Modeling and operation of dynamic membrane processes

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ICOM 2011

Book of abstracts

Welcome

It is our great pleasure to welcome you at the International Congress on Membranes and Membrane Processes (ICOM 2011) organized by the Membrane Technology Group of the University of Twente, The Netherlands and held at the RAI convention center in Amsterdam from July 23-29, 2011.

We tried to compose an interesting and inspiring program covering the broad spectrum of topics in the field of membrane science and technology. We invited three plenary speakers from areas closely related to, though still at a certain distance from the field of membranes, to broaden the scope of the program and generate discussion and new insights. The program covers 78 keynote lectures at the start of each conference session, giving an overview of the past and future developments in that specific field. Next to that, it consists of almost 400 oral and more than 600 posters presentations, from students as well as from senior scientists in the field.

The social program includes a welcome reception and an exclusive boat tour from the convention center, through the canals of the old city of Amsterdam, to the former stock exchange building where the conference dinner will take place.

We would like to take the opportunity to express our sincere gratitude to the members of the organizing committee for all their efforts and altruistic support at the expense of their own work. Thank you very much. Without your help, ICOM 2011 would not have been possible!

We are very grateful to our sponsors and we highly value their financial support. Finally we would like to thank all members of the membrane community for their contributions and help to make this conference a success. We appreciate your input.

We wish you a wonderful ICOM 2011 and hope you will have a great time!

Kindest regards,

Kitty Nijmeijer
Antoine Kemperman
Matthias Wessling

Chairs ICOM 2011

UNIVERSITY OF TWENTE.

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ICOM 2011 program outline

Sunday July 24, 2011

16:00-20:00	Registration
18.00-20.00	Welcome reception

Monday July 25, 2011

08.00-09.00	Registration
09.00-09.30	Opening
09.30-10.30	Plenary lecture Albert van den Berg (University of Twente)
10.30-11.00	Coffee break
11.00-12.50	Oral presentations
12.50-14.00	Lunch
14.00-15.30	Oral presentations
15.30-16.00	Coffee break
16.00-17.50	Oral presentations
18.30-21.00	Poster session 1

Tuesday July 26, 2011

08.30-09.30	Plenary lecture Wolfgang Marquardt (RWTH Aachen)
9.30-10.00	Coffee break
10.00-12.30	Oral presentations
12.30-13.30	Lunch
13.30-15.20	Oral presentations
15.20-15.50	Coffee break
15.50-17.40	Oral presentations
18.00-19.00	EMS general assembly
19.00-21.30	Poster session 2

Wednesday July 27, 2011

08.30-10.20	Oral presentations
10.20-10.50	Coffee break
10.50-12.40	Oral presentations

Thursday July 28, 2011

08.30-10.20	Oral presentations
10.20-10.50	Coffee break
10.50-12.40	Oral presentations
12.40-13.40	Lunch
13.40-15.10	Oral presentations
15.10-15.40	Coffee break
15.40-17.10	Oral presentations
17.30-20.00	Canal boat tour
20.00-22.00	Conference dinner

Friday July 29, 2011

09.00-10.00	Plenary lecture Jeff Long (UC Berkeley)
10.00-10.30	Coffee break
10.30-12.20	Oral presentations
12.30-13.00	Closure
13.00-14.00	Lunch

Network Young Membrains (NYM 13)

Prior to ICOM, the Membrane Technology Group of the University of Twente organizes the Network Young Membrains (NYM13) in Enschede, The Netherlands from July 21 until July 23, 2011. NYM aims at exchanging ideas on recent scientific developments in the field of membrane science and technology between young researchers from all over the world providing an excellent platform for exchange of ideas.

ICOM 2011 workshop program

As a part of the technical program for ICOM 2011, an international group of membrane experts conducts four 1-day workshops in key membrane technological areas. All workshops start at 8.00 and end at 17.00. Lunch and coffee breaks are included.

Saturday July 23, 2011

- Hydrodynamics and module design
  Prof. Thomas Melin, RWTH Aachen, Germany
- Membrane bioreactors
  Prof. TorOve Leiknes, NTNU, Trondheim, Norway

Sunday July 24, 2011

- Desalination
  Dr. Pierre Aimar, Université de Toulouse, Toulouse, France
- Membrane gas separation for industrial flue gases
  Ir. Paul Raats, KEMA Nederland B.V., Arnhem, The Netherlands

EMS General Assembly

Tuesday July 26, 2011
Emerald room
18.00-19.00

The EMS has published a special issue of the Membrane News dedicated to PhD theses carries out in the last three years all over Europe and neighboring countries. The pdf file of this issue is made available for ICOM 2011 participants through the EMS website. To get your electronic copy of this ICOM issue of the ‘Membrane News’, the Newsletter of the European Membrane Society, please click on ‘download Membrane News’ at the bottom left of the homepage of the European Membrane Society (www.emsoc.eu) and, upon request, use the password ‘ICOM2011EMS’.

Internet

Free wireless Internet is available in the Lobby of the Auditorium, the Ground Floor Auditorium, the Upper Lounge Auditorium, the Emerald Room and the Emerald Lounge. To access, please select the networkname ‘ICOM2011’ and enter the access code: icom2011

Student paper award

The European Membrane Society (EMS) has provided 4 oral and 4 poster prizes of € 500 each and the Membrane Society of Australasia has provided 2 oral and 2 poster prizes of AUS$ 500 each for young researchers in the field of membrane science and technology. All applications will be evaluated during ICOM 2011 and the winners will be announced at the end of the meeting on Friday July 29, 2011, during the closing ceremony of ICOM 2011.

Information for oral presentations

Each session room has a computer, a beamer, a laser pointer and a microphone. Speakers are kindly requested to respect the time. Time available for the plenary lectures is 1 hour. Keynote presentations last 25 minutes and 5 additional minutes for questions. Standard oral presentations are 15 minutes in length with 5 additional minutes for questions. Room G109 on the first floor is available for preview. Speakers are requested to put the presentation on the pc in the room of their presentation well before and no later than 1 hour before the start of their session.

Information for poster presentations

Presenters are requested to hang their poster either Monday morning (for the Monday evening Poster session 1) or Tuesday morning (for the Tuesday evening Poster session 2). Poster boards, tape and pushpins are available at the convention center. Posters MUST BE REMOVED by the author directly after each session has ended, otherwise they will be removed by the organization. The ICOM organization is not responsible for damage or los of the posters.

Poster session 1

Monday July 25, 2011; Onyx Lounge
Session time: 18.30-21.30

Topics:

1A. Carbon membrane
1B. Membranes for CO_2 capture
1C. Membranes for fuel cells
1D. Membranes for gas separation
1E. Hybrid membranes
1F. Inorganic membranes
1G. Membrane and surface modification
1H. Membrane bioreactors
1I. Membrane fouling
1J. Membranes for drinking water
1K. Mixed matrix membranes
1L. Molecular membrane design
1M. Membranes for waste water treatment

Poster session 2

Tuesday July 26, 2011; Onyx Lounge
Session time: 19.00-21.30

Topics:

2A. Membranes for biomedical applications
2B. Desalination
2C. Electromembrane processes
2D. Facilitated transport membranes
2E. Filtration under extreme conditions
2F. Membrane characterization
2G. Membrane contactors and reactors
2H. Membrane formation
2I. Membranes for biorefineries
2J. Membranes for energy generation
2K. Microfluidic membrane systems
2L. Membrane modeling
2M. NF/RO
2N. UF/MF

Social program

Sunday July 24, 2011
Welcome reception at the Amsterdam RAI Convention Centre.
All participants are invited to attend the welcome reception that will be held in the Lounge Auditorium at the Amsterdam RAI Convention Centre from 18.00-20.00 hrs.

Monday July 25, 2011
Poster session 1 (Drinks and snacks included)

Tuesday July 26, 2011
Poster session 2 (Drinks and snacks included)

Thursday July 28, 2011
Canal boat tour and Conference Banquet at the Beurs van Berlage (departure at 18:00 from the back side of the convention center; admittance with ticket only).

Canal boats
Amsterdam, capital of the Netherlands, is a bustling city. Few cities in the world have a historic center as large and untouched as Amsterdam and you will find only a few cities where water is as predominant as it is in Amsterdam. In 1.5 hour, canal boats will bring you from the RAI convention center to the former stock exchange building of Amsterdam, the Beurs van Berlage. While gliding through the old center of the city, a tour guide will guide you through the city.

Beurs van Berlage (Damrak)
In the Golden Age Amsterdam was the first place in the world to create a fixed location for the trade in stocks and shares. Three hundred years later Berlage built the third Amsterdam Stock Exchange; a building that generated a lot of controversy and, today, is considered the beginning of modern Dutch architecture: A fascinating location for the conference banquet in a pleasant atmosphere. After the banquet, take tram 4 in front of the Beurs van Berlage to return to the RAI Convention Center (or tram 9, 16 and 24 for other destinations in Amsterdam).

Amsterdam

Travel information

The Amsterdam RAI railway station is 300 m from the RAI convention center and has direct connections with railway stations Duivendrecht, Amsterdam Amstel, Amsterdam Zuid and Schiphol. Follow the signs Amsterdam RAI when you leave the station. Tram route 4 connects the city centre of Amsterdam, Amsterdam Central station and the RAI convention center (stop at Europaplein). From the Amstel railway station you can reach the RAI via metro 51 or bus route 15. Metro 51 also runs to Amsterdam Central Station.

Touristic highlights of Amsterdam
Source and more information: www.amsterdam.info

Oude Kerk: This old church with little houses clinging to its sides, remains a calm heaven at the heart of the freneric Red Light District. Its buildings, especially the Gothic-renaissance style octagonal bell tower, was used by sailors to get their bearings.

Dam square: The Dam is the very centre and heart of Amsterdam, although there are arguably prettier sights in the city. As an historical site however, it is fascinating and worth taking the time to appreciate. The Dam has seen many historical dramas unfold over the years, and was for example, the reception area for Napoleon and his troops during the 1808 take-over of the city. The Royal Palace which dominates the square, was originally used as the town hall and its classical facade and fine sculptures were intended to glorify the city of Amsterdam and its government. In contrast to its turbulent history, the square is now a peaceful place and is home to hundreds of pigeons and tourists resting their tired feet.

Amsterdam’s Canals: The number of canals have led Amsterdam to become known as “The Venice of the North”. And thus, a trip to Amsterdam is not complete without a boat cruise. A canal tour can be both fascinating and relaxing by day and enchanting and romantic at night when many of the houses and bridges are illuminated. The four main city center canals are Prinsengracht, Herengracht, Keizersgracht and Singel. There are also numerous smaller canals in the neighbourhood of Jordaan, of which the Brouwersgracht, the Bloemgracht and the Leliegracht are especially pleasant.

Rembrandt square: Rembrandtplein is lined with pubs, restaurants, cafes and hotels and is thus a tourist magnet. A popular centre for nightlife, it also includes traditional Dutch pubs which play real Dutch music. In summer, the terraces are packed with people enjoying a drink and watching the world go by. In the centre of the square is a small but pleasant park where you can relax or pay homage at the statue of Rembrandt. Around the area you’ll also find quality night clubs, gay venues, respectable diamond dealers and the inevitable tacky souvenir shops.

Leidseplein: The Leidseplein or Leidse-square is one of Amsterdam's most popular centres for nightlife. With many restaurants, clubs, coffeeshops, cinemas and theaters in the area, the Leidseplein is vibrant and colourful. On warm summer evenings, tourists and locals alike take advantage of the pubs' outdoor seating for a long, lazy drinks with friends. Street musicians, jugglers, fire-eaters and other performers liven up the square, often till the early hours.

Artis Zoo: Right in the center of Amsterdam, you can also find the oldest Zoo of Holland. It consists of four main areas: Zoo, Planetarium, Botanical Gardens and Geological and Zoological museum. In the zoo itself you will find animals from all over the world. In addition, a unique canal aquarium shows you which animals roam the canals of Amsterdam. The planetarium offers children a trip trough the universe. In the peaceful gardens, you can find many old trees and statues of contemporary artists and aswell as an impressive, tropical rainforest greenhouse. The Geological museum shows you how the planet has evolved over the past 4 billion years

Museums

Source and more information: www.amsterdam.info

Rijksmuseum Amsterdam: The Rijksmuseum is the largest museum in the Netherlands, with more than a million visitors each year. The Rijksmuseum is a familiar Amsterdam landmark and possesses an unrivalled collection of Dutch art, from early religious works to the masterpieces of the Golden Age. Location: Stadhouderskade 42, The museum quarter.

Stedelijk Museum: Housing the municipal collection of modern art, this important museum with wonderful collection of all biggest 20th C. artists, is going through the difficult phase of reconstruction and enlargement. Location: Paulus Potterstraat 13.

Van Gogh Museum: The museum houses some 200 paintings and 550 sketches showing Van Gogh in all his moods. These combined with hundreds of letters by Van Gogh to Theo, and selected works by his friends and contemporaries, form the core of the museum's collection. Location: Paulus Potterstraat 7.

Amsterdam Historical Museum: History of Amsterdam shown through fine paintings including one Rembrandt, various extraordinary 17th C. group portraits of foremost citizens and other admirable artifacts. Additionally, the museum usually presents interesting temporary exhibits. Location: Nieuwezijds Voorburgwal 357.

Anne Frank House: Anne Frank House in the center of Amsterdam is the hiding place where Anne Frank wrote her famous diary during World War II. The original of the diary is on display as part of the Anne Frank House's permanent exhibition. Location: Prinsengracht 267, Jordaan quarter near Westerkerk.

ICOM 2011

Oral Presentations

Abstracts

ICOM 2011

Monday, July 25th 2011

Plenary Lecture 1

Monday, July 25th 2011

ICOM1862

Labs-on-a-Chip for medical applications

Albert van den Berg
MESA+ Institute, University of Twente, BIOS/Lab on a Chip group, NL

The recent rapid developments in microfluidics technologies has enabled the realization of miniaturized laboratories. These Labs-on-a-Chip will play an important role in future medicine, both in point-of-care devices for drug or biomarker monitoring, as well as in early diagnostic devices. We developed a pre-filled ready-to-use capillary electrophoresis platform for measuring ions in blood. It is used to monitor lithium in finger-prick blood of manic-depressive patients, but can also be used for measuring calcium in blood for prevention of milk fever, or for measuring creatinine in blood or sodium in urine for early detection of ESRD. Another device was developed for analyzing male fertility by determining sperm concentration and motility in semen. It appears that the same device can be easily adapted to detect the presence of cells in milk, a good indicator for the presence of mastitis.For early detection of colon cancer, nanowire sensors for detection of hypermethylated DNA will be presented, showing label-free DNA detection. The small size of these nanowire sensors enables the integration of a complete lab in a pill, that may be used as a screwening tool for early diagnostics of intestinal cancer. Finally, some perspective for microfluidic devices for permeation studies of tissue and study of desalination processes will be presented.

Parallel Sessions

Monday, July 25th 2011

Morning Session, 11.00 – 12.50

Gas and Vapor Separation 1

ICOM1779

Pushing the Bounds: The Quest for Better Membrane Materials

Peter M. Budd
University of Manchester, School of Chemistry, GB

Membrane technology offers energy-efficient and cost-effective processes in many industries.[1] Most commercial membranes for gas and vapor separation are polymeric and, despite extensive research over the past decades, are based on a mere handful of polymers. However, if membrane technology is to penetrate new and demanding application areas, such as carbon dioxide capture from flue gases, better and more robust membrane materials are needed. Ways of generating improved membrane materials will be discussed, from the perspective of a polymer chemist.

For high-volume applications, high permeability is necessary in order to minimize membrane area. However, it is well known that high permeability is generally associated with poor selectivity, as illustrated by double logarithmic "Robeson" plots of selectivity against permeability.[2] The challenge is to push the bounds of membrane performance to higher permeability, whilst also achieving long-term stability under demanding conditions of use.

Permeability in polymers is related to the amount and distribution of free volume. For glassy polymers, the interrelationships between molecular structure, free volume distribution and transport properties, are complex. Nevertheless, in recent years there has been significant progress in the development of highly permeable polymers, including substituted polyacetylenes, certain perfluoropolymers, some polyimides, addition-type poly(norbornenes) and polymers of intrinsic microporosity (PIMs).[3] The effects of varying the polymer structure, through the use of novel monomers, through copolymerization and through chemical post modification, will be discussed with particular reference to PIMs. Post modification by thermal rearrangement, as demonstrated by Park *et al.*,[4] provides a route to promising materials that otherwise could not be processed into membrane form.

The possibilities for improving membrane performance through design of the macromolecular structure have not yet been exhausted. Nevertheless, a step-change in performance is most likely to come through a synergistic combination of materials. Thus, "mixed matrix" or "nanocomposite" membranes have been the focus of much recent research, as exemplified by the "DoubleNanoMem" project.[5]

1. Bernardo, P.; Drioli, E.; Golemme, G. *Ind. Eng. Chem. Res.* **2009,** *48*, 4638-4663.

2. Robeson, L. M. *J. Membr. Sci.* **2008,** *320*, 390-400.

3. Budd, P. M.; McKeown, N. B. *Polym. Chem.* **2010,** *1*, 63-68.

4. Park, H. B.; Jung, C.H.; Lee, Y.M.; Hill, A.J.; Pas, S.J.; Mudie, S.T.; Van Wagner, E.; Freeman, B.D.; Cookson, D.J., *Science*, **2007**, *318*, 254-258.

5. DoubleNanoMem (Nanocomposite and Nanostructured Polymeric Membranes for Gas and Vapour Separations) funded by the EC 7th Framework Programme (FP7/2007-2013) under grant agreement no. NMP3-SL-2009-228631.

ICOM646

Synthesis and Permeation Properties of Thermally Rearranged Polymers based on 3,3'-dihydroxy-4,4'-diamino-biphenyl and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (HAB-6FDA)

David Sanders[1], Zachary Smith[1], Ruilan Guo[2], Claudio Ribeiro[1], Donald Paul[1], Benny Freeman[1], James McGrath[2]
[1]The University of Texas at Austin, Chemical Engineering, Austin, TX, US, [2]Virginia Polytechnic Institute and State University, Chemistry, Blacksburg, VA, US

Thermally rearranged (TR) polymers have recently been seen as a promising family of polymers for gas separations. The initial work by Park et al. in 2007 showed high permeabilities, selectivities, and resistance to plasticization in CO_2/CH_4.[1] The combination of high
permeability and selectivity positioned these polymers well above the established upper bound for CO_2/CH_4 separation. These properties make TR polymers very suitable for CO_2 removal from natural gas.

Natural gas is the largest industrial gas separation with nearly 95 trillion standard cubic feet of gas used each year worldwide. This gas must not contain more than 2% CO_2, a common contaminant, in order to meet specifications for pipeline transport.[2] Membranes offer a desirable method of CO_2 removal when compared with amine absorption, the current industry standard, due to low energy costs, lack of hazardous waste, and small footprint. High performance polymers, such as TR polymers, can be used to improve membrane technology and make them even more enticing when compared with amine absorption.

The work to be presented focuses on the influence of preparation method on transport properties of TR polymers. Polyimides based on a non-fluorinated diamine 3,3'-dihydroxy-4,4'-diamino-biphenyl, and a fluorinated dianhydride, 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (HAB-6FDA) were synthesized. These polyimides were then subjected to thermal rearrangement conditions of 350, 400, and 450ºC for either one hour or thirty minutes. Thermogravimetric analysis and mass spectrometry were used to track the mass loss with time as the thermal rearrangement took place and monitor the evolved gas. Gel fraction measurements were also used to measure the chemical resistance of each of the resulting TR polymers. Permeation results on these materials showed large increases in the permeability of N_2, O_2, CO_2, CH_4, and H_2 at 35ºC for pressures from 30 to 220 psig as a function of thermal rearrangement.

References

1. Park, H.B., C.H. Jung, Y.M. Lee, A.J. Hill, S.J. Pas, S.T. Mudie, E. Van Wagner, B.D. Freeman, and D.J. Cookson, *Polymers with cavities tuned for fast selective transport of small molecules and ions.* Science, 2007. **318**(5848): p. 254-258.

2. Baker, R.W. and K. Lokhandwala, *Natural gas processing with membranes: An overview.* Industrial & Engineering Chemistry Research, 2008. **47**(7): p. 2109-2121.

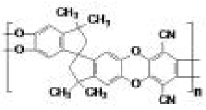
ICOM388

Highly gas permeable membranes based on polymers of intrinsic microporosity

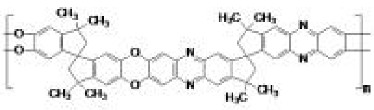
Michael Guiver[1,2], Naiying Du[1], Gilles Robertson[1], Mauro Dal-Cin[1], Ho Bum Park[2]
[1]National Research Council Canada, Institute for Chemical Process & Environmental Technology, Ottawa, ON, CA, [2]Hanyang University, WCU Department of Energy Engineering, Seoul, KR

The term 'Polymers of Intrinsic Microporisity' (PIMs) is currently used to describe high-free-volume microporous materials having rigid ladder-type polymeric structures incorporating contorted centers. These ladder polymers have very high surface areas, and are considered as promising materials for membrane gas separation. In a series of significant papers, Budd et al. and McKeown et al. reported 'PIM-1' and 'PIM-7' as the first high molecular weight microporous ladder polymers in this class.

PIM-1



PIM-7



PIMs exhibit very high gas permeabilities, though generally lower than the highest permeability microporous polymer, acetylene-based poly(trimethylsilyl propyne) (PTMSP). However, PTMSP membranes suffer from rapid aging and changes in properties, resulting from a collapse in free volume. One advantage of PIM-1 is that its aromatic ladder-type structure linked by a highly contorted spirobisindane centre has no rotational freedom, thus making it less prone to free volume collapse. Apart from PIM-1, very few other high molecular weight PIM polymers were reported until recently.

Structurally new PIMs of high MW, and their properties relating to membrane gas separation will be discussed. The PIMs derive from novel monomers or by post-polymerization modification. Since the molecular structures of PIMs have a strong influence on gas permeability and selectivity, the design of new PIMs allow the tuning of properties such as gas permeability and selectivity. Molecular structure variables that have been investigated include a) changes in the segmental distance between contorted centres, b) changes in the angle of contortion, c) incorporation of pendant groups d) hydrogen-bonded networks e) incorporation of strongly CO_2-philic groups that greatly enhance CO_2 permeability and CO_2 / N_2 selectivity, especially for mixed gases. In general, PIMs appear to have unusually high oxygen and carbon dioxide permeability, suggesting that they may be useful membrane materials for oxygen enrichment or carbon dioxide separations such as carbon capture.

ICOM1607

Water Vapor Transport in Carbon Nanotube Membranes

Yeny Hudiono[1], Jung Bin In[2], Costas Grigoropoulos[2], Aleksandr Noy[3], Olgica Bakajin[3], Sangil Kim[1], Francesco Fornasiero[1]
[1]Lawrence Livermore National Laboratory, Biosciences and Biotechnology Division, Livermore, CA, US, [2]University of California Berkeley, Department of Mechanical Engineering, Berkeley, CA, US, [3]Porifera Inc, Hayward, CA, US

The fundamental understanding of water vapor transport in the presence of other gases or molecules is important for a number of applications including breathable fabrics, protective clothing, and CO_2 capture. In particular, there is a strong need to improve the water vapor permeance of protective clothing that shield individuals from chemical or biological hazards, dust and/or organic contaminants. Current protective garments cannot provide high level of protection and high breathability simultaneously. Wearing these garments restricts the primary cooling mechanism for a human body in a hot environment, i.e. the evaporative heat loss, and leads to heat stress. Advancements in moisture – management performance of protective fabrics require new materials.

Recent study in our laboratory shows that carbon nanotube pore exhibits fast gas and water transport. Measured gas transport rates
through 1-2nm wide carbon nanotube (CNT) are two orders of magnitude faster than predicted by Knudsen diffusion theory [1]. This unique property of CNTs is expected to translate into very high breathability. Also, because of their narrow pore size, *engineered* CNT pores may be able to block large hazardous contaminants. Thus, incorporation of CNTs in a membrane may provide a quantum leap toward the development of next generation breathable and protective fabrics.

To investigate the water vapor transport in CNTs, we present here measurements of water vapor transport through well-aligned narrow CNT channels that function as the only pores of an impermeable matrix (silicon nitride or a polymeric material). Our measurements show that CNT/silicon nitride membranes provide water vapor transport rates that are comparable to those through state-of-the-art breathable fabrics, even if the moisture conductive pores are only 1-3nm wide and the membrane porosity is less than 1%. Incorporation of CNT in a flexible polymer matrix as selective, moisture conductive pores also results in highly breathable membranes. The measured water vapor flux of CNT-polymer membranes is more than an order magnitude higher than the breathability target for protective clothing. The results suggest that CNT membranes could provide a compelling alternative to current breathable membrane systems.

References:

1. Holt, J.K., et al., *Fast mass transport through sub-2-nanometer carbon nanotubes.* Science, 2006. **312**(5776): p. 1034-1037.

ICOM140

Partially pyrolyzed membranes (PPMs) prepared from copolyimides containing polyethylene oxide side chains

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Introduction

The use of polyimides that contain labile groups, suitable to be removed at relatively low pyrolysis temperature, can afford interesting materials for gas separation since the space occupied by the labile groups might keep as microvoids after the pyrolysis while the polyimide backbone prevails. We have recently demonstrated that COOH groups can be removed at 425-475ºC yielding partially pyrolyzed membranes (PPMs) with significantly higher P than the starting polyimide [1].

Here were report the effect of removing side polyethylene oxide (PEO) chains on the permeation properties of PEO containing polyimides (PIPEOs).

Experimental

PIPEOs were prepared by esterification of a copolyimide having COOH groups (**PIA**) using PEO with different Mw, 164, 550 and 1200 g/mol following a procedure previously reported [2]. The incorporation of PEO-164 was complete, whereas PEOs of 550 and 1200 g/mol yielded, partially modified copolyimides. The copolyimides were designated as **PIPEO-6**, **PIPEO-11** and **PIPEO-16** where the number indicates the final PEO content (weight percent) calculated by TGA and ^{1}H-NMR.

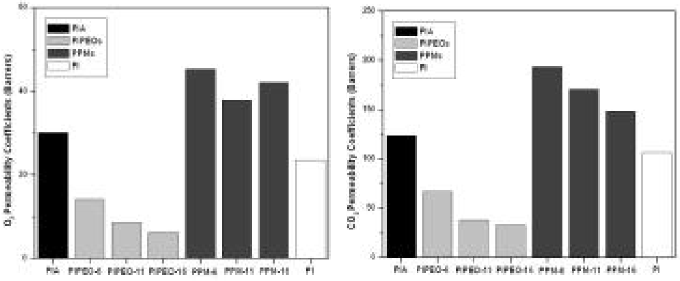
PPMs were obtained in a Carbolite CTF 1200 furnace heating the films up to 385ºC. According with the starting **PI-PEO** film used, the **PPMs** were nominated as **PPM-6, PPM-11** and **PPM-16**. The removal of PEO and COOH pendant groups was checked by TGA.

Results and Discussion

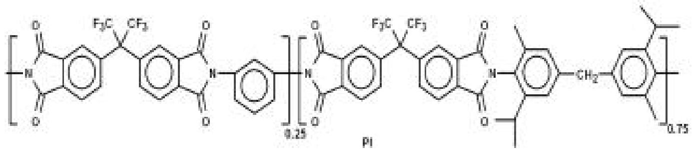
Permeability coefficients (P) to O_2, N_2, CH_4 and CO_2 were measured for all the membranes. Figure 1 shows the P(O_2) and P(CO_2). **PIPEO** membranes exhibited lower P than the starting copolyimide **PIA** which suggested that PEO groups did not cause separation of the polymer chains as other bulky groups do, but, because of its flexibility, they occupy the space of free volume of **PIA** preventing access of the gases. Furthermore, P decreased when the PEO content increased, confirming the above assumption.

When the PEO side chains were removed, P increased between 2.8 and 4.4 times, compared with the corresponding **PIPEO.**

The permeability coefficients to O_2, N_2 and CH_4 of the three **PPMs** were quite similar, while the P(CO_2) followed the same trend than that of **PIPEOs** films. These unexpected results seem to indicate that the polymer chains did not reach the molecular equilibrium in all the three films. The gas permeation properties will be evaluated after 1000 hours to check whether this unexpected behavior is transitory.



In principle, the elimination of the lateral chains should yield polyimides with the same structure in every case. This polyimide (**PI,** figure 2) was synthesized for comparative purposes and, as it is depicted in figure 1, its permeability values were lower than those of all **PPMs,** which revealed the positive effect of removing PEO side chains on gas separation properties.



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Membrane characterization 1

ICOM1858

Characterisation of porous structure in membrane materials - A short overview

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Transport properties and performance of porous membranes are directly related to their pore structure and surface characteristics. The physico-chemical and surface chemical properties (charge, hydrophilic-hydrophobic, chemical composition) may have a role in transport mechanisms and can, to some extent, predict the interactions between different types of molecules on the membrane surface. However, the characteristic parameters of the porous structure (including defects, if any) are of the utmost importance in relation with their impact on membrane performance. These parameters have to be measured and controlled, more or less drastically depending of the focused application.

The development of more complex and sophisticated membranes designs created a need for a better insight into the relationships between (a) the membrane synthesis route, (b) the membrane microstructure or morphological properties and (c) the permeation properties. This has been widely emphasized in the literature [1-3]. Recent developments are reported every 3 years in the abstracts of the International Symposiums on the Characterisation of Porous Solids (COPS) which bring experts from academia and industry together in order to discuss latest developments in this area. Information on membrane characteristics is essential for membrane users, manufacturers and scientists to choose an appropriate membrane for a specific application, to control membrane synthesis process parameters and membrane quality/stability (*ex-situ* or *in-operando*) or to understand transport mechanisms.

Four types of methods are classically used to characterize the porous structure in membrane materials. They can be ranked as i) stereology, ii) static intrusive methods, iii) static non intrusive methods, iv) dynamic methods, iv) coupled methods. Static intrusive methods (e.g. gas adsorption desorption or liquid intrusion porosimetry) are classically used for a first analysis of the membrane material porous structure. Non intrusive methods are adapted for the detection of non interconnecting pores, for the analysis of fragile materials or very thin membranes, but also for *in-operando* characterization of the membranes. Dynamic techniques provide an insight into the complex link between the membrane microstructure and transport behavior. These methods are not restricted by the limited quantity of membrane material and are sensitive to the active pathways through the porous structure, including defects. In this presentation several examples of developments in membrane characterization methods will be reported, with a particular emphasis on defect detection methods and on the characterization of very thin supported layers by coupled methods.

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ICOM865

Superimposed effects of nano-scale confinement and penetrant on behavior of ultra-thin glassy polymer membranes

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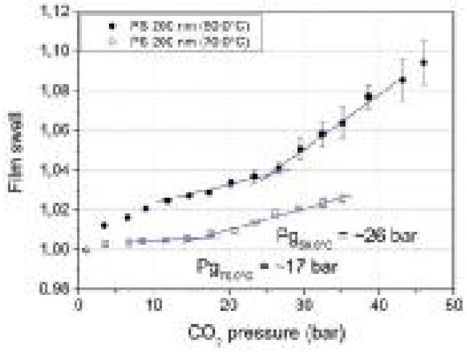
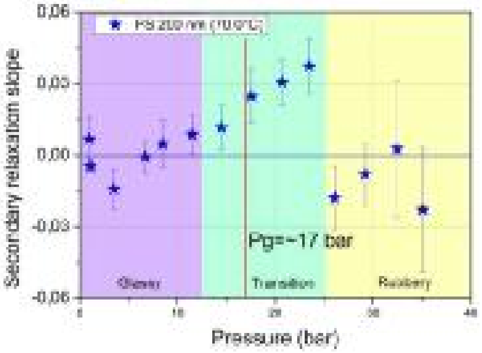
Reduction of the thickness of a glassy polymer to nano-scale dimension is known to have strong effects on its materials properties, such as a reduction in the glass transition temperature, a reduction of the Young's modulus and an enhanced rate of densification (physical aging). In addition to the abovementioned effects membrane separations involve substrate/film interactions as well as presence of highly soluble penetrants (organic solvents, vapors and gases). Such environment is anticipated to result in superimposed effects of reduced film thickness and penetrants' sorption which may significantly alter membrane performance over
its lifetime.

The research presented aims at fundamental understanding of sorption, relaxation and plasticization phenomena that occur in thin polymer films in the thickness range below 100 nm. Pressure induced glass transition as well as sorptive dilation behavior of ultra-thin model polymer systems is quantified based on optical and dielectric relaxation methods. Optical methods involve utilization of state of the art high pressure in-situ spectroscopic ellipsometry which enables to generate very accurate data on thickness and optical index behavior of polymer films down to the thickness of 30-40 nm. Optical index measurements can in turn be used to approximate the concentration of penetrant in ultra thin films, and therefore, evaluate sorption characteristics.

Figure 1 shows an example of dilation isotherms obtained for polystyrene (PS) films of thickness of 200 nm subjected to high pressure of CO_2.



It shows that this material can be plasticized at sufficiently high pressure or activity of the penetrant. By identifying the transition point between glassy and rubbery behavior it is possible to quantify pressure induced glass transition (P_g) – equivalent of isobaric glass transition (T_g). Sorption kinetics of the system can be closer investigated by looking at the rate of secondary relaxation in the polymer, as plotted in Figure 2.



It is caused by the material slowly accommodating penetrant molecules in the matrix causing it to dilate or increase thickness. It can be seen that the rate of relaxation is different depending on whether the polymer is in glassy, rubbery or in the transition state.

ICOM746

Ageing of ion-exchange membranes used in electrodialysis

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Ion-exchange membranes (IEMs), used in a food industrial electrodialysis (ED) application, were researched by measuring their static parameters, ionic permeability and mechanical resistance to evaluate the evolution of some physico-chemical properties before and after two years of use.

A major problem associated with the use of membranes, besides energy looses, is ageing. Indeed, more they are used, more their properties and performance change, particularly in ED processes, where a great part of the costs are related to the replacement of membranes.

A couple of cation-exchange membrane (CEM) and one of anion-exchange membrane (AEM) Neosepta® , made of polystyrene, crosslinked with divinylbenzene (DVB) and reinforced by a PVC cloth, were considered. Each pair was composed of a new membrane and another retired from an ED module after two years of use. The CEM contains sulfonated sites and AEM has quaternary ammonium sites.

The study of static parameters showed that capacities drop significantly after two years of use. The AEM appeared to be the most affected by the decrease of exchange capacity (-84%), which may be correlated with the large increase in water content (+40%) and thickness (+130%). For CEM when the exchange capacity decreased (-71%), water content and thickness also decreased in -16% and -9%, respectively.

Ionic permeability (P_s) was determined by the study of the diffusion of a strong electrolyte through a membrane in a transfer cell.

The ratio $P_s(new)/P_s(used)$ shows that the electrolyte permeability decreases dramatically after two years of use in ED, mostly for AEM than for CEM.

For AEM, the tensile test showed more than 93% of loss of polymer rigidity and 87% decrease on the breaking strength, comparing to 37% for the CEM, results that suggest damage in the polymer chain which was peeled off from the PVC cloth as it was also seen
on SEM images.

These experimental observations suggest inhibition and degradation of functional sites, fouling and degradation of the polymer. It is indicated then, that the use of IEMs over time leads to a change in their physico-chemical properties, exchange capacities, conductivity and therefore permeability, which definitely affects their performance in practical applications. The AEM is the most affected by these changes. The used membrane retains more water, its thickness increases and absorbs HCl, due to fouling in the interstices left free by macromolecular chains and disappeared ammonium sites. In addition it presents a decrease in permeability larger than that of CEM and greater damage in the polymer structure of the membrane.

Additional research is imperative in order to deepen knowledge on the long-term behavior of IEMs and to establish solutions to improve the stability of the ion-exchange polymers, mainly those of AEMs.

ICOM603

Conductometric and computational study of cation-exchange membranes in H^+ and Na^+ forms with the various hydration level

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The aim of this work is to investigate the influence of polymer morphology of cation-exchange membranes on thermodynamic state of water and electro-kinetic characteristics of counter ions (Na^+ and H^+). In this study we investigated: 1) experimentally the physico-chemical characteristics and concentration dependencies of electro-conductivity of commercial sulfonated membranes MF-4SK (analogous of Nafion), CM-1, CMX, MK-40 in NaCl and HCl aqueous solutions, 2) computationally the dependence of binding energy (BE) per water molecule of MF-4SK and MK-40 in Na^+ and H^+ forms on number of adsorbed water molecules (from 0 up to 9).

The membrane conductivity was measured by mercury-contact method using alternating current (AC) of high frequency (50-200 kHz). The computational study was carried out by ORCA Program [1]. The optimization of membrane model structure was performed using RHF method with 6-31G (d,p) basis set and tight optimization criteria. The calculations of the binding energy of the membrane-water complexes were carried out using LPNO-CEPA/1 method.

Based on approaches of the two-phase model [2] from the concentration dependences of specific conductivity we determined the volume fractions of the gel and inter-gel phase, the hydration capacity of gel phase as well as the iso-conductance point. Using Nernst-Einstein relation adopted for poly-electrolytes electro-kinetic characteristics as the molar conductivity ($\boldsymbol{\lambda}$) and self-diffusion coefficient ($\boldsymbol{D}$) of counter ions in gel phase were estimated. The highest $\boldsymbol{\lambda}$ and $\boldsymbol{D}$ of Na^+ and H^+ are observed for MF-4SK and the lowest ones for MK-40. $\boldsymbol{D}_{H+}$ in MF-4SK calculated from the conductivity data is $7{,}75 \times 10^{-6}$ cm^2/s, this value is quite comparable with $\boldsymbol{D}_{H+}$ in Nafion: $6{,}15 \times 10^{-6}$ calculated by Karo et al using molecular dynamic method [3] and $5{,}80 \times 10^{-6}$ determined experimentally by Perrin et al [4].

We detailed analyzed and discussed the computationally optimized structures of membranes MF-4SK and MK-40 in Na^+ and H^+ forms with various hydration degree. In MF-4SK the dissociation of the -SO_3H group occurs when the membrane contents three or more water molecules, while no dissociation was observed in MK-40 in whole investigated range of the hydration degree. BE of water molecules is higher in Na^+ than in H^+ form for both MF-4SK and MK-40. BE of water in Na^+ form for MF-40 and MK-40 practically does not differ, but in H^+ form of MF-4SK the water molecules are stronger bound than of MK-40.

We may conclude that fluorine in polymer matrix influences on the connectivity of water molecules and in this way promotes proton transport in membrane gel phase by Grotthus mechanism. The explanation of some higher molar conductivity of Na^+ in MF-4SK membrane than in other membranes needs further investigation.

The participance in the ICOM2011 is financially supported by Austrian Promotion Foundation (FFG), Project N 827559.

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ICOM1159

How an amphiphilic sulphonamide can modify microstructure and properties in a poly(ether-b-amide) membrane? Molecular Dynamic Simulations and Experimental Evidences

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Physical mixtures of copolymers and chemical additives have been used extensively to produce innovative membrane materials having combinations of properties that are normally not found in a single polymer. In choosing the appropriate blend systems, prediction of individual polymer miscibility aspects is important in view of their widespread industrial applications. In an effort to understand the miscibility/immiscibility behaviour of different materials, many attempts have been made to employ various theoretical and experimental tools.

A useful strategy for changing and improving the performance of raw materials consists of suitably incorporation of new structural and chemical elements into the polymer matrixes in order to control structure–property relationships.

In this sense, the classical simulation study at molecular level by using molecular dynamic simulations (MD) on polymer-additives and additives-additives interactions can powerfully support experimental studies about miscibility and morphological characteristics of such systems.

Improving performance of the modified membranes is achieved by determining the factors which control the miscibility and the morphology of systems at molecular level, i.e., the interactions among chemical additives, polymeric matrix and guest molecules. This aspect is crucial in identifying effective and targeted strategies for the synthesis of new materials in the science of nano-composites.

In the present work fully atomistic and experimental investigations of the microstructure in a poly(ether-b-amide) membrane (PEBAX®2533, Atofina) containing an amphiphilic sulphonamide (KET) have been performed.

In details, the compatibility between KET and PEBAX, the presence of nanoclusters of KET inside the matrix and the free volume distributions at different KET compositions have been studied at molecular level through modelling, DSC and IR analyses.

Also, the interactions between PEBAX and modifier in presence of dissolved water molecules have been analyzed, comparing data achieved at molecular level with experimental findings achieved at macroscopic level.

The integrated experimental-theoretical approach provided a more detailed investigation of three components complex systems, in which the macroscopic properties and morphologies are determined by interactions in the range nano scales, thus resulting in a reciprocal validation and useful correlations between MD and experimental analysis.

CO2 capture 1

ICOM1773

Membrane-Based CO_2 Capture at Power Plants: Process Design Considerations

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During the last century, the concentration of carbon dioxide (CO_2) in the atmosphere increased from 275 to 387 ppm. This increase is largely due to the combustion of fossil fuels and has already produced measurable increases in global temperatures. Climate models indicate that continuation of this trend will dramatically change the global climate by 2100.

Combustion of fossil fuels for power generation produces about 30% of world CO_2 emissions. One way to reduce CO_2 emissions to the atmosphere is carbon capture and sequestration (CCS). In this scheme, CO_2 is captured from large point sources, such as power plants, and sequestered underground in geological structures for long periods of time. A key to this approach is technology that can separate CO_2 from process gases cost effectively, allowing it to be sequestered without radically increasing energy costs.

Three pathways for CO_2 capture from fossil fuel power production are being considered by researchers: post-combustion CO_2 capture from flue gas, pre-combustion capture from syngas, and oxy-combustion, which produces a nearly sequestration-ready CO_2 effluent. In each of these approaches, membranes have the potential to play a role. However, attention to process design is crucial to guide membrane development.

The key challenge for post-combustion CO_2 capture with membranes is generating affordable pressure ratio. The high cost of compression or vacuum equipment will limit the affordable pressure ratio to about 5. Under these conditions, highly-selective membranes are not beneficial, but rather, high CO_2 permeance is critical to reduce system cost and footprint. As a consequence of affordable pressure ratio limitations, it is unlikely that a membrane-only approach can achieve the total separation for post-combustion CO_2 capture.

One way to generate CO_2 partial pressure driving force for flue gas with minimal energy input is to use combustion air as a sweep stream in a counter-current membrane contactor. In this selective-CO_2-recycle configuration, a membrane can function as a CO_2 pre-concentrator, and when used in combination with cyrogenics or absorption, offers promise to reduce post-combustion CO_2 capture costs. This process looks particularly attractive for natural gas combined cycle power plants.

For pre-combustion CO_2 capture with membranes, significant partial pressure driving force is readily available. As a result, high membrane selectivity is useful to reduce CO_2 capture costs. Process considerations show that H_2-selective membranes that can operate at high temperature are the most promising membrane syngas treatment approach, although CO_2-selective membranes can play a role in CO_2 purification.

In this paper, the impact of process design and membrane properties on the costs of pre and post-combustion CO_2 capture, and a comparison with conventional technologies, will be discussed. Field test results for current state-of-the-art membranes will also be reviewed.

ICOM1464

Tuning Microcavities in Thermally Rearranged Polymer Membranes for Hydrogen Separation

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Global warming and the resulting severe climate changes requests urgently the reduction of fossil fuels or capture of greenhouse gases such as carbon dioxide, methane and hydrocarbons, etc. At present, the most feasible method to reduce greenhouse gas, mostly CO_2, is to separate CO_2 from large emission sites like power plants. Among several CO_2 capture process from power plants, post-combustion, oxyfuel combustion, and pre-combustion process, the latter process called as integrated gasification combined cycle (IGCC) have been taken much interest as the most cost-effective process although post-combustion capture has advantages to be applied conveniently at the end of the present power plant system. Pre-combustion processes using coal or natural gas are comprised of coal gasification by steam reforming, desulfurization, water-gas-shift (WGS) reaction, and H_2/CO_2 separation. For H_2/CO_2 separation, membrane materials have been considerably restricted only to metal or inorganic materials due to the operation temperature higher than 200°C. However, thermally stable rigid-rod polymers can be also included as candidates of gas separation membranes due to the advantages of polymer materials such as low cost, easy mass production and high processibility if they have high separation performances as well as thermal and chemical stabilities.

Recently, we developed thermally rearranged (TR) rigid-rod polymers from ortho-functional polyimides by thermal treatment at around 450 °C, where thermal conversions of functional polyimides into polybenzoxazoles (PBO) at solid states occurred with chain rearrangement as resulting in increases of fractional free volume and extraordinary gas separation performances. The syntheses were different from conventional method to obtain PBO, where aromatic dicarboxyl acid reacts with bis(aminophenol) by one-step method in a strong acid like polyphorsphoric acid (PPA) at 180-200 °C. In this study, TR-PBO membranes were prepared by two-step method via poly(hydroxyl amide) (PHA) precursor as using diacid chlorides and bis(aminophenol)s to optimize hydrogen separation performances by the control of chain rigidity and free volume elements.

Three representative aromatic PHAs were synthesized by the condensation polymerization of diacid chlorides with bis(aminophenol) containing bulky hexafluoroisopropylidene group. Structural analyses were carried out by FT-IR, NMR and elemental analysis (EA). Thermogravimetric analysis (TGA) accompanied with mass spectroscopy showed that dehydration reaction was detected at around 330°C, revealing that chain rearrangement of PHA into TR-PBO occurred. The size and distribution of free volume elements were obtained from room temperature to 220 °C by positron annihilation lifetime spectroscopy (PALS). Gas permeation properties of TR-PBO membranes were investigated with temperature ranges of 30 to 220 °C. The polymer membranes showed temperature dependence as well as structure-property relationship on their H_2/CO_2 performances.

ICOM1150

The impact of phase-inversion polymer type on the development and performance of BSCF capillaries

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Oxygen-permeable perovskites with mixed ionic-electronic conducting properties can play an important role in the high temperature separation of oxygen from air which is needed in the oxy-fuel and pre-combustion technologies in fossil fuel power plants for the removal and capture of CO_2. When such gastight materials are exposed to an oxygen chemical potential gradient at temperatures typically higher than 700°C, they selectively transport oxygen in the form of oxygen ions from the high partial pressure side to the low partial pressure side of the membrane, without the need for electrodes and external electrical loadings. Since large-scale gas separation applications demand high membrane surface/volume ratios, membranes with capillary or hollow fiber geometry have a distinct advantage over tubular and flat sheet membranes.

In this work, we present the fabrication and performance of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) capillary membranes. The capillaries were made by a spinning technique based on phase inversion using a sulfur or non-sulfur containing polymer binder. The phase inversion technique is commonly used for the fabrication of polymeric membranes, but has been adapted by using a starting suspension loaded with a certain fraction of BSCF. Special attention was given to the polymer solution and ceramic spinning suspension in order to avoid macrovoids and achieve gastight membranes. The comparison of the performance of sulfur-free and sulfur-containing BSCF capillaries with similar dimensions revealed a profound impact of the sulfur contamination on both the oxygen flux and the activation energy of the overall oxygen transport mechanism. Also, the effect of activation layers on both types of capillaries will be shown. This work is performed in the framework of the 'MEM-BRAIN' project, aiming at the development of gas separation membranes for zero-emission fossil fuel power plants.

ICOM527

Asymmetric polybenzimidazole hollow fibre membrane for H_2/CO_2 separation at high temperature

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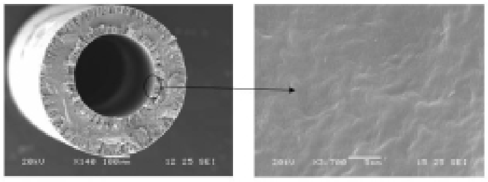
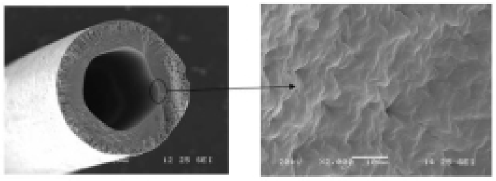
Polybenzimidazole, a class of heterocyclic polymer, is well known for its excellent thermo-chemical stability, high Tg and retention of its mechanical properties at high temperature. Due to these properties PBI have been extensively investigated for various applications viz., PEMFC, thermo-insulating materials, fire-fighting suits, etc. Owing to its rigid structure (T_g = 420 ˚C) and stability at high temperatures, PBI could be best suited for H_2/CO_2 separation application at high temperatures. Objective of the present study was to fabricate asymmetric PBI hollow fibre membranes by conventional dry-jet wet spinning technique and investigate the effect of temperature on H_2 and CO_2 separation performances.

Conventional polybenzimidazole, poly[2,2′-(m-phenylene)-5,5′-benzimidazole] was synthesized in house by solution polycondensation method. Asymmetric PBI hollow fibre membrane was prepared using dry-jet wet spinning process. A tube-in-orifice spinneret with outer diameter/inner diameter of the tube of 1.0/0.5 mm was used to spin the hollow fibres. The dope solution and the bore fluid were extruded at the predefined extrusion rate. The fibres were post treated by sequential solvent exchange technique with ethanol and hexane followed by air drying for about 24 h.

Two different bore fluid compositions were used and it was observed that the fibres spun with 20 % solvent in bore fluid (M1) results in a skin layer formation on the inner surface of the fibre that provides a sub-layer resistance for the fibre performance. Further increasing the solvent proportion in the bore fluid to 50 wt. % (M2) minimized this inner layer effect resulting in porous structure with significant improvement in flux for H_2 and CO_2.



(A) Overall morphology (M1) (B) Inner surface (M1)



(C) Overall morphology (M2) (A) Inner surface (M2)

Figure 1. SEM images of M1 and M2 fibres spun with different compositions of solvent in bore fluid.

The effect of temperature on gas permeance and selectivity of H_2 over CO_2 for PBI fibres (M2) is as shown below.

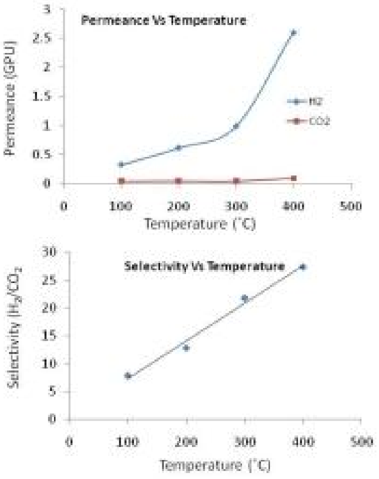


Figure 2. Performance of PBI hollow fibre membrane with temperature

With increase in temperature from 100 to 400 ˚C the gas permeance increases however, the extent of increase in permeance is more for H_2 than CO_2 resulting in increased permselectivity. The H_2 permeance at 400 ˚C was increased to 2.6 GPU by ~ 8 folds than its permeance at 100 ˚C. While the CO_2 permeance was relatively increased by just ~ 2 folds at 400 ˚C as compared to its permeance at 100 ˚C. This significant improvement in permeance of H_2 leads to H_2/CO_2 of 27.3 about 3.5 times higher than at 100 ˚C. This trend is opposite to the trend generally observed for the other polymers and could be attributed to the two things. First, is the rigidity of PBI which is retained even at elevated temperature due to its high thermal stability and second is the relatively higher increase in the diffusion of H_2 over that of CO_2 with temperature. Thus with increase in temperature if the polymer maintain its rigidity it is likely that the diffusivity of the smaller penetrant would benefit more than that of the larger penetrant. Development of such high performance polymeric asymmetric membranes can be best suited for high temperature applications such as water-gas shift reaction or reforming reactions for hydrogen production.

ICOM768

Synthetic Enzyme –Based CO_2 Separation Membrane

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Coal-fired power plants around the world emit ca. 9 billion tons of CO_2 each year, an amount large enough to raise concerns related to global climate change. However, capturing CO_2 at the power plant scale, toward sequestration or some form of utilization, is projected to be a difficult and expensive undertaking. Currently, the best available systems employ aqueous amine-based chemical scrubbing. In addition to their high capital and operating costs, these systems are problematic for a number of reasons including poor scalability, inflexible demands on installation footprint, costly consumables, offensive odors etc. From a power plant perspective, a passive, skid-mounted membrane-based separation system would indeed be a far more attractive solution.

In order to meet the dual goal of at least 90% capture combined with high purity of the CO_2 captured – and do so without a prohibitively large number of modules – it would be beneficial to utilize a membrane which has high selectivity as well as high permeance. Given the inherent difficulty to achieve this with typical organic or inorganic membrane materials, development of a fixed-carrier facilitated transport membrane is worth serious consideration, despite the poor track record of this concept with regard to commercial success.

To that end, a team led by United Technologies Research Center (UTRC) is developing a polymer-based membrane containing fixed carriers which interact with CO_2 selectively and reversibly. The fixed carriers are a “synthetic analogue” of carbonic anhydrase (CA), the enzyme used by all air-breathing organisms for CO_2 capture (at the cells) and release (at the lungs). The synthetic analogue, originally developed by Prof. Parkin of Columbia University, is a bio-inorganic compound which mimics the unique stereochemistry at the vicinity of the single zinc atom comprising CA's active site. Tests at Columbia and UTRC laboratories have confirmed the analogue's fast and reversible interaction with CO_2: this could provide a means to harness CA's power without the durability and cost implications associated with using the natural enzyme in a flue gas environment.

UTRC, in collaboration with Prof. Parkin, Hamilton Sundstrand, WorleyParsons, CM-Tec and GL Chemtec, was awarded one of the first-ever grants from ARPA-E, the new agency of the U.S. Department of Energy formed to fund high-risk / high-potential projects. The goal of the 2-year program is to evaluate technical and economic feasibility, with a target that the membrane-based separation system will result in ~30% lower incremental cost of electricity compared to amine-based systems. In addition to performance results to date, this presentation will discuss in more detail: 1) how the synthetic analogue mimics the active site of CA; 2) how it is being modified such that it can be incorporated into a polymer matrix; 3) a detailed separation system simulation which links membrane performance directly to cost of electricity; and 4) the effect of major flue gas contaminants (NO, NO_2, SO_2 and HCl) on membrane performance.

Membranes for extreme conditions 1

ICOM1803

Organic solvent nanofiltration, OSN – new frontier in technical scale molecular separation

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With the recent development of polymeric solvent resistant nanofiltration membranes, a new application area has emerged, known as organic solvent nanofiltration (OSN). A decade of developing OSN processes along with membranes of higher stability and performance has shown that the technology is capable of rejecting solutes from organic solvents as small as 200 g/mol. Generally speaking OSN is a pressure driven process in organic solvents, defined by a nominal molecular weight cut off (MWCO) between 200 and 1000 g/mol. The ability of separating on molecular scale at ambient or even sub ambient temperatures makes OSN interesting for versatile industrial applications. Several large scale OSN installation in different type of industries have already proven the significant cost savings through better purity, recovery, or throughput that this technology brings. Though the industry is rather reluctant to utilize new technologies, OSN is capable of generating significant benefit by providing unique separation solutions also in chemical, pharmaceutical and natural product industry. The main reasons that despite the clear process advantages only a few large-scale applications of OSN are established today are the limited quality of the first generation of OSN membranes and the lack of process know how. During the last years Evonik has explored the OSN technology in both laboratory and technical scale and helped to develop new generations of OSN membranes based on market leading polymer know how. The market-leading MWCO range and stability of the DuraMem^{TM} and PuraMem^{TM} series of membranes when combined with process integration provides a powerful tool for tackling a wide variety of separation challenges in the Pharma, fine chemicals and natural products sectors. Next to a market overview results of OSN membranes and OSN processes, as well as new developed applications will be presented.

ICOM428

High flux nanofiltration membranes for a broad range of organic solvents

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Organic solvent nanofiltration (OSN) is a straightforward tool for separation of substances from solvents. Since no phase change is needed the process consumes little energy, is of low cost and easy to perform. Inorganic membranes would be perfect for nanofiltration of organic solvents, however, besides higher costs often interact with solvents or solutes leading to fouling and low fluxes. On the other hand, organic polymer membranes swell in organic solvents and their selectivity and flux depend, therefore, on the solvent properties, i.e. polarity. Both forms porous membranes and dense thin-film composites are affected. So, polymer membranes may be suited only for similar organic solvents and hence limited in their application. To resolve this limitation cross-linking of the polymer is suited to limit the polymer swelling by solvents of differing polarity and standardize the properties of the membranes for organic solvent nanofiltration. High free volume polymers such as polyacetylenes or polymers of intrinsic microporosity (PIMs), are soluble only in a few solvents and swells considerably in other solvents. Their applicability for OSN was recently reported [1, 2]. We developed a simple method for targeted cross-linking by blending of the permselective polymer with a polyamine and heat treatment to yield solvent-stable thin-film composite membranes. SEM images shown in Figure 1 display the thin-film composite membranes of pure PIM-1 and a cross-linked PIM-1/polyethyleneimine (PIM-1/PEI) blend on polyacrylonitrile (PAN) support. The membranes were manufactured on a coating machine in square-meter quantities. The cross-linked PIM-1/PEI blend membranes were stable to all solvents including the solvent they are made from. The solvent stability of the PAN support only limits the use of the membranes. The retention and flux were measured applying polystyrene oligomers following a published procedure [3]. PIM-1 membranes without cross-linking showed a 90% retention at ~300 g/mol and >99% at ~400 g/mol with fluxes of 3 l/m^{2}hbar. The PIM-1/PEI cross-linked blend membrane was stable in THF and $CHCl_3$ and displayed in toluene a 90% retention at ~ 450 g/mol with flux of 3 l/m^{2}hbar.

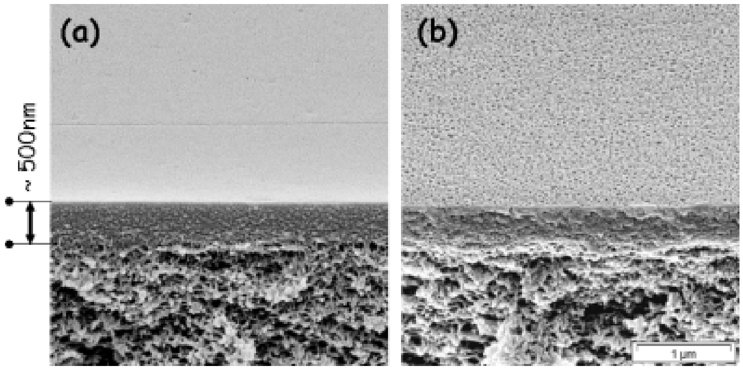

Fig. 1. Thin-film composite membranes on polyacrylonitrile support. Pure PIM-1 (a) and heat-treated, solvent-stable PIM-1/polyethyleneimine (8/2) blend (b).

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ICOM271

Organic Solvent Nanofiltration: a New Paradigm in Peptide and Oligonucleotide Synthesis

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In the last decade the market for peptide based pharmaceuticals has been growing rapidly. As of 2009 more than 60 synthetic therapeutic peptides have reached the American, European and/or Japanese pharmaceutical markets through a marketing authorization as APIs[1]. Antisense oligonucleotide (AO) and RNAi drugs are entering the market much slower – so far only a single AO drug (Vitravene) has been approved by FDA, but several are at phase III clinical trials. Despite series of failures big chemical and pharmaceutical companies as Pfizer, Eli Lilly, Evonik, Dow, Lonza are investing into synthetic oligonucleotide development[2]. Significantly, large-scale peptide/oligonucleotide manufacture faces important challenges related to molecular separation in between reaction cycles, and final product purification.

Nowadays solid phase synthesis is the dominant paradigm for peptide/oligonucleotide synthesis, used ubiquitously from discovery to production scale. However the solid phase approach produces coupling steps that may not be quantitative, introducing errors in amino acid/nucleotide sequences. It also entails an excess of reagents to overcome mass transfer limitations, and restrictions on solvent, coupling chemistry and protecting groups. Organic solvent nanofiltration (OSN) is a newly emerging technology capable of molecular separations in organic solvents. In this work we introduce a new technology platform which advantageously combines OSN with solution phase peptide/oligonucleotide synthesis, Membrane Enhanced Peptide/Oligonucleotide Synthesis (MEPS/MEOS). A first amino acid/nucleotide is linked to a soluble polymeric anchor. Through subsequent repeated coupling and de-protection steps, the peptide/oligonucleotide is extended to the desired length. The residual by-products and excess reagents after each reaction are removed by diafiltration through a solvent stable membrane which retains the peptide/oligonucleotide. The concept of Membrane Enhanced Peptide Synthesis (MEPS) is illustrated in **Figure 1**. Two pentapeptides are produced using this new technology. The purity of the peptides produced by MEPS is higher than that produced by solid phase synthesis, under the same conditions. This illustrates clearly that MEPS benefits from the advantages of solution phase synthesis, while avoiding the purification steps that have until now made solution phase synthesis practically difficult. A proof of concept example for di-nucleotide synthesis is also presented.

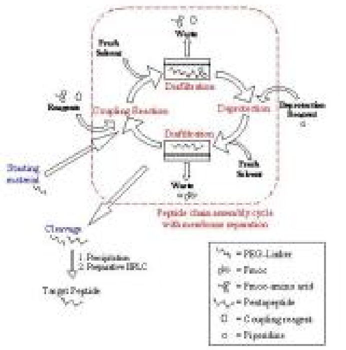

Figure 1: Schematic representation of the membrane enhanced peptide synthesis (MEPS) process[3]. Peptide chain assembly occurs via: 1) the coupling step; 2) a washing step for removal of excess reagents via constant volume diafiltration; 3) the deprotection step; 4) a washing step for removal of deprotection by-products and excess reagents. The cycle is repeated as many times as necessary, adding a further amino acid each cycle, until the desired peptide sequence is obtained. Reproduced by permission of The Royal Society of Chemistry http://dx.doi.org/10.1039/b926747f

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ICOM1475

Observations on the molecular weight cut-off of solvent resistant nanofiltration membranes.

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1. Background

Most of the studies on solvent stable membranes show that the transport mechanism for SRNF is much more complex than for NF in water. Organic solvents interact stronger with the membrane material as well as with the solute which sets high demands to a MWCO characterization method. Similarly to aqueous systems, the filtration of homologues series of oligomers seems to be an efficient way to determine the separation properties of SRNF membranes. However, the choice of solute and filtration conditions is still critical as is shown here.

2. Experimental

In this work the retention characteristic were studied systematically of two different SRNF membranes, dense composite α-alumina/PDMS hollow fibre (tailor made) and porous hydrophobic ZrO_2 membrane (purchased from HITK). We have chosen two broad range molecular weight oligomers, "rigid" polystyrene (PS) and "flexible" polyisobutylene (PIB). The retention characteristics of both membranes were tested in PS/toluene, PIB/toluene and PIB/n-hexane systems. In each case we performed permeation experiments under fully turbulent conditions in a cross-flow set-up operating at total recycle mode. The choice of the membranes was intentional, in order to study two extremes of SRNF membranes, the dense PDMS membrane with mostly solution-diffusion based transport and a porous ceramic with a dominant convective transport.

3. Results and Discussion

The MWCO of the -alumina/PDMS membrane was determined with toluene solution of 0.3% [w/w] PS and a similar solution of PIB. Toluene has a strong interaction with PDMS layer causing very strong volume swelling $\Phi_{toluene}=0.73$. The retention behaviour of the solutions as a function of pressure was determined and plotted:

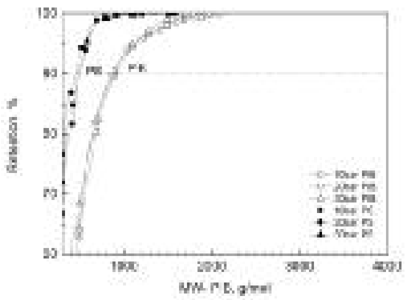

Figure 1: Retention curves of PIB and PS in toluene for composite α-alumina/PDMS hollow fibre membrane.

For both PS and PIB no significant effect of pressure on MWCO is found. Similar observations were made for the retention of composite α-alumina/PDMS capillary membranes in PIB/hexane system. The resulting MWCO for PS was 500Da, which was much lower than the one obtained using PIB; 900Da. The results show that, assuming a solution diffusion mechanism, the product of solubility x diffusivity for the PIB relates to that of PS having half the molecular weight.

Performing the same experiments for the porous hydrophobized ceramic membrane showed a stronger influence of pressure:

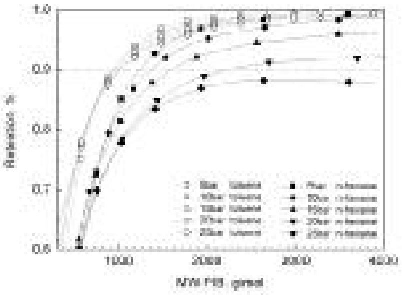

Figure 2: Retention curves of PIB in toluene and n-hexane for the ceramic hydrophobized zirconia membrane (HITK).

The dependence of the pressure of the molecular weight cut-off of PIB is remarkable. In both solvents PIB shows a decrease of retention with pressure. Of the two, hexane is the best solvent resulting in the largest radius of gyration of the oligomers. However, the retention is lower and decreases strongly with pressure. As leakage can be excluded a possible explanation could be found in the much higher flexibility of PIB. Deformation of the oligomers due to shear forces in the pores lowers the effective radius and increases the permeation. The results will be discussed and compared to include measurements and model calculations of concentration polarization effects.

ICOM1562

Decolorization of organic solvents with NF membranes

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In many processes in food, pharmaceutical and chemical industry solvents are being used as reaction and extraction medium of the end-product. Though the nature of the solvents is quite different they always have to be removed and recovered before the final end-product can be shipped. In the chemical and food processing industries there is a product need and a more or less regulatory driven need for environment-friendly low temperature processing for the recovery and re-use of organic solvents.

Membrane technology is a very suitable technique for such a requirement. Membrane systems can be operated in a wide range of aggressive organic solvents. A very robust membrane has been developed that can be used for a broad range of applications. This membrane is the heart of technical purification set-ups to be sold.

Particular use of this membrane technique is in decolorization of solvents. This as such includes many different industries again food additives, paints, lubricants. In these streams many other components are present, apart from the solvent. All these components influence the performance of the membrane. Sometimes components directly have an influence that is directly found in lab experiments. In other cases long-term piloting reveal the occurrence of fouling phenomena.

We will address the development of a process for decolorization of solvent starting from very small scale in the lab several years ago to current implementation on industrial scale. Aspects of scale-up, fouling and cleaning will be addressed.

Small scale filtration

Industrial unit yielding clean solvent

NF/RO 1

ICOM1831

Crosslinkable Chlorine Resistant Membranes for Reverse and Forward Osmosis (RO, FO)

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Collaboration between Virginia Tech and the University of Texas (Austin) was initiated about five years ago. It focused on transforming fundamental knowledge of polymer science to produce reverse osmosis membranes suitable for use in drinking water, wastewater purification and osmotic power. Our work has demonstrated that disulfonated poly (arylene ether sulfone) (BPS and BPSH) random and block copolymers are an interesting and novel platform for new RO and FO membranes . The materials have high water permeability, fouling resistance and good salt rejection, particularly at low ionic strength. Overall, they are highly tolerant of chlorine exposure, which has been an Achilles heel for polyamide RO membranes. The current state-of-the-art membranes are extremely sensitive to chlorine and are rapidly degraded by it. Hence, their ability to function as an RO membrane drops rapidly after exposure to even modest amounts of chlorine.

It has been of great interest to develop materials for highly chlorine resistant membranes as a very practical and inexpensive method of disinfecting water can be used in conjunction with RO to prepare safe drinking water. This has been demonstrated and has attracted the attention of both industry and government in the U.S., Europe and Asia. To exploit this finding and reduce it to practice, more fundamental studies are ongoing to explore the rejection properties of these materials to a variety of salts and salt mixtures of interest and determine whether or not such materials can be made into thin film composites.

Recently, we have been successful in preparing thin film composites (TFC) through the use of selective solvents for the ionomer relative to the traditional porous polysulfone support. We are also exploring novel supports which have recently been developed commercially and in our laboratory.

Synthesis and characterization of these materials, including post casting crosslinking studies are ongoing which are advantageous for generating smooth surfaces, controlling water swelling and increasing salt rejection. Several methodologies are being pursued and will be discussed . This new research is intended to develop membrane systems which are expected to have adequate permeability and improved sodium chloride rejection (>99%).

ICOM858

Preperation of biomimetic membrane using supported lipid bilayer as separating layer

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Seawater desalination by membrane filtration is operated using polymeric membranes in commercial scale. Recently, biomimetic membranes are receiving much attention as one of innovative technologies. In biological membranes, transportation of water and ion is mainly carried out by membrane-spanning proteins. This transpor-tation system has high selectivity and efficiency. Therefore, some biological membranes have higher permeability and selectivity than conventional polymeric membranes. However, biological membranes are usually driven by osmotic rather hydraulic pressure. Previous work has been reported about the feasibility of adopting biomimetic membranes for water treatment driven by hydraulic pressure. In the report, it was proposed to use a commercial nanofiltration (NF) membrane as a support for biomimetic lipid bilayer membranes. In this study, we prepared a supported lipid bilayer (SLB) on the NF membrane and incorporated a water channel into the SLB by self-assembling method.
First, positive charged liposomes were prepared. 1,2-Dimyristoyl-sn-glycero-3-phosphocholine, 1,2-Dimyristol-3-trimethylammoniumpropane, amphotericin B (AmB) and ergosterol was dissolved in a mixture of chloroform and dimethyl sulfoxide. 1,2-Dimyristoyl-sn-glycero-3-phosphocholine comprises lipid bilayer membrane and 1,2-Dimyristol-3-trimethylammoniumpropane is positive charged material. The combination of AmB and ergosterol is components for the formation of the water channel. Multilayered lipid bilayer was obtained on the wall of eggplant flask after evaporation of the solvents. Milli-Q water was added to the lipid bilayer and the flask was shaken to produce liposome. Freezing and thawing method and extruder was used to obtain the mono-disperse of liposome. Then, the liposome was placed in contact with a commercial NF membrane that has nega-tive charge. The liposome was then adsorbed on the NF membrane surface and self-assembled to form SLB by electrostatic interaction. The water permeability and rejection of obtained membranes were measured at 0.75 MPa using Milli-Q water and a 500 ppm NaCl solution, respectively.
The membrane prepared without water channel showed a water permeability of 6.6×10^{-3} L m^{-2} h^{-1} atm^{-1} and a NaCl rejection of 97 %. As the rejection of NaCl for support NF membrane is 60%, it is confirmed that dense structure was introduced on the support membrane. In the case of SLB prepared with ergosterol, water permeabil-ity increased to 3.2×10^{-2} L m^{-2} h^{-1} atm^{-1} as shown in Fig. 1. Fig. 2 represents that this membrane has a NaCl re-jection as high as 95%, which is slightly lower than SLB without the water channel. This is because fluidity of the SLB largely affects the membrane performance. The water permeability significantly increased to 1.4×10^{-1} L m^{-2} h^{-1} atm^{-1} in the case of SLB with water channel introduced by using ergosterol and AmB. This result suggests the combination of ergosterol and AmB makes effective channel in the liposome due to high affinity between them.

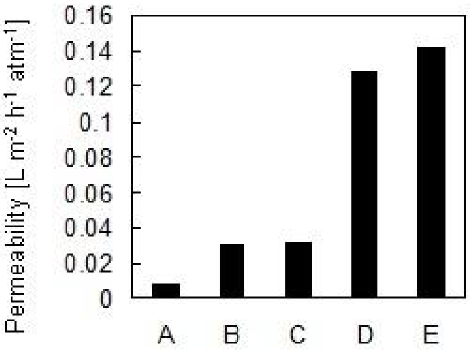

Fig. 1 Effect of SLB composition on permeability.
(A) SLB (without water channel).
(B) SLB with 10wt% ergosterol.
(C) SLB with 30wt% ergosterol.
(D) SLB with 14% ergosterol and 14% AmB.
(E) SLB with 20% ergosterol and 10% AmB

ICOM166

Lyotropic Liquid Crystal Polymer Membranes with Uniform, Sub-1-nm Pores for Molecular Size-based Water Separations: New Designs, Pore Size Control, and Processing

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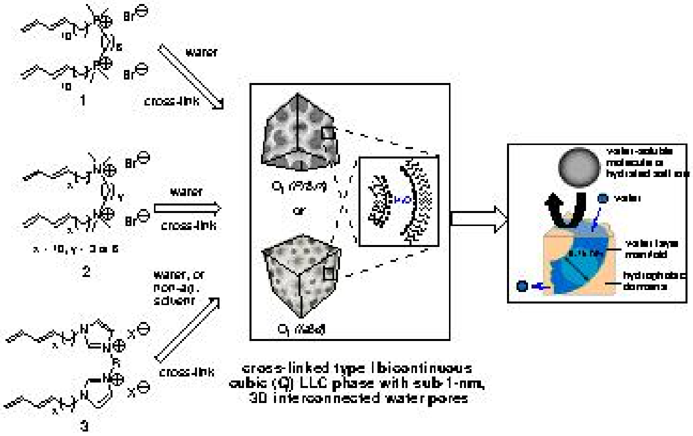
Aqueous separation processes employing polymer membranes with pore sizes in the 1 to 100 nm range are very important in industry and healthcare. Unfortunately, current porous membrane technologies afford extremely poor control over critical features such as pore size, pore architecture, and pore density in this small size regime. Our research team recently developed a new type of nanofiltration (NF) membrane material that contains uniform, sub-1-nm pores that can completely reject water-soluble molecules and hydrated salt ions larger than the pores. This new polymer material is made via the cross-linking of lyotropic (i.e., surfactant) liquid crystal (LLC) monomers that self-assemble in water into phase-separated assemblies containing sub-1-nm-scale water domains, affording a new type of water desalination membrane that operates by molecular sieving instead of traditional reverse osmosis. First-generation membranes of this type were based on a gemini phosphonium LLC monomer (**1**) that can be cross-linked in a type I bicontinuous cubic (QI) phase that has 3D interconnected, 0.75-nm wide annulus-like water channels. Although this material is able to perform water NF and desalination, monomer **1** is very difficult and expensive to synthesize and process. These features made monomer **1** impractical for scale-up or fundamental thin-film processing studies, which are both important for potential commercialization. In this presentation, we present several new advances in this area of nanoporous membrane materials research. First is the design of a new, easier-to-synthesize gemini ammonium-based, Q_I-phase LLC monomer (**2**) that significantly reduces the synthesis cost of the LLC polymer system. Monomer **2** has a slightly larger nanopore width of 0.86 nm. However, its more facile and modular synthesis allows convenient scale-up, entry into initial thin film processing studies, and even tuning of its structure to potentially modulate effective pore size. The aqueous NF performance of this new LLC material, and the results of studies to adjust its Q_I-phase effective pore size via systematic monomer modifications will be presented. Second is the design of several new gemini imidazolium-based LLC monomers (**3**) that not only have facile, inexpensive, and modular construction but also a propensity to form LLC phases with several non-aqueous solvents instead of water. The synthesis, polymerization, and water NF performance of supported membranes made from these 3rd-generation monomers will be presented. The results of studies to adjust their pore size via monomer modifications and the use of different non-aqueous solvents instead of water in the LLC phase formation will be presented. Initial results on preliminary thin-film processing studies for both the 2nd- and 3rd-generation Q_I-phase LLC monomers will also be presented. Finally, some speculative designs for new, more advanced Q-phase LLC monomers and polymers for water NF/desalination applications will also be discussed.



ICOM1611

Tuning Transport Selectivity in Carbon Nanotube Membranes with ALD

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Recently, several experimental investigations validated the MD prediction of an exceptionally fast fluid flow for both gases and liquids in carbon nanotube pores. For example, the measured water flow exceeds values calculated from continuum hydrodynamics models by more than three orders of magnitude; for gases, measured transport rates exceed Knudsen model prediction by two orders of magnitude [1]. These results generated great interest for the application of CNT as nanofluidic channels in several areas ranging from desalination and carbon capture, to drug delivery and single molecule sensing. For these applications, a fundamental understanding of the selectivity of these pores for specific molecules is needed and, unfortunately, still lacking. Also, robust strategies to precisely control the transport selectivity of CNTs are required.

In this work, we demonstrated that atomic layer deposition can be successfully applied to modify and improve the transport selectivity of carbon nanotube pores for small molecules. For our selectivity studies, we used a nanofluidic platform consisting of a silicon nitride membrane with well-aligned, sub 2-nm carbon nanotubes as pores [1]. Pressure-driven filtration of small ions is investigated before and after functionalization by atomic layer deposition and as a function of solution pH. Our results show that only a few ALD cycles are sufficient to tune ion selectivity of these membranes without loss of their ultra-fast transport rates. For example, sulfate ions are almost completely rejected by Al_2O_3 modified CNT pores when solution pH is above alumina *pKa*, whereas unmodified CNTs reject these anions only partially and for pHs greater than the *pKa* of carboxylic groups [2-3].

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS- 418587

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ICOM1612

Advanced RO/NF performance of TMC (trimesoly chloride)/MPD (metaphenylenediamine)-based polyamide membranes

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Water purification technology has attracted increasing attention because of water shortages and the lack of access to safe drinking water. Recently, new classes of functional materials have been applied to develop reverse osmosis (RO) and nanofiltration (NF) membranes with increased water permeability, high salt rejection, less fouling and excellent stability. Inorganic-organic nanocomposite membranes are quite interesting because they showed increased flux by incorporating inorganic materials as such as zeolite [1] and TiO_2 [2] without significant decrease in rejection. In this paper, our recent progresses in TMC (trimesoly chloride)/MPD (metaphenylenediamine) based polyamide (PA) RO and NF membranes will be discussed.

Thin film composite (TFC) PA membranes are typically prepared by interfacial polymerization (IP) of m-phenylene diamine (MPD) in aqueous phase and trimesoyl chloride (TMC) in organic phase on polysulfone ultrafiltration supports. Our strategy to enhance RO/ NF performance of TFC-PA membranes includes (a) addition of additives in organic phase [3], (b) inorganic-organic nanocomposite membranes with zeolite nanoparticles [4], (c) inorganic-organic nanocomposite membranes with metal alkoxides [5], and (d) two-step interfacial polymerization.

Polyamide membranes with controllable thin dense layer and effective "nanopores" were fabricated by adding co-solvent (acetone) to nonpolar organic phase (hexane), referred to as co-solvent assisted interfacial polymerization (CAIP), which exhibited a high water flux with no considerable salt rejection loss. Higher co-solvent added into the hexane solution resulted in a relatively large pore size as well as higher water flux. The best nanocomposite membrane that was prepared with a certain amount of acetone showed approximate 4 times higher water flux with no considerable rejection loss than that of polyamide membranes fabricated without acetone. [3]

A promising nanocomposite membrane was fabricated for use in water purification by pre-assembling zeolite nanocrystals on a polysulfone ultrafiltration support. Zeolite crystals were successfully incorporated into a polyamide membrane, which provided a preferential flow path through incorporated zeolites for water permeability. The as-prepared membranes exhibit 5-times high water permeability with no considerable loss of capacity for salt rejection (>95%). [4]

Inorganic-polyamide nanocomposite membranes were successfully prepared via metal-alkoxide-assisted IP, using three types of metal-alkoxides: titanium tetra isopropoxide, bis (triethoxy silyl) ethane and phenyl triethoxy silane. The best nanocomposite membrane that was prepared with phenyl triethoxy silane showed approximate 2 times higher water flux with no considerable rejection loss than that of pure polyamide membranes [5].

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Membranes for drinking water 1

ICOM1838

Innovations in membrane technology for drinking water treatment

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Only a few processes in the drinking water treatment technology are as strongly characterized of innovations as the membrane technology. In particular within the range of the low pressure membrane processes ultra- and microfiltration (UF and MF) it came in the last years due to the not standardised systems in this segment and the high stress of competition to a constant advancement. Membrane materials and membrane designs has being optimized with the goals of ensuring larger stability against membrane defects as well as for higher back wash fluxes and of achieving a higher removal rate for smallest colloids without decreasing permeability. Further on membrane materials and membrane geometry are adapted better to the appropriate treatment tasks as for example the pretreatment in seawater desalination. New module designs with higher packing densities allow the use of such materials, which are otherwise not competitive due to their specific price. The footprint of a membrane system will constantly be designed smaller, in order to minimize the attended costs, here in particular for the construction unit. Not only the systems have been continued improved consistently, but also the process itself. Back washing processes have been conducted more effective, sophisticated algorithms for controlling of filtration intervals and of recovery have been developed and above all synergistic potentials of hybrid treatment combinations have been investigated and used.

Within the range of the medium and high pressure membrane processes nanofiltration (NF) and reverse osmosis (RO) in particular the optimization and development of membrane material are advanced, in order to reduce further the power requirement by higher permeabilities, but also, in order to reduce the affinity to fouling. The modification of membrane modules, e.g. by optimization of the design of spiral elements spacer, has likewise the goal to reduce the fouling potential. In the last years the emphasis during the module development lay however on the enlargement of the membrane surface per element and the associated decrease of the required space. New or again discovered processes like membrane distillation, electrodialysis and forward osmosis have been intensively investigated, in order to exhaust their potential especially for drinking water treatment.

Due to the many advantages, achieved by membrane applications, these are dominant on the international market for the seawater desalination and for the advanced treatment of purified waste water. Here the low pressure processes MF and UF have been applied frequently as pre-treatment for an upstream sea water desalination system. Currently the investigation emphasis is set on the optimal trade-off of the two processes. Further on, the excellent scalability of membrane plants allows their use also for decentralized systems. Thus in the past years there were efforts to optimize the processes on the special requirements of small plants and to reduce the use of chemicals to a minimum.

The presentation will highlight especially the aspect of new materials for low pressure membrane systems and the synergistic combination with other treatment processes but will also cover briefly new developments in high pressure membrane processes for drinking water treatment.

ICOM624

FEASIBILITY OF DESALINATION OF BRACKISCH GROUNDWATER AND CONCENTRATE DISPOSAL BY DEEP WELL INJECTION

Nico Wolthek[1], Klaasjan Raat[2], Jan Arie de Ruijter[3], Antoine Kemperman[4], Ate Oosterhof[1]

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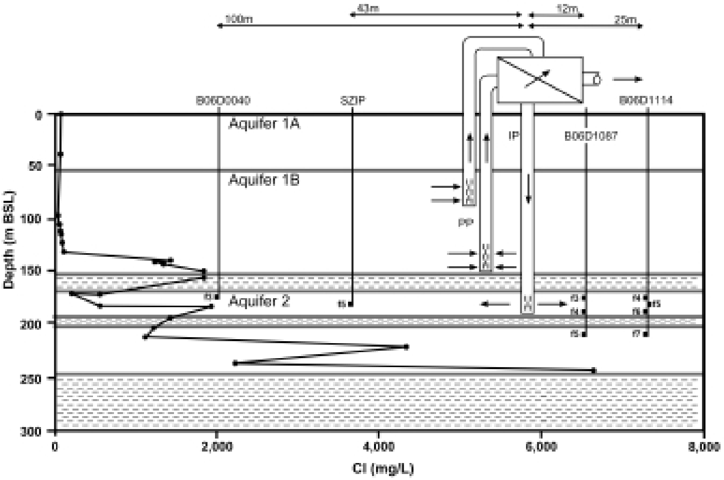
In the province of Friesland (in the Northern part of the Netherlands) problems have arisen with the abstraction of fresh groundwater due to salinization of wells by upconing of brackish water. A solution to this problem is to intercept (abstract) the upconing brackish water, desalinate it with BWRO and dispose the concentrate in a deeper, confined aquifer. The fresh-brackish interface in the source aquifer is stabilized by simultaneous abstraction of the fresh and brackish parts. After desalination, the abstracted brackish water provides an additional source for drinking water. To demonstrate the feasibility of this concept a pilot study was set up.



During one year about 220.000 m^3 of concentrate was produced and injected. The reverse osmosis installation was operated under anaerobic conditions without pre-treatment and antiscalant dosing. Despite the high iron concentrations (40 mg Fe/l) in the feed water the installation performed very stable. Although the concentrate was supersaturated towards carbonate and phosphate minerals (SI > 1), scaling or fouling of the membranes did not occur at recoveries of 50, 70 and 75 %. The mass transfer coefficient (MTC) or normalized flux (at 10 °C) was stable at $0.85 \cdot 10^{-8}$ m s^{-1} kPa^{-1}. Water quality changes in the target aquifer were monitored by two observations wells, at 12 and 24 m distance from the injection well. Also the injection of the supersaturated concentrate did not lead to mineral precipitation in the target aquifer, indicating that deep well injection is technically feasible without risks of injection well or aquifer clogging. The fresh-brackish water interface in the source aquifer remained stable by the simultaneous abstraction of fresh and brackish water. This showed that the so called “fresh-keeper” concept works in practise, providing a successful remedy against salinization of fresh water abstraction wells. Overall the pilot study showed that brackish groundwater provides an excellent , additional source for drinking water in the Netherlands or in other coastal areas worldwide, where fresh groundwater is scarce or where fresh water wells are threatened by salinization.The Dutch government supported this project with an innoWATOR grant. Partners in the project are Vitens, KWR Watercycle Research Institute, Hatenboer-Water and University of Twente.

ICOM1234

Additional Feed Pressure (Pulsation) to Increase Forward Osmosis Membrane Performance

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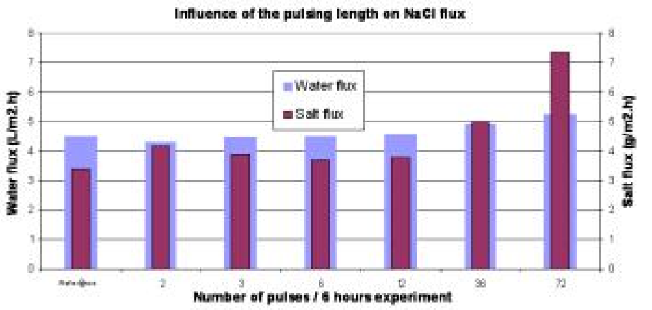
Forward osmosis (FO) is a concentration driven membrane process by an osmotic solution which gained a considerable amount of interest in the membrane research community in recent years. Advantages of FO are (i) low energy consumption, (ii) high product quality and (iii) lower fouling propensity compared to state of the art pressure driven membrane processes, such as reverse osmosis. Challenges include a limited flux due to internal concentration polarization, reverse salt transport (salt leakage) and a need for post treatment to recuperate or eliminate the osmotic solution. Flux optimization is carried out by improving membrane properties (thinner and more open support layers to reduce internal concentration polarization), optimizing osmotic solutions (NaCl and $MgCl_2$ are preferred solutions) and process related properties, e.g. temperature, flow conditions. In this paper the use of (i) additional hydraulic pressure at the feed side and (ii) pulsating feed pressure were applied in an attempt to reduce internal concentration polarization and increase FO membrane performance (water flux and reverse salt flux). Pulsation length and frequency was investigated. To the authors knowledge this is the first attempt to increase FO performance using these techniques.

FO laboratory experiments were carried out in a U-tube set-up in which the membrane (112 cm^2) was positioned in a membrane holder with additional support on both sides. The two compartments of the laboratory set-up contained respectively the feed solution (DI-water) and the draw solution (0.5 M NaCl and 0.33 M $MgCl_2$) which were circulated to diminish external concentration polarization. The pressure in the feed side compartment could be increased by air pressure and a pressure reducer (in a range of 0-1 bar). Pulsation was carried out by controlling an automatic valve at the pressurized air inlet, varying the pulsation frequency (in a range of 1x per 5 minutes .to 1x per 3 hours) and pulsation length (in a range of 1 to 30 minutes).

FO flux and reverse salt flux increased when the feed pressure increased. FO flux doubled when an additional feed pressure was applied of 0.8 bars. The reverse salt flux, however, increased more than this, resulting in an increase of the salt to water flux ratio in function of additional feed pressure. FO flux and reverse salt flux increased in function of feed pressure pulsation only at high frequencies (> 1x per 30 minutes)



. The salt to water flux ratio increased in function of the feed pressure pulsation.

Because of the increase in (reverse) salt to water flux as a result of additional feed pressure and feed pressure pulsation these techniques to improve the performance of FO membrane does not seem to be successful. In future these techniques will be investigated to diminish the potential negative effects of fouling in FO. Furthermore, possible mechanical breakdown due to additional feed pressure and feed pressure pulsation might be an issue.

ICOM621

HORMONE SORPTION ONTO POLYMERIC MEMBRANE MATERIALS

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The presence of steroidal hormones in surface water is becoming a major concern as current wastewater treatment technology does not effectively remove these compounds (1).

Polymeric membranes, considered as physical filters, can remove micropollutants without chemical addition. Nanofiltration (NF) in particular has been studied for the removal of hormones in the past few decades (2,3).

The retention of hormones with NF varies significantly depending on many factors such as retention mechanisms, membrane characteristics, hormone characteristics and operating conditions. Retention mechanisms affecting the performance of the NF membranes for hormone removal can be summarized as size exclusion, charge repulsion, sorption/diffusion, solute-solute interactions and adsorption. Several studies have shown that adsorption plays a very important role in hormone retention by NF membranes (2,3).

Hormone adsorption to membrane polymers is highly dependent on the physical and chemical characteristics of the material and the interaction mechanisms between these two (4). Chemical interactions such as hydrogen bonding and hydrophobic interactions are considered the mechanisms responsible for sorption. However, none of these interactions can explain the difference between the hormone sorption affinities of different polymers. Moreover, these interactions have neither been systematically investigated nor quantified in water samples.

Sorption affinity of several commercially available polymers (polyamide (PA), polypropylene (PP), polysulphone (PSU), polyethylene naphthalate (PEN), polystyrene (PS), polyethylene terephthalate (PET), cellulose (CEL), PVDF, polyethylene high density (HDPE), polyethersulphone goodfellow (PES GF), poly(2,6 dimethyl 1,4-phenylene oxide) (PPO), polyethersulphone Radel (PES R), polysulphone Udel (PSU U) and poly(methyl methacrylate) (PMMA)) is investigated for steroid hormones. Four different types of hormones, estradiol (E2), estrone (E1), testosterone (T) and progesterone (P), are used and sorption isotherms are determined for each polymer and hormone at different pH conditions. A selection of results is presented in Figure 1 showing that affinity of E2 to PA is the highest compared to other polymers. PES is another polymer type with relatively high E2 sorption affinity. Kinetic experiments show that the sorption process takes half an hour to reach equilibrium for all polymers.

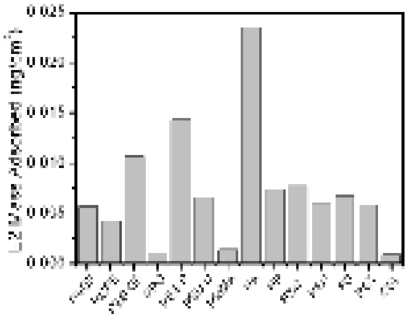

Figure 1. Estradiol (E2) sorption to different polymer materials

Responsible interaction mechanisms are systematically investigated for each hormone and specific polymer by studying the bonding affinities. Hydrogen bonding, hydrophobic interactions and π-π interactions are considered the main responsible mechanisms for hormone sorption on polymers. Quantification of these interactions are investigated and proposed to be used in membrane characterisation.

Understanding and quantifying the sorption capacity of different polymers as well as the interaction mechanisms between specific type of polymer and hormone will both help improving the removal of steroids from water by improving membrane selection and allow more specific manufacturing.

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ICOM572

Improvement of anti-fouling potential of anion exchange membrane by surface modification with polyelectrolyte in electrodialysis system

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The desire to make drinking water by treating ground water, surface water, seawater and so on has been increasing. An electrodialysis (ED) is one of the useful methods and has applied to make the drinking water as well as RO and NF membranes. Especially ED is utilized to deionize harmful ions like F^- and NO_3^-. Most of organic compounds contained in these feed waters (humate, surfactants, proteins and others) have a negative charge and cause a fouling of anion exchange membrane (AEM). The fouling of AEM causes increase of membrane resistance and is a very serious problem in ED. If AEM is given a negative surface charge, the anti-fouling potential will be improved by an electric repulsion between surface charge and foulants. In this paper, the improvement of anti-fouling potential of AEM is tried by modifying the AEM surface with a negative polyelectrolyte. AMX (Astom Corp.) was used as AEM and poly(sodium 4-styrene sulfonate) (PSS) as negative polyelectrolyte. Sodium dodecylbenzene sulfonate (SDBS) is used as foulant. One surface of AMX was modified by contacting with PSS solution for 30 min. After modified surface was rinsed with water, AMX was set in the experimental cell. Figure 1 shows the experimental setup.

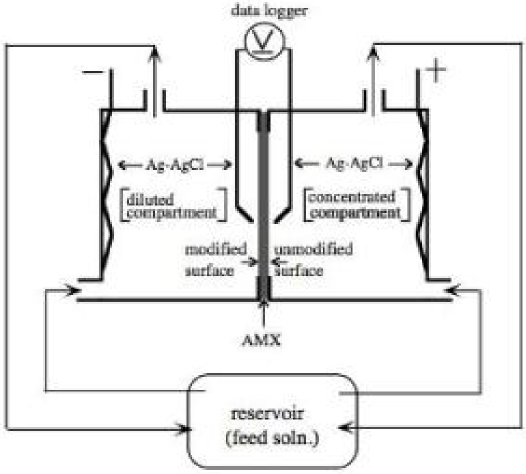

Fig. 1 Experimental setup

0.05 M NaCl + x mg/l SDBS aqueous solution was used as a feed solution. Here, x is variable. The electric current was constant as 0.2 mA/cm^2. The fouling was detected by the increase of a potential difference across AEM, ΔE. ΔE is constant if the fouling does not take place, since the diluted solution is not changed during ED. The elapsed time until the fouling (transition time) was measured from the time course of ΔE. There was an optimum concentration of PSS to improve the anti-fouling potential and it was 0.3 g/l. The optimum condition is determined by a combination of the charge density and the hydrophobicity of AMX surface. Figure 2 shows the transition time for unmodified membrane and modified membrane with 0.3 g/l PSS as a function of SDBS concentration.

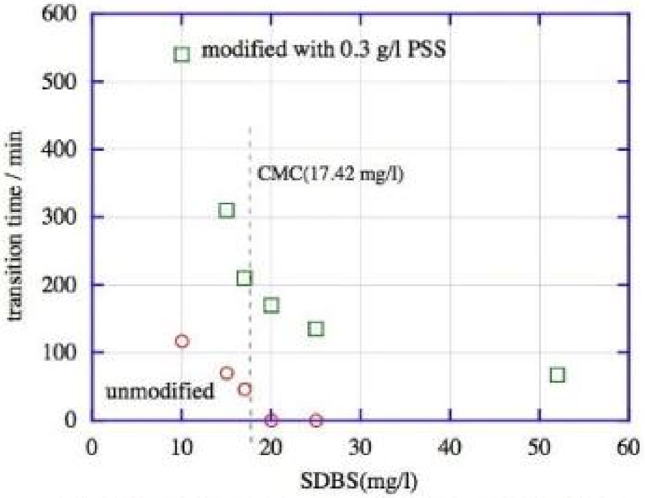

Fig. 2 Transition time for unmodified and modified AMX

From Fig.2, it is found that the transition time decreased with SDBS concentration and became zero over CMC for unmodified membrane. This phenomenon indicates that the fouling is due to micell. On the contrary, the transition time for modified membrane is longer than that for unmodified membrane. The transition time for modified membrane is not zero over CMC. It is clear that the anti-fouling potential of AMX is improved by the surface modification with PSS.

Parallel Sessions

Monday, July 25th 2011

Afternoon Session 1, 14.00 – 15.30

Membrane and surface modification 1

ICOM1776

Membrane and Surface Modifications

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The most compelling reasons why it is attractive to modify existing synthetic membranes rather than develop a new polymer *a priori* are cost and speed for implementation. Several approaches have been pursued and will be addressed including wet chemistry, polymer phase separations and irradiating methods like ultraviolet light and low-pressure plasma. The most challenging aspect for membrane and surface modification is selection of the appropriate chemistry for optimizing the performance of a particular application. To meet this challenge, we offer a novel high throughput method for synthesis and screening of customized protein-resistant surfaces. This method is an inexpensive, fast, reproducible and scalable approach to synthesize and screen protein-resistant surfaces appropriate for a specific feed. The method is illustrated here by combining a high throughput platform (HTP) approach together with our patented photo-induced graft polymerization (PGP) method developed for facile modification of commercial poly(aryl sulfone) membranes. We demonstrate that the HTP–PGP approach to synthesize and screen fouling-resistant surfaces is general, and thus provides the capability to develop surfaces optimized for specific feeds. Surfaces were prepared via graft polymerization onto poly(ether sulfone) (PES) membranes and were evaluated using a protein adsorption assay followed by pressure-driven filtration. We have employed the HTP–PGP approach to (i) confirm previously reported successful monomers, (ii) develop new antifouling surfaces from a library of 66 monomers for four different challenges of interest to the biotechnology community: hen egg-white lysozyme, supernatant from Chinese Hamster Ovary (CHO) cells in phosphate buffered saline (PBS) solution as a model cell suspension, and immunoglobulin G (IgG) precipitated in the absence and presence of bovine serum albumin (BSA) in high salt solution as a model precipitation process, (iii) optimize grafting of polyethylene glycol using solvents, and (iv) determine optimal surface chemistries for biotechnology (e.g. substrata for stem cell proliferation without differentiation) and a medical application (e.g. mucus resistance). Besides these applications, advantages, limitations and future plans to address some of the limitations will also be discussed.

ICOM888

Membrane Hydrophilization Using Electron Beam and Plasma Techniques

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Today, micro- and ultrafiltration membranes are predominantly fabricated from synthetic membrane materials such as polyethersulfone (PES), polyvinylidene fluoride (PVDF), or polyamide (PA). The diversity of applications necessitates the modification of the polymer in order to avoid any fouling of the hydrophobic membrane surfaces or to achieve a functionalized membrane.
Here, we present two different methods using electron beam irradiation and combined plasma and electron beam treatment for permanent hydrophilization of polymer membranes. No catalysts, photoinitiators, organic solvents or other toxic reagents were used, and no additional synthetic or purification steps are required.

1. Electron Beam Modification

A new method for the straightforward and permanent functionalization of polymer membranes, using small molecules bearing diverse hydrophilic functionalities (Figure 1) was developed.[1] The approach combines surface activation of the matrix polymer and the simultaneous immobilization of small molecules by use of low-energy electron beam (EB) in an aqueous system. The procedure guarantees for the permanent immobilization of hydrophilic small molecules on the membrane polymer. It neither requires any preceding surface functionalization nor the use of catalysts/photoinitiators or other toxic reagents. In addition, it prevents the synthesis of hydrophilic monomers/polymers, thus avoiding additional synthetic and purification steps as well as the use of organic solvents.

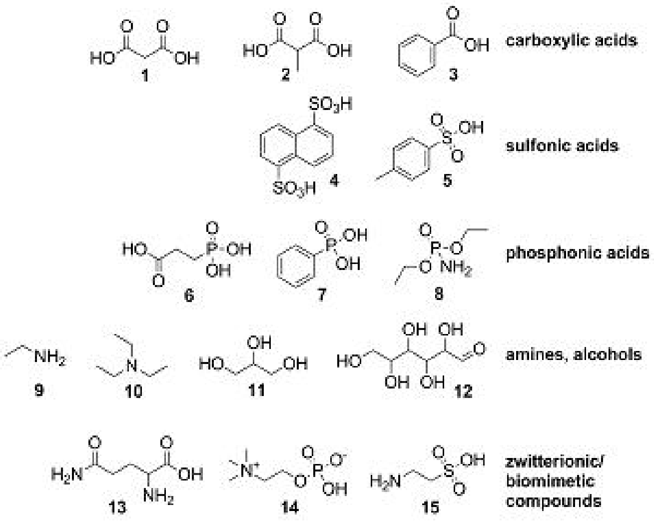

Figure 1 Functional molecules that were used for membrane modification.

Since the use of EB activation allows for operating independently from specific functionalities present at the matrix polymer's surface, the method can be adopted to a vast variety of base membrane polymers, e.g., PES or PVDF. Furthermore, EB is capable of interpenetrating polymeric membranes. This way, the inner surface of the membrane is also activated for the desired modification reactions.
With selected functional molecules, this simple modification procedure resulted in significantly increased flux and hydrophilicity accompanied by decreased fouling and protein adsorption at the membrane surface as demonstrated for different proteins.

2. Combined Plasma and Electron Beam Treatment

Plasma modification is a powerful method for hydrophilization of polymer surfaces. However, after common plasma treatment hydrophobic recovery is very often observed leading to increasing contact angles within several days or even weeks.[2-4]

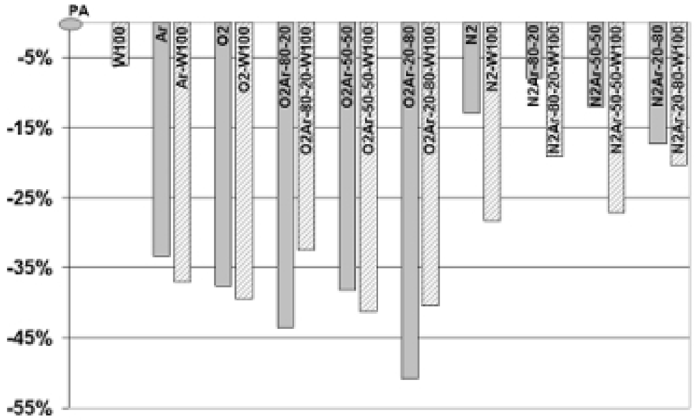

Figure 2 Variation of water contact angle at the surface of PA membranes treated with 100 kGyEB and/or selected mixtures of O_2/Ar and N_2/Ar gases plasma for 5 min. (PA is the untreated membrane; W100 corresponds to the EB wet treatment and for plasma treatment volume ratios are indicated after the gases mixtures).

In the present study, plasma modification was "fixed" by subsequent EB irradiation due to cross-linking of the polymer chains to prevent any macromolecular motions. The plasma gases used in this study were O_2, N_2, Ar and various mixtures thereof. The membranes are soaked in water few minutes after plasma treatment and then exposed to EB irradiation. The modified membranes were characterized through measurements of water contact angle, flux and protein adsorption.

Plasma treatment followed by EB irradiation in wet condition always improved the wettability (Figure 2) and reduced the protein adsorption at the surface of the membrane compared with the use of plasma treatment alone.

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ICOM1511

Multivalent Immobilization of Antimicrobial Peptides on Reverse Osmosis Membranes as a Promising Approach to Reduce Biofouling

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Because of the growing demand for fresh drinking water in the world, there is a necessity for improving desalination techniques, such as reverse-osmosis (RO) and nanofiltration (NF). A major problem in RO and NF is fouling, and the most rigorous type of fouling is biofouling. Numerous strategies have been used to resolve the biofouling problem; however, an effective solution for overcoming biofouling has not yet been developed.
Here we describe a novel approach to reduce biofouling by the inhibition of biofilm formation on RO and NF membranes, in which a construct of multivalent antimicrobial peptides (AMPs) is attached to the membrane surface (Figure 1).

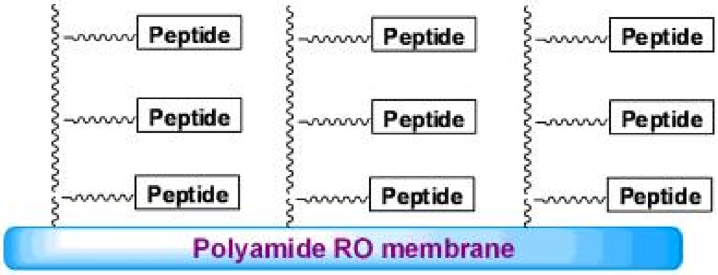
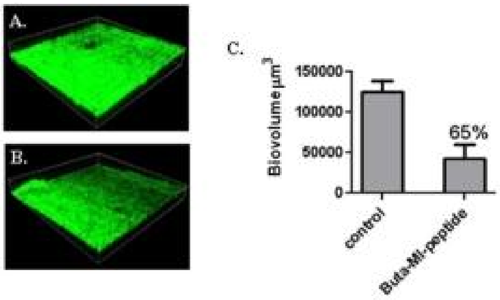


Figure 1: *A schematic representation of our approach to the multivalent immobilization of antimicrobial peptides on RO membranes.*

Antimicrobial peptides were chosen because they are active against a wide range of bacteria, bacteria do not develop resistance to them and they are non-toxic to humans. The present work is focused on design and synthesis of multivalent structures of AMPs attached to the surface of RO membranes, through the use of graft polymerization of acrylic monomers, as was shown previously by S. Belfer and her coworkers in our department [1].
Initially, we converted the surface of the BW-30 RO polyamide membrane into a multivalent structure through graft polymerization of methacrylic acid and polyethylene glycol methacrylate to create polymer-brushes. Subsequently, we attached to the polymer construct the AMPs Modelin-1 and Hexapeptide-4, which were recently found in our lab to be active in high-salinity solutions [2]. Characterization of the modified membrane surface was done by ATR-FTIR and water-drop contact-angle techniques. Evaluation of the inhibition of biofilm growth of *Pseudomonas aeruginosa* on the membranes was performed by CLSM quantification. It was found that multivalent immobilized AMPs successfully inhibit biofilm growth on the RO membrane surface (Figure 2).



<u>Figure 2</u>: *Biofilm growth detected on* ***(A)*** *unmodified membrane (control),* ***(B)*** *membrane modified with graft polymerization, 1,4-butadiamine, MI and C-Modelin-1,* ***(C)*** *volume of the biofilm formed on the examined membranes.*

This study is an important step toward development of a novel approach for the inhibition of biofilm growth and biofouling of aromatic polyamide RO and NF membranes.

Acknowledgements:

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of Industry, Trade and Labor for financial support; we thank Ms. Roza Fainshtein (BGU) for assistance in graft polymerization on RO membranes.

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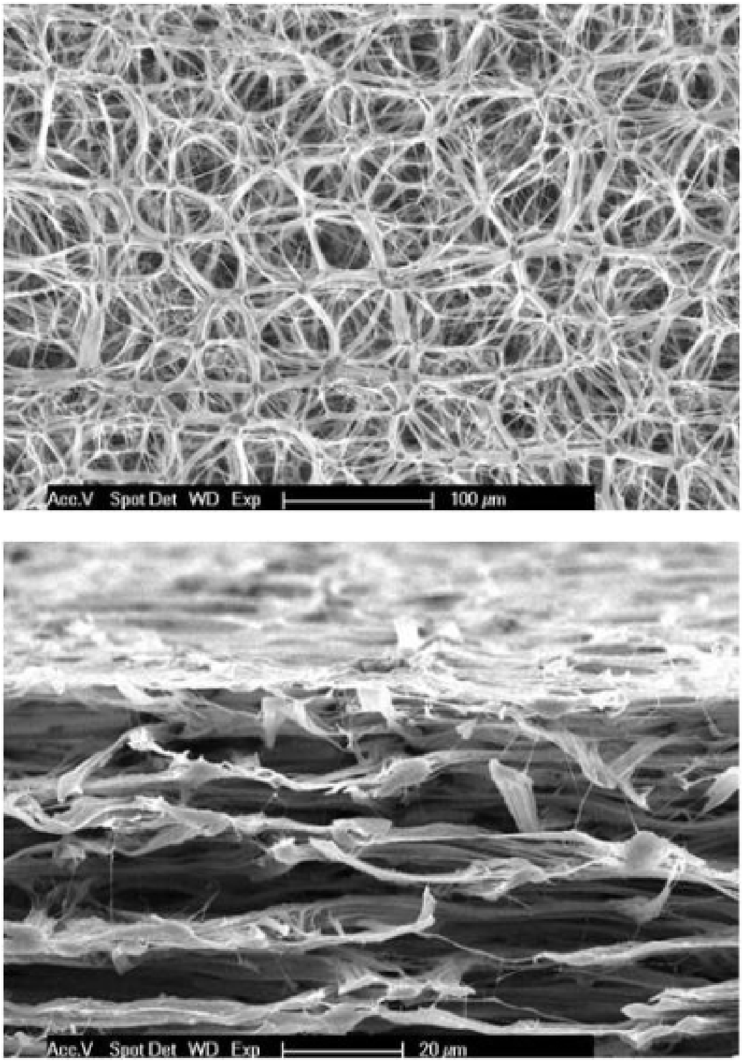
ICOM1411

New hydrophilic UHMWPE SOLUPOR® membranes

Magda Avramescu, John op den Kamp
Lydall Solutech, Heerlen, NL

Made from Ultra High Molecular Weight Polyethylene (UHMWPE), using an unique patented proprietary manufacturing technology, our strong SOLUPOR® membranes are highly porous with high gas, air and liquid permeability. These membranes are successfully used in various separation processes due to their numerous advantages, in particular their high chemical and mechanical resistance, excellent abrasion and impact resistance, biocompatibility and low cost. The microporous Ultra High Molecular Weight Polyethylene Solupor® membrane combines a microstructure with an internal nanostructure for excellent strength, high efficiency and low pressure-drop. The application of polyolefin membranes is however, limited by their hydrophobic nature which renders the membrane non-wettable and reduces their water permeability. Furthermore, polyolefin membranes tend to have large flux decline caused most probably by membrane fouling as a result of solute adsorption and pore blocking.



SEM-micrographs for SOLUPOR® membranes: 1: top surface; 2: cross-section

Some simple methods for hydrophilization of polyolefin membranes such as: organic solvent pre-wetting, blending with hydrophilic polymers, physical adsorption of various surfactants or hydrophilic polymers onto membrane surface, have the disadvantage that the hydrophilic components tend to desorb from the membrane during prolonged permeation, resulting in a decrease of hydrophilic properties. Often, chemical etchants and irradiation based methods like UV-irradiation, γ-ray irradiation, electron beam irradiation or plasma techniques are used to activate and/or to graft hydrophilic polymers onto the membrane surface. However, as a result of the treatment, the membrane structure may damage to a certain extent, depending on the strength of the etchant or the irradiation intensity and irradiation source. There is therefore a need to provide a process for increasing the hydrophilicity of polyolefin membranes that overcomes the disadvantages of the above mentioned methods.

Our paper presents a new family of modified Ultra High Molecular Weight Polyethylene SOLUPOR® membranes prepared by using a patented novel technology. The developed technology is flexible and offers the possibility to easily adjust the membrane pore size and porosity, as well as the functionality of the membrane surface. Excellent results have been achieved for the hydrophilization of our microfiltration flat-sheet UHMWPE SOLUPOR® membranes. For instance, a modified hydroxylated membrane surface renders the membrane highly hydrophilic with low protein binding.

The newly prepared SOLUPOR® membranes were characterised with respect to their morphology, porosity, hydrophilicity, permeability and retention properties. Contact angle measurements showed excellent water wetting properties. In contrast to the untreated UHMWPE SOLUPOR® membranes, a hydrophilic 0.45 mm mean pore size treated membrane (based on beads retention measurements) exhibit high water permeability (> 15.000 (lxhxm^2) at 10 psi) even after repeated drying. Depending on the used treatment, the membranes have a high porosity (>80%) and are EtO and gamma sterilization resistant. Furthermore, being prepared without the use of surfactants, our hydrophilized SOLUPOR® membranes have a low level of extractable (maximum 0.002 mg/cm^2), making them very suitable for analytical or bio-applications.

Membrane bioreactors 1

ICOM1809

An overview of membrane bioreactors (MBR): state-of-the-art, current and future directions of R&D

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Development and commercialization of membrane bioreactors (MBR) for advanced treatment of wastewater has seen an exponential growth in the last 10-15 years. Market growths have been in excess of 10% per year and have essentially been driven by the municipal sector, in particular by the construction of the larger plants with installed capacities above 5.000 m^3/d. MBR technology is now a cost competitive option for municipal and industrial wastewater treatment, where the applications require exceptional specifications such as enhanced water quality (*i.e.* bathing water regulations, water reuse etc.), reduced footprint or where the technology is used to upgrade existing plants. In particular, the driving factor for this market growth is water scarcity, both physical and economic scarcity, founded on a specific need for water reuse and recycling strategies.

MBRs are commonly understood as the combination of membrane filtration and biological treatment using activated sludge (AS), where the membrane primarily serves to replace the clarifier in the wastewater treatment system. MBRs are complex units of operation that include biological processes, physical / chemical processes and their interactions, where the key elements of this process are matching biological conversions with membrane separation technology. Several challenges have been identified that are specific to MBR processes and which may viewed as the main constraints of this treatment option. Membrane fouling is an inherent phenomenon in all membrane systems, and particularly a problem in AS-MBRs since the process deals with liquors having high concentrations of total solids as well as dissolved compounds such as extracellular polymeric substances (EPS). Fouling is defined as reversible, *i.e.* can be removed by air-scouring and/or backwashing strategies, or as irreversible, *i.e.* fouling which is only recoverable by chemical cleaning, where the dominating fouling mechanism subsequently determines the performance of the process. Optimizing fouling control and cleaning strategies is therefore an important aspect of developing and designing MBR processes. Energy demands are also of concern, where aeration both for the biological stage and aeration for operation of the membrane filtration unit represent up to 80% of the total energy demands in MBR systems. Other challenges are related to operation aspects, monitoring / control of the process, and costs and market acceptance in general. Although much R&D has been conducted, key bottlenecks of the technology are still being investigated; gaining a better fundamental understanding of membrane fouling and fouling control, reducing the energy demand and consumption, and reducing allover costs through improved operations and increase in system lifetime. This presentation will highlight the key elements and bottlenecks in MBR technology, state-of-the-art of the process, current and future directions of R&D based on recent research efforts reported, and a give a general overview of the technology.

ICOM611

A study on ion exchange membrane bioreactor for perchlorate removal from highly contaminated aquifers

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In recent years perchlorate, a highly hazardous substance which particularly affects pregnant women and young children, has become a major concern globally as a ground water contaminant from activity of military and aerospace industries and in some cases as a natural contaminant. Perchlorate is a highly soluble and stable molecule, and as such it rapidly spreads through the aquifer. In Israel, the coastal aquifer in the Ramat Ha'Sharon area is severely contaminated by perchlorate in the saturated and unsaturated sediments. Authorities are now proposing pumping and treating this water to prevent it jeopardizing the water quality of hundreds of millions m^3 of adjacent groundwater.

A novel ion exchange membrane bioreactor (IEMB) developed by Crespo and Reis has shown its efficiency in the removal of low concentrations (< 1 mg/L) of perchlorate ion from water. IEMB combines both removal and degradation techniques; perchlorate is removed from the contaminated feed stream into a biological reactor through an ion exchange membrane by applying the Donnan dialysis. Velizarov et al (2003) developed a model for the different operational parameters of the IEMB (e.g. membrane thickness and flow regime in the IEMB). In the reactor, the microbial degradation of perchlorate to Cl^- takes place. There is no contact between the treated water and the bioreactor, making the treatment effluent suitable for drinking water.

The present study examines the performance of the IEMB in removing perchlorate at the level of 100's of mg/L, typical of highly contaminated ground water. A series of experiments was conducted using a water chemical composition similar to contaminated ground water with increasing perchlorate concentrations. The perchlorate flux across the membrane was obtained by performing a mass balance across the device based on perchlorate measurements of each stream. The flux results were compared to the prediction of the model developed by Velizarov et al (2003) for describing the Donnan flux across the ion exchange membrane as a function of concentrations of the counter-ion (ClO_4^-) in the feed (see Figure 1).

The model predicts that high concentrations of counter-ion in the feed side will result in higher fluxes.

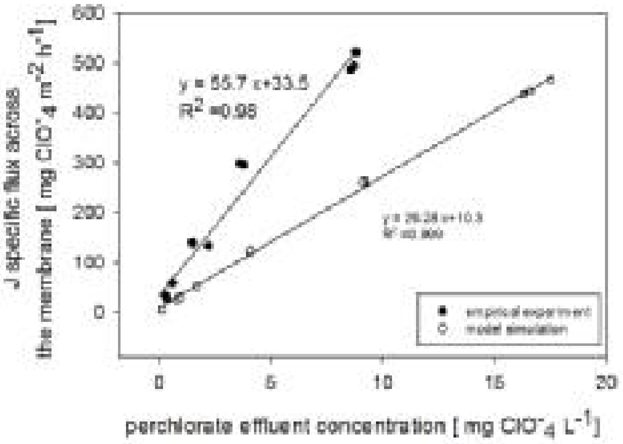

Figure 1 Donnan dialysis of high concentration perchlorate feeds, empirical results vs. model simulation

The empirical results were fifteen percent higher than the prediction of the model. This observed flux enhancement relative to the model is attributed to the fact that the model was formulated for a monovalent ionic system (chloride-perchlorate with common sodium cation) while the experiments were conducted with complex solutions containing various multivalent anions and cations as well.

In the follow-up experiment, acclimatized bacteria from sediments from a contaminated site in Ramat Ha'sharon were introduced into the bio compartment. High degradation rates of perchlorate were observed in the bioreactor resulting in 91% treatment efficiency for contaminated water. Given that the perchlorate level in the biocompartment dropped below the detection limit, we concluded that the rate-controlling process is the passage of perchlorate from the feed side to the bioreactor.

ICOM932

A parallel comparison of aerobic, anaerobic, and attached-growth membrane bioreactor systems

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Water sustainability is essential for meeting human needs for drinking water and sanitation in both developing and developed countries. Reuse, decentralization, and low energy consumption are key objectives to achieve sustainability in wastewater treatment. Consideration of these objectives has led to the development of new and tailored technologies in order to balance societal needs with the protection of natural systems. Membrane bioreactors (MBRs) are one such technology. In this investigation, a comparison of MBR performance is presented. Laboratory-scale submerged aerobic MBR (AMBR), anaerobic MBR (AnMBR), and attached-growth aerobic MBR (AgMBR) systems were evaluated for treating domestic wastewater under the same operating conditions.

The AnMBR system required three months of acclimation prior to stable operation, compared to one month for the aerobic (AMBR and AgMBR) systems. COD removal for the three systems was in the range of 85% and TOC removal for the three systems was in the range of 95% (Figure 1). With regard to biomass production, the AnMBR system did not produce excess biomass while the AMBR and AgMBR systems produced approximately 0.21 and 0.28 g MLSS/g COD removed, respectively. Excess biomass produced within the process must be disposed of and may contribute to up to 60% of the total treatment facility operating costs. Therefore, operating costs of an AnMBR system could be significantly lower and AnMBRs could contribute towards a more sustainable treatment scheme. On the other end, the higher excess biomass produced by the AgMBR system (because of the attached-growth media) could hinder the development of AgMBRs because of added operating costs.

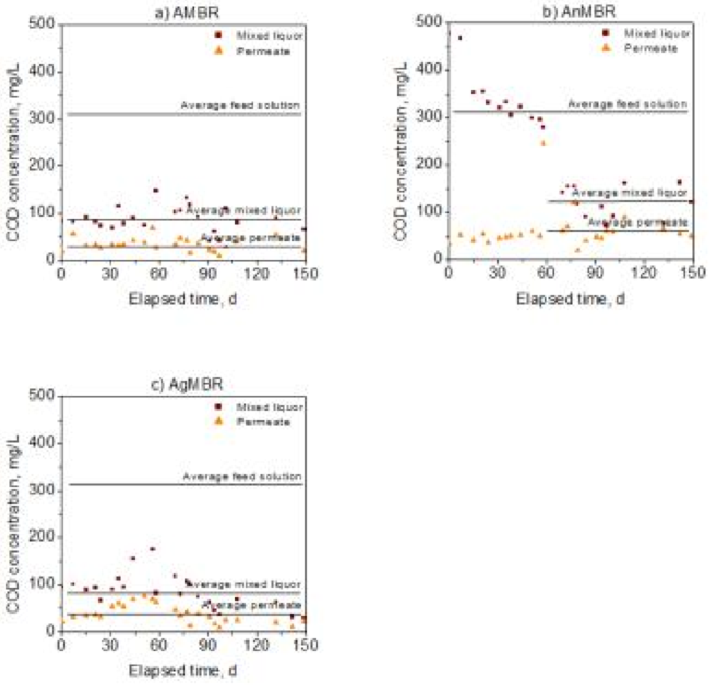

Figure 1. Feed solution (average), mixed liquor, and effluents COD concentration in the a) AMBR, b) AnMBR, and c) AgMBR systems.

The AMBR and the AnMBR systems had similar critical flux values, while the AgMBR system had a 30% higher critical flux value (Figure 2). This suggests that the attached-growth media had a positive role in controlling membrane fouling in MBR systems. This would make it possible to operate AgMBR systems at higher water fluxes, which could result in reduced membrane area requirements and lower subsequent capital costs. Overall, the three systems evaluated have their tradeoffs and system selection would depend on the specific weighting of capital and operating costs. Compared to AMBR systems (today's standard in terms of MBRs), AnMBR systems require longer acclimation time but are likely to have lower biomass production and comparable water flux values, while AgMBR systems are likely to have higher biomass production and higher water flux values.

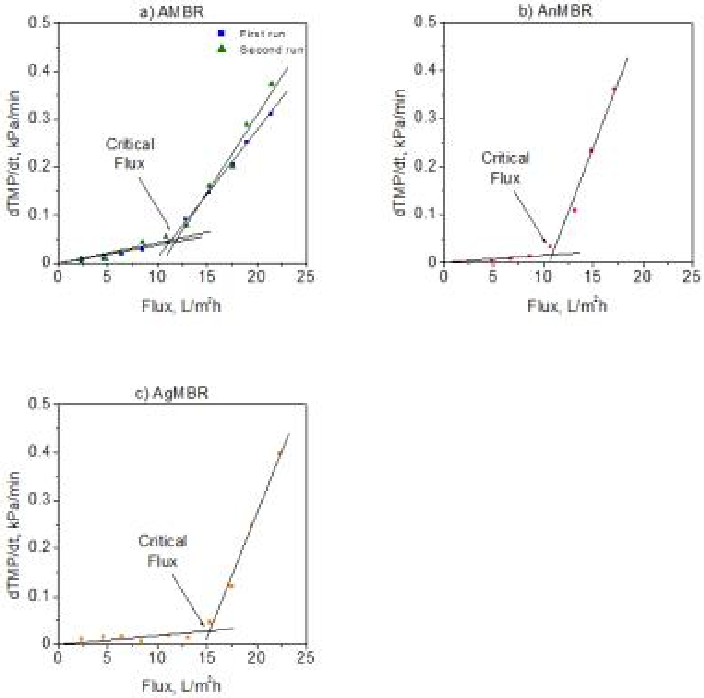

Figure 2. Critical flux in the a) AMBR, b) AnMBR, and c) AgMBR systems.

ICOM1520

Effect of temperature shocks on membrane fouling in membrane bioreactors

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Temperature influences the biological performance of conventional activated sludge systems. In membrane bioreactors, temperature not only affects the bioconversion processes but also membrane performance. Seasonal variations in membrane fouling, with more severe membrane fouling at lower temperatures, have been reported for several full scale systems [Miyoshi et al., 2009]. Also in a MBR pilot increased filtration resistance was observed for a small temperature shift (17-18 ºC to 13-14 ºC), even after correcting for permeate viscosity [Jiang et al., 2005]. Four phenomena were mentioned to explain this effect: (1) increased sludge viscosity, reducing shear stress by coarse bubbles, (2) intensified deflocculation, reducing biomass floc size and releasing extracellular polymeric substances (EPS) into the solution that can cause membrane fouling, (3) lower backtransport velocity and (4) lower degree of biodegradation of (wastewater) COD. Although this higher membrane resistance at low temperatures has been reported in several papers, the relation with supernatant composition has not been investigated before.

In this paper, the composition of the soluble fraction of the mixed liquor is related to membrane performance after exposing the sludge to temperature shocks. Flux-step experiments were performed at 7, 15, and 25 °C in an experimental system with sludge that was continuously recirculated from a pilot scale membrane bioreactor. Home made PVDF membranes with a nominal pore size of 0.1 µm were used. The soluble fraction was analysed for polysaccharides, proteins and submicron particle size distribution.

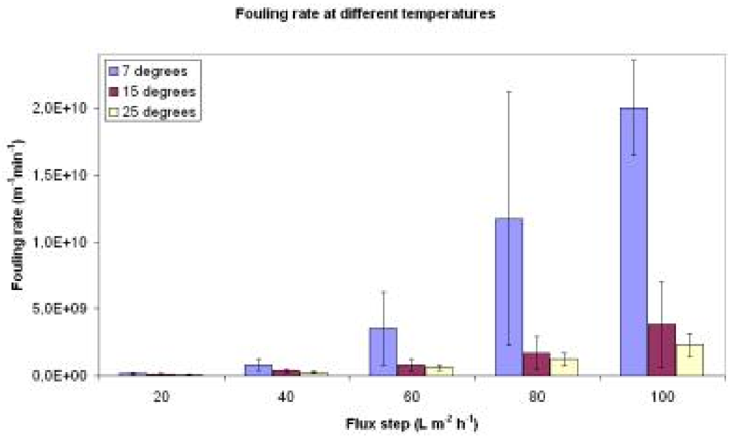

Figure 1 Average fouling rates for different flux steps at three different temperatures.

After correcting the permeate viscosity for temperature, higher membrane fouling rates were observed for the lower temperature (Fig.1), in combination with a lower fouling reversibility.

High polysaccharide concentrations were found in the experimental system as compared to the MBR pilot, while no differences were found for proteins. Upon decreasing the temperature of the mixed liquor, a shift was found in particle size towards smaller particles (Fig.2). Because these smaller particles are very similar in size as the membrane pore size, fast pore narrowing or pore blocking could explain the low fouling reversibility.

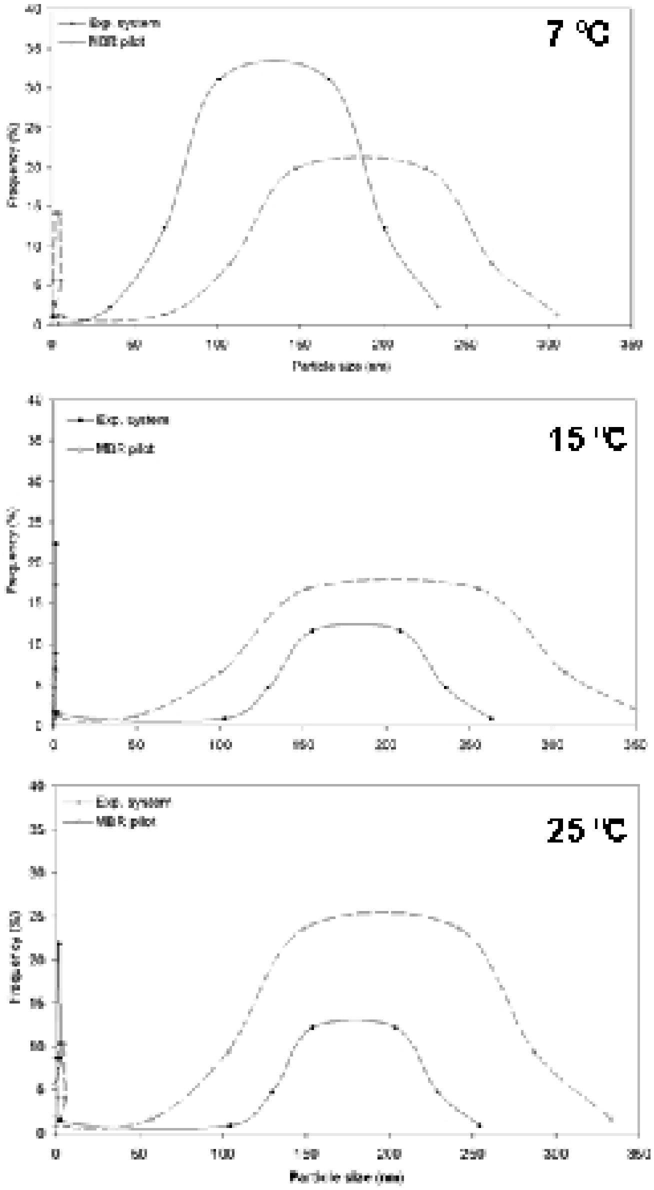

Figure 2 Particle size distribution in the soluble fraction of the MBR pilot (open symbols) and experimental system (filled symbols) at three different temperatures

These results strongly indicate that the release of polysaccharides and submicron particles from sludge flocs could explain the increased membrane fouling at low temperatures. They also show that temperature should be taken into account when designing a membrane bioreactor. Long term temperature effects, such as a change in microbial diversity and microfauna, should be studied as well. Microbial diversity of different sludge fractions and its relation to membrane fouling is currently investigated in our laboratory.

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Membrane contactors and reactors 1

ICOM1863

Membrane contactors & membrane reactors

Mary Rezac

ICOM908

Development of Catalytic Hollow Fibre Membrane Micro Reactor for On-Board Hydrogen Generation

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The future of the hydrogen economy rests on a clean and efficient hydrogen generation along with the development of new technologies which enable a safe storage and transport of the H_2 [1] . Ethanol has been regarded as a promising renewable source of H_2 because it can be easily decomposed in the presence of H_2O to produce H_2. The chemical and physical properties of ethanol liquid at room temperature and atmospheric pressure, along with its non-toxicity make it possible to be used as a "storage-molecule" of H_2 for on-board applications[2]. However, the main problem of EtOHSR reaction is that it produces a significant amount of CO_2, which is one of the most important contributors to the greenhouse effect. It has also been known that the presence of CO_2 in the anode stream lowers the performance of the fuel cells. Therefore, hydrogen must be purified before being used in the fuel cell and the CO_2 produced during the reaction must be captured and stored. In order to avoid these problems, conventional catalytic membrane reactors (CCMR) have been proposed a few years ago as a promising solution. Nevertheless, the big size of the CCMR prevents its use in small-scale on-board H_2 applications such as laptops or mobile phones. Based upon this, in this work, asymmetric yttria stabilized zirconia (YSZ) hollow fibre has been used as a support for both 10%NiO/MgO/CeO_2 and Pd/Ag membrane in the development of a catalytic hollow fibre membrane micro-reactors[3] (CHFMMR) for on-board high purity CO_X free hydrogengeneration by ethanol steam reforming (EtOHSR) reaction. The fact that YSZ hollow fibre lengths as short as 1-10 cm can be employed to develop the CHFMMR, allows its use in small-scale on-board H_2 applications. The CHFMMR was characterised using SEM, SEM-EDS, BET, XRD and Hg porosimetry. The catalytic activity tests were carried out under atmospheric pressure and between 350-600 °C, in a fixed-bed reactor, the catalytic hollow fibre micro-reactor (CHFMR), and the CHFMMR. The ratio between C_2H_5OH/H_2O was 1 to 5 with a space velocity ranging of 720 L/g.hr. The results showed that the ethanol conversion obtained in the EtOHSR reaction using the CHFMMR was four fold higher than in a conventional fixed-bed reactor and two fold higher than in a CHFMR. A high purity CO_X free H_2 generation (50.0 ml/mg.hr) is achieved at 550 °C using a sweep gas of 60 ml/min in the CHFMMR.

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ICOM1397

One-stage production of high purity *p*-Xylene from *m*-Xylene isomerisation in an extractor-type catalytic membrane reactor equipped with a tubular nanocomposite membrane

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Production of high purity *p*-Xylene in industry involves *m*-xylene isomerization in Fixed-bed reactors (FBRs) followed by separation to augment the market demands. This process is energy intensive and in some cases, the separation step is repeated several times before high purity *p*-Xylene could be obtained [1]. This contributes to high energy consumption, translating into significant operating costs. Recent research trends in membrane processes has shown, through process intensification, that extractor-type catalytic membrane reactors (e-CMRs) could potentially alleviate this problem by producing high purity *p*-Xylene [2-5]. However, acceptability of this intensified process by the industry depends on the availability of robust, easily reproducible high selectivity membranes with appreciable membrane fluxes. Also, the system will be more attractive to the industry if production of high purity product (e.g. *p*-Xylene) could be obtained in one stage.

In this work we demonstrated one-stage production of high purity *p*-Xylene via *m*-Xylene isomerisation in an e-CMR equipped with a nanocomposite MFI-alumina membrane, synthesized via pore-plugging hydrothermal technique [6] on a α-alumina support, as a separation unit. During the *m*-Xylene isomerisation, *m*-Xylene, saturated in N_2 gas was fed into the reactor (packed with 2.18 g of a commercial Pt-HZSM-5 catalyst) at 10 mL(STP)/min and the permeate side was swept with N_2 gas at 5 mL(STP)/min. For comparison, an equivalent fixed-bed reactor (FBR) was operated at the same conditions.

At a reaction temperature of 473 K, the results revealed 18 % increase in *p*-Xylene yield, 33 % increase in *m*-Xylene conversion and *p*-Xylene purity >99% in the e-CMR if compared to the equivalent FBR. Also, the membrane displayed ~100% selectivity to *p*-Xylene in the permeate side at all the temperatures (473 K-573 K) investigated. However, ~ 20% xylene loss was observed, due to disproportionation of *m*-Xylene, indicating the need for developing e-CMR adaptable catalysts with high selectivity for *m*-Xylene isomerisation. The results presented in this study have demonstrated the possibility of one-stage production of high purity *p*-Xylene in e-CMRs. These results support the possibility of cutting down operating costs, through a reduction in energy consumption and by space conservation, during the production of high purity *p*-Xylene in an e-CMRs. The production of reproducible high-flux membranes with high *p*-Xylene selectivity could potentially fast-track the development and industrial acceptability of this technology.

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ICOM1076

Application showcases for a small scale membrane contactor for fine-chemical processes.

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The transition from batch to continuous processing in fine-chemicals industries offers many advantages; among these are a high volumetric productivity, improved control over reaction conditions resulting in a higher yield and selectivity, a small footprint and a safer process due to a smaller reaction volume. Pilot studies of continuous microstructured reactors in a production environment have been presented over the last few years by chemicals producers collaborating with equipment developers. It makes, however, little sense to shift only the reactor to continuous operation and not the work-up because this would result in accumulating reaction intermediates and products in storage vessels.

The next logical step is the introduction of continuous microstructured separation equipment that has a similar performance with respect to separation efficiency as continuous reactors regarding productivity. Consequently for multistep chemical synthesis a toolbox of separations has to be developed based on the classical operations of evaporation, extraction and crystallization. Potential benefits versus conventionally applied stirred tank vessels include: a small footprint because of high productivity, less product degradation volume and increased safety due to a small because of the lower volume (for example less solvent) and the potential to reduce the number of down stream processing steps. Issues for the development of these separations are multi-purpose applicability and scalability by modular design.

Membrane contactors are potentially beneficial for small scale separations in fine-chemical applications. Potential benefits of pertraction are: a stable interface and therefore less foam / froth problems, less solvent use because of a asymmetric volume ratio up to 100:1 (for process stream: solvent stream), it allows for streams with small density difference because no gravity based settler is required, a small footprint due to a high specific surface area, flexible with respect to scale-up because a modular construction is possible, multi-applicable by choice of solvent, no moving parts resulting in low maintenance cost and finally proven technology in water applications. Issues that have to be addressed before pertraction can be applied in the core of fine-chemical processes are the use of chemically resistant materials and scale-up at low cost to sufficient large modules.

To initiate the development of a pertraction module for fine-chemical processes three showcases for potential chemical applications were demonstrated experimentally. The first application was a solvent switch of a compound from one solvent into another. The second application was an aqueous work-up of a solvent reaction mixture, aiming for removal of spent acids or bases. The aqueous work-up can be carried out without the formation of an emulsion and potentially with a smaller volume of washing water. The third application was the dehydration of a reaction mixture, with the objective of removing both dissolved and dispersed water. In the latter case the test system was an esterification reaction between hexanol and hexanoic acid with lipase as catalyst. For all cases the mass transfer coefficient was determined in order to calculate the surface area of membrane required for a small scale industrial pertraction module. Finally, module design and construction aspects (a.o. stacking) will be considered.

Hybrid membranes 1

ICOM1846

New directions for the HybSi® membrane concept

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Hybrid membrane systems have been a research topic for a long time. Examples include polymeric membranes in which inorganic particles have been dispersed, membranes that are supported by a different type of material. Since over 15 years, attempts have been made to combine both organic and inorganic moieties on a molecular level. One of the first attempts has been to modify pure silica membranes with terminating units [1]. The motivation of this work was to enhance the limited stability un der hydrothermal conditions. These developments had a limited success, as the maximum application temperature in de dehydration of butanol was increased to ~100°C [2]. More recently, a more successful approach was developed. In this case, part of the inorganic Si – O – Si bonds were replaced by $Si – C_mH_n – Si$ bridges [3]. It was found that especially these bridging moieties are an essential structural element for the hydrothermal stability of nano-porous hybrid silica membranes. The unprecedented stability is apparent from the dehydration of butanol at 150°C under pervaporation conditions for a period of 1000 days without failure [4]. Also the acid stability [5] of these so-called HybSi® pervaporation membranes is higher than many other inorganic membranes.

The presence of the hydrocarbon bridges offers the possibility to fine tune the porosity, properties, pore size and interactions with the medium to be separated. In this way a wide variety of applications can be targeted using one single membrane concept. Through careful selection of precursors and sol-gel chemistry, the nature of this family of compounds can be controlled in an effective manner [6]

These HybSi® membranes were originally been developed for high-temperature pervaporation applications. The optimal bridging group in this case were short linear chains such as $–CH_2–$ and $–C_2H_4–$ [5]. In this way high selectivity, could be combined with high hydrothermal stability and high fluxes. The origins of the high hydrothermal stability can be found in the higher crack propagation energy [7], and in the fact that the bonding between silicon and a hydrocarbon group is not sensitive to hydrolytic attack. More recently, other separations such as gas separations were explored [8] .

In this presentation, an overview of the versatility of this family of membranes is given and the precursor–performance correlations will be highlighted. For the bridging moieties, various alkanes, alkenes and aryl groups will be treated. For the terminating groups, alkyl groups and functionalized alkyl groups will be discussed. We will demonstrate that the nature of the organic fragment has a direct effect on membrane pore size, polarity, and therefore on the membrane behavior.

In the light of these new findings potential new applications in the fields of nanofiltration, organophilic pervaporation and gas separation will be discussed.

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ICOM426

Gas separation using hybrid inorganic-organic silica membranes

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Inorganic membrane-based gas separation offers an environmental-friendly alternative to conventional separation technologies due to its high energy efficiency and high performance, i.e., flux and selectivity, at elevated temperatures. In this paper, we report on sol-gel derived microporous hybrid inorganic-organic membranes for gas separation.

Membranes were prepared by acid-catalyzed co-hydrolysis and condensation of the ethylene-bridged bis-silyl precursor 1,2-bis(triethoxysilyl)ethane (BTESE) and, subsequently, dipcoating of the polymeric sol on an alumina-based multilayer support. Inspection of the membranes, after calcination at 400-550 °C in either nitrogen or air, using optical microscopy showed formation of a continuous, crack-free and smooth surface. TEM analysis showed that the hybrid membranes had a thickness in the range of 100-180 nm.

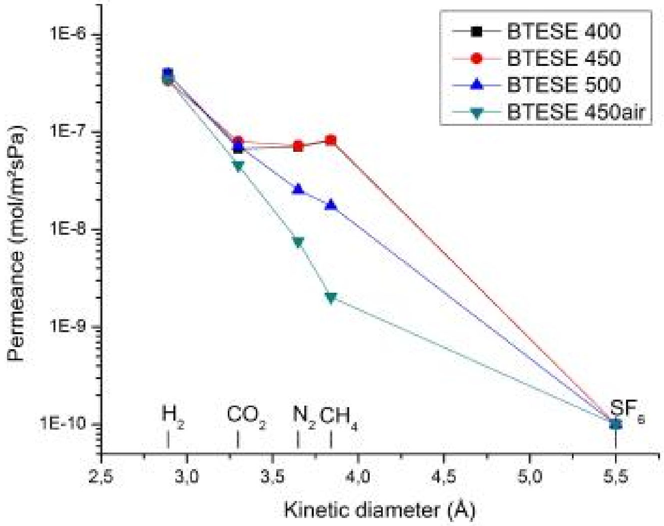

Figure 1: Single gas permeation measurements of the BTESE membranes, calcined under different conditions. Measurements were conducted at 200 °C and $\Delta p = 2$ bar.

Results of single gas permeance measurements at 200 °C are shown in Fig. 1. Membranes calcined in nitrogen at 400 and 450 °C showed Knudsen selectivity. Given the fact that the permeance SF_6 is found below the detection limit, the pore size of the membranes is estimated below 5.5 Å. Membranes calcined in air at 450 °C showed comparatively high H_2/N_2 and H_2/CH_4 selectivities (46 and 203, respectively), i.e., far above the corresponding Knudsen values (3.7, and 2.8, respectively).

Contact angle measurements indicated that the membranes calcined in air at 450 °C showed an enhanced hydrophobicity over those calcined in nitrogen. Hydrothermal tests of the membranes are presently conducted, and results will be presented at the conference.

ICOM814

Nanocomposite functional membranes – increasing the IQ of intelligent textiles

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In the last years membranes have attracted a great interest in the textile industry and have been mainly used for applications where increased comfort is required. Here we give an overview of of different membrane developments, able to increase the functionality of textile materials for protective and medical applications.

New nanocomposite membranes based on supramolecular **po**lyoxo**m**etalate clusters and **po**ly**m**ers (POM-POM) have been synthesized in our lab. The inorganic moieties display hydrophilic nano pores which allow the passage of water molecules but prevent the transport of organic solvent molecules. As such we have demonstrated a 1.5 fold increase in the breathability (water vapor transmission rate- WVTR) of the membranes, while maintaining the permeation of polar and apolar solvents extremely low. These types of membranes will be applied in chemical protective equipment, ensuring high levels of protection while providing an increased comfort for the user.

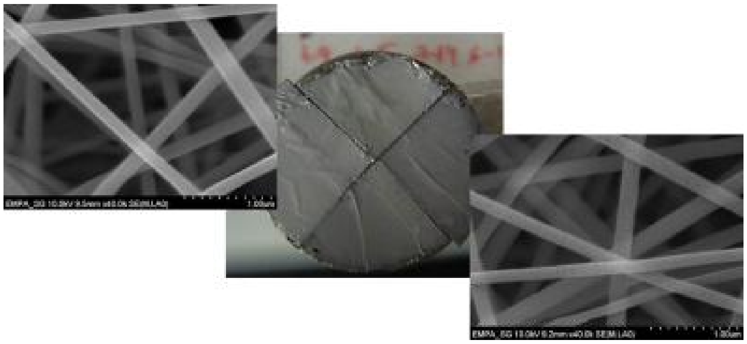

Figure 1 - Morphology of POM-POM as evidenced by TEM, showing a homogeneous distribution of [Mo132] crystals

A different direction we explored was the production of adaptive membranes for textile physiological applications and to this extent we have synthesized polymer-polymer composite membranes by grafting thermo-responsive polymers on porous polyester supports. Oligoethylene methyl methacrylate-based polymers display high biocompatibility and their transition temperature can be tuned by varying the molar percentage of monomers with different hydrophilicities in the composition. Upon functionalization we have obtained membranes with temperature-dependent permeability. These systems can be applied in medical textiles as on-off gating systems for drug reservoirs and we show this effect using caffeine as a model system. Additionally, the thermo-responsive WVTR through these membranes was investigated as to assess the suitability of these “smart” membranes for modulating thermal and wet-comfort inside the clothing in function of the external conditions.

Finally we show the possibility of obtaining non-woven membranes which display structural colors and a method for modifying this structural color in function of the temperature. These membranes can be used as end of service indicators for heat-protective suits, as to indicate the eventual thermal damage in a non-destructive manner.

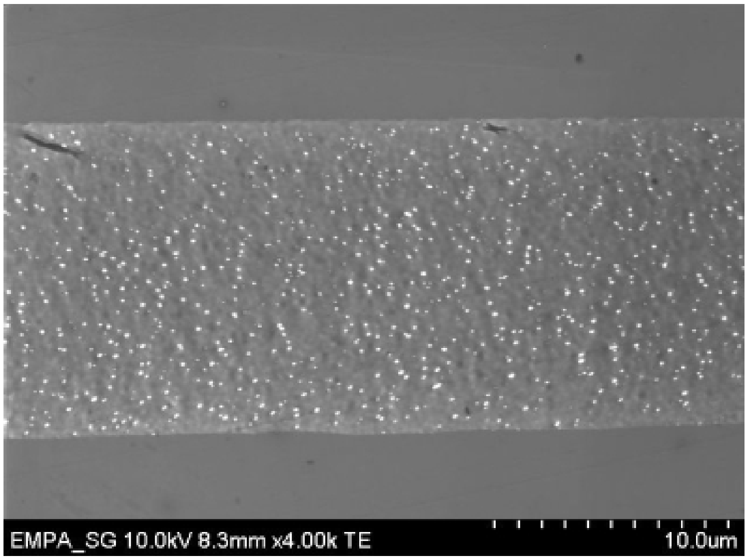

Figure 2 – Color change of non-woven membranes upon exposure to temperature and corresponding SEM images of the nanostructured nanofibers responsible for the color change

ICOM496

Polymer-embedded metal-organic framework membranes for gas separation applications

Constantinos Dimitrakakis[1,2], Matthew Hill[2], Bradley Ladewig[1]
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Metal-Organic Frameworks (MOFs) are an emerging class of highly porous materials consisting of metal linked by organic ligands into well-defined porous networks. Much interest has been expressed in applying MOFs as adsorbents or molecular sieves for gas separation. Within this class of materials are the *zeolitic imidazolate frameworks* (ZIFs), which adopt structures analogous to aluminosilicate zeolite networks and exhibit good chemical and thermal stability up to ~400°C, making them suitable for harsh environments typically encountered in industrial
gas separation processes such as post-combustion carbon dioxide capture.

In order to harness the potential for ZIFs to perform efficient gas separation, efforts have focused on the fabrication of membranes incorporating the ZIFs into a flexible membrane, which has been achieved by growing a crystalline layer of ZIFs onto a flexible, highly porous support and then depositing a thin layer of polymer over the top. The ZIF layer is grown through a solvothermal synthesis technique and optimised through manipulation of the surface chemistry of the supporting polymer substrate.

By coating the crystalline layer with a non-porous polymer and removing any excess to expose the surfaces of the ZIF crystals, the selectivity of the membrane can be optimised by preventing the leakage of gas through non-selective paths through cracks and grain boundaries within the crystalline layer (Figure 1). However, it becomes important to ensure that the coating polymer is compatible with the ZIF chemical structure to ensure good interfacial bonding to prevent leaks. Alternatively, by coating the membrane in a highly porous polymer, additional structural integrity and flexibility can be given to the membrane while maintaining high throughput in a manner similar to mixed-matrix membranes.

This presentation will describe the membrane fabrication process, including the ZIF layer synthesis technique and manipulation of the coating polymer. The effect of the polymer coating on the gas separation performance of these membranes will be explored.

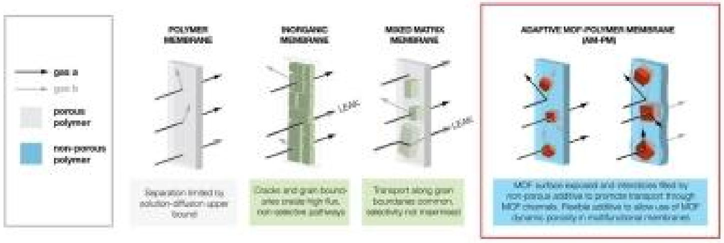

Figure 1 - Comparison of the proposed membrane architecture compared to current organic, inorganic and mixed matrix membranes.

Membrane formation 1

ICOM1774

Of Micelles and Membranes

Klaus-Viktor Peinemann[1], Suzana P. Nunes[2], Madhavan Karunakaran[1]
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Molecular self-assembly of di- and triblock copolymers is a powerful method for manufacturing highly ordered structures with nano-sized patterns. Films with regular monodisperse nanopores and ultrahigh porosity are needed in applications, which vary from water purification, sensors, information storage, as templates for nanowires, scaffolds for tissue engineering and controlled drug delivery. Block copolymer self-assembly has been proposed as formation method for artificial highly selective membranes since many years. This presentation will review the recent progress in this field. Fascinating membrane structures could be manufactured, but the techniques applied were in many cases time consuming and complicated. Till today an up-scaling of the self-assembly process for membrane manufacturing was not possible. The combination of the most common membrane formation process (non-solvent induced phase separation, NIPS) with block copolymer self-assembly was first described in 2007 /1/. But the mechanism was not well understood and the reproducibility with other polymers was insufficient. We showed later that micelle formation in the membrane casting solution was the key to a successful asymmetric membrane formation /2,3/.

The order of block copolymer micelles as part of the membrane has been demonstrated making use of transmission electron microscopy tomography. The micelles have a fundamental influence on the morphology. They assemble themselves forming regular pores with a bidimensional hexagonal structure. The membrane pore response to pH, acting as chemical gates, was investigated by using different microscopy methods (AFM, cryo and environmental microscopy). Due to the extremely high porosity the water flux through the membrane is higher than through any other membrane with comparable pore size. The critical steps for the NIPS assisted self-assembly from very small laboratory scale to membrane manufacturing on a continuously operating casting machine will be described. Machine made self-assembled block copolymer membranes will be shown for the first time.

/1/K.-V. Peinemann et al., Asymmetric Superstructure in a Block Copolymer via Phase Separation, Nature Materials 2007, 6(12) 992

/2 /S. Nunes et al., Ultraporous Films with Uniform Nanochannels by Block Coppolymer Micelles Assembly, Macromolecules 2010, 43, 8079

/3/ Nunes et al., Switchable pH-Responsive Polymeric Membranes Prepared *via* Block Copolymer Micelle Assembly, ACS Nano 2011, DOI: 10.1021/nn200484v

ICOM1438

A new strategy to prepare nanoporous membranes via selective swelling of amphiphilic block copolymers

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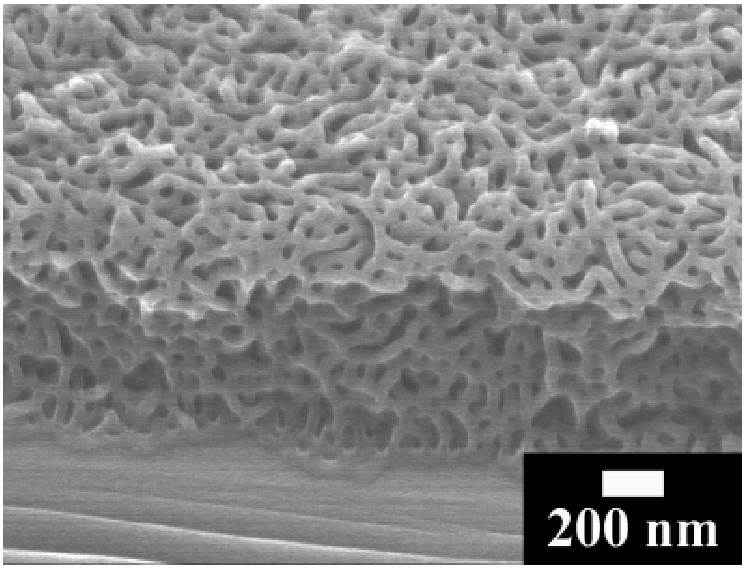
It is highly desired to have a simple but effective method for the preparation of nanoporous polymer membranes or films with well-defined, three-dimensionally interconnected porosity without the involvement of tedious, multiple synthesis steps. In this work we demonstrated an extremely facile route for the fabrication of bicontinuous, nanoporous polymer membranes through the selective swelling of amphiphilic block copolymers (BCPs). The originally separated hydrophilic domains in BCP films were selectively swollen and connected with each other when exposed to polar solvent, and bicontinous nanopores were generated upon drying due to loss of polar solvent. The obtained nanoporous polymer membranes have regular, bicontinuous nanopores spanning the whole depth of the film and the pore walls are hydrophilic because the chains of the polar blocks are immigrated to the surface during swelling. The pore size can be tuned in the range of 10-50 nm, and the thickness of the membrane can be as thin as <100 nm. We obtained composite membranes by coating BCP solutions on the surface of support membranes filled with water. Because of the polyelectrolyte nature of the polar blocks, the obtained membranes show a stimuli-responsive property.



ICOM328

Molecular design of the cellulose ester-based forward osmosis membranes for desalination

Sui Zhang[1], Kai Yu Wang[2], Tai-Shung Chung[1,2], Y. C. Jean[3], Hongmin Chen[3]
[1]National University of Singapore, NUS Graduate School for Integrative Science and Engineering, Singapore, SG, [2]National University of Singapore, Chemical and Biomolecular Engineering, Singapore, SG, [3]University of Missouri-Kansas City, Department of Chemistry, US

Forward osmosis (FO) has drawn worldwide attention in recent years as an alternative desalination technology. With osmotic pressure as the driving force, FO offers the unique advantages of low energy consumption, low fouling propensity and high rejection towards ions. However, currently membranes for FO suffer from insufficicent water permeability and severe concentration polarization (ICP) due to their thick and low-porosity support layer, which leads to significant reduction in the efficiency of osmotic driving force. Therefore, innovations are urgently required in the design and fabrication of membranes that are structurally feasible for FO.

Meanwhile, the phase inversion mechanism of cellulose ester membranes has been widely studied over the past decades. However, most of them focused on the formation process of a dense layer at the top surface (between membrane and air) of the membrane. Very limited attention has been paid to the bottom interface between polymer solution and casting substrate. It is thereby quite interesting and technocally innovative to investigate the possiblity and process of forming a selective layer the the bottom interface.

This work has investigated the fundamental science of phase inversion and formation mechnism of cellulose ester membranes at the interface between polymer and casting substrate. It also explores the desired membrane preparation conditions for FO applications in seawater desalination. With the aid of positron annihilation spectroscopy (PAS) and molecular simulation, the similarity in physicochemical properties between the polymer and substrate was found to play a key role in determining the bottom surface morphology. The structure of the dense interfacial layer was also strongly dependent on membrane thickness and solvent composition. Experimental results surprisingly reveal that the original pore size of the as-cast membrane is critical for the final performance of the subsequent annealed membrane. In addition, since a threshold pore size exists during annealing above which pores become difficult to down size, we have found that a thin dense selective layer integrally in an asymmetric membrane may not always be the best option for FO applications. A balanced membrane structure consisting of a thin porous support and a thin dense layer with a small structural parameter has been developed which shows low ICP in the FO process. Therefore, a relatively high water flux was obtained when seawater was employed as the feed, indicating that the membrane has great potential for desalination.

ICOM467

Preparation and application of interfacially formed membranes

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An improved method for preparing thin-film composite membranes via interfacial polymerization was presented in this work. Poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA), a side-chain active polymer, was employed as polymeric amine. A solid-liquid interfacial reaction between a preformed solid PDMAEMA layer and a *p*-xylylene dichloride (XDC) solution was exploited for film formation. Compared to the conventionally used liquid-liquid interfacial reaction for membrane formation, this procedure has numerous advantages: 1) due to existing backbones in the polymer, a defect-free membrane can be easily obtained, 2) since a polymeric amine is used instead of a monomeric amine, the penetration of the amine solution into the pores of the substrate is minimized, resulting in a substantial reduction in the mass transport resistance in the substrate, 3) the possible formation of microvoids caused by solvents involved in the liquid-liquid interfacial reaction is eliminated, 4) uniform distribution of fixed charges from the functional groups can be achieved, and 5) by controlling the crosslinked networks, the membrane can be finely-tuned for use in nanofiltration, gas separation and pervaporation. When tested in nanofiltration with an aqueous solution containing 0.1 wt% $MgSO_4$, a permeation flux of 30 L/(m^2.h) and a $MgSO_4$ rejection of 90 % were obtained at 0.8 MPa and 30^{o}C. A CO_2 permeance of 85 GPU and a CO_2/N_2 permeance ratio of 50 were achieved at 23^{o}C and 0.4 MPa feed pressure, and such a permselectivity is very favorable when compared to other gas separation membranes reported for flue gas separation. The membranes also showed good permselectivity for ethylene glycol dehydration by pervaporation. At 30^{o}C, a permeation flux of ~1 mol/(m^2.h) and a permeate concentration of 99.7 mol% water were achieved at a feed water content of 1 mol%.

Waste water treatment 1

ICOM1850

The role of membrane processes in wastewater treatment and reuse

Thomas Wintgens
University of Applied Sciences Northwestern Switzerland, School of Life Sciences, Institute for Ecopreneurship, Muttenz, CH

Advanced wastewater treatment and water reuse present promising options to mitigate the growing pressure on water resources in many areas of the world. However, the implementation of these concepts faces obstacles that include insufficient public acceptance, technical, economic and hygienic risks and further uncertainties caused by a lack of awareness, accepted standards, uniform guidelines and legislation. Rapid urbanization, global climate change and increasing awareness related to hygienic and chemical quality of natural water bodies are driving forces for significant developments in the areas of wastewater treatment and provide a strong motivation for the closing of local to regional water cycles.

Membrane processes are regarded as key elements of advanced wastewater treatment and reuse schemes and are implemented in a growing number of schemes world-wide including prominent examples such as agricultural irrigation in Kuwait, managed groundwater recharge in Orange County/California, indirect potable reuse schemes Torreele/Belgium and Singapore as well as for industrial process water production like in Wollongong/Australia, just to name a few. For centralised treatment options and high water quality requirements dual membrane processes, including e.g. micro- or ultrafiltration as tertiary treatment or membrane bioreactors are used followed by a reverse osmosis stage for desalination and removal of dissolved organic compounds. There is also a huge number of small scale membrane bioreactor systems providing high quality treatment for single households, small communities or residential complexes. Next to water reuse the discharge of effluent into sensitive water bodies, e.g. used for bathing, is a motivation for producing a high quality effluent with membranes.

Membrane processes have already proved to be reliable and viable options in advanced wastewater treatment schemes providing excellent treatment effectiveness and paving the way to further polishing or direct reuse. But the main drawbacks are still in the additional energy demand and in the case of dense membrane processes the concentrate stream generated.

The paper will provide an overview on the status of implementation of membranes processes in wastewater treatment and reuse world-wide and depict their potential role in promoting more sustainable water use patterns. The major technology trends will be described in terms of membranes and module systems utilized and operational experiences gained. Form the vast range of research activities conducted on membrane processes in wastewater treatment and reuse some major results will be highlighted including aspects of fouling characterization and control, membrane cleaning, integrity testing, removal performance with respect to different classes of contaminants, system design and simulation. The paper will conclude with an outlook on new developments and research needs.

ICOM1104

Integration of reverse osmosis and electro-oxidation for degradation of antineoplastic agents in wastewaters

Patrícia Oliveira, Svetlozar Velizarov, João G. Crespo, Carla A. M. Portugal
Requimte - CQFB, Departamento de Química, FCT – Universidade Nova de Lisboa, 2829-516 Caparica, PT

The antineoplastic agents are pharmaceutical compounds with high genotoxicity applied in cancer and autoimmune diseases therapies. Their presence in hospital and domestic wastewaters are potentially due to the excretions of patients under treatment and to laboratory activity. Their low biodegradability [1] explains the inadequacy of the processes generally applied in wastewater treatment plants for the destruction of these pollutants and their persistency in the ecosystems.

Incineration guarantees the chemical degradation of the antineoplastic agents, through high energy consumption, leading simultaneously to the emission of dioxins, furans and heavy metals [2].

The implementation of an eco-efficient and economic sustainable process allowing for the degradation of these compounds becomes a priority in order to prevent their accumulation in the ecosystems and avoid their adverse effects on the environment and human health.

The present work aims at developing an integrated reverse osmosis (RO) / electro-oxidation process for the degradation of the antineoplastic agents and their metabolites. This process integration methodology will benefit from the reduction of wastewater volume through reverse osmosis while achieving a dynamic control of the processing conditions, namely the salinity level and the concentration of antineoplastic agents (Figure 1).

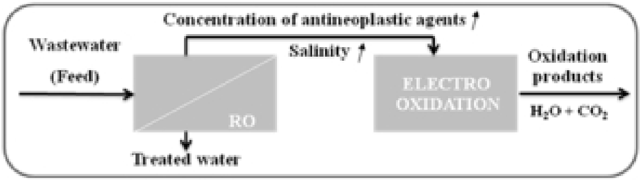

Figure 1: Integrated reverse osmosis (RO) / electro-oxidation process for the removal and degradation of antineoplastic agents from wastewater.

In this work, permeation studies were performed using a reverse osmosis flat membrane, SW30 (Filmtec, Dow) operated under cross flow mode, in order to determine the transport and the membrane rejection characteristics towards antineoplastic agents.

These studies were performed using a model solution of 5-aminouracil (5-AU), which is a less toxic chemical analogue of 5-fluorouracil (5-FU), one of the most frequently applied antineoplastic agent in cancer treatments. The selection of 5-FU as a model compound was based on its molecular weight (130 g/mol) and its octanol-water partition coefficient of -0.81. Indeed, 5-FU is the antineoplastic agent with one of the smallest molecular weights among the large diversity of antineoplastic agents. These studies aimed at understanding the influence of different processing parameters, such as: transmembrane pressure, hydrodynamic conditions, pH, concentration (Figure 2) and chemical nature of different salts (usually present in urine), on the RO membrane rejection properties.

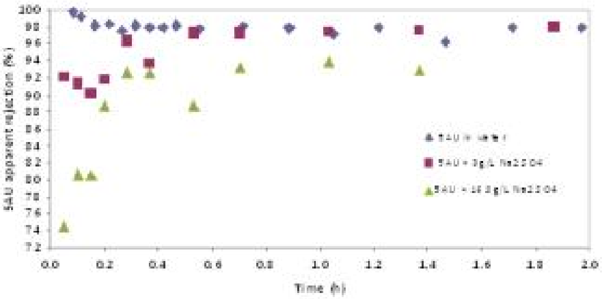

Figure 2: 5-AU apparent rejection in a SW30 (Filmtec, Dow) membrane, using feeds solutions with different saline concentration.

Studies on the degradation of 5-AU were also performed using an electro-oxidation cell equipped with a boron-doped diamond (BDD) anode (Adamant Technologies DiaCell®). In order to obtain a better comprehension of the reaction kinetics and mechanisms inherent to the 5-AU anodic oxidation, ongoing studies for the identification of the degradation products obtained at different processing times are being performed through LC-MS/MS analysis.

Acknowledgements:
The financial support from *Fundação para a Ciência e a Tecnologia (FCT-MCTES)* through research project PTDC/AAC-AMB/100960/2008 is acknowledged. P.I.C.Oliveira acknowledges *FCT-MCTES* for the PhD grant SFRH/BD/47587/2008.

References:

[1] Steger-Hartmann, T. (1997), Ecotoxic. Environ. Safety, 36, 174-179.
[2] http://www.noharm.org/europe/issues/waste/alternatives.php [accessed 13 July 2009]

ICOM335

Integrated forward osmosis and membrane distillation module with in-situ draw solution regeneration for water reclamation: Enhanced flux and trace organic removal

JIN SONG ZHANG[1], WINSON CHEE LOONG LAY[1,2], Shuwen Goh[1,2], Rong Wang[1,2], Chuyang Tang[1,2], Anthony Gordon Fane[1,2]
[1]*Nanyang Technological University, Singapore Membrane Technology Centre/NEWRI, Singapore, Singapore, SG,* [2]*Nanyang Technological University, School of Civil and Environmental Engineering, singapore, singapore, SG*

The integration of forward osmosis (FO) and membrane distillation (MD) in a single FO-MD module has shown significant potential for application in treatment of used water and water reclamation. The schematic diagram of the FO-MD module is shown in Figure 1. The FO process is a membrane separation process using dense semi-permeable membranes that allows water molecules to pass through while retaining bigger size solutes. The driving force for water transport is an osmotic pressure gradient achieved by using an osmotic 'draw solution' (DS) on the downstream side of the membrane. The MD process, on the other hand, uses microporous hydrophobic membranes that allow water vapour to pass through the dry pores, while retaining the non-volatile constituents. The vapour pressure gradient between the heated feed and cooled permeate provides the driving force for water transport.

The FO-MD module captures the complementary advantages provided by FO and MD in a single step. The MD membrane can provide complete retention and hence in-situ regeneration of the DS, when the DS is non-volatile, such as NaCl solution. The module is a three-channel arrangement with DS in the middle channel. The feed to the FO would be in the top channel while the permeate flow of the MD would be in the bottom channel. Other arrangements are possible, including FO and MD hollow fibres in a shell containing DS. The FO-MD module is able to reject salt, volatile and nonvolatile organic compounds.

In this study, the feed to the FO-MD module was synthetic feed water, which had a composition of 0.5g/L NaCl and 5 different types of pharmaceutical compounds (Carbamazepine, Naproxen, Ibuprofen, Diclofenac And Sodium 2-(4-Chlorophenoxy)-2-Methylpropionic Ac) at a concentration of 25ppb each. The DS was 0.5M NaCl and its temperature was maintained at 55°C. The permeate flow in the MD channel was maintained at 20°C by a chiller. The experimental results showed that permeate of the FO-MD process was ultra clean water. The removal of the pharmaceuticals was extremely high (> 99%) by the FO-MD integrated module. The conductivity of the permeate was less than 3µs/cm, confirming that the DS was completely retained by the MD membrane. In addition, by maintaining the temperature of the DS at 55°C, flux inefficiency due to internal concentration polarization of the FO membrane was reduced due to increased diffusion coefficient. As a result, the FO flux was double that obtained at 25°C.

This study demonstrated that the FO and MD processes can be synergistically coupled into one module and showed the feasibility of using this integrated module for water reclamation with enhanced water production and rejection of low molecule weight organics at trace level.

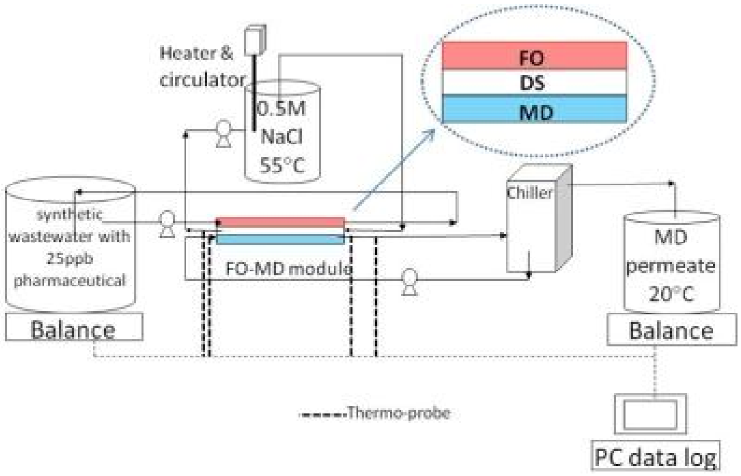

Figure 1 Integrated FO/MD Module and FO-MD process

ICOM1669

Valorization of waste water from potato starch production

Mika Mänttäri[1], Elsi Koivula[1], Jussi Lahti[1]
[1]Lappeenranta University of Technology, Chemical Technology, Lappeenranta, FI, [2]Lappeenranta University of Technology, FI, [3]Lappeenranta University of Technology, FI

Potato fruit juice is released from potatoes during production of starch. Actually it is waste water which has huge chemical oxygen demand and significant eutrophical effect in the receiving water ways. In this study valorization of potato fruit juice by membrane filtration has been studied. The aim was to reduce the volume of the waste water and to produce concentrated streams which can be utilized e.g. as production of biogas or as a fertilizer. The target was also to reduce the environmental load of the starch production plant.

Various membranes (ceramic and polymeric) as well as different modules (low and high shear modules) were tested to fractionate potato fruit juice into concentrated fractions and permeate that can be treated more efficiently in a biological waste water treatment process. Ultrafiltration (UF) and microfiltration were used to concentrate suspended solids and high molar mass compounds (e.g. proteins). Their permeate solutions were further filtered using reverse osmosis (RO) membranes to concentrate dissolved compounds (e.g. potassium ions).

The potato fruit juice contains dry solids about 4% and its potassium concentration was 4.5 g/L. UF at a recovery of 90% produced the concentrate stream which dry solid content was approximately 24%. The average permeate flux was 110 kg/(m^{2}h) at 2.5 bar when a high shear cross-rotational UF was used. Potassium ions permeated completely UF membranes. This means that they were not bound by suspended solids. In RO (recovery of 88%) the dry solid content increased from 4.6% up to 22 % and potassium concentration from 4.5 g/L to 31.4 g/L. Two stage membrane process (UF +RO) recovered about 75% of potassium in the RO concentrate. The best RO membrane produced permeate which COD content was about 2 g/L and potassium 1.6 g/L when the concentrate COD was 209 g/L. The results showed that membrane filtration is a promising method to valorize waste water from potato starch production to concentrated by-products.

Parallel Sessions

Monday, July 25th 2011

Afternoon Session 2, 16.00 – 17.50

Membrane fouling 1

ICOM1848

Advanced tools to study biofouling in spiral wound membrane systems

J. S. Vrouwenvelder[1, 2], C. Picioreanu[2], A. I. Radu[2], J. C. Kruithof[1], M. C. M. Loosdrecht[2]
[1]Wetsus, Centre of Excellence for Sustainable Water Technology, Leeuwarden, NL, [2]Delt University of Technology, Faculty of Applied Sciences, Dept. of Biotechnology, Delft, NL

The objective of our studies was to relate biomass accumulation in membrane systems with membrane performance and determine parameters influencing biofouling.

Problem analysis in 15 full-scale reverse osmosis and nanofiltration installations showed a need for tools to enable a reliable evaluation of the development of biofouling. An innovative set of tools was developed to monitor and characterize biofouling: membrane fouling simulator, sensitive pressure drop measurements, Magnetic Resonance Imaging and a three-dimensional numerical model to simulate biofouling and hydrodynamics. These tools have been used to increase the understanding of biofouling.

An important finding was the crucial role of the membrane spacer in fouling processes. The critical flux concept was shown to be not applicable for reverse osmosis fouling. Flow channeling has been shown as the dominant processes for concentration polarization and the resulting decreased water flux combined with increased salt flux over the membrane.

The presentation will contain advancements on fundamental understanding of biofouling processes, including potential new ways for their control.

ICOM565

Calcium Phosphate Mineralization Inspired by Surface Functional Groups in Membrane-based Wastewater Treatment Processes.

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[1]Ben Gurion University, Desalination and Water Treatment, Beer Sheva, IL, [2]Ben Gurion University, Biotechnology Engineering, Beer Sheva, IL

Worldwide the amount of fresh water is limited hence improvements in waste water reclamation are necessary. It has been shown that formation of biofilms and calcium phosphate scaling on reverse osmosis (RO) membranes limits the desalination of secondary waste water effluents. Here we studied the effect of specific components representing biofilm-EPS (extra-cellular polymeric substances) on calcium phosphate mineralization at the molecular level. Our results show that calcium phosphate mineralization is accelerated by different functional groups. Mineralization in simulated secondary effluent (SSE) solution which is oversaturated with respect to calcium phosphate, simulating the concentration present on the surface of RO membrane, was studied on self assembled monolayers of alkanethiols modified gold substrates, and on Langmuir films. Mineralization was accelerated in the order of: $-PO_4$> -COOH~ $-NH_2$> -COOH: NH_2 1:1 mixture> -OH> -ethylene glycol. X-ray diffraction of the scale showed a peak at $2\theta = 31.7^{\circ}$, and ATR-FTIR peaks at 1059 and 1179 cm^{-1} that are characteristic of hydroxyapatite. Results imply that surfaces possessing low charge density groups, or equally distributed positively and negatively charged groups tend to scale less. Gold wafers coated with biopolymer components of the EPS, incubated in SSE solution for 10 and 20 days showed that the rate of mineralization is accelerated in the order: alginic acid>fibrinogen> BSA> medium MW chitosan= low MW chitosan. ATR-FTIR characterization of the scale showed intense peaks of hydroxyapatite. This data provides an insight towards understanding the effect of the various chemical functional groups in EPS biopolymers on scaling mechanisms. It is also expected that this study will contribute to the development of novel low-scaling RO desalination membranes.

ICOM803

Critical flux in algal biopolymer fouling of forward osmosis membranes - role of feed solution chemistry and draw solution types

Qianhong She[1,2], Xue Jin[1,2], Chuyang Y. Tang[1,2]
[1]Nanyang Technological University, School of Civil and Environmental Engineering, Singapore, SG, [2]Nanyang Technological University, Singapore Membrane Technology Centre, Singapore, SG

Forward osmosis (FO) is an emerging membrane separation process that has recently been explored for various environmental applications, such as wastewater treatment and seawater desalination. The growing interests in FO raise the need for systematic research in FO membrane fouling which may limit its applications. Critical flux, below which no fouling would occur, has been studied extensively for the fouling of pressure-driven membrane processes. However, the critical flux concept may be different in the osmotically-driven FO process due to the complexity induced by draw solution. This study aims to systematically investigate the role of feed solution chemistry, draw solution type and membrane orientation in the critical flux in alginate fouling of FO membranes.

A commercially available FO membrane, provided by Hydration Technologies, Inc. (Albany, OR), was used as the model FO membrane. Alginic acid sodium salt (Sigma-Aldrich) was selected as the representative of algal biopolymer. Accelerated fouling experiments were carried out in a lab-scale cross-flow flat-sheet FO membrane cell. Water flux and reverse diffusion of draw solution salt were monitored with time.

Results show that FO fouling was more severe in the active layer facing draw solution (AL-DS) orientation in all cases. The presence of Ca^{2+} in the feed water significantly enhanced alginate fouling whereas the presence of Mg^{2+} had little influence in flux behavior. Moreover, results from fouling experiments confirmed that draw solution type dramatically impacts the fouling extent. The critical fluxes under different types of draw solution in alginate fouling decreased as $NaCl \geq MgCl_2 > CaCl_2 > Ca(NO_3)_2$. The observed different fouling behaviors with different types of draw solution can be dominated by reverse diffusion of the solute from draw solution to feed water, which can further result in (1) the interaction between the reverse-diffused draw solute and alginate in feed water and (2) the increase of the osmotic pressure in feed water and thus reduced osmotic driving force. We will discuss the relationship between critical flux and the physicochemical characteristics of draw solute. Our results further suggest that there is a critical draw solution concentration value below which no fouling would occur in FO process. The ratio of critical flux over critical draw solution concentration may be introduced to evaluate the efficiency of draw solution.

ICOM1680

Biofouling of reverse osmosis membranes: Effect of permeate flux on biofilm architecture, adherence and viscoelasticity

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Major obstacles in membrane processes used for treatment of any type of wastewater are different types of fouling. Our project focuses on biofouling, the major challenge in wastewater reclamation (Xu et al. 2010). Biofilm formation results in an increased energy requirement of the feed water pumps, a lower flux, and a decrease in permeate quality (Jarusutthirak and Amy 2006). Recently it was found that species belonging to the Sphingomonas family initiate and dominate RO biofilms (Bereschenko et al. 2010). A model strain, *Sphingomonas wittichii* RW1, is used in this study.

The current work examines abiotic and operational system parameters, attributed to the RO process, and their effect on the initial bacterial adherence and biofilm buildup. The effect of permeate flux and concentration polarization is examined. Changes in the rate of RO biofilms development and structure together with EPS adherence and viscoelasticity are characterized.

It was found that permeate flux affects several key parameters in the course of biofilm development: (1) mode of microcolonies dispersion during initial stages of sessile cells proliferation; (2) mature biofilm volume; (3) biofilm roughness and porosity; (4) live/dead cells ratio in the biofilm; (5) extracellular polymeric substances (EPS) composition and (6) EPS adherence and viscoelastic properties as analyzed in a quartz crystal microbalance with dissipation (QCM-D). In addition, permeate flux decline was enhanced by the rate of biofouling process in two ways that are interrelated with the initial flux: (1) at higher initial permeate flux, a higher rate of biofilm development was observed and (2) biofilm enhanced concentration polarization (BEOP) phenomena was more pronounced.
Under higher flux, the protein portion in the EPS increased and the EPS became more viscoelastic. Biofouling layers subjected to a higher flux contained EPS which is more elastic and the ratio of cells volume to EPS volume decreases. This observation is explained by absence of selection of relatively sticky EPS components, such as polysaccharides, at higher permeate flux.

Even though pressure and the associated permeate flux are important and well studied parameters in membrane separation processes, in the RO tertiary effluents reclamation process, their effects on the physical and the physiological properties of the RO biofouling layers have not been thoroughly investigated. Our findings shed light on the biofilm development of a model strain that is found to initiate and dominate biofilms on RO membranes under desalination conditions of tertiary wastewater. Results to be discussed may assist process improvement and development of appropriate and target-aiming biofouling control of RO membranes.

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ICOM1227

Biofilm development in spacer filled channels in reverse osmosis membrane processes

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Reverse osmosis (RO) is the most common method for desalination and water reclamation. However, its success has been hindered by biofouling where biofilm grows inside the membrane module and increases energy requirements [1]. Biofilm on the membrane surface may increase the resistance (R_f) and cause enhanced concentration polarization (CP) [2]. This results in higher trans-membrane pressure (TMP), needed as the driving force. The biofilm can also increase channel pressure drop (ΔP) where biofilm grows inside the feed channel due to the presence of spacer [3]. Recently, we have shown that spacer reduces the TMP rise in RO applications, which shows that biofouling in RO is a membrane related problem [4]. A more in depth study was done to investigate the role of feed channel spacer towards biofouling in a spacer filled channel.

The objective of this study is to observe biofilm development in a spacer filled channel. Experiments were conducted at constant flux and biofouling was observed by the increase of TMP and autopsy. Fouled membranes and spacers were analyzed for bacterial counts and EPS content. *In situ* observation with confocal light scanning microscopy (CLSM) was also conducted to visualize biofilm patterns inside the module.

Figure 1 shows the development of biofilms in the membrane module as the TMP increased steadily with time by ~40% after 10 days. Separate experiments with the same conditions were conducted at different durations (3 and 6 days). The spacer caused uneven growth across the membrane area. Percent coverage by biofilm increased from 30% (3 days), to 73% (6 days), and 85% (10 days). Biofilm was primarily found on the membrane and started to appear on the spacer after 6 days.

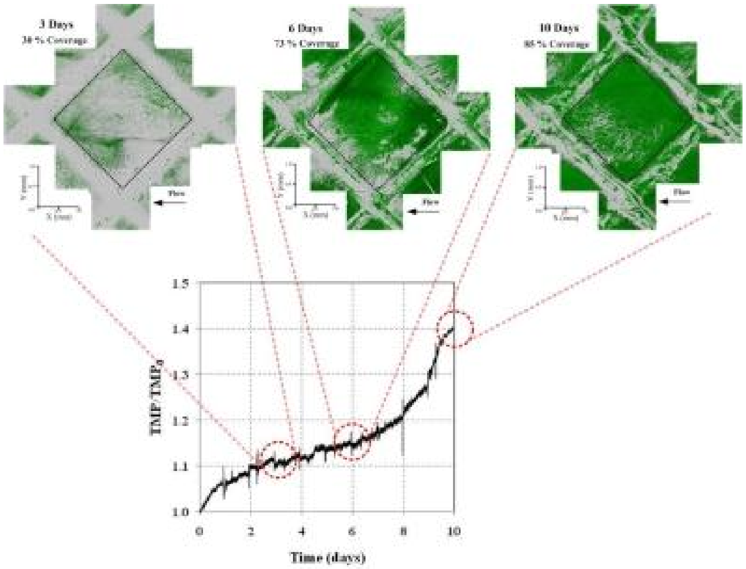

Figure 1. Successive events of biofilm development in a spacer filled channel and causes increase of observed TMP. Flux = 35L/m2/h, cross flow velocity = 0.17 m/s, diamond type spacer. Image analysis with CLSM method and LIVE-DEAD staining.

Different patterns of biofilm were observed when different types of spacer (diamond and ladder) were used. Figure 2 shows that ladder type spacer gives less biofilm coverage (~50%) compared to diamond type spacer (~70%). Ladder spacer seem to provide better biofouling reduction.

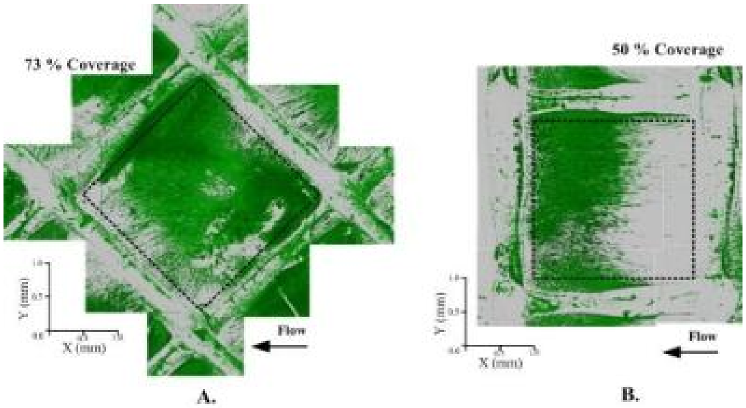

Figure 2. Microscopic images of biofilms on the membrane and spacer with A. Diamond type spacer and B. Ladder type spacer. Flux = 35L/m2/h, cross flow velocity = 0.17 m/s. 6 days experiments observed with CLSM 10x objective and 0.6x zoom.

This study shows that biofouling starts on the membrane and appears on the spacer in latter stages. The presence of spacer affects the biofilm development and its configuration influences the development of the biofilm. It appears that biofouling in RO is both membrane and spacer problem.

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Membranes for fuel cells 1

ICOM1864

Nanofiber Composite Ion-Exchange Membranes

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There is a need for high performance polymeric ion-exchange membranes for proton-exchange membrane and alkaline fuel cells. Such membranes must possess the requisite transport properties (e.g., high ionic conductivity and low gas/fuel permeability) and have outstanding durability (i.e., enhanced mechanical, chemical, and thermal stability in both the wet and dry states). Past strategies for developing new fuel cell membranes have included: (1) the synthesis of new polymers with a high ion-exchange capacity, (2) the use of block copolymers which self assemble into nano-phase domains, where one block provides selective ion transport pathways and the second block imparts mechanical strength to the membrane, (3) combining the desirable properties of two different polymers in a single membrane by blending the polymers prior to membrane casting, (4) impregnating a functional polymer into a microporous inert support, where the support provides the mechanical properties that the functional polymer does not possess, and (5) crosslinking the polymer to limit/control solvent swelling. While these approaches have resulted in some successes (e.g., the GoreSelect® membranes from W. L. Gore & Associates for fuel cell applications where perfluorosulfonic acid polymer is impregnated into a porous Teflon support), there all inherent difficulties and drawbacks in most of these schemes. For example, the use of block copolymers is limited by polymer chemistry (it is difficult to covalently attached very different blocks to one another) and by the availability of a suitable solvent for solution casting membranes from the resulting block material. Also, there is no guarantee of high-level (long range) organization of phase-separated domains in a block copolymer after membrane casting.

An alternate approach is to use polymer nanofiber electrospinning as a "forced assembly" technique to generate a highly desirable phase separated composite membrane nanomorphology[1-3]. Two different membrane morphologies are possible: (1) ion-exchange polymer nanofibers surrounded by an inert (uncharged) polymer matrix and (2) inert (uncharged) polymer nanofibers surrounded by the charged polymer. In the present talk, both membrane structures will be discussed, in terms of: (a) membrane processing, where uncharged and ionomeric nanofibers are electrospun simultaneously with follow-on mat processing into a defect-free membrane, (b) membrane characterization (e.g., ionic condutivity, membrane swelling, and mechanical properties), and (c) membrane applications for hydrogen/air and alkaline fuel cells.

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ICOM1013

Surface nano-coated hydrocarbon proton exchange membrane for fuel cell

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Proton exchange membrane (PEM) determines the electrochemical performance of membrane-electrode assembly (MEA) as it delievers protons and blocks fuel gases at the same time. Proton conductivity and dimensional stability of PEM are required for high performance and duarability of MEA in fuel cell operation. Hydrocarbon membranes including sulfonated polysulfone and sulfonated poly (arylene ether sulfone) have high proton conductivity came from high ion exchange capacity and high degree of sulfonation when it is fully hydrated due to effective water channels formed by the phase separation of hydrophilic domains and hydrophobic domains between polymer chains. Although this high proton conductivity improves the electrochemical performances of MEAs, it can bring excessive swelling of polymer matrix, losing its dimensional stability and detoriating the long-term durability of MEAs. Moreover, under low relative humidity (RH) conditions below 50%, they show the drastically decreased proton conductivity due to the dehydration inside membranes. Finally, single cell performances of hydrocarbon membranes are decreaed under low humidity below 50% RH in comparison with the membranes in fully hydrated condition. This weak point of PEMs has retarded the commercialization of proton exchange membrane fuel cell (PEMFC) for vehicles and stations, requiring the complexed humidification system such as balance of plant (BOP) and humidifier.

In this study, surface nano coating technology was applied to hydrocarbon membranes to improve the electrochemical performances of MEA in low relative humidity conditions. Sulfonated poly (biphenyl sulfone) (BPSH) polymers with variations of degree of sulfonation 20, 40 and 60 were selected for the surface treatment. Nano-coating treatmenat changed the hydrophilicity and morphology of membrane surface according to the degree of sulfonation and the intensity of treatments. Nano coated layer on membrane surface was confirmed by measuring contact angles and several surface analysis images. This modified surface of BPSH membrane provides high water uptake in low relative humidity condition sustaining its dimensional stability. Consequently, it resulted in the increased proton conductivity under relative humidity of 50% and much higher electrochemical performances of MEA in I-V curves, comparing to the performances of BPSH membrane itself. Therefore, surface nano-coated hydrocarbon membrane suggests another way to enhance the electrochemical performance in low humidity, which is resulted from the surface modifications having self-humidifying properties without sophisticated polymer synthesis for well-ordered proton conducting channels.

ICOM981

Theoretical Studies of Proton Transfer on Surface of Strong Acidic Nanoparticles for Polymer Electrolyte Fuel Cells

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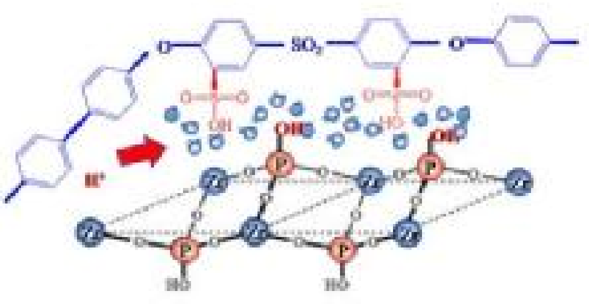
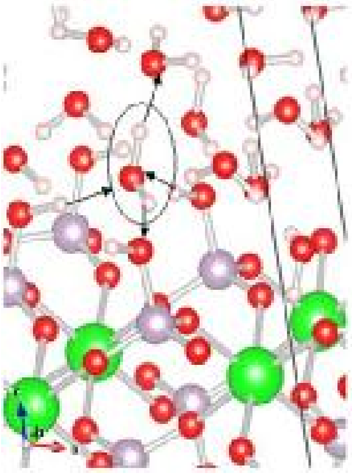
The development of fuel cells is increasingly important because fuel cells have the potential to reduce CO_2 emissions as a result of their high energy efficiency. In particular, polymer electrolyte fuel cells (PEFCs) have been studied as portable or stationary power sources and also as an energy device for automobiles. One of requirements is to simplify the humidification device of the PEFC electrolyte membranes that provide high performance under low-humidity conditions.
Recently, strong acidic zirconium phosphate (ZrP), zirconium sulphophenylphosphate (ZrSPP) is blended finely to sulfonated polyether sulfone (SPES) and show high proton conductivity at low-humidity condition. The interface of SPES and ZrP/ZrSPP particles causes the high conductivity, because the composite shows higher proton conductivity than the sum of the conductivities of ZrP/ZrSPP and SPES. In the interface of ZrP/ZrSPP and SPES, acid groups are considered to be concentrated, which leads to better performance. However, there is no clue for this phenomenon.



To examine the origin of the high proton conductivity at the organic-inorganic interface, the proton hopping mechanism at the surface of water-adsorbed ZrP, ZrSPP, and zirconium sulphate (ZrS), has been theoretically investigated as a first step in our research. Proton transfer path and activation energy, which determine the proton conductivity, are examined by quantum chemistry calculations. In particular, the effects of adsorbed water molecules and acid groups on the proton conductivity are analyzed by examining the interaction energy between the acid groups and the adsorbed water molecules, the charge of the proton and oxygen atom and also the O–O distance along the proton-transfer path.
As a result, it has been clearly shown that the interaction between the acid groups at the surface of ZrP/ZrSPP/ZrS nanoparticle and the adsorbed water molecules are relatively large and a strong hydrogen-bond network is generated locally.



Because of the strong interaction, water molecules can be attached to the nanoparticle and the O–O distance becomes shorter and the charge of atom is more delocalized than that in bulk water systems. Because of the short O–O distance and the delocalized charge of each atom, the activation energy of proton transfer at the surface of nanoparticle decreases and causes high proton conductivity. Based on the above studies, the origin of the high proton conductivity at the organic-inorganic interface is also discussed.

ICOM1068

Proton conducting interpenetrating polymer networks as new PEMFC membranes

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PEMFC systems are of prime interest for automotive applications. The current standard membrane for use in PEMFC applications remains Nafion® due its high proton conductivity (ascribed to its well-defined microphase separated morphology) combined with excellent chemical stability. Its suitability for the transport sector is however limited due to the reduced performance and lifetime at high temperature (T > 90°C) and low relative humidity (RH < 50%). Conditions which are typical for automotive utilization. As an alternative, aromatic polymers are generally considered to have suitable properties to serve as a membrane material. Many aromatic polymers are currently already used in a variety of technical applications under very demanding conditions and have important properties, such as high thermal stability as well as excellent mechanical properties. To be able to serve as a proton conductor, these aromatic polymers are substituted with acidic groups (generally sulfonic acid groups). The acidic groups ensure swelling of the polymer membrane by water and enable the effective proton transport. Although swelling is essential it generally results in dramatic changes (losses) in the mechanical properties. The essential high proton conductivities require high degrees of sulfonation and thus an apparent paradox exists between membrane performance and membrane stability.

In the frame of the French national project AMEIRICC, funded by National Research Agency, original proton conducting interpenetrating polymer networks (IPNs) are investigated in order to increase the performance and durability of PEMFCs, especially for the hard operating conditions found in automotive applications. IPNs are defined as a combination of two or more polymer networks synthesized in juxtaposition. The main thought behind the IPN concept is the separation of the two required membrane functions into two different polymeric structures. The first, generally a sulfonated aromatic polymer, ensures high proton conductivity, while the second, generally a perfluorinated polymer, provides the mechanical and chemical stability. Two different polymerization routes (e.g. UV photopolymerization and polyaddition) are used to ensure that two distinct polymer networks are created. The entanglement of two crosslinked polymers leads to forced 'miscibility' compared with usual blends and the resulting materials exhibit good dimensional stability. Ultimately, the interpenetrating polymer network mimics the microphase separated morphology, which is characteristic for the perfluorosulfonated proton conductive ionomers, such as Nafion®.

In this contribution we discuss the synthesis of these interpenetrating polymer networks and elaborate on the results relative to morphology, proton conductivity, water swelling, chemical and mechanical stability and hydrogen permeability. Furthermore their fuel cell performance with membrane electrode assemblies (MEA) manufactured with commercial gas diffusion electrodes will be presented.

ICOM542

High performance anode-supported micro-tubular SOFC prepared from single-step fabricated dual-layer hollow fibres

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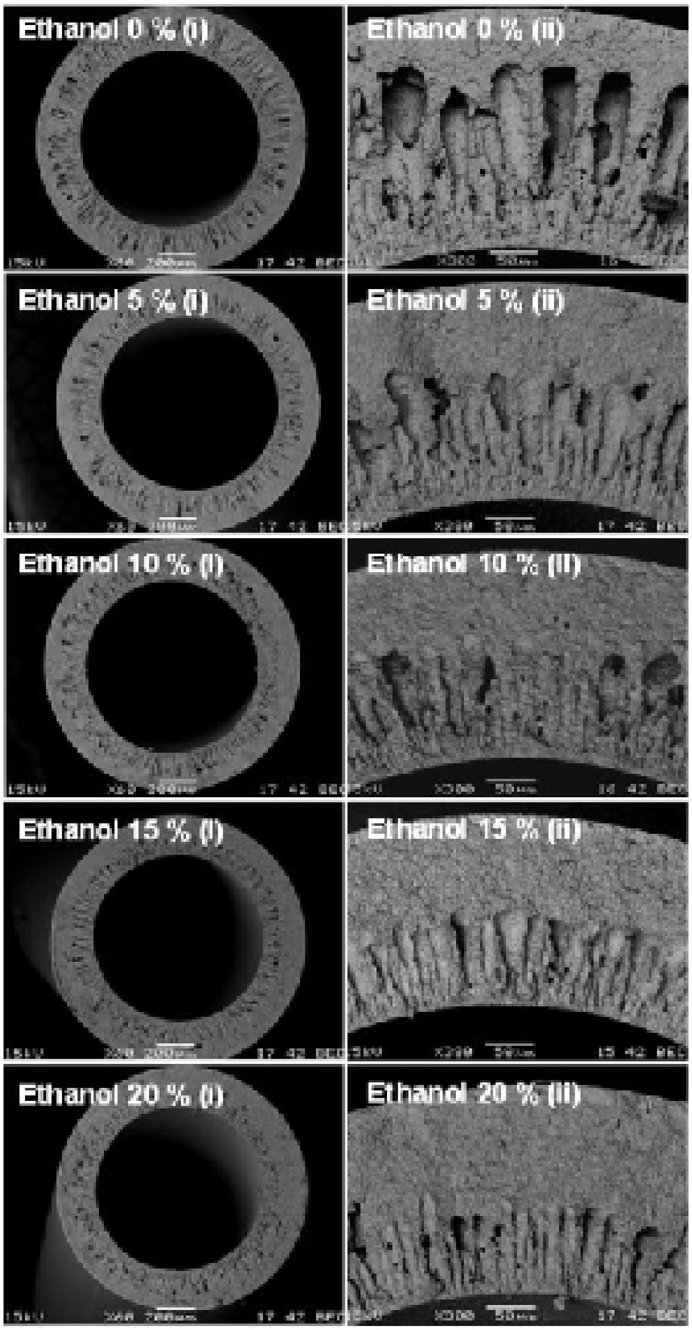
The development of micro-tubular solid oxide fuel cells (SOFCs) has received more and more attention recently due to a number of advantages of this configuration, such as high volumetric power output and rapid start-up/down. Significant efforts in fabricating micro-tubular SOFC have been achieved by our research group [1-3], where an advanced dry-jet wet extrusion technique, i.e. co-extrusion process, was employed. By using this technique and followed by a co-sintering process, a cerium-gadolinium oxide (CGO) electrolyte/nickel (Ni)-CGO anode dual-layer hollow fibre (HF), distinguishes by an electrolyte outer layer of approximately 80 µm supported by an asymmetric structure anode inner layer with 35 % finger-like voids thickness, has been developed in a single-step [1]. The resultant micro-cell produced the maximum power density of 5,864 W m^{-2} at 570 ^{o}C [2].

Further effort to reduce the thickness of the defect-free electrolyte outer layer to as thin as 10 mm resulted in the increase of the maximum power output to 11,100 W m^{-2} at 600 ^{o}C [3]. Although it proved the potential of dual-layer HF as a promising support for SOFC, the value of powder density was still slightly lower than the value previously reported in literature (12,940 W m^{-2} at 600 ^{o}C) [4]. One of the major reasons for the lower power output was the less effective porosity in the anode of HFs fabricated in this study due to short finger-like voids structure (~35 %).

Realising the finger-like voids can simply be controlled by the co-extrusion technique, therefore the study on the effect of anode structures on cell performance is the main concern in this work. The use of ethanol in the spinning suspension allows the control over the asymmetric structure of the anode layer, i.e. finger-like voids covering about 50-85 % of the anode layer, as can be seen in Figure 1. The presence of finger-like voids significantly facilitates the mass transfer inside the anode, and as a result, the maximum power density increases from 18,391 W m^{-2} to 23,244 W m^{-2}, when the finger-like voids is increased from 50% to 70% of the asymmetric anode layer. However, further growth of finger-like voids to 85% of the anode layer dramatically reduces the number of triple phase boundary (TBP) region and conductivity in the anode, which consequently decreases the maximum power density to 9,863 W m^{-2}. Based on the results obtained, therefore, dual-layer HFs with 50-70% of finger-like voids in the anode can be considered as the ideal structure for producing high performance micro-tubular SOFCs.



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Desalination 1

ICOM1785

Developments and Challenges in Membrane Desalination

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Reverse Osmosis is now the favoured technology for desalination. This has come about thanks to continuous improvements in membranes, modules and systems, as briefly reviewed in this presentation. Developments include RO membranes with improved water permeability and lower solute transmission, modules with improved spacer design and system hybridization to more evenly distribute flux. Pretreatment for membrane desalination appears to be moving to low pressure membranes.

Membrane desalination is nominally a 'mature' technology, yet there are challenges and opportunities that require future change. Novel membrane concepts include those based on mixed matrix formulations, carbon nanotubes, biomimetics and antifouling surfaces. The spiral wound module continues to evolve with input from CFD analysis. Although we have learnt to live with it, fouling in RO desalination continues to limit efficiency. A better understanding of biofilms offers promising control of biofouling based on biofilm manipulation, such as quorum 'quenching'.

Interest in 'non-RO' desalination is also strong. For example recent developments in ED –based desalination may offer energy savings. The low pressure processes, membrane distillation (MD) and forward osmosis (FO) offer interesting possibilities, including the use of low grade heat in desalination. Developments in MD include improved membrane hydrophobicity, enhanced performance of hollow fibre modules and novel flat-sheet MD concepts. MD coupled with RO could greatly increase water recovery. FO is experience a renaissance with significant developments in membrane performance. Draw solute optimization is required for a viable FO desalination process. However there are other opportunities, such as FO coupled with RO to exploit the chemical potential of the brine concentrate.

The presentation ends with a final look into the crystal ball.

ICOM564

Osmotically Assisted Desalination: A Low Energy Integrated Desalination System

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Development of alternative desalination processes is essential in light of the continuous increase in demand for drinking water. Membrane processes, and especially reverse osmosis (RO) and electrodialysis, are leading among seawater desalination processes. However, each has it own shortcomings, including high energy requirements and limitations to the feed water salinity that can be handled.

A novel hybrid desalination process is presented. The process, called osmotically assisted desalination (OAD), utilizes a high-pressure membrane desalination process (i.e., reverse osmosis (RO)) that in combination with a pressure-retarded osmosis (PRO) subsystem achieves water desalination at lower energy expenditure. In the OAD system (Figure 1), treated wastewater, or another source of impaired water, is used as an energy source that is manifested during mixing with concentrated brine (draw solution) before ultimate discharge of the mixture back into the ocean. There are several advantages associated with the OAD system:

· The only external energy input required is to pressurize water from approximately 350 to 600 psi (ΔP = 250 psi). This is much less than the external energy input required for conventional seawater RO which requires pressurization from approximately 0 to 600 psi (ΔP = 600 psi). Otherwise, the energy for the system is supplied through pressure exchangers that convert the osmotic pressure difference in the OAD to hydraulic pressure in the desalination process (osmotic pumps). **From the energy standpoint, the osmotic pressure difference between the draw solution (generated by the desalination process) and the wastewater is the source of hydraulic pressure that is used in the desalination process to overcome the osmotic pressure of the feed water to the RO process; therefore, the net energy demand of the RO process is used for the purpose of producing purified water only and not to overcome the osmotic pressure of the feed water to the desalination process.** Therefore, in the OAD a booster pump is used to enhance water recovery at very low energy expenditure.

· The draw solution is used in a completely open loop and therefore accumulation of contaminants in the system is unlikely.

· The brine generated during the desalination process is being diluted in the PRO process and subsequently being discharged back to the ocean at the same ambient concentration; therefore mitigation adverse environmental impact on marine ecology/habitat. Also, being mixed with purified water from the PRO process, the diluted brine is discharged to the ocean at higher water quality compared to the ambient seawater.

· The impaired water and RO product water are in completely separate circuits so there is no contact of impaired water with drinking water.

A pilot-scale OAD system is currently under construction and it will be deployed to the test field in spring 2011. When completed, the OAD system will be the first PRO system operating in the United States. In this presentation, details about system construction, and results from experiments and modeling will be presented.

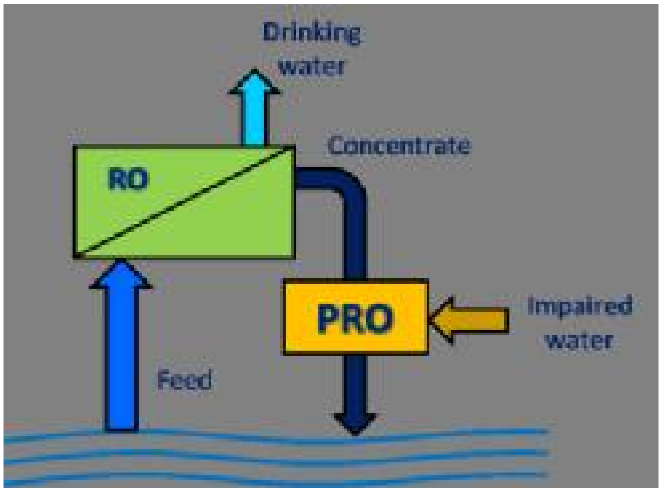

Figure 1: Schematic illustration of an OAD system.

ICOM435

DCMD Studies in Crossflow Membrane Modules and Cascades using Coated Hollow Fiber Membranes: An Overview

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Abstract: We have recently developed novel hollow fiber membranes and devices for recovering pure water from hot brine via direct contact membrane distillation (DCMD). Hot brine undergoes rectangular crossflow over the outer surface of highly porous hydrophobic polypropylene hollow fibers whose outside surface was coated with porous plasma polymerized silicone-fluoropolymer coating to mitigate pore wetting and distillate contamination as cold distillate flows through the bores of fibers having a large wall thickness. The DCMD studies were successfully carried out at three levels: small laboratory modules, large laboratory modules, larger pilot plant units. Extended pilot scale operation demonstrated no salt leakage, stable and repeatable performance with synthetic solutions having salt concentrations of 10% as well as with sea water concentrated up to 20% salt via batch recirculation.

The scaling behaviors of scaling salts such as $CaSO_4$ and $CaCO_3$ in small crossflow hollow fiber modules were studied extensively using supersaturated solutions having high SI values. The highly encouraging results will be summarized. In addition the scaling behavior of polymeric solid hollow fiber-based heat exchangers potentially usable in DCMD processes was experimentally evaluated.

If such a technique is to be used to further concentrate the reverse osmosis desalination process concentrate, we should know how it behaves with antiscalants. Extensive scaling experiments with the addition of antiscalant were conducted to see the effects of concentration and different kinds of antiscalants on inhibiting scaling from deposits of $CaSO_4$ and $CaCO_3$. The parameters of the induction period, calcium concentration, distillate conductivity and water vapor flux were investigated.

Cost-efficient desalination technology was also developed successfully by integrating a countercurrent cascade of the novel crossflow DCMD devices and solid polymeric hollow fiber-based heat exchange devices. Simulations have been carried out for the whole DCMD cascade to project values of gained output ratio (GOR) as a function of the number of DCMD stages as well as other important factors in the cascade vis-à-vis the temperatures and flow rates of the incoming hot brine and cold distillate streams. The simulation results were verified with the experimental results from cascades consisting of 2 to 8 stages. An artificial sea water was concentrated 8 times successfully when a countercurrent cascade composed of 4 stages of the DCMD modules and a heat exchanger was employed during the DCMD process in the batch recirculation mode. Numerical calculations will also be reported for the case where a number of such cascades are utilized in series for substantial concentration of saline water on a continuous basis.

ICOM414

Brackish water desalination by forward osmosis: Effects of working temperature on separation performance, membrane scaling and cleaning

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Over the past 40 years reverse osmosis (RO) has drawn increasing attention in water desalination because of its excellent separation capability. However, RO is still facing the problems of high energy and cost inputs, as well as low water recoveries partly due to membrane fouling. To mitigate these problems, this study proposes using forward osmosis (FO) for inland brackish water desalination. It is supposed that FO has many advantages over other pressure-driven processes, such as low energy consumption, low membrane fouling, high quality of product water due to its multi-barrier protection, high water recovery and thus minimizing brine volume.

In the current study, a bench scale FO system was operated to evaluate the effects of temperature on separation performance (e.g. water fluxes and recoveries), membrane scaling and cleaning in brackish water desalination. Both local brackish water with total dissolved solids of 3970 mg/L and simulated brackish water with NaCl only were used as the draw solution in FO at temperatures of 25, 35 and 45 °C. The effects of temperature on FO performance in terms of permeate fluxes, system recoveries, membrane scaling and cleaning effects were systematically investigated. Bench-scale FO experiments showed that higher temperature would afford higher water fluxes, higher water recoveries and higher concentration factors, but also caused more adverse effects on membrane fouling and cleaning. For example, shows that the membrane scaling became more severe with the increase of the operation temperature. From , it can be seen that higher temperature will result in more severe FO scaling and also more adverse affect on water cleaning, even though it can lead to a higher initial water flux. These findings have significant implications for optimizing the working temperature, which involves in many factors such as permeate fluxes, water recoveries and membrane scaling in FO process for brackish water desalination.

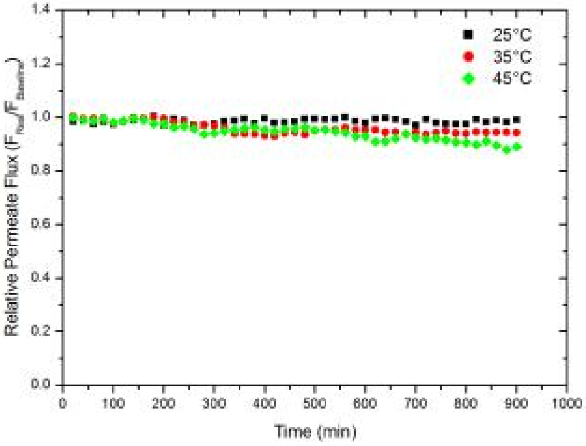

Table 1. Effects of temperature on membrane scaling and cleaning in FO.

Temperature (℃)	Pure water volume flux, J (L/m^{2}h)			Flux ratios [a]	
	Initial, J_0	After fouling, J_1	After cleaning, J_2	Fouling effect, r_1	Cleaning effect, r_2
25	15.13	14.52	15.08	0.960	0.997
35	19.79	14.67	16.80	0.741	0.849
45	22.09	15.00	17.50	0.679	0.792

[a] $r_1=J_1/J_0$; $r_2=J_2/J_0$.

ICOM484

Highly Effective Polyamidoamine Denrimers-Based Draw solutes for Forward Osmosis

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Forward osmosis is a new desalination process that utilizes the osmotic pressure difference as the driving force for water transfer across a semipermeable membrane. Since it is a natural process, the water transfer does not require the input of energy, thus is termed as a green, environment-friendly and energy-efficient process. The process has not been applied in desalination in industry because of the separation of draw solute from the transferred water is energy-intensive. Moreover, it has been found that the draw efficiency of the FO process can be as less as 10% of theoretical prediction which is mostly ascribed to the concentration polarization, especially the internal concentration polarization.

It is generally recognized that small molecules are more effective in reduction of the internal concentration polarization. Here we report the use of globular polyelectrolytes as draw solutes in a FO process. The use of a home-made, nearly double-skinned CTA membrane and a Dow RO membrane were used to evaluate the draw efficiency of the solutes. The draw efficiency of the draw solutes of different generation was evaluated at different draw concentration and compared with NaCl. The osmotic pressures of the draw solutions were measured. The theoretical water flux and experimental fluxes were compared. It was found that with the increase of dendrimer generation, the draw efficiency decreased, but for G0 generation, a draw efficiency of about 50% was observed, which is significantly higher than many small molecules considering the high pure water flux: 28.1 $Lm^{-2}h^{-}L$. In the desalination process, when 0.1M NaCl solution was used as the feed and 0.4 M G1 dendrimer solution was used as the draw agent, a pure water flux of 16.3$Lm^{-2}h^{-1}$ was observed with a rejection rate of 99.5%. These results indicate the potentials of globular polyelectrolyte for use as draw solutions for FO processes.

Membranes for biorefinery applications 1

ICOM1847

Sustainable, energy efficient and economic biorefineries by membrane enhance processes

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Biomass conversion processes to produce fuels, power, heat, and value-added chemicals are becoming more and more important with increasing prices of fossil fuels, the problem of global warming caused by combustion of fossil fuels and the risk of nuclear power plants.

Bioethanol production plants are the best known examples of biorefineries. Actually bioethanol is produced mainly from sugarcane (Brazil), corn (USA), wheat and other grains (Europe). Till bioethanol from lignocelluloses raw materials will be competitive not less than 1 decade will be still required for further development. Therefore it is necessary to improve the processes with the main raw materials utilized today. Membranes are able to improve different parts of the whole bioethanol production process.

A first benefit can be achieved in the saccharification process by separating sterile glucose via an ultrafiltration membrane. On this way the enzymes can be kept in the saccharification process. The process can be run at much higher enzyme concentrations resulting in a reduction of process time from 72 hours down to less than 10 hours. At the same time pure yeast as a valuable byproduct is formed in the following fermentation process [1].

After fermentation a distillation is required to concentrate the ethanol followed by an additional dewatering step to overcome the azeotropic point. Conventional dewatering techniques, as azeotropic distillation or pressure swing adsorption, are energetically consumptive and cause high investments costs. As an alternative to the conventional techniques water selective membranes can be used. The membrane process enables the continuous and energetically efficient dewatering by pervaporation or vapor permeation. Different types of water selective membranes have been reported. Most promising results have been achieved on the basis of NaA-zeolite membranes by Mitsui Engineering and Shipbuilding (MES) [2] as well as Hermsdorf Institute of Technical Ceramics (HITK) with its subsidiary inocermic GmbH [3]. HITK and inocermic GmbH merged with Fraunhofer Institute for Ceramic Technologies and Systems (IKTS) in 2010.

An additional benefit can be expected from a hydrophobic membrane able to remove ethanol from diluted fermentation broth. Such a membrane would enable the use of cellulosic feedstocks instead of starch. The membranes reported so far are mainly polymer membranes with limited ethanol fluxes [4].

In all these examples the success of membrane implementation depends not only on the membrane performance but on the integration of the membrane process in the complete bioethanol production.

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ICOM1074

Process Intensification by Pulsed Diafiltration for In-Situ Product Recovery

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Objectives

Fossil fuels will be depleted in the near future so that the development of new biofuels is crucial to ensure future mobility. Within a larger consortium on "Tailor-Made Fuels from Biomass", we investigate the sustainable production of platform chemicals from biomass to synthesize renewable biofuels.

Cellulose derived from green biomass is fermented to yield the platform chemical itaconic acid, which serves as a building block for the biofuel. For the fermentation process, a continuous operation mode with cell retention is desired which benefits have been reported in literature [1]. We present a new submerged diafiltration membrane system integrated into the bioreactor. Some of the advantages of integrating the membrane are

· achieving higher productivity and yield,

· the provision of a continuous cell-free product stream and

· the prevention of oxygen limitation that often occurs when placing the membrane externally.

The diafiltration process yields a product stream which is withdrawn from the bioreactor by an ultrafiltration hollow fibre membrane (outside-in filtration mode). Additionally, the same amount of feed is supplied through the same membrane and serves as nutrient supply for the microorganisms. The same membrane fiber serves as a withdrawing as well as feeding membrane and the liquid level in the bioreactor remains constant. The feeding simultaneously prevents cake layer build-up during the continuously operated fermentation process by the continuous reversal of filtration direction. It is the challgenge to provide a constant product recovery at these highly dynamic process conditions. An overview of the membrane bioreactor process is shown in Figure 1.

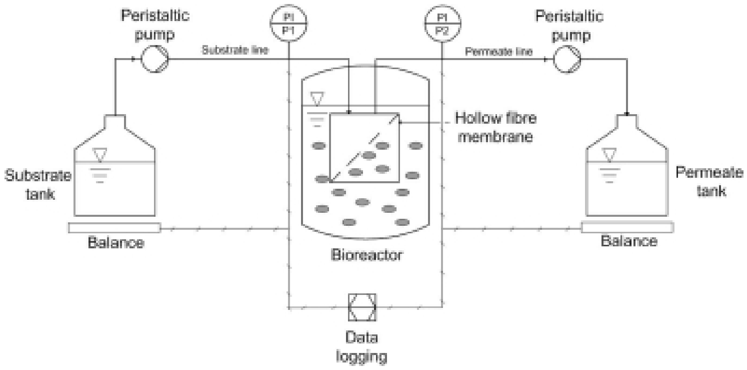

Figure 1: Experimental set-up of the submerged diafiltration membrane process

The presentation will show that the pulsed diafiltration process operated on a fermentation suspension showed indeed very stable filtration stability with hardly any permeability decline over a time period of a few days. We will describe in detail how various process parameters such as pumping interval and flow rate influence product recovery. Experiments are carried out with model solutions as well as with fermentation suspension. Results show that the pulsed diafiltration process enables continuous product recovery without cake layer built-up.

Acknowledgements

This work was performed as part of the Cluster of Excellence "Tailor-Made Fuels from Biomass", which is funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities.

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ICOM1431

Pervaporation separation of ethanol/ETBE and methanol/MTBE mixtures using poly(lactic acid) based membranes

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The separation of organic-organic mixtures is one of the main application areas of pervaporation. A particular area of interest is referring to the use of new fuel oxygenators which have been gradually introduced to avoid lead dissemination and to limit the aromatic (benzene) content in gasoline.

Ethyl *tert*-butyl ether (ETBE) is usually obtained from the reaction of a large excess of ethanol with isobutene to ensure a high isobutene conversion towards ether production while methyl *tert*-butyl ether (MTBE) is produced by the reaction of isobutylene with methanol. The obtained EtOH/ETBE and MeOH/MTBE mixtures are difficult to separate by conventional technologies like distillation because of azeotrope formation of 20/80wt% and 14/86wt%, respectively. Pervaporation process could be used to break the azeotrope in a hybrid distillation-pervaporation system or even alone to produce pure ETBE and MTBE.

In spite of the acceptable PV reported results, challenging the new polymers and materials in order to include some other advantages is always of researchers' interest. Poly(lactic acid) (PLA) is a natural source polymer and only recently the authors started to investigate its PV properties [1, 2]. This polymer is considered to be a suitable replacement for numerous petroleum-based polymers in the future.

In the current work, PLA membranes have been first produced and characterized and then PV tests have been performed with MetOH/MTBE mixtures. EtOH/ETBE was also investigated at the azeotropic concentration using PLA/PVP membrane blends. SEM cross-sectional images showed a porous structure at higher PVP shown in figure 1.

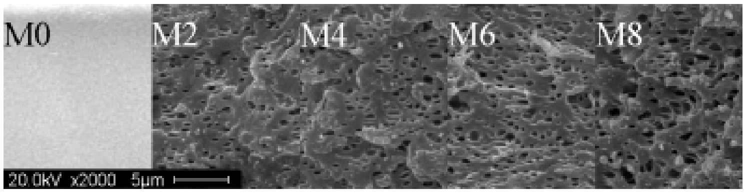

Figure 1. Cross sectional SEM image of M0 to M8 (0-21 wt% PVP)

The decreasing of water contact angle from 74° to 54° confirmed higher hydrophilicity and alcohol affinity at higher PVP contents. Unmodified PLA membranes were able to selectively separate low concentrations of methanol and ethanol from MTBE and ETBE. Separation factors dropped drastically from more than 30 and became almost constant (around 5) for MeOH concentration higher than around 10 wt%. In case of the PLA/PVP blends, the degree of swelling as well as the permeation flux gradually increased when the PVP amount increased to 21wt%. On the other hand, the EtOH separation factor initially raised to 16 using 3wt% PVP and then decreased to 3 using 21 wt%PVP. The more porous morphology and the plasticization effect resulted in selectivity decrease. This was also in agreement with the observed mechanical behavior of the blends. At higher EtOH concentrations and PVP contents, the elastic modulus of the membranes decreased, contrary to the membrane elongation.

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ICOM309

Membrane processes in bulk fermentation: From antibiotics to biofuels and biochemicals

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1. Introduction

The end of the 20th century was marked by the start of the third and so far final wave of biotechnology, the so-called white biotechnology, aiming to substitute chemical processes based on C_2/C_3 chemistry of oil and gas by biotechnological processes. The standard conversion process in biotechnology is fermentation, which is used to produce bulk products such as antibiotics, enzymes, bioethanol and organic acids. This presentation will provide a brief overview on the current status of membrane processes in the bulk fermentation inudstry and then focus on the latest trend in this industry - biorefineries. Details on the different processes and process conditions will be given.

2. Current status

The use of membrane processes in the production of bulk fermentation products is widely established since the 1970-ies. At the front-end of the production, microfiltration/ultrafiltration with diafiltration can be used for separation of the active ingredients from the fermentation broth. After this separation, ultrafiltration, nano-filtration, and reverse osmosis are used for concentration/purification of the active ingredients. An example for membrane opportunities in the antibiotic production is shown in Figure 1.

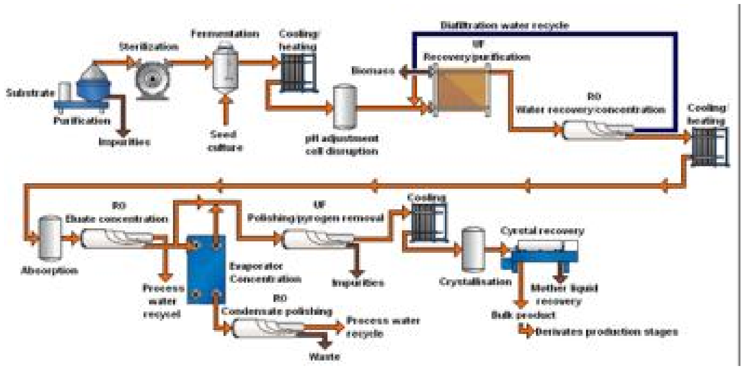

Figure 1: Antibiotics production with selected membrane opportunities

3. Future biorefineries

Biorefineries are integrated biotech facilities aiming on full utilization of feedstock for the simultaneous production of e.g. food, biofuels and biochemicals. Examples are the integrated production of biofuels and/or biopolymers from sugar and/or cellulose-based feedstock as part of sugar/starch factories or pulp mills. Depending on the raw material, e.g. wood biomass or starch, the initial step is the pre-treatment and conversion to sugars. The sugars - if diluted - can then be concentrated by reverse osmosis and polished by microfiltration/ultrafiltration before fermentation. During fermentation, the biofuels/biochemicals are produced and can be continuously removed by e.g. microfiltration/ultrafiltration/pervaporation to prevent product inhibitions from stopping the fermentation. Subsequently, microfiltration, ultrafiltration, nanofiltration, reverse osmosis and pervaporation can be used for concentration/polishing of the biofuels/biochemicals. In Figure 2, an overview of different membrane opportunities is given.

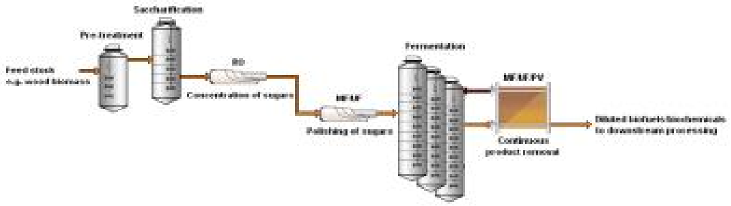

Figure 2: Biorefineries with selected membrane opportunities

4. Outlook

Overall, this paper shows that cross-flow membrane processes have established themselves in the bulk fermentation industry and further have a great potential in biorefineries.

ICOM323

In situ biobutanol recovery by organophilic pervaporation

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Butanol is an important commodity chemical used as a solvent and as a precursor for chemical synthesis. In addition, 1-butanol holds tremendous promise as a second-generation biofuel. It has a considerably higher combustion value than ethanol and its chemical properties allow blending in fuels more readily than ethanol, therefore it is a genuine “drop-in” biofuel.

The production of n-butanol with solvent-producing strains of *Clostridium*, commonly known as ABE (acetone-butanol-ethanol) fermentation, is one of the largest biotechnological processes ever developed. The inability of the fermentation process to compete with the booming petrochemical industry in the 1950s and 1960s has lead to its almost complete demise.

The economics of the ABE fermentation are hampered by two important bottlenecks: the high cost of the substrates (i) and butanol toxicity leading to cell inhibition, low product accumulation, low space-time-yields and high purification costs (ii). Improvements can be expected both from process and metabolic engineering. VITO's research and development efforts are focused on improving the fermentation by process engineering. The default technology for recovery of biobutanol is distillation, establishing the most energy intensive step in the entire process. Significant economic gains are expected by increasing the efficiency of the recovery step. Therefore, integration of the first step of the downstream separation process with the fermentation by using a suitable *in-situ* product removal (ISPR)technique offers an interesting strategy to overcome this bottleneck. Pervaporation is identified as one of the most promising unit operations for *in situ* product recovery of 1-butanol based on energy requirements of the recovery step.

Organophilic pervaporation membranes selectively remove organics from dilute aqueous streams thanks to the higher affinity for, and/or quicker sorption of organic compounds in the hydrophobic membrane. The driving force for selective mass transport is achieved by maintaining a vacuum or applying a sweep gas at the permeate side of the membrane.

To study the butanol recovery from ABE fermentation broths, a dedicated, integrated bench-scale unit for continuous ABE fermentation and ISPR has been designed and built. It consists of two bioreactors, an intermediate ultrafiltration unit for cell removal, and a pervaporation set-up for butanol removal.

A comparison is made between a state-of-the-art composite commercial membrane and a novel in-house developed composite membrane consisting of a thin, silica-filled organo-selective poly(1-(trimethylsilyl)-1-propyne) (PTMSP) separating layer applied on top of a porous support.

Modelling 1

ICOM1780

Modeling transport in porous membranes for separation tailoring

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The design of novel membrane materials and the improvement of existing ones requires in-depth understanding of the mechanisms that underlie the transport, sorption, and eventually the separation process itself. Most of these mechanisms relate to the precise features of the internal structure of the membrane. The demand for continuously improving separation efficiency necessitates better control of the transport phenomena at the nanoscale and, in many cases, at the level of the precise shape of the molecules to be separated and the shape of the pores or interstitial features of the membrane structure. Advanced modeling and simulation efforts are invited to elucidate this interrelationship between structure and transport.

To cope with the large number of scales between the nanofeatures and the eventual membrane unit, multiscale models and simulators are needed. Upscaling aims to predict the macroscopic behavior of an engineering process from first principles. Down-scaling approaches nanoscale phenomena staring from macroscale, engineering variables. In any case, computational techniques can guide investigations across scales in a well-structured fashion and are nowadays considered indispensable -in combination with sufficiently accurate experimental techniques- in membrane material design and synthesis. Notable examples include new or modified molecular sieves, porous membranes with controlled hydrophilicity, tailored pore networking within otherwise dense membranes, ionic liquids in membrane matrices etc.

A particularly challenging scientific issue arises when dealing with gas separation in nanoporous membranes. The classical continuum approximation breaks down in nanopores and alternative but sufficiently fast molecular or pseudo-molecular approaches are required to simulate such rarefied flows. Direct Simulation Monte Carlo (DSMC) is a mesoscopic technique that essentially performs rapid, yet coarse, molecular dynamics-type computations at relatively confined pore regions. Recently, progress was made in the direction of utilizing faster mesoscopic techniques (e.g., lattice-Boltzmann) in such computations without sacrificing significant accuracy, provided that a careful mapping of physicochemical properties is designed and implemented in a code that can treat realistic length scales. In the membrane distillation case, for instance, modelling allows the calculation of the transport rates as functions of the membrane thickness, air gap size, and temperature differences across the unit. To this end, two-phase flow simulation of the liquid-vapor interface at the entrance of the membrane can be conducted using the lattice-Boltzmann technique. The additional feature of gas phase simulation under rarefied conditions (Knudsen number between 0.1 and 1) is coupled to the lattice-Boltzmann two-phase flow simulator to simulate evaporation and vapour transport through the narrow pores of the membrane.

ICOM279

Comparing Sieving and Sorption Retention Mechanisms in Modeling Transient Particle Microfiltration

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The retention performance of microfiltration membranes in liquid streams often depends on the particular application. In order to classify and compare membranes with different properties, they are sometimes tested in a controlled environment with standard particles of a certain size in a defined fluid stream. One of these model systems is the filtration of mono dispersed spherical polystyrene latex beads in an aqueous fluid. It has been observed that the removal efficiency with these polystyrene beads can significantly decrease over time. This behavior may be explained by a sorption-type retention mechanism, which is determined by the interaction of particles and membrane material, rather than by sieving retention. However, most filter media are comprised of pores with a wide pore size distribution and may also include pores that are larger than the particles to be filtered. This leads to the penetration of particles into the filter media and possibly passage of a fraction of those particles even with a sieving retention mechanism. This fractional passage will change over time as smaller pores are being filled by retained particles, thereby making them unavailable for filtration of subsequent particles. The purpose of this study was to compare the calculated decrease of retention performance by a sorption and a sieving model.

Transient latex bead retention data were generated for a variety of membranes by analyzing small fluid volumes sampled throughout the filtration experiment. The applied sorption model includes probabilistic adsorption and desorption transport terms to account for the possibility of releasing previously captured particles. The model incorporates a variety of adjustable parameters, which were fitted to the experimental data. While some aspects of the experimental observations can be described satisfactorily, the model predictions are inconsistent across a series of experiments with changing conditions [1]. The sieving model is based on a two dimensional representation of the membrane pore structure and the transport of particles through the filter is simulated by applying probabilistic pore selection rules to move to the next pore in the network. Retention of particles is determined by comparing the size of the penetrating particle to the local pore size. Model input parameters include pore size distribution coefficients and pore selection rules. It has been observed that individual retention experiments can be described very well using an appropriate selection of these input parameters [2].

Model calculations for both models will be compared to transient experimental bead retention data across a variety of experimental conditions. Conclusions will be drawn on the sensitivity of the input parameters for either model and the significance of the retention mechanism, sieving or sorption, on the model analysis.

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ICOM378

Contribution of pore structure to membrane fouling

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In the membrane processes used in drinking water production, the fouling stays the main limiting phenomenon. One of the ways to minimize this issue is the choice of the membrane. The chemical properties and the pore size distribution are often taken into account. Nevertheless, the local properties of the membrane are rarely considered because of the lack of knowledge about their impact on the fouling.

By coupling the numerical simulation with some experiments with a microfluidic device, the present study aim at reaching the pore scale and at better understanding the contribution of the pore structure to membrane fouling. The used geometries mimic membrane structure by a simpler way (cf. figure 1). Filtrations of latex particles have been performed through these media. During these experiments, images have been acquired using a high-sensitive camera. The dynamic of the pore clogging at the single pore scale could then be studied using the recorded images. With these results, the contribution of the local properties (tortuosity and pore connectivity for example) can be discussed. In parallel, numerical simulations of these filtrations have been carried out (cf. figure 2). In these simulations, the latex suspension is modelled as spherical particles and its capacity to stick to the surface is considered by the Hamaker theory. The effect of captured particles on the hydrodynamics is also taken into account. The comparison between the experimental results and the numerical simulations allows testing the validity of the numerical simulations and more especially the interactions between membrane and particles.

At time where a large range of membrane structure is available for the drinking water production, it is necessary to understand their effects on the hydrodynamics and on the fouling. With this present work, a way to zoom on the membrane local properties is proposed. This type of numerical simulation is promising, notably, using the modeling of membrane thanks to the X-Ray tomography.

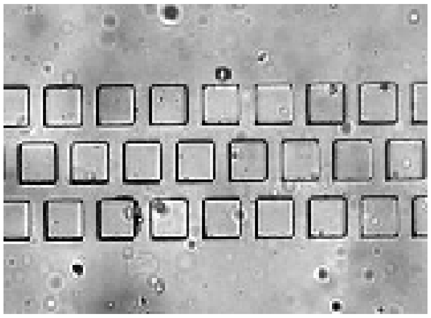

Figure 1: one of the used geometry

Figure 2: Results with the geometry presented above

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ICOM1032

Numerical simulations of fluid flow in a dead end hollow fibre filtration module

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The aim of this study is to analyze the influence of hollow fibre module design, especially packing density, and filtration operating mode on the filtration performance. To this end, a numerical model based on the finite element method is used to compute the flow in the fluid / porous domain and subsequent filtration velocity along the fibre. The flow in the fluid and porous regions is governed by Navier-Stokes and Darcy-Brinkman models, respectively. An overall pressure difference is considered as boundary conditions at the inlet and the outlet of the module. Simulations are performed on a representative unit element of the module which consists of a single cylindrical fibre surrounded by a fluid envelope, assuming a homogeneous behaviour of the module and a regular arrangement of the fibres.
A first model takes advantage of Happel's free surface model to allow the internal space (fluid), membrane (porous) and external space (fluid) to be considered as concentric cylinders. Thus the computation domain is finally simplified as a two dimensional axisymmetric domain. Simulation results in terms of filtrate flux are found to be in good agreement with experiments performed with two modules of different packing densities. Then the model is applied to study the effect of fibre density on the hydrodynamic conditions, both for inside/out and outside/in filtration modes. A modification of the axial filtration velocity profile with packing density is clearly demonstrated [1].
A more complete model is developed to study three dimensional fluid flow on a geometric domain which takes into account the exact external fluid envelop surrounding a fibre. According to the symmetry of the problem, the representative unit element of the module consists of a triangular prism (Fig 1) thus considerably reducing the computation mesh. Arced sections represent the inside, membrane and outside of the fibre. Simulations results of 2D and 3D models compare well each other. The simulations obtained with the 3D model for inside / out filtration mode highlight a non uniform angular profile of the radial velocity component along the fibre (Fig 2). Minimum velocities do not reach 0.0ms^{-1} to indicate that there are no stagnant areas of fluid. Flow preferentially occurs at the open end of the fibre for low packing densities and at the closed end of the fibre for high packing densities for inside / out filtration regime. On the contrary flow has a preference to take place at the open end with a high packing density and at the closed end with a low packing density for outside / in filtration regime. At an intermediate fibre density (Fig 2), results exhibit a significant difference at three positions along the fibre and signify that filtrate flow is higher towards the middle of the fibre.

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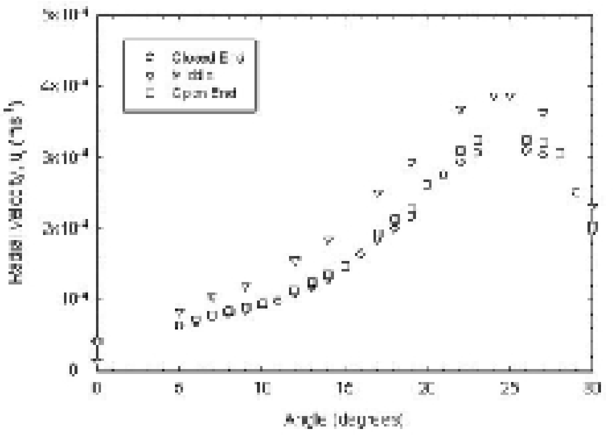

Fig 1: Plan (left) and 3D (right) views of 3D model geometry

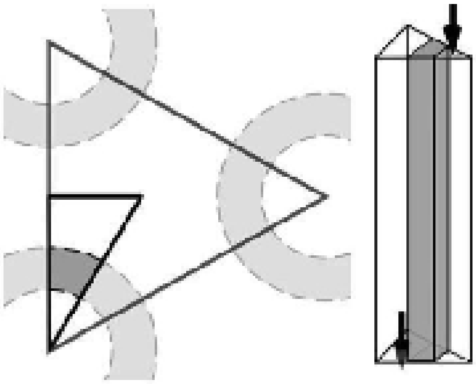

Fig 2: angular profile of radial velocity for outside / in filtration regime

ICOM1212

Fractionation of monodisperse and bidisperse suspensions

Martijntje Vollebregt[1], Ruud van der Sman[1], Remko Boom[2]
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Fractionation of suspensions and emulsions in their, often more valuable, components is an important processing step in a wide variety of processes. Microfiltration is one of the fractionation techniques used in food processing and is viewed as a mild process compared to other methods of fractionation. However, during membrane microfiltration accumulation of components on the membrane surface and inside the membrane pores takes place, resulting in a decrease of the flux through the membrane, a change in the membrane selectivity and in the necessity to use chemicals, water and energy to clean the membrane. This makes the process less mild. Our interest lies in process design for microfiltration with increased performance for various food applications.

In order to obtain a better understanding of the physical processes a model of microfiltration from first principle physics has been formulated. The model is formulated in such a way that it describes the properties on the feed as being a mixture. This provides a link between the model parameters and measurable properties of the feed.

The microfiltration model includes the flow of the feed along and towards the membrane as well as the permeate flow through the membrane. The flow properties are of importance, since these influence the migration of the components along and perpendicular to the membrane. The migration perpendicular to the membrane is due to different interactions between liquid and particles: drag towards the membrane due to the transmembrane pressure, and the counteracting effects of the interactions between flow filed and particles resulting in for instance lift, shear-induced migration and Brownian motion. The interactions depend on properties of the flow, the geometry (channel height, membrane length and resistance) and the feed (component concentration and size). The interactions are included in a model formulation for microfiltration of mono- and bidisperse suspensions. The model is applicable to strongly driven soft matter systems, a subject of increasing scientific interest. The resulting model requires less assumptions than the currently used models for microfiltration. This enlarges the applicability of the formulation to, for instance, the start-up regime in filtration processes.

The simulations reveal characteristics of the fouling processes, such as of the development and thickness of a concentration polarization layer and of the development and thickness of the cake layer in time along the membrane. The simulations for a monodisperse suspension are compared with experimental data, and good agreement is obtained. Also some implications of bidispersity are given.

UF/MF 1

ICOM1861

Pores getting smaller, markets getting bigger! *From Microfiltration to Nanofiltration in perspective of the history of X-Flow*

L. Broens, H.D.W. Roesink
X-Flow, NL

X-Flow started in the mid eighties as a spin-off from the University of Twente. The authors, Broens and Roesink were strongly involved in this process. The initial idea was to develop hydrophilic capillary membranes, that could be used in the pre-treatment for reverse osmosis [RO] systems. In that time a revolutionary view on the optimalisation of this desalination process. Though perfect hydrophilic microfiltration membranes, based upon polyethersulphone polyvinylpyrrolidone blends were developed and still produced, the first successful applications could be found in the food and beverage area, i.e. wine and beer clarification, but also in waste water treatment, oil water separations etc.

The breakthrough for X-Flow in the water market started in 1995, after the crypto outbreak in the USA. Legislation forced the water companies to invest in new technologies that removes microorganisms from all kinds of feed water. Though the focus initially was on cryptosporidium, already very fast removal of viruses was an issue, so that the membrane suppliers were forced to shift to ultrafiltration. This was also done by X-Flow, were the ultrafiltration membranes were incorporated into the world wide accepted XIGA Concept.

This XIGA concept is now typically used for large scale water treatment and forms the basis for the fact that X-Flow is now the market leader in pre-treatment RO. Here the ultrafiltration concept is used to remove all suspended solids, microorganisms, colloids, in order to facilitate an optimal RO process for the lowest possible operational costs.

The actual focus in water treatment is still on desalination, but also on the presence of so called micropollutants, a large family of pesticides, residual medicines, hormones, flame retardants, etc. These compounds are typically present in low concentrations, but do demonstrate a negative effect on the aquatic life and, and consequently on human health, reason why legislation also here is coming up very strongly. A new generation of membranes here should be developed to cope with this issue, were also biological processes, adsorption via activated carbon, or destruction via advanced oxidation are possible candidates to get rid of these micropollutants. X-Flow picked up this challenge and the first results of this development will be presented here on the ICOM.

ICOM711

How to reduce both the capital investment and operationnal costs of the water filtration plants by using a new and unique very large pressurized hollow fiber membranes module

Olivier Lorain, Franc Saux, Isabelle Duchemin, Jean Michel Espenan
POLYMEM, Toulouse, FR

Ultrafiltration and microfiltration are now widely used in water and wastewater treatments. Over the years, the investment and maintenance costs of such membrane systems have dramatically decreased and are now cost competitive with the conventional media filters. This was possible thanks to both module manufacturing and associated process improvements. In this field, hollow fiber membranes, with a high packing density and an easy assembly in bundles and modules, are the most cost competive solution. However, since the size of standard modules are, today, relatively small (from 4 to 12 inches), huge numbers of modules and huge number of associated connections and modules supports are necessary. It's a drawback for cost reduction which today tends to reach a plateau. A way, to re-start costs saving, is to pass to larger pressurized module diameter. In this paper, a new and unique very large pressurized hollow fiber membranes module, developed recently by Polymem, is presented.

In a first part, the module features are presented and the impact of size increase on the capital investment and operating costs, discussed. The figure 1 presents a view of this module. Its diameter is 600 mm (24 inches) with a heigth of 1.5 m.

Figure 1 : 24 inches Gigamem^{TM} module, internal assembly, bundled removal and unit design

The module develops more than 500 m^2 of membrane filtration area. The module is set directly on the ground, reducing the needs
of supports and skids for the modules. Further more, since the inlet of raw water and the outlet of treated water are both located at the top of the module, only two headers, located at the top are needed. Hollow fibers are gathered in individual bunldes which facilitates the maintenance of the membranes: removal of bundles, fiber integrity check, membrane replacement. During membrane
replacement, only the bundles will be replaced without changing the shell of the module. All these design improvements lead to important capital investment costs saving. The design of the module allows to use an efficient air-scouring in the feed side during the backwash sequences which permits to reduce the permeate water consumption and involves better recoveries. The fiber is opened at the top end and closed at the bottom end. The material of fibers can be changed so the unit can be upgraded during its lifetime with the latest best available membrane material.

In a second part, hydraulic and rejection studies achieved on this large module, are presented. During the presented studies, various membrane materials with various pore size (UF and MF) have been tested. Permeate turbidity was always lower than 0.1 NTU. Virus and bacteria rejections up to 7 log were achieved for UF membranes.

Several full size plants are constructed or under construction. Fields of application are drinking water production, seawater filtration before reverse osmosis and tertiary filtration of municipal and industrial wastewaters.

ICOM174

Enhancement of crossflow filtration by ultrasound: application to colloidal suspensions

nicolas hengl[1], Romain Mollard[1], Frédéric Pignon[1], Christian Pétrier[1], Nicolas Gondrexon[1], Stéphane Baup[1], Albert Magnin[1], Laurent Michot[2], Erwan Paineau[2]
[1]Université Joseph Fourier, Laboratoire de Rhéologie, Grenoble, FR, [2]CNRS-Nancy Université UMR 7569, Laboratoire Environnement et Minéralurgie, Vandoeuvre, FR

The combination of ultrasound systems and crossflow filtration is more and more used to minimize the phenomenon responsible of the decrease of the transmembrane flux: the concentration polarization effect and the fouling [1]. Indeed, the ultrasound waves create a succession of compression and depression in the whole solution; thus it causes turbulence in the fluid which modifies the formation of agglomerates of particles resulting in a raise of the permeation flux.

In this study we present a new filtration process coupling crossflow filtration and an *"in situ"* ultrasound system for the enhancement of mass transfer. The figure 1 shows a description of the ultrasound system in the experimental set up.

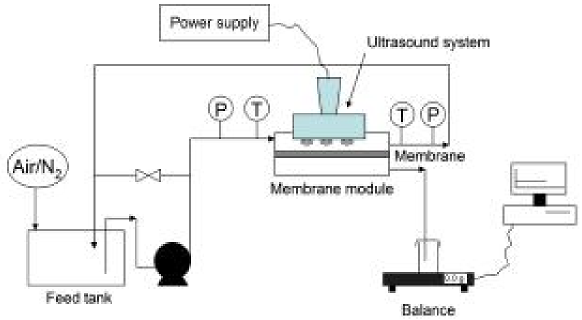

Figure 1. Experimental setup of crossflow filtration process coupled with in situ ultrasound system.

In our process, a thin Titanium vibrant blade is immerged in the feed compartment and placed above the flat membrane at a distance of 5 mm, contrary to most of other set up already developed using ultrasound bath. Indeed, applying ultrasound waves directly close to the membrane leads to a better instability of the polarization layers.

The figure 2 depicts the results of filtration obtained with three different aqueous colloidal model suspensions: the Na-Wyoming Montmorillonite clay (f_v=0.37%, 1.10^{-4} NaCl, platelets with a thickness of 1 nm, and a length of 75 nm) [2], the Laponite suspension disc shaped particles with a diameter of about 30 nm and thickness of 1 nm (f_v=1%, 6% tspp in 1.10^{-3} M NaCl) [3], the Colloidal silica Ludox HS-40 (40 wt%, spherical shape with an average diameter of 12 nm).

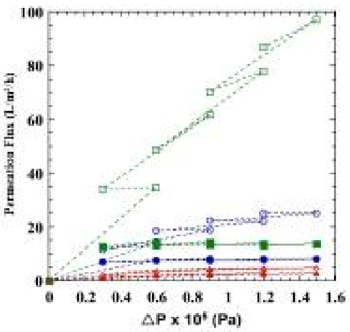

Figure 2. Permeation flux versus transmembrane pressure during crossflow filtration of colloidal suspensions without ultrasound (plenty symbol) and with ultrasound (empty symbol): (■) Na-Wyoming (T3), (●) Laponite, (▲) Colloidal silica. (Qv = 0.45 l.min^{-1}, T = 25-30° C, polysulfone sulfonated membrane 100 kD, pressure step method).

When ultrasound system operates, the transmembrane flux increases strongly (7 times higher at a pressure of 1.5 x 10^5 Pa for the Na-Wyoming (T3)). These results show the efficiency of the system for the control of the accumulation of the particles in the polarization layers, but also on the fouling process. Moreover it appears that this efficiency depends on the structural properties of the particles in the suspension.

In addition, by combining this system with membrane modules allowing an observation *"in situ"* (close to the membrane surface) by small-angle x-ray scattering (SAXS) [4,5], it will be possible to study the effect of the ultrasound system on the degradation of the polarization layers and on the dynamic of the involved phenomenon, and especially at very small scale (few nanometers).

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ICOM1670

Computational fluid dynamics and the electrochemical method to characterize membrane permeation modules

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This work investigates the behavior of the fluid flow inside a membrane module by Computational Fluid Dynamics (CFD) and the experimental determination of the mass transfer coefficient by the electrochemical method (EM). The study was carried with a new configuration for membrane modules, using flow patterns generated in hydrocyclones to reduce the polarization layer near the membrane surface by increasing the liquid velocity.

CFD has been widely used to design and evaluate Membrane Separation Processes (MSP). It can be used, for instance, to simulate the velocity field and to determine the mass transfer coefficient inside the modules. EM is an experimental technique useful for the evaluation of the mass transfer coefficient and is based in an electrochemical reaction that occurs when the liming step is the diffusion of ions towards the electrode. Under this condition, the electrical current generated from the reaction allows the calculation of the mass transfer coefficient in the liquid phase.

The CFD package ANSYS CFX was used in the simulations. The methodologies SSG and SST were used to characterize the velocity field inside the module configuration under steady state condition. From the observation of the velocity field, we identified areas of recirculation inside the module configurations, as well as zones of stagnated fluid. The same behavior was also deduced experimentally from results of the electrochemical method.

The CFD simulations successfully characterized the velocity field in a microfiltration module designed for separation of suspensions. The electrochemical method allowed the calculation of the mass transfer coefficient close to operational conditions. However, the
high computational time for the simulation is still a limitation of CFD. The combination of CFD and EM revealed to be useful tools for evaluation and optimization of new configurations for permeation modules.

ICOM516

Novel Rectangular Membranes with Multiple Hollow Holes for Ultrafiltration

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We have demonstrated, for the first time, rectangular membranes with multiple hollow holes, a hybrid of flat sheet membranes and hollow fibers, have been successfully produced for ultrafiltration. The spinning process was carried out with a specially designed spinneret with a rectangular slit for the polymer solution and seven injectors for the bore fluid. The fabrication process of rectangular membranes is similar to that of single-layer hollow fiber spinning but the spinning conditions are not as diverse. The experimental results show that the membrane microstructure, outer surface contour and shapes of lumen holes strongly depend on the spinning conditions such as dope formulation, bore fluid composition, air-gap distance and external coagulants. The evolution of membrane morphology as a function of spinning conditions has been elucidated by light transmittance. By carefully tuning the spinning parameters, polyacrylonitrile (PAN) rectangular membranes with a pure water permeation flux of 238 L/m^2·h·bar for ultrafiltration have been manufactured This performance is comparable to some literature works when considering only simple binary dope formulation and no modifications being applied to the membrane. In addition, compared to hollow fiber and flat sheet membranes, rectangular membranes do show a combination of the characteristics in terms of mechanical strengths. (Please

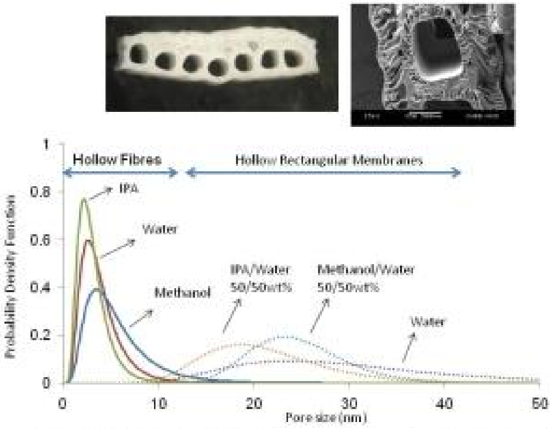

Fig. 1 Comparison of the pore size and pore size distribution of rectangular membranes and hollow fiber membranes spun from different coagulants

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ICOM 2011

Tuesday, July 26th 2011

Plenary Lecture 2

Tuesday, July 26th 2011

ICOM1800

The Biorenewables Opportunity – Towards Next Generation Process and Product Systems

Wolfgang Marquardt
RWTH Aachen University, AVT – Process Systems Engineering, DE

Different scenarios have been published recently which predict the depletion of fossil carbon resources for the production of fuels and chemicals in face of the increasing demand of a growing world population. Despite the uncertainty of such predictions, the switch from fossil to biorenewable carbon feedstock seems to be inevitable, if we aim at equilibrating global CO_2 binding and release to stop the increasing trend of the average surface temperature on our planet. This switch of feedstock provides a unique opportunity to redesign the value chain from raw materials to new molecular and functional products if we are willing to exploit the rich molecular structure of biomass to the extent possible.

Rather than breaking the molecular structure of the biomass into C_1 building blocks either by gasification to synthesis gas (CO and H_2) or by anaerobic fermentation to a methane-rich gas (CH_4, CO_2 and H_2), the synthesis power of nature should be preserved by refunctionalizing the existing molecular structures in biorenewable feedstock into new chemicals, materials and fuels. Such future products should differ from current products by their oxygen content. Current molecular products contain little oxygen because the processing effort to oxygenate fossil carbon feedstock is avoided if possible. In contrast, future bio-based products will contain higher oxygen content. Surplus oxygen has to be released in biorenewables processing. Reduction of the highly oxygenated raw material can be either reached by releasing CO_2 or H_2O. While the former reduces the carbon efficiency and contributes to the climate problem, the latter requires large amounts of hydrogen, which has to be produced sustainably, e.g. by means of solar water splitting.

Such future perspective calls for a radical change in chemical and biochemical catalysis, in the associated process technologies, and in the strategies towards novel molecular and functional products. The presentation will concentrate on evolving process systems engineering problems in this context. We will argue that a holistic systems approach orchestrating experimental and model-based methods and tools in a complementary manner offers an enormous potential for sustainable, first-time-right solutions.

In particular, we will touch on the production of carefully selected or even specifically tailored raw materials, on novel methods for biomass pretreatment, on the design of novel reaction pathways, processes, equipment and supply chains, as well as on an integration of process design with product design. These research issues will be put into the context of both, a large collaborative research project aiming at the development of 3rd generation biofuels, and the strategic reorientation of chemical engineering research at RWTH Aachen University.

Parallel Sessions

Tuesday, July 26th 2011

Morning Session, 10.00 – 12.30

Gas and vapor separation 2

ICOM1802

Strategies for Development of Advanced Membranes for Gas Separations

Ingo Pinnau
King Abdullah University of Science and Technology, Advanced Membranes and Porous Materials Center, SA

The first commercial membranes for water desalination and gas separation applications were developed between 1960 and 1980. During this period, revolutionary fabrication methods were developed for integrally-skinned asymmetric as well as thin-film composite membranes. A significant portion of the events which has led to the development of advanced membranes was based on serendipity rather than scientific principles – three notable examples are the groundbreaking discoveries of a) defect-free, ultrathin-skinned asymmetric cellulose acetate membranes by Loeb and Sourirajan at UCLA, b) interfacially polymerized thin-film composite membranes by Cadotte at Midwest Research Institute/FilmTec and c) multicomponent asymmetric membranes for gas separations by Henis and Tripodi at Monsanto.

In the past thirty years gigantic advances have been achieved in fundamental understanding of structure/gas transport property relationships in polymeric as well as inorganic membrane materials, membrane formation and modification principles, thin-film- and nanotechnology. Although the commercial market size for membrane-based gas systems has grown steadily, surprisingly few new membrane types have been introduced. This presentation will highlight some strategies to facilitate development and implementation of novel membranes for commercial gas separation applications.

ICOM833

Separation of CO_2 from Biogas by Gas Permeation: a Comparison with Competing Technologies

Torsten Brinkmann, Jan Wind, Thorsten Wolff
Helmholtz-Zentrum Geesthacht - Centre for Materials and Coastal Research, Institute of Polymer Research, Geesthacht, DE

The use of biogas as a source of renewable energy is steadily increasing. However, the majority of installed plants employ the produced gas as a feedstock for decentralised energy production. The problem of this approach is that there are typically not enough consumers for the produced heat. Hence the upgrading of biogas to meet natural gas standards and the subsequent feeding of the gas into the natural gas grid is an application of interest to the biogas plant construction and operating companies. Different technologies are being employed to separate the CO_2 from biogas. These include physical and chemical absorption, pressure swing adsorption as well as gas permeation processes.

Whilst there is a host of literature comparing the different technologies qualitatively e.g. [1, 2] and investigating the single processes individually e.g. [3, 4], a quantitative comparison using identical boundary conditions appears to be missing. Furthermore appears the performance of membrane technology underestimated in the qualitative studies [1, 2], probably due to outdated membrane performance data. In this work different absorption, adsorption and membrane processes for the separation of CO_2 from biogas are compared quantitatively. For the gas permeation processes, permeation data of current high performance membranes are employed. The data has been experimentally validated in laboratory and pilot scale. The required data for the absorption and adsorption processes is taken from literature or from the databases of commercial process simulators as Aspen Plus® [5]. The comparison is carried out by implementing the different processes into the commercial process simulators Aspen Plus® and Aspen Custom Modeler® [5]. The optimisation tools provided by the simulators are employed to identify the optimum design. For the simulation of the gas permeation processes a purpose developed model implemented in Aspen Custom Modeler® is employed. Different single and multi stage membrane process designs will be introduced. An example is shown in Figure 1, where the performance data of a three stage process employing membrane modules equipped with CO_2 selective MATRIMIDE® and POLYACTIVE® are depicted.

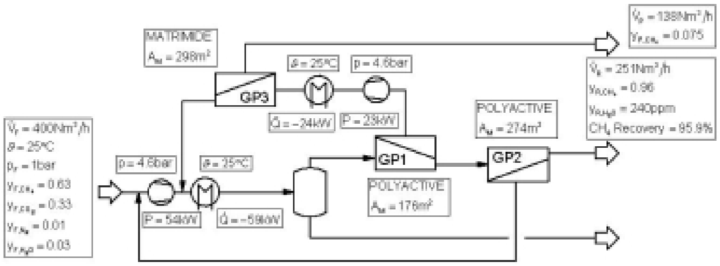

Figure 1: Three stage membrane process for the separation of CO_2 from biogas

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ICOM263

Carbon monoxide removal from argon atmosphere

Thomas Harlacher, Marco Scholz, Matthias Wessling, Thomas Melin
RWTH Aachen University, Chemical Process Engineering, Aachen, DE

Carbon monoxide results from incomplete combustion of carbonic compounds. In chemical manufacturing processes such as the ceramic synthesis of SiC, carbon monoxide occurs as a by-product enriched in the argon reaction atmosphere. Because of the impact on the reaction equilibrium and its toxic properties carbon monoxide has to be separated continuously. Argon as a high-value gas needs to be retained in the reaction.

The investigated process design consists of a polymeric membrane gas separation unit following a water gas shift reaction. While adding water vapour, carbon monoxide is shifted to carbon dioxide and hydrogen. The gas has to be cooled down to adjust it for the membrane unit. Condensing water is separated. In the gas separation unit carbon dioxide and hydrogen are separated, while argon and non reacted carbon monoxide are partly rejected and recycled to the reactor (Figure 1).

We present commercial membranes and their permeation properties with respect to single gases and gas mixtures.

Data were collected for binary mixtures up to a four gas mixture with compositions equal to conditions for pilot plant tests. The results were used to verify module simulations based on a proprietary Aspen Custom Modeler® model. We show that a simple model considering the module geometry, the mass transfer along the membrane and the pressure losses on feed and permeate side reflects the experimental results very accurately over a wide temperature and pressure range (low feed pressure applications).

The use of water vapour as a reactant in the water gas shift reaction causes a wet inlet gas stream for the membrane process. Therefore the influence of water vapour on the separation performance was investigated and implemented in the model as well.

The membrane module simulation was finally imported into Aspen Plus®. Different module configurations were simulated and the best performance was chosen for the implementation in the pilot plant.

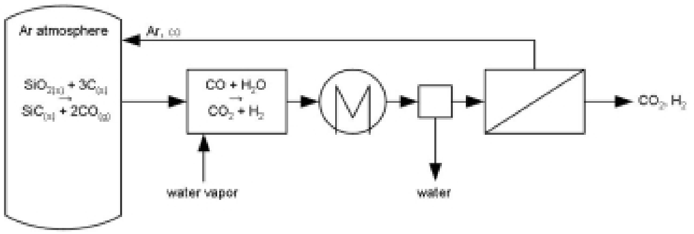


Figure 1. Schematic representation of the considered process design for carbon monoxide removal from argon atmosphere.

ICOM275

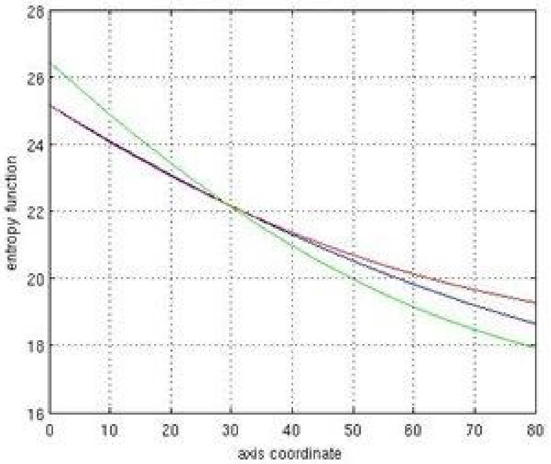
Membrane separation processes and energy efficiency: a critical reassessment

Eric FAVRE, Christophe CASTEL
LRGP CNRS, ENSIC, Nancy, FR

The concept of energy efficiency is one of the key performance characteristics of a separation process which governs its selection or rejection for a given application [1]. The recent evolution of the energy framework strengthens the importance of this criteria and the rigorous comparison of the energy efficiency among different separation processes is a key issue. This presentation intends to provide a critical analysis of the pros and cons of membrane separation processes compared to other separation equilibrium based separation processes (distillation, absorption, adsorption). Membrane separations are indeed alternatively presented as offering a high [2] or low energy efficiency [3].

This paradoxical situation will be analyzed based on the concept of minimal work of separation W_{min} which is classically proposed in order to assess the energy efficiency of a given process towards the separation performances of a homogeneous mixture. A modified criterion, which takes into account the target purity y of the separation has been developed for that purpose. A comparison of the energy efficiency of different separation processes for gas (i.e. air separation) and liquid (i.e. water desalination) separations will be proposed based on this parameter.

In a second step, the different strategies which can be proposed for membrane processes to achieve minimal energy dissipation will be presented and discussed. The energy dissipation function provided by Irreversible Processes Thermodynamics approaches [4] has been applied to different gas separation operations. This engineering tool, which, to our knowledge, has not been applied to the design membrane separations up to now, may offer unique opportunities to tackle the conditions (structural and operating) which govern the overall energy dissipation. The application to an isothermal membrane gas separation operation for tow compounds noted 1 and 2 leads to the local dissipation function which can be used in order to analyze the location and profile of energy dissipation. An example is shown on Figure 1, where the evolution of the local dissipation function along the axial coordinate of a gas separation module is compared for different hydrodynamic conditions.



: Evolution of the local dissipation function vs the axis coordinate of a gas separation module for different hydrodynamic conditions: conter-current (green curve), cross plug flow (blue curve), co-current (reed curve).

The possibilities offered by this approach and the questions which remain open on pushing the energy efficiency of membrane separations to the upper limits will be discussed.

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ICOM1483

Low Methane Emission membrane process for Biogas upgrading to Biomethane with new highly selective SEPURAN ® Polyimide Membranes

Markus Ungerank[1], Jörg Balster[3], Goetz Baumgarten[2]
[1]Evonik Fibres GmbH, Lenzing, AT, [2]Evonik Degussa GmbH, Performance Polymers, Fibres and Membranes, Marl, DE, [3]Evonik Degussa GmbH, Process Technology & Engineering, Reaction Technology, Membrane Processes, Marl, DE

The first industrial application of gas separation membranes, i.e. the recovery of hydrogen from purge gas streams, was introduced 30 years ago. Currently, the most important applications of these membranes are in the generation of nitrogen, hydrogen recovery, air drying, and removal of sour gases from natural gas.

One key use of gas separation membranes is the removal of CO_2. CO_2 is found in natural gas and biogas and must be removed before the gas can be used. So far Biogas upgrading to Biomethane and injection into the gas grid or usage as a fuel was mainly done by other separation techniques even though current membrane processes show very low energy consumption. Membrane based separation processes are easily scalable to smaller and bigger sizes, can be started and stopped within minutes and do not need any auxiliaries such as amines or water or regeneration.

In general, current gas separation membrane systems consist of either a single stage system or the dual stage system with a recycle stream. In both cases an OFF gas stream (> 7 % of Methane) is produced that contains remarkable amounts of Methane which is

· Lost in the process and lowers the yield of Biomethane

· Cannot be emitted into the atmosphere without any further post combustion due to regulations and the fact that methane has a very high green house gas potential

The OFF gas is treated either by sending it back to a Combined Heat and Power plant (CHP) or by burning it in a Regenerative Thermal Oxidation (RTO) step.

If the major portion of Biogas is upgraded to Biomethane and the OFF gas is mixed with the Biogas the percentage of Methane in the Biogas for the CHP will become too low for a reliable process of the CHP. Therefore the CHP won't be able to consume the OFF gas any more. Then the gas has to be treated with a dedicated post combustion system like a FLOX burner or a RTO.

In addition, post combustion needs further investments and therefore increases the cost per m3 Biomethane especially for smaller plants in the range of 100 to 300 m3/h raw Biogas.

We will show a new multistage membrane process with one compressor which can be applied to low and high volume gas streams. This process allows a simultaneous generation of Biomethane with pipeline quality and an OFF gas stream with very low Methane concentrations (< 0,7 %). We will show how the cascade is set up, how it works and how it reacts on fluctuating biogas compositions and how the capacity can easily be adjusted to the actual production of Biogas of the Biogas plant.

We will also show the influence of the selectivity of the membranes used in the new Multistage process on the economics of the process. We will also introduce the new highly selective Evonik Polyimide gas separation membrane.

ICOM348

On board electricity generation through a membrane reformer fuel cell process

Johannes Völler, Timo Mittag, Michael Follmann, Matthias Wessling, Thomas Melin
RWTH Aachen University, AVT.CVT, Aachen, DE

Today, heavy duty trucks generate electricity during idling by running diesel engines. Due to rising fuel prices and stronger environmental protection regulations, alternatives to the generation of on board electricity is desired.
Fuel cellbased auxilliary power units (APU) are such an alternative and one of the most promising mobile applications for fuel cells. To avoid a dedicated H_2-storage, the H_2 needs to be generated on board by hydrocarbon reforming.
Figure 1 (top) depicts a conventional fuel cell system, comprising a reforming unit, which generates a synthesis gas consisting mainly of H_2O, H_2, CO, CO_2 and some CH_4. CO is a catalyst poison for low temperature fuel cells. It is converted to H_2 in two shift stages (high temperature shift, HTS, and low temperature shift, LTS) by the water gas shift reaction. The remaining CO is oxidized in a selective oxidation unit (SELOX). The reformate stream is used to generate electricity in a polymere electrolyte membrane fuel cell (PEM-FC).
An alternative system purifies the hydrogen by physically separating hydrogen from the other reformate gases using a highly selective palladium membrane (Figure 1, bottom). The hydrogen is generated by steam reforming of diesel fuel yielding higher efficiency than alternative concepts such as partial oxidation or autothermal reforming. Furthermore, the hydrogen partial pressure in the reformate gas from steam reforming is higher. Thus, the membrane is used more efficiently for hydrogen separation. The high purity hydrogen gas can be completly used in the fuel cell and, as no poisoning takes place, a higher efficiency of the fuel cell is expected within this setup compared to a conventional fuel processor.
We model the overall system efficiency for the membrane reformer system under different operating conditions. The system is dimensioned with respect to a target H_2 production rate of 0,06 kg/h (corresponds to 2 $kW_{thermal}$). The model of the membrane reformer was implemented in FORTRAN and interfaced with Aspen Plus.

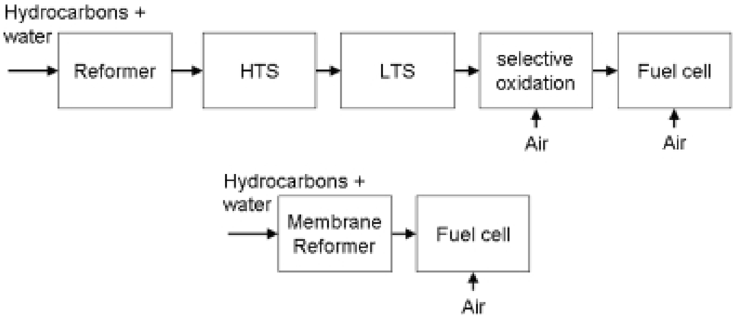

Figure 1. State of the art fuel cell based APU system (top) and novel membrane reformer system (bottom).

For mobile applications, all water needed in the system must be recovered from the offgas streams. The temperatures to which the offgas streams have to be cooled for the water recovery were calculated. Setting the minimal coolant temperature, that a vehicle can reliably supply, to 70 °C, the impact of the modified operation conditions on the APU system efficiency is calculated.

ICOM1255

Mixed-gas CO_2/CH_4 and CO_2/N_2 separation with sulfonated PEEK membranes derived from sulfonated monomer

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CO_2 removal from mixtures containing CH_4 and N_2 is of interest for wide variety of industrial applications such as natural gas separation, flue gas cleaning, and syngas processing. Polymeric membranes have received tremendous attention due to their advantages, such as low cost, high energy efficiency and low ecological footprint. One of the goals in the development of polymeric membranes is to overcome the limitation of the established 'upper bound' of the permeability-selectivity relationship. CO_2 induced plasticization, leading to swelling of the polymer due to increased sorption of CO_2 in the polymer matrix, is another problem which drastically affects the membrane separation performance. Chemical modification of the polymeric material offers a possible method to surpass this limitation. Polymer sulfonation in specific has been found to be an effective way of increasing the membrane performance.

This paper reports the first application of lab-made sulfonated aromatic poly (ether ether ketone) (S-PEEK) membranes, directly prepared from the sulfonated monomer, for CO_2 separation from gas mixtures containing N_2 or CH_4. Dense membranes with different degree of sulfonation were prepared via solvent evaporation. SEM and AFM were used as characterization techniques for the synthesized membranes. Both single and mixed gas permeabilities and selectivities were measured for the membranes to study the coupling between the permeating species. Increasing degree of sulfonation simultaneously improved the permeability and selectivity for both gas pairs. The effect of counterions was investigated by converting S-PEEK membranes from the Na^+-form in which they are prepared, to the H^+ and multivalent cationic forms. Gas permeability and selectivity for polymers with divalent and trivalent counterions were higher than those for polymers in the monovalent and H^+-forms. In order to study the stability and potential industrial application of these membranes, they were tested at different conditions of feed pressure, temperature and CO_2 feed concentration. Polymer sulfonation also proved to be effective in imparting anti-plasticization properties to the polymer by shifting the plasticization pressure from 11 bar to beyond the highest tested pressure (40 bar), thereby proving S-PEEK membranes as an interesting candidate material for gas separation applications.

Inorganic membranes 1

ICOM1843

Sol-gel processing of porous ceramic membranes for advanced molecular separation

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Amorphous silica network structure allows permeation of the smallest molecules such as helium (kinetic diameter: 0.26 nm) and hydrogen (0.289 nm), but not larger molecules such as nitrogen (0.364 nm).[1)] Although silica membranes for hydrogen separation were first reported in 1989 by CVD[2)] and in 1990 by sol-gel processing[3)] and have been developed for the last two decades, there still remain two technical challenges: pore size control and hydrothermal stability.[1)]

In order to improve hydrothermal stability of silica membranes, organic-inorganic hybrid alkoxides such as methyltriethoxysilane (MTES) were used for fabrication of hybrid silica membranes.[4)] Recently, Castricum et al.[5)] developed hybrid silica membranes using bridged bis-silyl precursor, bis (triethoxysilyl) ethane (BTESE), bis (triethoxysilyl) methane (BTESM)) and MTES, which showed superior hydrothermal stability in comparison with MTES/TEOS-derived membranes because of incorporation of organic linking groups (Si-C-Si, Si-C-C-Si unit) in silica networks.

We recently proposed a new strategy to control pore sizes of silica membranes using bridged alkoxides.[6-8)] Bis (tri-ethoxysilyl) ethane (BTESE), consisting of ethane group between 2 silicon atoms ($-Si-CH_2-CH_2-Si-$) as the minimum unit in hydrolysis and condensation reaction, was found to lead to loose silica networks. BTESE silica membranes showed about one order magnitude high H_2 permeance ($\sim 10^{-5}$ mol/(m^2 s Pa)) compared with previously reported silica membranes using TEOS, and a high H_2 to SF_6 permeance ratio of approximately more than 1,000 with a low H_2 to N_2 selectivity (~10). Another bridged alkoxide, bis (tri-ethoxysilyl) methane (BTESM), consisting of methane group between 2 silicon atoms ($-Si-CH_2-Si-$) was used and evaluated for gas permeation properties. Moreover, disiloxane compounds, including 1,1,3,3-tetraethoxy-1,3-dimethyl disiloxane (TEDMDS) and hexaethoxy disiloxane (HEDS), were also investigated for tuning silica networks.[8)]

Normalized Knudsen-based permeance (NKP) was proposed for the determination of membrane pore sizes less than 1 nm, which is based on the gas translation model originally proposed by Xiao and Wei, and Shelkhin *et. al*., and verified with gas permeance of MFI and DDR zeolite membranes.[8)] Judging from NKP fitting curves for TEOS, TEDMDS, BTESM, and BTESE-derived silica membranes, the order of silica membranes could be estimated as follows: TEOS < BTESM < BTESE, TEDMDS-derived silica membrane. Silica membranes created by a Si unit alkoxide (TEOS) showed smaller pore size distribution than silica membrane prepared by bridged alkoxide units such as $-Si-CH_2-CH_2-Si-$, $-Si-CH_2-Si-$, and Si-O-Si. These results suggested that the pore size of silica membranes can be tuned by spacer technique with bridged alkoxides.

Applications, including gas separation (hydrogen separation, organic gas) and liquid phase separation, will be introduced.

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ICOM398

Tailoring the molecular separation properties of hybrid organosilica membranes

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We have recently developed a hybrid organic-inorganic molecular sieving material with unprecedented stability under hydrothermal conditions [1]. Even after a period of almost 3 years, the hybrid material has not suffered from failure in the presence of water at very high operating temperatures (150˚C). High stability under realistic operating conditions is essential for the application of membrane technology for molecular separation. While the architecture of the hybrid material is mostly similar to that of inorganic silica, a substantial part of the Si–O–Si bonds has been replaced by organic Si–R–Si bridges. To be utilized in a broad range of applications, advanced control over the separation properties of hybrid silica membranes is required.

We will report how hybrid organosilica membranes can be tailored towards a wide variety of specific molecular separation applications by changing the structure of the bridging group. Both (flexible) linear alkyl and (rigid) aryl bridges were investigated. The type of bridging group has a major influence on the reactivity of the silsesquioxane precursor, the formation of colloidal nanoparticles and the processability towards membranes. We developed a generic procedure that leads to a colloidal structure optimized for thin-film processing, taking into account differences in precursor reactivity. Thin-film coating with these colloidal sols resulted in defect-free nanoporous molecular separation membranes that cover a range of porous structures. Colloidal sols were characterized with Dynamic Light Scattering (DLS) and Small-Angle X-ray Scattering (SAXS) to determine particle size and fractal dimension. The permeability of membranes to various molecules was found to be related to the size, shape and electronic structure of the organic bridging group.

We will present the factors that determine successful applicability of hybrid organosilica membrane materials, and indicate directions fur further tailoring toward specific separation applications. The overall conclusion that the separation performance of organosilica membranes can be tailored through the variation of the organic bridging group gives excellent prospects for an extensive range of industrial applications, *e.g.* for carbon capture and biofuel production applications.

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ICOM1282

Nb_2O_5 improved $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ mixed conducting oxides for oxygen separation at intermediate temperature

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Perovskite-type mixed ionic-electronic conducting (MIEC) membranes used for oxygen separation from air has received considerable attentions. These ceramic dense MIEC membranes have 100% selectivity for oxygen, delivering high-pure oxygen product (>99%). However, a high operation temperature (normally higher than 800 ℃) was required which would lead to a high energy consumption. To lower the operation temperature (below 600 ℃) is imperative and challenging for practical application. $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) with high oxygen flux is an excellent candidate for intermediate temperature application. However, this kind of cobalt-containing material shows very limited structure stability in low oxygen partial pressure. Therefore, it's critical to develop high flux MIEC material with high stability and better performance at intermediate temperature.
In this study, a new series of Nb_2O_5-doped (0.5, 1, 3, 5 and 10 wt.%) $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ mixed conducting materials were synthesized by the solid-state reaction method. The crystal structure, surface morphology, phase stability, oxygen desorption behavior, thermal expansion behavior, electrical conductivity and oxygen permeability of the prepared materials were systematically investigated. Doped Nb_2O_5 was totally incorporated into the SCF structure while effectively suppressed the coexisted orthorhombic phase in bulk cubic SCF and perovskite-brownmillerite transition at low oxygen partial pressure ($pO_2=1\times10^{-5}$ atm). SCFNb0.5 (slightly doped with 0.5 wt.% Nb_2O_5) with a cubic perovskite structure has the smallest cell parameter, the lowest thermal expansion and the highest oxygen flux (3.38 ml min^{-1} cm^{-2} was at 900 °C). A better intermediate temperature performance with 0.23 ml min^{-1} cm^{-2} oxygen flux for disk-shape membrane (1 mm thickness) was obtained at 600 °C. More Nb_2O_5 dissolved into the SCF lattice was served to decrease the electrical conductivity and oxygen flux, increase the thermal expansion and remarkably suppress the grain size of membranes.

Acknowledgment

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ICOM733

A new supercritical CO_2 process for micro/mesoporous silica-based membrane preparation

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Supercritical carbon dioxide (SC-CO_2) based processes are attractive for ceramic materials preparation and were initially developed in our group for the synthesis of oxide ceramic nanopowders [1-5]. During the last 15 years, we investigated a wide range of materials (TiO_2, ZrO_2, Y-ZrO_2, CeO_2, Gd-CeO_2, SiO_2…) and applications (photocatalysis, catalysis, solid oxide fuel cells, gas purification, cosmetics…). We are currently focusing on ceramic oxide processing, especially for preparing gas-separation membrane, either by powder post-processing or by direct on-stream deposition in supercritical media.

In the context of pure hydrogen production, gas separation membrane technology has gained considerable attention in the last years. A great deal of research is namely focused on silica-based molecular sieve membranes which exhibit attractive properties regarding hydrogen separation at intermediate temperature. The deposition of thin silica membrane top-layers on inorganic porous substrates can be typically achieved by either sol-gel or Chemical Vapor Deposition (CVD) techniques. The SC-CO_2 deposition process described here can gather the advantages of both techniques, since it is based on both cluster transport using SC-CO_2 as carrier fluid (close to CVD method) and cluster condensation at the substrate surface (sol-gel like process).

Chosen because of its attractive transport properties and easily adjustable solvent power, SC-CO_2 acts as a solvent in which alkoxide precursors are solubilized and then transported to the inorganic porous support where deposition occurs. Thanks to this new deposition process, it seems possible to repare, in one-shot, porous ceramic membranes, with few defects, coated on or infiltrated into a tubular porous substrate. Deposition process and coated membrane quality can be monitored by following the evolution of transmembrane pressure (between permeate and retentate sides). Deposit localization as well as membrane thickness and homogeneity can be controlled by adjusting process parameters like pressure, temperature or CO_2 flux… During the presentation, deposition mechanisms will be discussed and correlated to transmembrane pressure evolution, process parameters and membrane characteristics.

This original on-stream deposition process is very versatile and easily adjustable for modification of a variety of porous substrates with various ceramic, metal or polymer precursors, providing they are soluble in SC-CO_2 media.

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ICOM135

Thin film mixed ionic electronic conducting membranes for oxygen separation

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All scenarios about the future global energy requirements anticipate an increasing power demand, which can most likely only be met by considerable exploitation of fossil fuels. However, fossil fuel power plants are by far the biggest individual sources of CO_2 and contribute with more than 40 % to the worldwide anthropogenic CO_2 emissions. Carbon Capture and Storage (CCS) in fossil power plants is an important means to reduce CO_2 emissions, hence allowing future electricity supply to be environmentally safe and sustainable.

In particular in an Oxyfuel power plant, pure oxygen is used to combust a carbon containing fuel (e.g. coal, gas, biogas) forming primarily CO_2 and H_2O making it much easier and cheaper to capture the CO_2 than by the use of air for combustion process. An advanced way to produce the required oxygen are ceramic Oxygen Transport Membranes (OTMs), which lead to significantly lower efficiency losses compared to conventional cryogenic separation technologies. OTMs are gastight Mixed Ionic Electronic Conductors (MIEC), which allow oxygen diffusion through lattice vacancies and simultaneous conduction of electrons in the opposite direction.

Obviously a key issue is the progress in the development of gastight oxygen separation membranes, which should fulfil the characteristics of (i) high oxygen permeability (ii) infinite oxygen selectivity and (iii) reliable long term operation in terms of thermo-chemical and thermo-mechanical aspects. In order to address all of these goals simultaneously, the use of surface activated thin film membranes appears to be essential. However, the application of gas-tight membrane layers on a porous support by thick film technologies such as screen printing or tape casting as well as thin film technologies, such as Physical Vapour Deposition (PVD) or sol-gel techniques is very challenging.

The presentation covers the development of thin (20-70 µm) and “ultra-thin” (1-2 µm) membrane layers on porous supports. Besides manufacturing and functional properties mechanical issues are addressed, which has shown to be of outstanding importance due to the very complex thermo-mechanical behaviour of the considered perovskite materials. Mechanical aspects cover the temperature dependent mechanical properties of the supporting substrate materials in terms of elasticity, creep and failure relevant behaviour as well as statistical aspects with respect to failure probabilities. The linkage of design relevant aspects and failure is briefly discussed.

ICOM1763

Hydrogen Transport Membrane Technology for Ethylene Production

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Ethylene, the largest volume commodity chemical manufactured today, is currently produced by pyrolysis of ethane in the presence of steam. Pyrolysis of ethane also produces significant amounts of greenhouse gases (CO and CO_2) in the reactor section, because carbon directly contacts steam. Thermodynamically limited in terms of its equilibrium conversion, this process requires substantial energy input. The Chemical Bandwidth Study conducted by the U.S. Department of Energy (DOE) Office of Industrial Technologies Program (ITP) compared recoverable energy potential across fifty-three chemical technologies and listed ethylene at the top of the list with a recoverable energy potential >250 x 10^{12} Btu/yr. A subsequent study by DOE-ITP concluded that pushing the cracking equilibrium to higher conversion by removing hydrogen as it is formed would give a substantial energy intensity advantage and would represent a fruitful avenue for future research. Our project offers a new approach for producing ethylene, wherein a hydrogen transport membrane (HTM) selectively removes hydrogen during the dehydrogenation of ethane, thereby shifting the equilibrium toward ethylene production. Preliminary laboratory experiments show that the new approach can afford ethylene yields significantly above the thermodynamic equilibrium limit, even at high ethane conversion, while eliminating production of greenhouse gases in the reactor section. Moreover, the new approach results in a much simpler product slate than that obtained from today's pyrolysis technology. This simpler product slate affords an opportunity to lower the cost of the “back end” purification train. In addition to significant energy savings, feedstock and capital cost savings, and overall cost reduction are expected in this ethylene production.

In our approach, a disk-type dense ceramic/metal composite (cermet) membrane is used to produce ethylene by dehydrogenation of ethane at 850°C. The gas-transport membrane reactor combines a reversible chemical reaction (e.g., hydrogenation/dehydrogenation) with selective separation of one product species and leads to increased reactant conversion to the desired product. In an experiment ethane was passed over one side of the HTM membrane and air over the other side. The hydrogen produced by the dehydrogenation of ethane was removed and transported through the HTM to the air side. The air provided the driving force required for the transport of hydrogen through the HTM. The reaction between transported hydrogen and oxygen in air can provide the energy needed for the dehydrogenation reaction. At 850°C and 1-atm pressure, equilibrium conversion of ethane normally limits the ethylene yield to 64%, whereas in our experiment under the same conditions, we obtained an ethylene yield of 69% with a selectivity of 88%.

Further improved HTM materials will lower the temperature required for high conversion at a reasonable residence time, while the lower temperature will suppress unwanted side reactions and prolong membrane life. Thus, the approach simplifies overall product purification and processing schemes, and results in greater energy efficiency. The results of our work will be discussed at this talk.

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ICOM853

High-performance inorganic membranes produced by rapid heat treatments

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The required time to produce state-of-the-art inorganic membranes is commonly dominated by the duration of the heat treatment steps requisite for structure consolidation. Using a novel heat treatment process in which the membrane precursor is placed in a preheated chamber for short times, we show that the manufacturing time of high-performance inorganic membranes can be decreased by an order of magnitude (see figure 1).

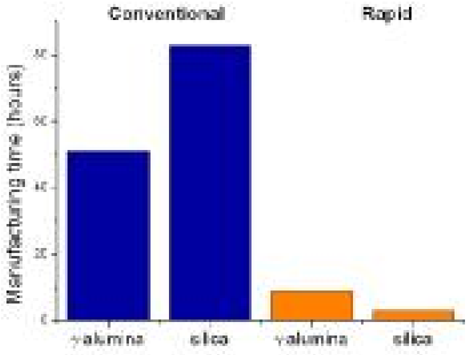

Figure 1: Manufacturing time of a silica membrane using conventional and rapid heat treatments. By rapid heat treatments, the manufacturing time is reduced to 10% of the original.

The heat treatment method was tested using microporous silica and mesoporous γ-alumina as model membrane layers. After the rapid heat treatment, the quality of these γ-alumina and silica membrane layers is comparable to that of membranes that were processed conventionally. The resulting silica membranes show good selectivities (see figure 2), indicating that the layers contain only a limited amount of defects. The process can easily be extended to films of other materials, e.g., titania or hybrid organic-inorganic membranes. The versatility of our technique allows for rapid screening of new materials and can be applied in existing production processes to drastically reduce process time and energy requirements.

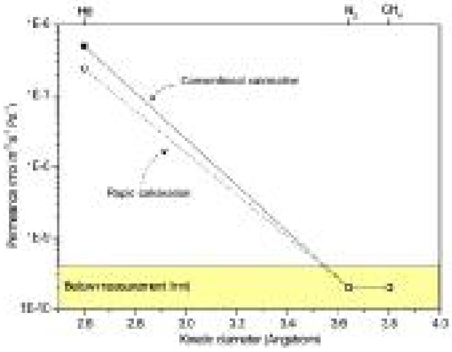

Figure 2: Permeance and selectivity of a rapidly calcined silica membrane are comparable to those of a benchmark membrane that is calcined conventionally (De Vos and Verweij, *Science* 279, 1998, pp. 1710-11).

Biomedical membrane applications 1

ICOM1778

All for one, one for all? Requirements for membranes in medical application. The current situation of haemodialysis

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Currently more than 900 dialyser types are available in the market. The question arises, whether there are common features attributable to all dialyser types or whether there are clinical needs to specify properties to achieve the best possible outcome.

The artificial kidney represents a global success story of the use of polymers and membranes in medical application. The number of kidney patients requesting such a medical device is increasing by 6% annually, a figure that is five times higher than the relative increase in the world population. Apart from the associated technical aspects of logistics, membrane application has to be adapted to the well known demographic variations either. The current age of patients beginning with dialysis is steadily increasing in the Western hemisphere. This change implies additional co-morbidities, such as diabetes, increased vascular calcification and heart problems with a need for therapy adaptation. However, improved modern devices and optimised therapy mo-des enable kidney patients on haemodialysis to expect long survival times. As an example, more than 10.000 patients undergo haemodialysis for more than 20 years in Japan.

Which factors determine the current market place and therapy situation? Some poly-mers, which dominated the membrane market in recent years are not yet available anymore. Among them are a) membranes from regenerated cellulose, namely Cupro-phan®, to be explained by its alleged lack of blood compatibility and b) membranes with low UF-coefficients. The latter lost considerable market chair due to the introduction of new therapy modes (haemodiafiltration, HDF) following medical needs to remove toxins with larger molecular weights under conditions of increased solvent drag.

Thus, actual requirements for mem-branes in dialysis refer to high blood compatibility, proven biostability, but also to specific performance features. Two examples may illustrate this notion. Major concerns in the medical community refer to possible inflammatory stimuli originating from either water contaminants or polymer leachables.

Polymers with the capacity to adsorb endotoxins and do not activate the contact phase of coagulation are now available and increasingly used. Sterilisation techni-ques, such as online steam sterilisation avoid the presence of membrane oligomers, which can be isolated in some cases from g-irradiated devices. secondly, membranes with high UF-coefficients allow for their use in therapy modes, such as haemodiafil-tration. The underlying mechanism of HDF is “solvent drag” which allows for the removal of a large spectrum of uremic toxins, even if they are not yet identified until now..

Conclusion: The heterogeneity of the current patient population, as well as the future changing medical needs due to demographic variations and varying co-morbidities request a high variability of membranes to be used in clinical application.

ICOM383

Bi-soft segment poly (ester urethane urea) membranes for ExtraCorporeal Blood Oxygenation Devices: Gas Exchange and Hemocompatibility

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CardioPulmonary Bypass (CPB) for open heart surgery and Extra Corporeal Membrane Oxygenation (ECMO) for longer-term lung support are clinical practices that make use of Membrane Blood Oxygenators (MBO). These devices have at their very core membranes that separate the patient's blood from gases and that allow oxygen to enter and carbon dioxide to leave the bloodstream. More than 98% of commercial oxygenation membranes are made from polyolefines coated with anticoagulant materials to improve hemocompatibility. Even though MBOs have been used in CPB for over 30 years, and in ECMO support devices for less than 10 years the insufficient hemocompatibility of the materials remains a problem and hazards of CPB and ECMO include bleeding disorders, systemic inflammatory reactions, multiorgan failure, pulmonary dysfunction and abnormal pressure gradients across the oxygenator mainly due to fibrin deposits. Presently, research efforts are directed towards improving the hemocompatibility of membranes, reduce the costly coating of the MBO's and CPB circuitry and develop new membranes with tailored optimal surface/bulk morphologies with high gas permeation properties and enhanced hemocompatibility
capable of sustaining lung support for lengthier periods of time. Biomedical polyurethanes are associated to high hemocompatibility and fatigue resistance. These block copolymers typically have an ether or an ester soft segment with an aromatic or aliphatic
hard segment and a urethane or urethane/urea linkage. Despite numerous studies on biocompatibility of polyurethanes there is scarce literature on the biocompatibility of polyurethanes containing two soft segments as the ones of the membranes under consideration in this work. The type of soft segments and the ratios of hard-to-soft and soft-to-soft segments are investigated in order to get tailored polyurethanes with improved gas transfer, physical and mechanical properties. Over the last years the structural versatility of polyurethanes with two soft segments has been subject of intense investigation in our group for the synthesis of both symmetric[1-4] and asymmetric gas permeable membranes. Having in mind the incorporation of these membranes in blood contacting devices and namely in membrane blood oxygenators, two main goals drove the synthesis of bi-soft segment polyurethane
membranes: i) The enhancement of O2 and CO2 gas permeation rates, and ii) The enhancement of the hemocompatibility. This work focuses on the synthesis of bi-soft segment poly (ester urethane urea) (PEUU) membranes suitable for ECMO devices. Gas permeation properties of dense and integrally skinned PEUU membranes are evaluated and membrane surface characterization is investigated at the sub-micron level. Furthermore a strong correlation between membrane surface properties and blood compatibility
is established contributing to the enhanced hemocompatibility of PEUU asymmetric membranes through the tailoring of top dense surface morphologies.

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ICOM367

Biomolecular recognition polymer using aptamer and dissociation of dsDNA for gating membrane

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Molecular recognition gating membranes can open and close their pores, and control a solution flux in response to molecular recognition of receptors. The gating membranes have a short response time and high sensitivity, and can be operated easily. Therefore, if the receptors can recognize biomolecules, the gating membranes can be useful biosensor used in medical care. The gating membranes' pores opening and closing are triggered by a swelling and shrinking of stimulus-recognition polymers grafted on the surface of the pores. Therefore, a biomolecular recognition polymer that can swell and shrink in response to a specific biomolecule is desired to develop a biomolecular recognition gating membrane.

We propose a novel biomolecular recognition polymer using an aptamer and dissociation of a double strand DNA (dsDNA). The concept of this polymer is shown in Figure 1. This polymer is thermo-responsive copolymer with a pendant single strand DNA (ssDNA). Thermo-responsive polymers exhibit a swelling/shrinking phase transition in aqueous solution due to temperature change. The ssDNA sequence is complementary to an aptamer strand, and forms a dsDNA. Aptamers are synthetic oligonucleotides, and can bind a certain target molecule specifically. An aptamer is used as a specific receptor in the molecular recognition polymer. In the presence of a target molecule, the aptamer specifically recognizes and binds the target molecule, and the dsDNA dissociates. When the dsDNA dissociates, hydration of the thermo-responsive copolymer is changed as previously reported. On the other hand, hydration change of a thermo-responsive polymer can induce a swelling/shrinking phase transition of the polymer. Therefore, aptamer's molecular recognition triggers shrinking of the thermo-responsive copolymer due to less hydration of the copolymer. If this molecular recognition polymer using an aptamer is used in a gating membrane, the gating membrane could be used for specific, easy, and rapid detection of various target biomolecules.

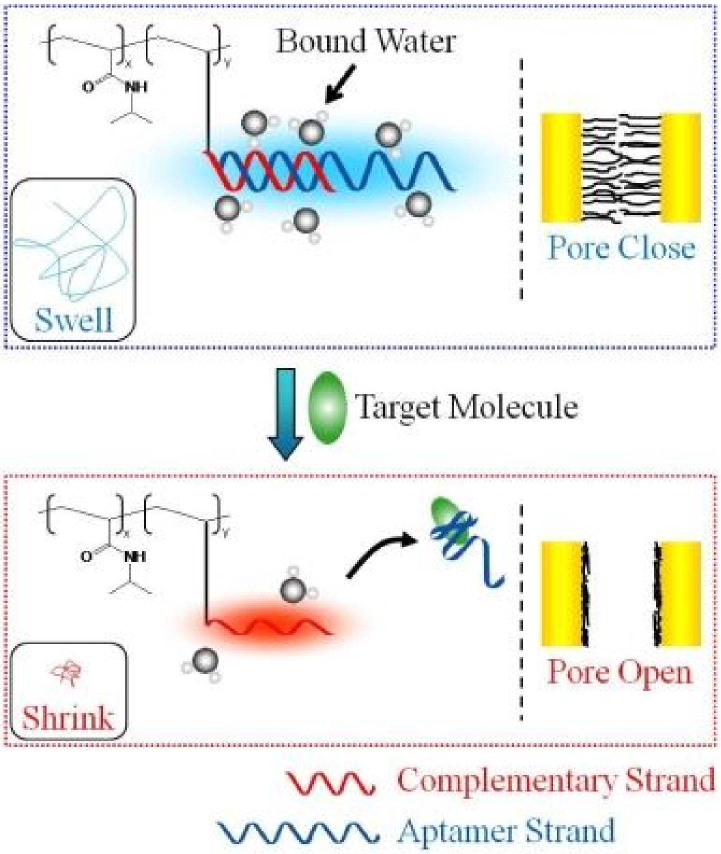

Figure 1. The concept of the biomolecular recognition polymer.

In this study, we prepared linear thermo-responsive copolymers with a pendant ssDNA or dsDNA, and confirmed swelling/shrinking phase transition of the copolymers caused by dissociation of a dsDNA.

First, a vinyl monomer containing thiol-activated group pyridyl disulfide was synthesized, followed by copolymerization with a thermo-responsive monomer. Then, conjugation of a terminated-thiol single strand DNA (ssDNA) to the copolymer was performed. Then, an aptamer contained dsDNA conjugated polymer was prepared by addition of a DNA aptamer strand to ssDNA conjugated polymer. Shrinking properties of the DNA conjugated polymers were measured as absorbance of the polymers solutions at heating process using UV-vis spectrometer.

Absorbance measurements of DNA conjugated polymers are shown in Figure 2. Increase in absorbance represents turbidity of solution, and means shrinking of the polymers. The figure shows that the ssDNA conjugated polymer became more shrunk than the dsDNA conjugated polymer did. This result shows that dissociation of a conjugated dsDNA can trigger the shrinking of the thermo-responsive copolymer. Thus, in the future, the proposed gating membrane could open its pores in response to a target molecule when an aptamer recognizes the target molecule followed by dissociation of the aptamer from a conjugated dsDNA.

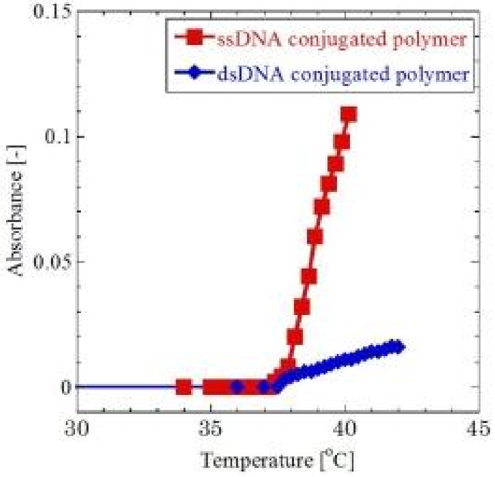

Figure 2. Shrinking properties of the ssDNA and dsDNA conjugated polymers

ICOM1674

Experimental evaluation and theoretical analysis of convective affinity adsorbers for chromatographic applications

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The use of convective affinity media, such as membranes and monoliths, for chromatographic separations is an innovative technique that is receiving increasing attention by the biotechnology industry. Compared to chromatographic processes performed on resin beads, convective media are not limited by diffusion as convection is the main transport mechanism through the porous structure. For this reason they are particularly suitable for purifying large biomolecules such as monoclonal antibodies, DNA fragments and viruses. This work presents the purification of immunoglobulin G (IgG) in columns packed with convective media (e.g. membranes and monoliths) and discusses the enhanced performance versus packed bead columns. The stationary phases studied derive from the functionalization of membranes and monoliths with natural and synthetic affinity ligands that show high specificity towards IgG. Among the supports investigated in our research group, we would like to focus on affinity membranes with immobilized Protein A and Mimetic Ligand™ B14, as well as CIM (convective interaction media) Protein A monolithic columns.

The affinity materials are completely characterized through adsorption, washing and elution cycles. The separation performance of the affinity supports has been determined by feeding both pure IgG solutions and a cell culture supernatant containing IgG. Several tracer molecules covering a large range of molecular weights have been tested in pulse experiments. The chromatographic peaks obtained have been analyzed using the moment method, and the mass transfer parameters and column efficiency have been evaluated through the height equivalent of a theoretical plate (HETP). The frontal analysis approach in the staircase mode was successfully applied for the first time in monolithic media to determine the dynamic binding isotherm for human IgG. In addition, elution was performed over a range of operating conditions to determine the critical pH needed to initiate desorption and subsequently the effects of pH and flow rate on the recovery of the bound IgG.

Relevant process parameters, such as maximum adsorption capacity, affinity equilibrium constant and selectivity, are evaluated and carefully compared among the different affinity supports.

The experimental data collected have been used for the validation of a proposed simulation model. Such chromatographic model is based on species mass balance equation over the convective medium, coupled with a suitable kinetic equation which represents the interaction between the IgG target molecule and the ligand immobilized on the porous support. Model simulations are in good agreement with all of the experimental affinity cycles, demonstrating the accuracy of the model to describe the transport phenomena in the column and the adsorption binding mechanism.

The scale-up of the improved affinity materials for industrial applications is also addressed.

ICOM1126

Electrolyte transport through nanoparticles-incorporated membranes

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Membrane modification with biomaterials and encapsulation of different therapeutically active molecules are attractive fields of research for developing new devices such as biosensors and controlled-release delivery systems [1]. Lipid nanoparticles (LNPs) represent a promising class of particulate matrices for bioactive organic molecules due to their temporal and thermal stability, high loading capacity, preparation simplicity and low production costs [2]. The insertion of intact lipid nanoparticles in the structure of different membrane supports is studied in this work as a way to improve material biocompatibility and to characterized potential drug releasing systems for topic applications.

Functionalized lipid nanoparticles (FLNPs) loaded with the sunscreen active 2,4-dihydroxybenzophenone or DHB were inserted in the structure of two different kinds of commercial membranes: i) a dense regenerated cellulose matrix; ii) a PVDF porous support. FLNPs were incorporated to the membrane supports by immersion in an aqueous dispersion of nanoparticles in the case of the dense sample [3], while nanoparticle dispersion was filtrate through the porous support. DHB encapsulation efficiency in the FLNPs of around 8 % was determined by HPLC.

Impedance spectroscopy measurements with dry samples were performed to determine changes in characteristic membrane material parameters (resistivity and dielectric constant) by comparing the results obtained with originals and functionalized membranes, while salt diffusion and membrane potential measurements carried out with NaCl solutions at different concentrations allow the determination of the effect of the FLNPs on characteristic electrolyte transport parameters (diffusion coefficient, fixed charge and ion transport numbers) [4], but they also give valuable information on the stability of the modified membranes depending on both solution concentration gradient and membrane-solution contact time. These results indicate a reduction in mass and ions transport across both functionalized membranes independently of their dense or porous structure and the stability of the systems, which supports their potentiality as drug delivery systems.

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ICOM1457

Membrane adsorbers can lower the cost of downstream purification

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Membrane chromatography has taken hold in the biotechnology marketplace as a worthy replacement for anion exchange chromatography resins. Several commercial products are being offered by the major membrane manufacturers as well as smaller companies that attempt to offer differentiated products. The possibility of functionalities other than anion exchange has also
been discussed and several academic publications have outlined the possibilities.

While the reduction in cost of goods (CoGs) possible by the one to one replacement of a chromatography resin by a membrane adsorber has been recognized, this study explores in more detail the potential CoGs advantages as a function of membrane adsorber performance and product cost. Such calculations are being used to guide product development, for example by stressing the relative importance of capacity and purification versus cost of media. It is important to challenge simple-minded assumptions about membrane properties and place them within the broader context of cost per gram of produced recombinant protein.

One of the enabling properties of novel membrane adsorbers is their high strength of binding which allows their use immediately after a cation exchange purification step, eliminating a hold tank. This property can lead to connected processing and the advantages in terms of reduced infrastructure and shorter processes with reduced labor requirements will be quantified. Some of the intangible benefits inherent in the use of a single-use product that does not require column packing will also be addressed.

This holistic view of how membrane adsorbers are actually used is essential in promoting the adoption of membrane chromatography and is necessary given the competition from established chromatographic unit operations. The trade-offs inherent in DSP process design will be illustrated with several examples.

The power of sophisticated CoGs software (Biosolve by Biopharm Services, Ltd) is exemplified through various scenarios that leverage all possibilities of cost reduction and provide guidance to both product development and process optimization teams.

ICOM261

DEVELOPMENT OF BIOACTIVE MEMBRANES FOR AN INTRADIALYTIC BIOLOGICAL KIDNEY SUPPORT DEVICE

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Introduction

Despite hemodialysis therapy, many end-stage renal disease patients (ESRD) have uremic complications that result in high morbidity and poor quality of life. Uremia is caused by the retention of a large group of molecules with different physical and chemical properties that are not sufficiently cleared by hemodialysis. In the native kidney, these protein-bound toxins are actively secreted in the renal tubule by renal tubular epithelial cells[1]. In our study, we aim to develop a bioactive composite membrane permeable to albumin bound uremic toxins.

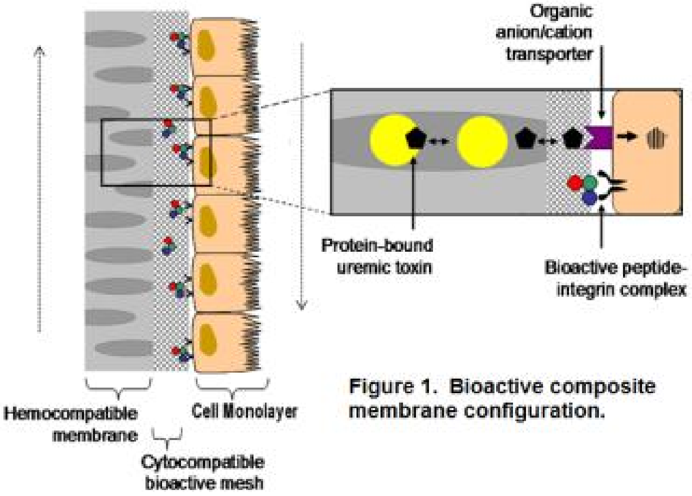

Figure 1. Bioactive composite membrane configuration.

This composite consists of two membranes: a hemocompatible membrane permeable to albumin bound toxins and a cytocompatible nanofibrous mesh that acts as a support for renal epithelial cells. Our bioactive membrane will selectively remove albumin bound toxins and regulate the cell monolayer integrity and cell viability under uremic conditions.

Materials and Methods

The membranes for the selective transport of albumin bound toxins were prepared using polysulfone based polymers which are commonly used in blood purification.[2] Various polysulfone based membranes were produced by phase inversion and different coagulation baths were employed. For reference, albumin permeable commercial membranes were studied, as well. A polycaprolactone (PCL) based fiber mesh was produced by electrospinning and later integrated directly into selected membranes to support a tight renal epithelial cell monolayer. The morphology of the produced membranes was investigated via Scanning Electron Microscopy, whereas the membrane transports properties were studied using pure water and model protein solutions at selected pressures.

Results and Conclusion

During membrane fabrication, several parameters control the membrane morphology, therefore, selected conditions (coagulation bath composition, for instance) were applied upon casting. As a result, membranes with controlled pore sizes that allow the passage of the albumin molecule, were produced. In fact, various polysulfone based membranes with water permeability in the range of 2000 – 4500 L/hr/m^2/bar and high bovine albumin sieving coefficient were obtained. These values are similar and/or higher than those of the commercial membranes tested. The more permeable membranes were acquired when the coagulation bath composition was mainly constituted of water due to the fast solvent/non solvent exchange.

Figure 2. A) Cross section of a membrane with spongy structure; B) Fiber mesh morphology obtained by electrospinning; C) Cross section indicating the tight adhesion between membrane and fiber mesh.

These membranes often had macrovoids. However, membranes coagulated in NMP/H_2O have more spongy structure [figure 2A]. During electrospinnning, specific parameters (height, voltage and polymer feed rate) were tailored in order to obtain different fiber mesh morphologies [figure 2B]. Successful integration between the porous membrane and the electrospun PCL mesh was achieved without the use of bonding agents [figure 2C].

In the future, cell culture with renal epithelial cells on the composite membrane will be performed and their performance in a bioreactor will be evaluated.

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Molecular membrane design 1

ICOM1833

SYSTEMS MEMBRANES - DYNAMIC SELECTION OF HYBRID MEMBRANE SYSTEMS

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Dynamic Interactive Systems[1] are defined by networks of continuously exchanging and reversibly reorganizing connected objects (supermolecules, polymers, biomolecules, biopolymers, pores, nano-platforms, nanotubes, surfaces, nanoparticles, liposomes, materials, cells). They are operating under the natural selection to allow 4D spatial / temporal and structural / functional adaptability in response to internal constitutional / affinity or to stimulant external factors.

Herein we will disscuss some selected examples of hybrid organic/inorganic SYSTEMS MATERIALS, covering a) the sol-gel resolution of constitutional architectures from Dynamic combinatorial libraries[2] and b) the generation of Dynamic Hybrid Materials[3] and SYSTEMS MEMBRANES able to evolve insidepore exchanging architectures via ionic stimuli so as to improve membrane transport functions.[4]

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ICOM938

Stimuli-responsive membrames from the self-assembly of block copolymers

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Superassemblies of nanobuilding blocks have found many promising applications in photonics, electronics and sensing due to a control of the material architecture at a nanometric level. In order to produce stable superstructures, it is necessary to control the building block design in terms of morphology, mechanical properties and inter-block interactions. Herein, we report on the facile preparation of stable nanostructured and nanoporous superassemblies in one step from homogenous solutions of block copolymers (Fig.1).

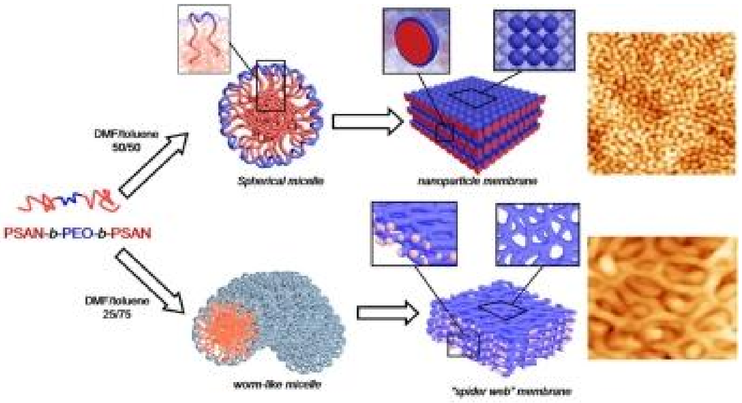

Figure 1. Schematic depiction and AFM pictures of the self-assembly of PSAN-*b*-PEO-*b*-PSAN into nanoparticle and "spider-web" porous superstructures.

The success of this strategy is essentially due to the design of very stable micelles prepared and self-assembled *in situ* in few seconds by solvent evaporation. It is known that preparing micelles from ABA triblock copolymers with a solvent system that preferentially dissolves the middle B block yields to a very stable morphology composed by a core of the A block and a corona of the B block. We designed the triblock copolymer poly(styrene-*co*-acrylonitrile)-*b*-poly(ethylene oxide)-*b*-poly(styrene-*co*-acrylonitrile) as a 'hard' PSAN core is expected to bring good mechanical property to the material and the soft corona of PEO to ensure efficient binding between the building blocks. The porosity of the assembly is controlled by the interspace between the self-assembled nanoobjects. The transport of water through the nanomaterials has been carried out in order to understand the porosity/nanostructure relationship. In function of the water pressure applied on the membrane, the pore size could be changed thanks to the particular structure of the nanobuilding blocks. Also when applying a pressure exceeding 3.5 bars, the membrane morphology could be tuned from spherical to cylindrical micelles, enabling the access to a huge range of pore size (Fig. 2).

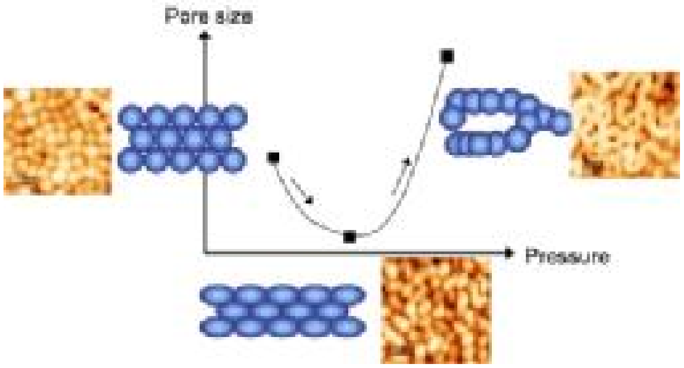

Figure2: Schematic evolution of the pore size in function of the water pressure

ICOM543

Reaction media for molecularly imprinted membranes for acid removal in biorefinery

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Introduction
The removal of trace components from aqueous bulk streams is an important separation in chemical industries. Despite its high energy consumption, distillation is the most frequently used separation technology. This project aims developing a low energy consuming membrane-based process using molecularly imprinted membranes (MIM).

Molecular imprinting (Figure 1) is a versatile technique to introduce high selectivity in membrane adsorbers. In order to create 3 dimensional cavities in a polymer, the formation of a bond between template (trace component) and functional monomer is essential (complex formation). Formation of the complex and its effectiveness in the application depend on the nature of the reaction medium, as this determines the type of bonds formed (ionic, hydrogen) and therefore the shape, strength and stability of the 3D complex structure. The use of MIMs for biorefinery applications requires recognition properties in aqueous environments. Here the effect of common reaction media and pH are studied to mimic such aqueous applications.

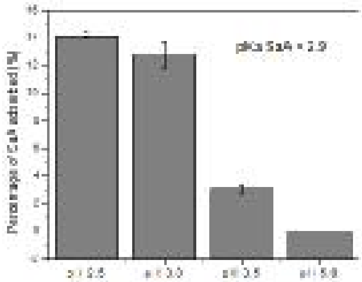

Figure 2: Adsorption of SaA [%] as function of pH

Experimental part
The ratio template (salicylic acid, SaA) to functional monomer (4-vinylpyridine, 4VP) in the complex was determined from Jobs plots using methanol, acetonitrile and 2-butanol. The equilibrium constant between SaA and 4VP towards the complex in methanol was determined by the Rose-Drago method.

MIMs were made by adsorption of a photoinitiator on the surface of a porous polypropylene support after which the support was placed in the reaction mixture (functional monomer (4VP), template (SaA), crosslinker (ethyleneglycoldimethacrylate) and solvent (methanol or methanol:water, pH 2.5)) and crosslinked by UV light. Non-imprinted membranes (NIM) were prepared accordingly but without template.
Adsorption experiments were performed by filtrating 2 ml of a $1 \cdot 10^{-5}$ M SaA solution (methanol and water pH 2.5-5.0) through the membrane. The effect of molecular imprinting was determined by comparing the adsorption of SaA with the adsorption of 3-methylsalicylic acid (3M-SaA) in NIMs and MIMs.

Results and discussion
The Jobs plot showed that methanol is the best solvent for complex formation because of its functional monomer to template ratio (2:1), which makes molecular recognition more effective. The equilibrium constant for the complex ($1 \cdot 10^{4}$ M^{-1}) in methanol is strongly towards the complex.

The results show that adsorption of SaA from methanol is limited. Adsorption from water is pH dependent (Figure 2). Although the use of methanol during MIM preparation results in complex formation, methanol apparently not sufficiently mimics complex formation in the application. Adsorption from aqueous media is high below the pKa of SaA (pKa 2.9), but rapidly decreases at higher pH (deprotonation of acid).

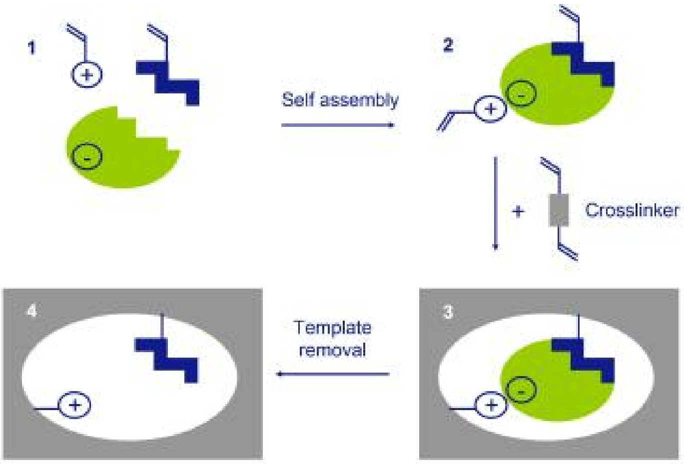

Figure 1: Illustration of molecular imprinting: 1, mixing of template and reactants; 2, self-assembling of template and reactants (complex formation) ; 3, stabilization of template molecule by crosslinking; 4, extraction of template molecule.

Lowering the pH of the reaction medium shows a positive effect on molecular imprinting. Although adsorption of SaA in the MIM is lower than in the NIM, adsorption of 3M-SaA is much lower in the MIM than in the NIM consequently increasing selectivity towards SaA.

This research shows molecular imprinting is a powerful tool to develop highly selective membrane adsorbers for biorefinery applications. Reaction medium and conditions are essential and allow tailoring required functionalities and selectivities.

Acknowledgements
This is an ISPT (Institute for Sustainable Process Technology) project.

ICOM272

Molecular Design Aspect of Thermally Rearranged (TR) Polymers for Gas Separation Membranes

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With the increasing emphasis on energy efficient technology, membrane mediated gas separation has emerged as an important fast-growing separation technology offering many advantages over traditional processes, namely, low energy consumption, low operating costs and high flexibility. There have been widespread gas separation applications utilizing polymer membranes, such as air separation, CO_2/Methane separation, and H_2 recovery. As being realized, the biggest challenge for gas separation membranes is the strong trade-off relationship between permeability and selectivity defining the so-called "upper bound".[1] Over the years, substantial research efforts have been directed to expanding the performance envelope defined by the "upper bound" via designing novel polymer structures. It was recently reported that polybenzoxazole (PBO) structure derivatized from molecular thermal rearrangement (TR) of ortho-hydroxy aromatic polyimides (API) exhibited unprecedented performance in CO_2/CH_4 separation as well as high resistance to plasticization.[2] However, very high processing temperatures (>400°C) are essential for current TR process making it less practical in real applications. In this regard, molecular design and synthesis of new API precursor structures and investigation of synthetic variables effect on PBO membrane properties define the research scope of this study.

In this study, we design and synthesize a series of ortho-functional API precursors via polycondensation of carefully selected aromatic bisaminophenols and dianhydride monomers.[3] Bisaminophenols introduce the ortho-functionality in precursor structures facilitating TR process and chemical modifications. Dianhydrides containing various bridging/linking units provide structural variables in terms of chain rigidity and/or free volume, which represent crucial conformational parameters on the effectiveness of molecular design. By manipulating the monomer combinations, polyimides with manageable conformational and thermal characteristics are prepared and solution cast into tough films. TR processes of APIs are monitored with time and temperature via recording FTIR, TGA, DMA and gel fraction measurements. It is shown that efficient TR temperature of imide-to-benzoxazole rearrangement greatly depends on the Tg of precursors. APIs with high Tg's require high TR temperature to be efficiently converted to PBOs. In this regard, efficient TR temperatures are successfully reduced by up to 100℃ by simply altering the structure of dianhydrides. This finding represents a significant leap in the development of practical applications of TR membranes for gas separations. It is also demonstrated in this study that the nature of ortho-positioned functional groups in the precursor structure plays an important role in the formation of benzoxazole structure and gas permeation properties of resulting TR membranes. Presumably larger leaving groups result in larger cavity size in TR membranes leading to higher gas permeability. In summary, the integration of polyimide molecular design with chemical modification of the ortho-functionality generates synergistic effects for optimizing and fine tuning the gas separation performance of TR polymer membranes.

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ICOM477

Novel composite membranes with switchable ultrafiltration functions

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Conventionally, due to their permanent pore size, micro- and ultrafiltration (MF, UF) processes separate only two or two groups of components; one being obtained in the permeate and the other in the retentate [1]. One way to improve these processes is via pore-filling functionalization using temperature-responsive hydrogels; e.g., poly(*N*-isopropylacrylamide) (PNIPAAm). The hydrogel network on one hand imposes a sieving structure and may be used to enhance size selectivity processes. On the other hand, filling the macropores of base membranes with smart hydrogel allows for a tailored and switchable barrier, i.e., from UF to MF and vice versa as the crosslinked PNIPAAm swells or deswells in the vicinity of its lower critical solution temperature (LCST; 32 °C).

In this work, hydrogel pore-filled composite membranes (HPFCMs) were prepared using commercial polyethylene terephthalate (PET) track-etched membranes (nominal pore diameter 200-5000 nm, Oxyphen AG, Switzerland). PET membranes were equilibrated in solutions containing 10 or 15 wt% NIPAAm with same degree of crosslinking (5 % relative to monomer, methylenebisacrylamide as crosslinker) and photoinitiator, followed by UV-irradiation (5-20 mins, λ > 300 nm, intensity □ 30 mW/cm^2).

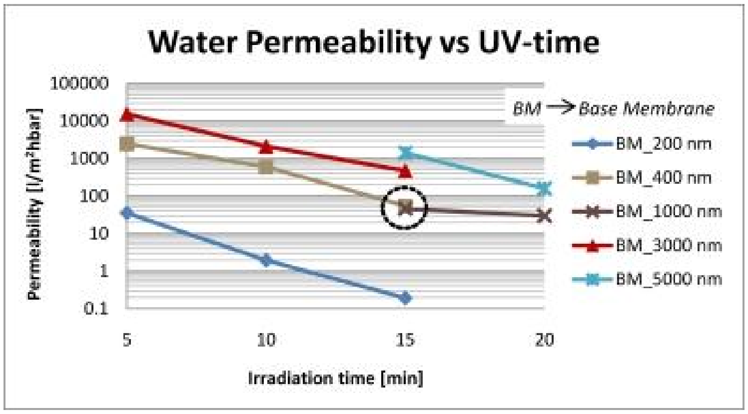

Fig. 1: Water permeability at 25 °C of HPFCMs as a function of irradiation time and pore size of base membrane at constant monomer concentration (15 wt%).

After functionalization, the water permeabilities measured below LCST were significantly reduced; i.e., by □ 3-4 orders of magnitude depending both on pore size of base membranes as well as irradiation time (Figure 1). The degree of functionalization (DOF) between 500-750 µg/cm^2 was obtained and interestingly functionalization with 15 min resulted in same DOF (□ 700 µg/cm^2) for all pore sizes.
Nevertheless, higher resistance towards permeability was observed for smaller membrane pores which can be explained by confinement effect.

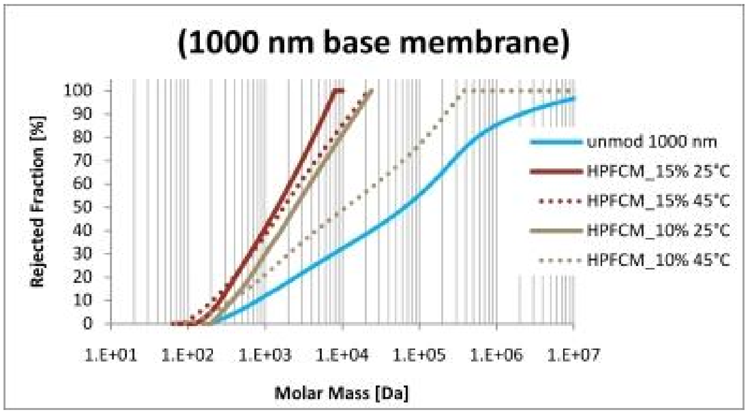

Fig. 2: Rejection curve of unmodified membrane vs HPFCMs (10 and 15 wt%) after 24 h diffusion of a dextran mixture in water.

HPFCMs demonstrated size-selectivity features; i.e., an apparent molecular weight cut-off (*a*MWCO) under diffusive flow (solution of a mixture of dextrans with molar masses between 4 and 2000 kDa) which is tunable by synthesis conditions and also temperature (Figure 2). The *a*MWCO was well correlated to the hydrogel network determined from Darcy model (Darcy model; *c.f.* [2]). Most importantly, HPFCMs also revealed switchable *a*MWCO; more pronounced switching was observed for HPFCMs prepared with smaller monomer fraction, i.e. comprising a “looser” network.

To conclude, the tunable transport through HPFCMs was due to the very large reversible change of effective size-selective barrier properties of the pore-confined hydrogels in response to temperature change as a stimulus. Such novel approach is of course very important since it could overcome the single size limitation with respect to retention of components by conventional MF or UF processes.

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ICOM444

Chiral Separation with Molecularly Imprinted Polysulfone-Aldehyde Derivatized Nanofiber Membranes

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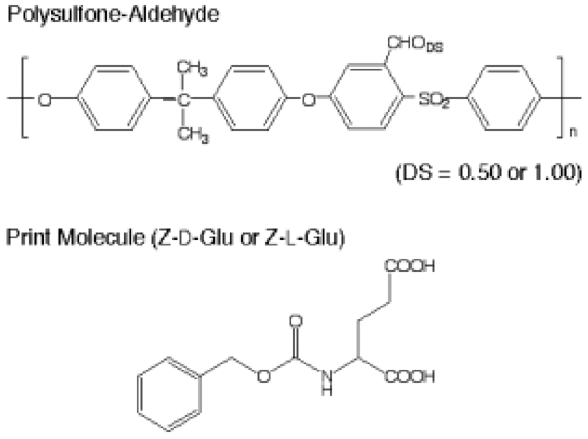
Various polymeric materials, such as synthetic polymers [1], derivatives of natural polymers [2], oligopeptide derivatives [3], and natural polymers [4], were converted into molecular recognition materials (membranes) by applying an alternative molecular imprinting. Molecularly imprinted membranes with a higher surface area can be expected to give higher flux and permselectivity compared with those prepared by conventional molecular imprinting technique. Electrospray deposition is one plausible method to obtain molecularly imprinted membranes with a large surface area. To this end, novel molecularly imprinted nanofiber membranes were prepared from carboxylated polysulfone (PSf-COOH) [5] and cellulose acetate [6] by applying an electrospray deposition and an alternative molecular imprinting during the membrane preparation process. In the present study, modified polysulfones having aldehyde moiety (PSf-CHO) were adopted as candidate polymers for molecularly imprinted nanofiber membranes. In the present paper, results of molecularly imprinted nanofiber membranes and usual molecularly imprinted membranes from PSf-CHO will be reported.

PSf-CHO's with the degree of substitution of 0.50 (DS = 0.50) and 1.00 (DS = 1.00) were adopted as candidate materials in the present study [7]. N-α-Benzyloxycarbonyl-D-glutamic acid (Z-D-Glu) or N-α-benzyloxycarbonyl-L-glutamic acid (Z-L-Glu) was employed as a print molecule. Enantioselective transport was studied by using concentration difference or potential difference as a driving force for membrane transport.


Polysulfone-Aldehyde

Print Molecule (Z-D-Glu or Z-L-Glu)

Figure 1 Chemical structures of polysulfone-aldehede and print molecules.

The results obtained in the present study suggested that molecularly imprinted nanofiber membranes enhance both permslectivity and flux, which are generally perceived to show a trade-off relationship. The flux for the present molecularly imprinted nanofiber membranes were about two orders of magnitude higher than the usual molecularly imprinted membranes, while the molecularly imprinted nanofiber membranes also showed permselectivity. The present study revealed that molecularly imprinted nanofiber membranes have potential that both permselectivity and the corresponding flux can be simultaneously enhanced.

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ICOM521

Phosphonated polymers: synthesis and application as PEMs

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Phosphonated polymers as alternatives to sulfonated ones have the advantage of being simultaneously proton donors and acceptors. This makes them suitable candidates for membrane systems based on water-free conductors. However, in order to build-up a continuously conducting phase (channels) one should provide a high local concentration of protonogenic functions into membrane structure. This can be done by both the use of highly functionalized polymers or self-segregation of the polar segments of less functionalized polymer. Both strategies are described at the current research: (i) synthesis of a novel highly phosphonated polymer and (ii) preparation of a phase-separated polymer blend.

(i) The synthesis of highly phosphonate polymers was done utilizing both strategies: “monomer-first” where monomer is initially phosphonated followed by its polymerization; and “polymer first” where a non-phosphonated polymer is obtained followed by its post-phosphonation. In the framework of the “monomer-first” approach, the phosphonation of perfluorinated monomers is presented. In the “polymer-first” strategy, phosphonation of partially fluorinated polymers and their blending with polybenzimidazole is presented as well.

(ii) Preparation of a phase separated polymer blend system is possible through all the methods that retard the polymer “freezing” in a solid polymeric membrane. Particularly, reducing the rate of evaporation of the solvent during the polymer film preparation is extending the relaxation time of the polymer mixture. This is giving a higher possibility for the self-segregation between the polymer chains which differ in chemical nature. Properties of the so obtained phase separated membranes are presented here.

The polymer membranes possessing the best characteristics are tested under fuel cell operating conditions.

The synthesis of novel highly functionalized polymeric materials together with the optimization of a PEM structure and properties are the two approaches followed in the present study. We believe that the success of both approaches and their combination will give us an access to a PEM suitable for low- to mid-temperature fuel cell applications.

Membrane fouling 2

ICOM1781

Strategies and Challenges of Membrane Fouling Control

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Fouling remains a dominant limitation of membrane filtration processes. We highlight the emerging understanding of the fouling process and their consequences for future strategies for polymer membrane modifications and operational strategies to control fouling. In addition, often-neglected impacts of cleaning on long-term membrane performance are discussed in relations to membrane ageing and residual deposition. Constraints and opportunities for future implementation in membrane systems are outlined from the perspectives of water and wastewater treatment applications.

ICOM994

An On-line Instrument for Assessing the Integrity of Pre-filtration Membranes

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This paper discusses the design and performance evaluation of a low cost, sensitive, on-line sensor for assessing the integrity of membrane modules used for water treatment, membrane bioreactors and pre-treatment prior to nanofiltration or reverse osmosis. The operating principle of this Integrity Sensor is based on continuously sampling the effluent from the upstream pre-filtration module. The sample stream flows under pressure across a microfiltration membrane in the Integrity Sensor. The permeate then flows through a valve whose resistance is equal to that of the initially unfouled membrane. The membrane resistance gradually increases owing to rejection of trace particulates in the sample stream. However, if the pre-filtration module is compromised, the resistance of the membrane will increase rapidly owing to the larger concentration of particulates. The integrity of the pre-filtration modules can be assessed by continuously measuring the pressure drop across the membrane relative to the pressure drop across the valve. The Integrity Sensor response is quantified by the C-metric, defined as the ratio of the difference between these two pressure drops divided by their sum. This ratio is independent of the permeation rate through the membrane and valve.

The time rate-of-change of the C-metric correlates well with the Silt Density Index of feed water of different blends of treated and untreated water from the Bedok Water Treatment Plant in Singapore. The sensitivity of the Integrity Sensor is demonstrated by simulating a failure in a pre-treatment module by shifting the feed from UF permeate to that from the same UF module for which one of the 1500 hollow fibers was cut. Figure 1 shows the C-metric as a function of time. Initially the C-metric increases slowly in time. A linear regression through these data gives a slope of 7.06×10^{-4} min^{-1}, which corresponds to an SDI of 0.54, thereby implying a feed stream with negligible particulates. At 20 minutes the feed was shifted to that from the compromised UF module. Within three minutes the C-metric begins to increase markedly. A linear regression through the data in the range $20 \leq t \leq 60$ gives a slope of 2.13×10^{-3} min^{-1}, which corresponds to an SDI of 1.64.

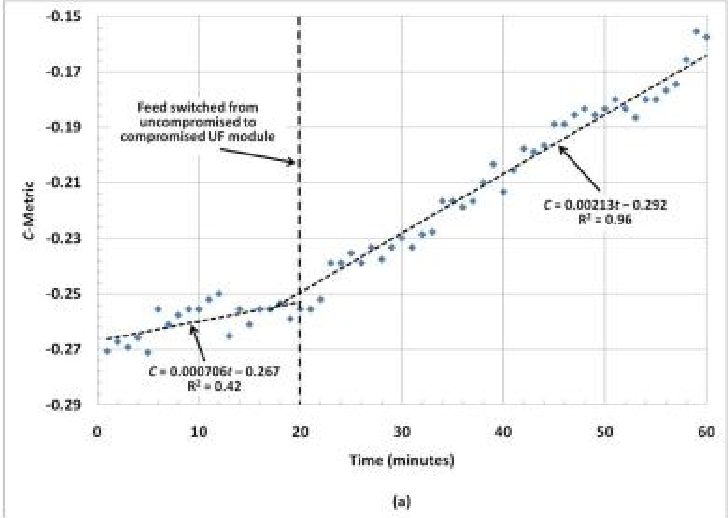

Figure 1: *C*-metric as a function of time for an experiment in which the feed to the Integrity Sensor was switched at 20 minutes from an uncompromised UF module permeate to permeate from the same module for which one of the 1500 hollow fibers was cut to simulate failure of a pre-treatment module; the marked change in the slope from 7.06×10^{-4} min^{-1} to 2.13×10^{-3} min^{-1} implies a change in the Silt Density Index from 0.54 to 1.64.

A prototype Integrity Sensor developed by MINT (Membrane Instruments and Technology Pte. Ltd.), the commercialization arm of the Singapore Membrane Technology Center, will be shown. The ability of this instrument to provide long term reliable sensing, to be conveniently retrofitted on water treatment facilities, and to provide reliable sensing of pre-filtration modules at a low cost will be discussed.

ICOM613

Direct visualization of protein fouling inside a hollow-fiber membrane by fluorescent microscopy

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Ultrafiltration using a hollow fiber membrane is increasingly used in water treatment for the removal of particles, turbidity and microorganisms to meet stringent water quality requirements. In ultrafiltration processes, protein adsorption has been considered as one of the main causes of membrane fouling and also still a poorly understood phenomenon. There's a growing interest in the control and elimination of the foulant during filtration and also in membrane remediation by physical or chemical cleaning after filtration. The protein permeation through hollow fiber membranes is affected by various filtration conditions. During filtration, the labile nature and complex structure of proteins increase the difficulty of understanding fouling and cleaning mechanism. The possibility of protein denaturation and aggregation resulting in radically different deposition also brings additional challenges in fouling characterization. While many studies have focused on permeation flux and the foulant deposited on a membrane, there was little report describing the internal protein deposition in the pores of a hollow fiber membrane. In this study, we aimed to directly observe the membrane fouling using fluorescent microscopy. Fluorescently-labeled protein was used as a model foulant. After filtration, the cross section of the fouled membrane was observed by a fluorescent microscope to reveal the protein deposition in pores.

We adopted bovine serum albumin (BSA), casein (from bovine milk) and lysozyme (from egg white) as model protein foulants and modified them with fluorescein isothiocyanate (FITC). An aqueous solution containing a fluorescently-labeled protein was filtrated to a PES hollow-fiber membrane (10 kDa, 30 kDa, 150 kDa and 300 kDa) from the membrane outside. The cross-sectional microscope images of the membranes showed that three types of proteins showed completely different fouling behaviors although the flux declines of these protein solutions were similar to each other during filtration.

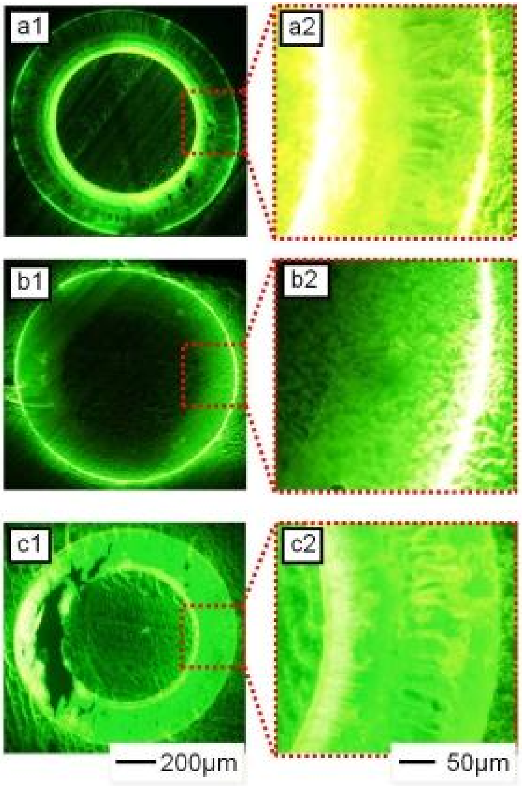

Fig. 1 Fluorescent images of the whole (1) and the magnified (2) cross section of the fouled hollow-fiber membrane. (a) A polyethersulfone membrane (MWCO 30 kDa) was fouled by the filtration of 50 ppm FITC-BSA solution for 2 h at 0.5 atm, with the final relative permeability of 0.23 and with the rejection of 95.1%. (b) A polyethersulfone membrane (MWCO 300 kDa) was fouled by the filtration of 20 ppm FITC-casein solution for 2 h at 0.5 atm, with the final relative permeability of 0.12 and with the rejection of 53.1%. (c) A polyethersulfone membrane (MWCO 10 kDa) was fouled by the filtration of 100 ppm FITC-lysozyme solution for 2 h at 0.5 atm, with the final relative permeability of 0.25 and the rejection of 5%.

For example, fouled casein located only on the outer surface of the membrane, while BSA formed a thin cake layer on the membrane surface and also entered into the membrane. In contrast, lysozyme only entered into membrane pores and was homogeneously distributed inside of the membrane. Interestingly, lysozyme did not form a cake layer on the membrane surface. These microscope observations first revealed the fouling behavior inside the membrane.

To clean the membrane fouled with FITC-labeled BSA, backwashing using various cleaning agents was carried out and the cross-sectional images were observed using the fluorescent microscope.

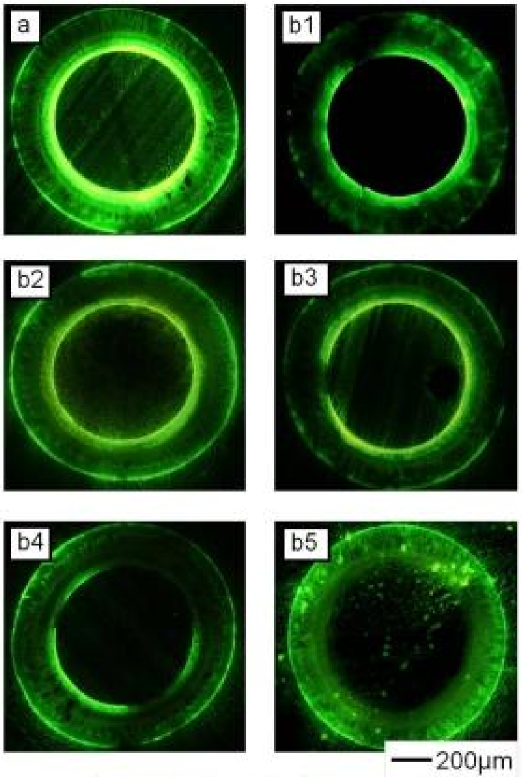

Fig. 2 Fluorescent images of the polyethersulfone hollow-fiber membrane (MWCO 30 kDa) fouled with FITC-BSA before (a) and after backwashing for 1 min at 1atm (b). The fouled membrane was backwashed using 8M Urea (1), 500 ppm NaClO (2), 0.01M NaOH (pH 11) (3), the mixture of 1 wt% SDS and NaOH (pH 10) (4), and 1wt% SDS (5). The backwashing efficiency was 49.1%, 42.9%, 24.2%, 27.1% and 14.7%, respectively.

The recovered flux was drastically influenced by cleaning agents. Among these cleaning agents used, urea and NaClO exhibited the effective backwashing. More importantly, fluorescent observation clearly revealed which part of the membrane was cleaned and where the foulants were removed (cake layer or deposits inside).

Our present study succeeded in the direct visualization of protein fouling inside a membrane and also provided novel clues for better understanding of the membrane fouling.

ICOM499

Monitoring of Membrane Filtration Processes for Drinking Water Production using Fluorescence Excitation-Emission Matrix Analysis

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Membrane-based treatment systems are increasingly used for the production of drinking water as an effective mode of removing particulate matter, reducing natural organic matter (NOM) and water-borne disease causing organisms. The application of this technology is however constrained by membrane fouling, which contributes to increased operational costs associated with decreased membrane permeability, higher trans-membrane pressure and the need for frequent chemical cleaning, as well as shortened membrane service life. NOM and colloidal/particulate matter in water are considered as the major membrane foulants and therefore their characterization is essential for improving our understanding of membrane fouling in drinking water treatment applications. Implementation of effective and reliable foulant characterization techniques could also serve for developing fouling control strategies that have applications in industrial-scale membrane filtration systems.

In this study, the fluorescence excitation-emission matrix (EEM) approach was used for characterization of the major natural water foulant species, humic substances (HS)–like, protein-like and colloidal/particulate matter in water samples drawn from different steps of the full-scale controlled membrane pilot facilities at GE in Burlington, Ontario. A library of fluorescence EEMs of Hamilton Bay water (Burlington, Ontario, Canada), coagulant-added Bay water (feed for the pilot membrane filtration systems), permeate and reject water collected after back-pulsing and scouring of membranes was created. Samples were collected on a weekly basis over extended period of time. Liquid Chromatography - Carbon Detection (LC-OCD) was utilized as a complimentary characterization method for selected water samples.

The results from these analyses revealed how the addition of the coagulant polyaluminum chloride contributed to the reduction of HS-like foulant species and the increase in the colloidal/particulate content in membrane feed water. In addition, removal of protein-like, HS-like and colloidal/particulate foulant species from the surface and/or within the pores of the membranes during membrane back-pulsing and scouring were also observed. These results were then correlated with the corresponding trans-membrane pressure readings to identify possible correlations that merit further investigation with regards to developing fouling control protocols.

These results will provide GE a better understanding as to how individual and combined contributions of the major foulant components present in water source contribute to membrane fouling , facilitate the improvements of membrane performance by developing operational strategies for fouling control, and allow operational changes to be implemented proactively for its industrial-scale membrane systems.

ICOM1208

Development of a new method for the characterisation of electrokinetics properties of fouling deposits during the filtration

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Although the electrokinetic characterisation of fouling deposits during filtration is of a great importance for better understanding of the membrane/foulant and fouling layer/foulant interactions, few methods have been developed for performing this characterisation so far. Moreover, they are not applicable to the case of complex fouling layers such as compressible fouling layers. The present study focuses on the description and validation of a new method for in situ and real time electrokinetic characterisation of cakes. This method is based upon simultaneous measurements of transversal streaming potential (SP) and permeate flux before and during the cake formation. The measurements of the SP at a constant pressure have been preferred to those obtained by pressure steps in order not to modify the cake structure. Indeed, a densification of the cake structure with pressure steps might lead to pressure-dependent SP coefficients. Mono-disperse suspensions of (negatively charged) polystyrene latex and (positively charged) melamine at various particle concentrations were filtered in a dead-end mode through negative polyethersulfone membranes forming a narrow channel. It was found that the global SP coefficient increased in absolute value with the deposited latex quantity, whereas it decreased and changed of sign during the filtration of melamine suspensions.

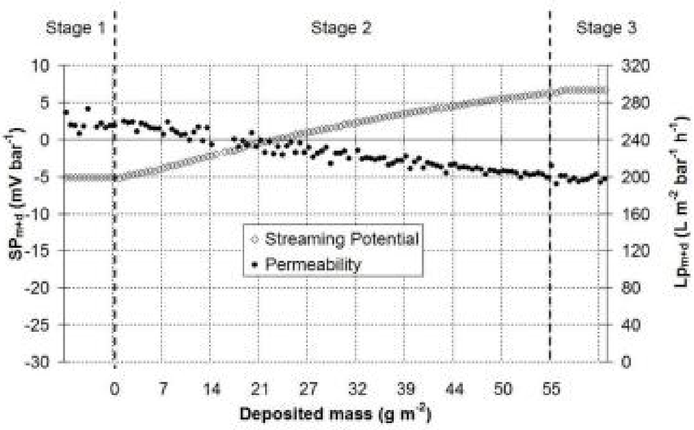

Fig. 1: SP_{m+d} and permeability (Lp_{m+d}) versus deposited particle mass during filtration of a melamine suspension (C = 450 mg L^{-1}, 0.001 M KCl. Stages 1 and 3: filtration of a 0.001 M KCl solution.

By considering a resistance-in-series model, the SP coefficient of the alone deposit was deduced from the electrokinetic and hydraulic measurements performed through the membrane and "membrane + deposit". The charge sign obtained for latex and melamine deposits as well as the independence of the SP coefficient of deposits on both deposit thickness and growth kinetics validates the method at constant pressure, as well as reliability of the proposed procedure.

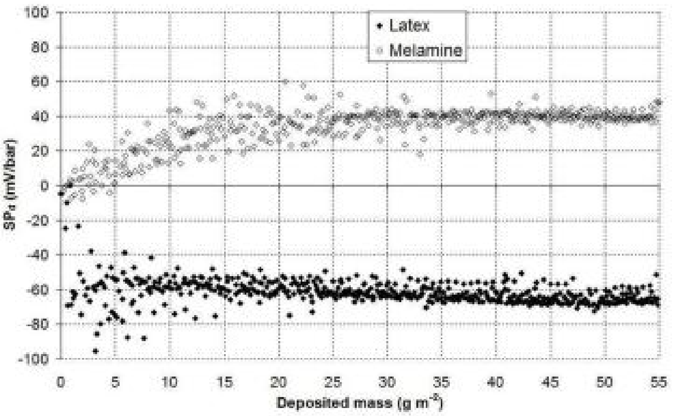

Fig. 2: SP coefficients of latex and melamine deposits (SP_d) versus deposited particle mass. Particle concentration: 150, 450 and 750 mg L^{-1}.

Indeed, if particles, which are rigid, pile up one upon another in an identical way during the filtration, then the mean pore size of the deposit should not vary during its growth. In these conditions, it is quite normal that the SP coefficient of deposits varies neither with its thickness nor with its growth kinetics, since they are the same particles with the same surface charge density that participate in the cake growth. It was also found that the porosity of deposits levelled off rather quickly, i.e. for deposit thickness greater than ~15 mm. Porosities of 31 and 33% were obtained for latex and melamine deposits, respectively. These values indicate that deposits have a compact structure of body-centred cubic type, which is not uncommon in the case of mono-dispersed rigid spherical particles. As a conclusion, it was shown that this method is able to evaluate the SP coefficient of the single deposit without disturbing its build-up. Such a tool should help to better understand the cake formation in conjunction with operating conditions.

ICOM423

Effect of air/water cleaning frequency in the control of biofouling in spiral wound RO membranes

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Introduction

Membrane filtration is getting increasingly popular in (drinking) water treatment. Despite several merits, Reverse osmosis (RO) and nanofiltration (NF) membranes suffer from membrane fouling (particularly biofouling) resulting in operational problems and possible product quality loss. Membrane fouling can be controlled by periodic membrane cleaning. The effectiveness of membrane cleaning depends strongly on the hydraulic conditions in SWM elements [1]. To improve hydraulic conditions, periodic air/water cleaning (AWC) is introduced in vertically positioned SWM elements. The first experiences of the use of periodical air/water cleaning (AWC) were very promising, resulting in an effective restoration of the membrane performance after air/water [2]. In the current study the effects using daily versus monthly intervals of AWC was investigated while operating at a fixed feed pressure.

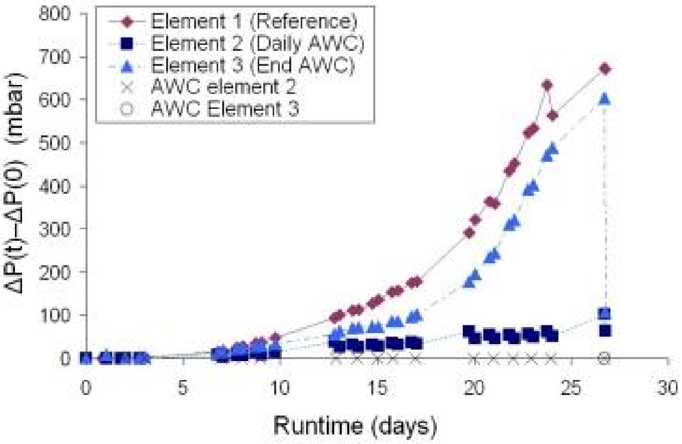
Experimental part

A pilot study was carried out using three parallel 2.5-inch SWM elements (2521 and 2540 elements) with a fixed feed pressure (3.4 and 10 bar) in cross-flow operation at a recovery of 10% per element i.e.; (i) a reference element, (ii) an element with daily AWC (except for the weekends) and (iii) a third element with AWC after a month. The pilot is depicted in the following figure.

The three elements were fed with pre-filtered tap water (without disinfectant residual) enriched with acetate to promote biomass development while operational parameters (e.g. relative pressure drop, MTC, retention) were investigated. At the end of the experiments membrane autopsies were performed to analyze the biological (ATP, TDC and carbohydrates) and inorganic (Iron + Manganese) deposition on the membrane surfaces.

Results

The evolution of the feed-channel pressure drop in time is shown here.



The feed-channel pressure drop in elements 1 and 3, without AWC increased exponentially. After AWC, performed after one month, the pressure drop was 107 mbar for element 3. For element 2 (daily AWC), no exponentially increase of the pressure drop was observed. At the end of the experiment the relative pressure drop was 64 mbar. Other operational parameters (not shown here) like the MTC evolution and the retention remained almost unaltered for the 3 elements.

After the experiment a membrane autopsy was conducted (results not shown here). The autopsy results confirmed the results of the operational parameters. The amount of ATP, TDC, carbohydrates, manganese and iron was more pronounced in the reference element than in the element with AWC after a month. The lowest depositions were on the element with the daily AWC.

Conclusion

Air/water cleaning is an effective cleaning method to maintain the membrane performance. Current study shows that performing a daily AWC the membrane performance will not be restored for 100%. From autopsy studies it appeared that daily AWC is more effective in removing biomass and inorganics compared to AWC after one month.

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ICOM440

Impact of suspension properties and membrane permeation flux on *in-situ* determined cake structural properties and growth kinetics

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Indirect characterization (permeate flux monitoring), *ex-situ* analysis, and numerical studies have shown that the particle/particle interactions and the permeation rate through the membrane are influencing some structural properties (thickness, porosity) of a fouling consisting in a filtration cake. However, to date, the impact of those parameters on filtration cakes structure has never been studied *in-situ* during filtration. As cake structural properties are responsible for filtration process global performances, a better understanding of the morphology of particle-based fouling deposits in relation with operating conditions is a key issue for further optimization of filtration processes. The objective of this study was thus
to evaluate, *in-situ* and on real time, the impact of particle nature (material, charge, size), solution chemistry (ionic strength) and convective flow rate through the membrane (permeate flux) on the morphology (thickness, porosity) of fouling deposits built on the surface of membranes during dead-end filtration in a confined geometry. The Laser-Sheet at a Grazing Incidence Method that was previously developed [1] has been adapted and used to allow a measurement of fouling layer thickness at different locations of the membrane surface during each filtration run with a resolution of is 3µm. From these measurements it was possible to determine cakes growth kinetics. Monitoring the permeate mass on time, it was possible
to link local structural properties with global parameters (permeate flux, hydraulic resistance).

Impact of particle nature has been assessed using suspension of negatively charged latex and positively charged melamine particles of same diameter (500nm). The particle surface charge was changed by adjusting the ionic strength at different values (10^{-5}-10^{-3}M). Influence of particle size was evaluated by comparing the filtration of 500nm and 1800nm melamine particle suspensions. In order to study the impact of permeate flow rate through the membrane, three different polyethersulfone membranes were used. They had different cut-off (mean pore size of 0.01µm and 0.1µm and MWCO of 100kDa respectively) leading to a different permeability (60 to 250l/h.m^2.bar). Applying the same transmembrane pressure through the three membranes, it was thus possible to generate fouling deposits under different convective permeate flow rates. The influence of applied pressure was also evaluated by performing filtrations at different transmembrane pressures (0.5 to 1bar). Filtrations were performed in dead-end mode.

The impacts of these operating conditions on structural properties (thickness, growth
kinetic porosity) of fouling deposits have been studied both in time (along cake thickness) and space (along filtration surface). It has been shown that particle's surface properties have an important impact on both cake growth kinetics and on cake porosity variation. Fouling deposits made of big particles were more porous than the one made of small particles and present a high average porosity variation along the channel length. Using membrane with different initial permeabilities, it was shown that for a given deposited mass, the less permeable the membrane is, the greater the growth kinetics and porosity are. These experimental data are essential results for further validation of different numerical studies that are presented in the literature.

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Membrane and surface modification 2

ICOM1844

Polymeric membranes with tailored barrier and surface properties

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Membrane technologies have been established in a wide range of industrial processes. However, in advanced separation and reaction engineering, membranes applied as separator or contactor can offer yet many more distinct advantages [1]. The majority of synthetic membranes are made from polymers because barrier and surface properties can be variied in wide ranges with help of established scalable manufacturing processes. Significant efforts have been made to further improve membrane performance by focussing on barrier properties (high selectivity, high flux) or surface properties (antifouling, biocompatibility, affinity). Important strategies include the development of novel membrane polymers which can form ordered self-assembled structures, or membrane surface and pore functionalization with controlled functional macromolecular architectures. Membranes with "smart", i.e., stimuli-responsive barrier or surface properties can also be created by such strategies. All these developments had been critically reviewed [2-4].

In this lecture, important recent trends in the field will be discussed and illustrated with examples from own research. One focus will be on ultra- and microfiltration membranes with pH- or temperature-responsive barrier or surface properties. Such membranes can be obtained by phase separation of polymer solutions, either using block copolymer additives to established membrane polymers (e.g. [5]), or by using such block copolymers as membrane material (e.g. [6]). Surface functionalization of membranes from standard polymers is an alternative, and using tailored block copolymers as surface modifiers is again an option which had until now been less explored [7,8]. Thin-film or pore-filling hydrogel composite membranes, with sieving properties which are determined by the added functional hydrogel, are another very promising route (e.g. [9,10]). Finally, some novel approaches toward membrane surfaces with mimimized fouling and biofouling propensity and, hence, reduced need for cleaning will be highlighted (e.g. [11]). Such approaches have relevance for most of the established or novel membrane applications with aqueous feed streams.

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ICOM972

Novel chemical surface modification to enhance hydrophobicity of polyamide-imide (PAI) hollow fiber membranes intended for use in gas-liquid membrane contactor

Yuan Zhang[1,2], Rong Wang[1,2], Shouliang Yi[2], Lauren Setiawan[1,2], Tony Fane[1,2]
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The membrane wetting by the liquid absorbents is a major concern in gas-liquid membrane contactor process. In order to develop a novel hydrophobic membrane that can be used in the hollow fiber gas-liquid membrane contactor, a hydrophobic surface modification method for Torlon® polyamide-imide (PAI) membrane was explored, which has not been reported previously. The asymmetric porous PAI hollow fiber membranes were fabricated via the non-solvent induced phase-inversion process. The reactions between the PAI hollow fiber membranes and the modification agents which include a coupling agent and a fluoro-compound, have been confirmed by experiments.

Effect of the modification time on the resulting membrane structure, contact angle, mechanical strength, surface porosity, liquid entry pressure (LEP_w) and CO_2 absorption performance were investigated. The PAI membrane is less hydrophobic in nature with the contact angle of ~76°. The modified membranes exhibited much higher hydrophobicity and wetting resistance. The newly developed PAI#1 membrane showed contact angle of 110° with the liquid entry pressure of 2.7 bar, while PAI#2 membrane showed contact angle of 117° with the liquid entry pressure of 4.0 bar. The CO_2 absorption test using distilled water as the liquid absorbent was conducted for both PAI#1 and PAI#2 membranes. The PAI#2 membranes showed a lower CO_2 absorption flux than that of PAI#1 because they experienced a longer modification time, which resulted in a denser top layer. Nevertheless, both membranes showed much higher CO_2 absorption flux than that of the commercial polypropylene (PP) and polytetrafluoroethylene (PTFE) hollow fiber membranes. Moreover, the modified membranes presented better tensile strength compared to the original PAI membranes. This study provides a simple and effective hydrophobic modification method to make highly hydrophobic PAI membranes. The results indicate that the modified PAI membranes have great potential to be used in membrane contactor applications.

ICOM1695

Development of a surface mimetic for aromatic polyamide reverse osmosis membranes and its potential use in studies of membrane fouling

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A major problem in reverse osmosis (RO) technology is membrane fouling, which is the accumulation and adherence of colloidal organic matter, inorganic salts (scaling), or bacteria that form biofilms (biofouling). Understanding engineering and physicochemical aspects of fouling is important for mitigating this obstacle. One promising strategy for studying molecular mechanisms of fouling is based on foulant adsorption experiments to surfaces with well-defined and homogeneous chemistry. In this paper we describe the design and synthesis of a stable oligoamide layer on gold coated wafers, that mimics the surface chemistry of RO aromatic polyamide films and that can be tested in fouling and adsorption studies using a wide range of physical methods.

The synthesis of the oligoamide film[1] was performed by self-assembly of cysteamine on gold surface primarily, followed by alternately coupling 1,3,5-benzenetricarbonyl trichloride (TMC) or *meta*-phenylenediamine (mPD). Repeated successive TMC and mPD couplings produced thick oligoamide films, with chemical structures depicted in Fig. 1.

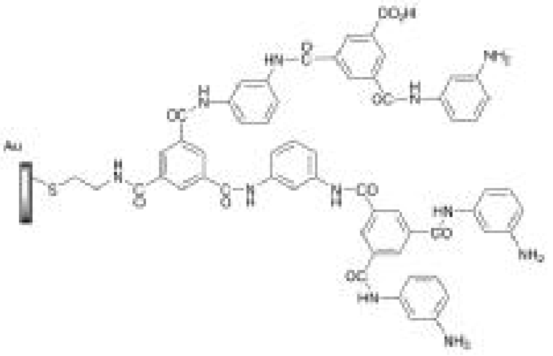
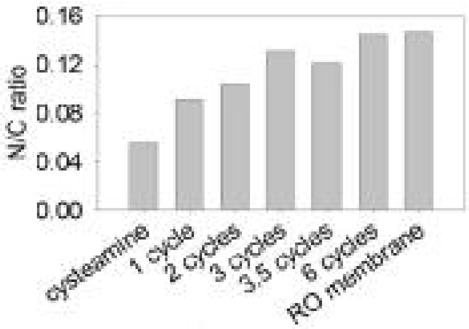


Figure 1: *Chemical structure of two-reaction cycles oligoamide film prepared in this study on gold-coated silicon wafers.*

The chemical composition of the oligoamide layers on gold was measured by X-ray photoelectron spectroscopy (XPS) and compared to a commercial RO membrane. The N/C weight ratio increased almost linearly with the number of complete reaction cycles (Fig. 2). N/C ratio for the 6-cycles product was almost identical to that of a commercial RO membrane[2], of 0.145 and 0.149, respectively (Fig. 2).



<u>Figure 2</u>: *Nitrogen to carbon weight ratio as measured by XPS surface analysis of oligoamide films on gold, in comparison to aromatic polyamide RO membrane.*

The resultant surface chemical composition, wettability, and chemical nature of the oligoamide films prepared in this study, were comparable to aromatic polyamide films of RO membranes. Hence, the oligoamide-coated wafers may be used in adsorption/fouling studies as a surface mimetic of RO membranes, and will therefore facilitate understanding of fouling processes in membrane-based water treatment systems with the goal of developing better antifouling strategies.

(1) Z. Steiner, J. Miao and R. Kasher (2011). *Chemical Communications*, in press; available online at: http://dx.doi.org/10.1039/c0cc04379f.

(2) Flat-sheet brackish water RO LE membranes were kindly provided by FILMTEC Membranes, Dow Water Solutions.

ICOM569

High performance nano-structured NF/RO membranes – synthesis, surface characterization and performance

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Effective use of RO/NF membranes in brackish desalination and water reuse applications requires adequate suppression of membrane fouling and mineral scaling. Traditional strategies for producing membranes of low fouling propensity have relied on alteration of membrane surface chemistry and topography by addition of a permselective polymer thin film, coated or graft polymerized, that could act as both a separation layer and a physical boundary to reduce adsorption of foulants. In the present study, the recently developed atmospheric pressure plasma-induced graft polymerization (APPIGP) method was utilized to generate a high surface density of active surface sites on a polyamide membrane for subsequent graft polymerization using suitable water soluble vinyl monomers. Surface structuring via graft polymerization was then employed to form a brush layer of polymeric chains that are terminally and covalently attached to the polyamide surface of an optimized (with respect to flux and salt rejection) of a thin-film composite (TFC) polyamide (PA) membrane. The chemical and physical features of the resulting surface nano-structured (SNS) TFC-PA membrane was tuned by the selected vinyl monomer chemistry, as well as the reaction conditions, to achieve the desired surface architecture to reduce fouling and scaling, while achieving the target membrane performance with respect to flux and rejection. The presence of the grafted polymeric brush layer was confirmed by XPS and Fourier Transform Infrared (FTIR) Spectroscopy. Graft polymerization kinetics were determined, for a number of different candidate water soluble monomers, with respect to the evolving grafted polymer layer thickness with reaction time and initial monomer concentration. The change in surface energy (a measure of the degree of surface hydrophilicity/hydrophobicity) was quantified via contact angle measurements and surface charge was determined by analysis of streaming potential measurements in a specialized RO cell. Performance evaluation of the SNS-TFC-PA RO/NF membranes was carried out by examining their mineral salt scaling and biofouling propensities. Membranes effectiveness in retarding organic- and bio-fouling was assessed via flux decline studies with model proteins and polysaccharides solutions and utilizing secondary treated municipal waste water effluent. Reduction in membrane mineral scaling propensity was quantified from both flux decline studies (using salt solutions supersaturated with respect to the target mineral salt scalant) and via direct observations of the evolution of mineral scaling on the membrane surface in an optically transparent high pressure RO cell. The results of the present study demonstrated that it is feasible to tailor-synthesize SNS-TFC-PA membranes of high permeability (by up to a factor of ~2 compared to commercial membranes of the same level of salt rejection) with the added benefit of reduced mineral scaling propensity and increased fouling resistant.

ICOM1666

Surface modification of commercial thin film composite membrane support layers for engineered osmosis applications

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The shortage of energy and water resources is a grand challenge facing humanity during this century. Engineered osmosis (EO) technologies have been increasingly investigated as alternative means of sustainable water and energy production. These membrane technologies exploit the gradient of osmotic pressure between a dilute feed solution and a concentrated draw solution as a driving force for water treatment (forward osmosis, FO) and electricity generation (pressure retarded osmosis, PRO). However, EO development has been hindered by the lack of well-designed membrane that exhibits high water flux, superior selectivity, chemical stability, and adequate mechanical strength.

Thin film composite (TFC) membranes comprised of an ultrathin dense selective layer formed over porous support membranes have been broadly used in reverse osmosis. However, the thick support layers of traditional TFC-RO membranes are for EO because they hinder salt diffusion internally, which is referred to as internal concentration polarization. In order to mitigate this problem, composite membranes are needed with thinner and highly porous support layers. The support layer also needs to be more hydrophilic than traditional TFC-RO membranes, while retaining appropriate physical, chemical, and thermal stability. In this study, the support layers of two commercially available thin film composite reverse osmosis membranes were modified to enhance their hydrophilicity. The membrane support layers were coated with polydopamine, a novel bioinspired hydrophilic polymer. This resulted in increased hydrophilicity and a corresponding increase in 'wetted porosity' and reduced internal concentration polarization. The modified membranes were then characterized for contact angle, salt rejection, hydraulic permeance, salt flux, and osmotic flux. The results were promising, indicating that the modified reverse osmosis membranes exhibited an **eight to twelve fold increase in flux** performance under test conditions when compared to an unmodified membrane. This modification method, which is scaleable, has the potential to enable the use of existing thin film composite membranes for engineered osmosis.

ICOM896

Modification of PVDF porous membrane by blending amphiphilic block copolymer P(MMA-b-MAA)

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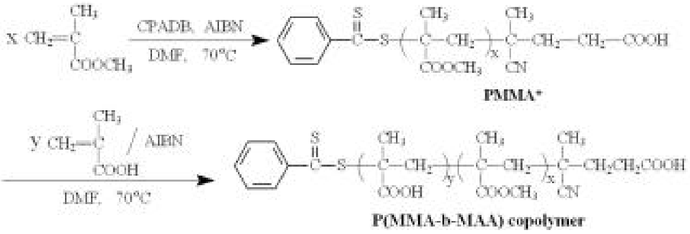
PVDF membrane is a kind of important filtration material in water treatment. Endowing the membrane with hydrophilicity, antifouling and high flux is necessary to realize its high performance. Among the several routes, blending hydrophilic components into membrane is an efficient method with lower production cost and simpler manufacture process. PEG and PVP have been widely adopted as hydrophilic component. However, these polymers can be leached out during membrane preparation and filtration process due to their good solubility in water. In mechanism, the amphiphilic polymer with proper structure and composition should be better stabilized in membrane and yield better reliability of membrane performance. In this work, a new type amphiphilic block copolymer of poly(methyl methacylate-block-methacrylic acid (P(MMA-b-MAA)) was proposed as blending candidate for PVDF membrane. The modification effects on membrane performance were discussed basing on corresponding measurements.



Characterization data of synthesized copolymers

Copolymer	M_n	M_w	M_w / M_n	MAA content (wt%)
Copolymer a	107700	133300	1.23	15.2
Copolymer b	141000	179500	1.27	20.2
Copolymer c	166300	247900	1.49	49.2

Figure 1 Synthesis and characteristic of amphiphilic P(MMA-b-MAA) copolymers

P(MMA-b-MAA) copolymers were successfully synthesized following a reversible addition fragmentation chain transfer (RAFT) polymerization route. By changing MMA/MAA monomer ratio, three copolymers with different content of MAA block were obtained (Figure 1). The flat PVDF/P(MMA-b-MAA) blend membranes were prepared via a typical formed via non-solvent induced phase inversion(NIPS) process method using PVDF/P(MMA-b-MAA)/DMF (14.2/2.5/83.3 weight by) mixtures as cast solutions and water as non-solvent. After being leached in water for 48h at 25°C and dried at 60°C in vacuum, the membranes were used for characterization. Membrane ID Ma, Mb and Mc presents that the used P(MMA-b-MAA) is copolymer a, b and c respectively.

Three prepared membranes had comparable structure (thickness: 100±10mm, porosity: 70±5%, BSA rejection: 90±2%). The ratio of copolymer content in surface layer to that in whole membrane for the three sample was 2.09, 2.02 and 1.88 respectively, which suggests the obvious enrichment of P(MMA-b-MAA) in surface layer. Such enrichment was attributed to a surface segregation effect during membrane formation process, in which the amphiphilic copolymer migrated to surface under the strong interaction between water and MAA block. This surface enrichment substantially refers efficiency of copolymer in improving hydrophilicity (Figure 2a). The water contact angle for blend membranes (70-75°) was much lower than that of pure PVDF membrane (110±5°). To investigate the retaining stability of P(MMA-b-MAA), the membranes was immersed in water (60°) and shaken continuously. The contact angle changes little with shaking time revealed that P(MMA-b-MAA) could be stably retained in membrane. Such stability of P(MMA-b-MAA) potentially ensured the reliability of blend membrane in real water filtration application.

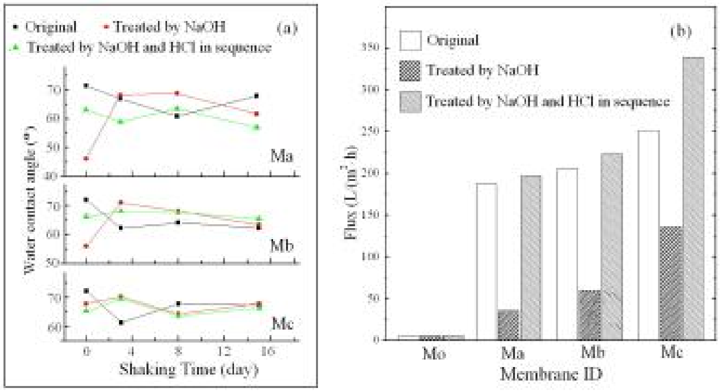


Figure2. Water contact angle (a) and flux (b) changes of PVDF/P(MMA-b-MAA) membranes

The flux of blend membrane was much higher than pure PVDF membrane and increased with MAA content in P(MMA-b-MAA). Interestingly, the flux decreased greatly after being immersed in aqueous NaOH solution (3wt%, 25 °C, 48h). Once being further treated in aqueous HCl solution, the flux increased to a value higher original membrane (Figure 2b). Comprehensively, the reason of this performance should be generated from the fact that hydration effect of –COONa is higher than –COOH. The out-stretching state of more hydrated block chain containing –COONa yielded the pore-size-reduction function.

ICOM1598

High Throughput Discovery of New Fouling-Resistant Surfaces

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Rational design of low fouling membrane surfaces for specific applications remains elusive. Here, we offer a new approach to rapidly, efficiently, and reproducibly develop and select optimal polymeric surfaces for particular applications, offering the potential
to gain understanding for future design of surfaces. The new method adapts a high throughput platform (HTP) the facile modification of poly(ether sulfone) (PES). We combine HTP with our patented photo-induced graft polymerization (PGP) method using 66 commercially available vinyl monomers to produce new polymeric synthetic membrane surfaces. We have employed the HTP-PGP approach to confirm previously reported successful monomers and to develop new anti-fouling surfaces for different challenges of interest to the biotechnology and water treatment communities. These include bovine serum albumin (BSA) and hen egg-white lysozyme as model proteins, supernatant from Chinese Hamster Ovary (CHO) cells in phosphate buffered saline (PBS) solution as a model cell suspension, immunoglobulin G (IgG) precipitated in the absence and presence of bovine serum albumin (BSA) in high salt solution as a model precipitation process, and humic acid as a model natural water foulant. We have tested these newly
modified PES membrane surfaces in a 96-filter well format in quadruplicate using either 1) ultrafiltration of feed solution, or, 2) ultrafiltration of deionized (DI) water or phosphate buffered saline (PBS) after solute adhesion as challenges. This paper presents the *method* and the *new chemistry findings* – surfaces having optimal surface chemistry. We demonstrate that the HTP-PGP approach to synthesize and screen fouling-resistant surfaces is general, and thus provides the capability to develop surfaces optimized for specific feeds. For selected feeds we have also evaluate the scalability of the HT format using bench scale experiments to evaluate fouling kinetics. Fouling kinetics have been modeled and the correspondence between fouling at different scales will be discussed in the context of fouling mechanisms.

Reference: Zhou, M.Y.; Liu, H.W.; Venkiteshwaran, A.; Kilduff, J.E.; Langer, R.; Anderson, D.G.; Belfort, G. High Throughput Discovery of New Fouling-Resistant Surfaces. *Journal of Materials Chemistry*, 21, 693-704 (2011).

Parallel Sessions

Tuesday, July 26th 2011

Afternoon Session 1, 13.30 – 15.20

Gas and vapor separation 3

ICOM1795

The role of free volume in membranes for gas and vapour separations

Anita J. Hill, Aaron W. Thornton
CSIRO Materials Science and Engineering, AU

Membranes are becoming the technology of choice for gas and vapour separations because they are cost-effective, have a small footprint, and are simple to operate and maintain. The economics of a separation membrane process are largely determined by the membrane transport properties of permeability and selectivity for a specific component in a mixture. Ideally, membranes should exhibit high selectivity (product purity) and high permeability (productivity). For most membranes, however, as selectivity increases, permeability decreases, and vice versa, creating a performance tradeoff.

This paper examines the role of free volume in the tradeoff between high permeability and high permeability selectivity of membranes. Diffusivity and permeability, and therefore permeability selectivity can be predicted using a free volume model. Free volume in membrane materials can be examined using positron annihilation lifetime spectroscopy (PALS), and the results compare extremely well with experiment and theory. Membranes with tailored free volume architectures are shown to be able to overcome the performance tradeoff. Theory and experiment will be compared for polymers and other hybrid and inorganic membrane materials, and avenues for further research exploration will be suggested.

ICOM1589

High flux SAPO-34 membranes for CO_2/CH_4 separation at high pressure

Begum Tokay, Yanfeng Zhang, Ryan Smith, Hans Funke, Richard Noble, John Falconer
University of Colorado, Department of Chemical and Biological Engineering, Boulder, CO, US

The efficient removal of carbon dioxide from methane at high pressures is an important step in natural gas processing since CO_2 is corrosive in pipelines and decreases the heating value of the natural gas. Polymer membranes with high fluxes are available but their selectivity decreases at the high pressures required for pipeline feeds due to swelling, and they are often susceptible to various degradation mechanisms due to impurities in the feed. In contrast, SAPO-34 membranes, which consist of crystals of the SAPO-34 molecular sieve, can remove carbon dioxide with high fluxes and high selectivities at pressures as high as 7 MPa. The membranes were grown by seeded hydrothermal synthesis as thin, continuous layers (3-5 μm thick) on porous tubular ceramic supports. For a 50:50 CO_2/CH_4 feed at a pressure of 4.6 MPa, CO_2 fluxes were as high as 370 kg/m^2/h (>10^{-6} mol/(m^{2}sPa)) with CO_2/CH_4 selectivities greater than 80. Their performance was stable after storage for extended time periods. The fluxes and selectivities are significantly above the boundary of the Robeson plot (Fig.1), indicating their potential for commercial application. At lower pressures, the permeances were higher than 4x10^{-7} mol/(m^{2}sPa) with selectivities above 200.

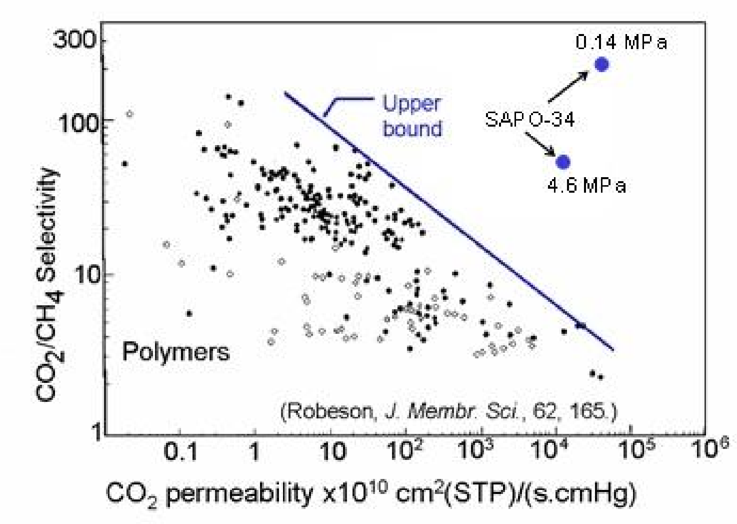


Figure 1: Robeson plot shows SAPO-34 membranes perform better than polymer membranes

The high fluxes were obtained by using two templates and small seed crystals. Membrane fluxes doubled when the structure-directing templates were removed in an inert gas or in vacuum. This is in contrast to template removal in air, which has been used for essentially all other zeolite membranes. Temperature-programmed desorption and oxidation showed that the templates were removed at lower temperatures in an inert gas, apparently because partial oxidation products formed in air that were more stable than the original templates. The membranes did not have many defects larger than a few nanometers, as determined by permporometry. A small number of small defects may not have much effect on separations at low pressures, but they can significantly decrease selectivities at high pressures. The SAPO-34 membranes were scaled up from 5-cm to 25-cm lengths without significant loss in performance.

ICOM818

Microscopic Free Volume Theory for Molecular Diffusivity Prediction in Polymeric Membrane Systems: Application and Further Extension

Hidenori Ohashi, Takanori Tamaki, Takeo Yamaguchi
Tokyo Institute of Technology, Chemical Resources Laboratory, Yokohama, Kanagawa, JP

Molecular diffusivity in polymer matrices is an important dynamic physical property for membrane transport. The establishment of predictive methodology of the dynamic property should greatly enhance gas and vapor permeation design of polymeric membrane. In response to the requirement, recently we have developed diffusivity prediction model in polymeric systems. Microscopically, molecular self-diffusive motion originates in the common microscopic mechanism of molecular collisions with adjacent molecules. Microscopic molecular collisions results in free space around a penetrant (diffusing molecule), and the space is used for molecular diffusive motion. Thus, free space around a penetrant molecule can be regarded as the representative of microscopic molecular collisions, and is defined as shell-like free volume in this study. By introducing the microscopic notion into the existing free volume theory, a novel prediction model that can estimate molecular diffusivity in polymeric systems using only pure component parameters have been developed for the first time.

The newly proposed model requires pure component parameters of free volume, molecular surface area, and molecular core volume for diffusivity prediction. We derived the free volume parameter using viscoelastic properties of polymer and solvent, molecular surface area using quantum chemical calculation, and molecular core volume using group contribution method that can estimate molecular volume at 0K, respectively.

In our presentation, we will show that the combination of the model and the single component parameters used succeeds in self-diffusivity prediction in various polymeric systems: from binary and multicomponent systems, wide temperature and composition range, to various shapes of penetrant molecule. In general, the diffusivity prediction is satisfactory quantitative, and it means the model will be applied to design of polymeric devices including membrane permeation. Furthermore, we will introduce the influence of strong interaction between penetrant and polymer on penetrant diffusivity, by introducing a new microscopic notion.

ICOM343

Hydrogen separation using membranes based on natural zeolites

Hrishikesh Keshavan[1], Anthony Ku[1], Steven Kuznicki[2], Weizhu An[2], Paul Swenson[2], Lan Wu[2], Terri Waller[2]
[1]GE Global Research, Ceramics and Metallurgy, Niskayuna, New York, US, [2]University of Alberta, Department of Chemical and Materials Engineering, Edmonton, Alberta, CA

Zeolite membranes for gas separation have been studied for decades, but are not sufficiently robust for widespread practical application. We examine an unusual natural clinoptilolite material which has been compacted over time into crystalline blocks containing essentially no macroporosity. When sectioned, this material behaves as a solid, continuous molecular sieve membrane. Untreated membranes sliced from this dense material were found to have as much as two times higher ideal selectivity for H_2 over CO_2 than would be predicted by Knudsen diffusion. We will present the effect on H_2 selectivity and permeance at elevated temperatures and pressures. These unique natural zeolite membranes have the potential to be engineered for high-temperature, energy-efficient industrial separation and purification applications including hydrogen separation, and to serve as a model for the development of robust synthetic zeolite membranes with superior separation characteristics. We will also discuss the prospects for scalable manufacturing of synthetic membranes based on these materials.

ICOM120

Selective nano-fibrous membranes for water vapour transport applications

Ryan Huizing[1,2], Walter Mérida[3], Frank Ko[4]
[1]University of British Columbia, Materials Engineering, Vancouver, BC, CA, [2]DPoint Technologies, Vancouver, BC, CA, [3]University of British Columbia, Clean Energy Research Centre, Vancouver, BC, CA, [4]University of British Columbia, Advanced Materials and Process Engineering Labratory, Vancouver, BC, CA

Membranes with high water vapour permeation have several applications, including protective clothing, dehydration, and humidification. One interesting application is energy recovery ventilation for buildings. Energy recovery ventilators (ERVs) improve building energy efficiency by transporting heat and water vapour between incoming and outgoing air streams in buildings, effectively 'recycling' the energy utilized to condition building air. Membranes for these devices must have high vapour permeation rates, and be selective for water vapour over other gases and contaminants that may be present in the outgoing indoor air.

Current high performance membrane materials for ERV devices are based on coated microporous membranes. Improved water vapour permeation performance in these materials is desirable, both to improve latent recovery efficiency of ERVs and to decrease their size and cost. Our analysis of commercially available materials indicates that currently used microporous substrate materials contribute significant resistance to vapour transport in the membrane (greater than 50%). Higher porosity substrates with similar pore sizes to current materials would be desirable.

Recent studies have identified nano-fibrous materials as promising membrane substrates since they offer very high porosity (>80%) with essentially no dead-ended pores, and their pore size can be controlled to facilitate application of a coating layer. By coating these nano-fibrous substrates with a dense water vapour permeable polymer layer, selective nanofibre membranes can be created with improved water vapour permeability over current materials.

In this study, nano-fibrous substrates of varying density were fabricated from polyacrylonitrile using electro-spinning techniques; these fibers were deposited onto polyester non-woven supports. These substrates were then coated with cross-linked polyether-polyurethane copolymers. These polymers are known to have hard and soft segments in which the hard urethane segments provide mechanical strength and can be cross-linked, and the soft PEO segments allow high moisture transport rates and sufficient selectivity. The nano-fibrous membranes created demonstrate a new type of membrane for selective water vapour transport.

These materials were analyzed by SEM to measure fiber diameter, pore size, and surface porosity, and to determine coating effectiveness and thickness in the membrane samples. The coating lay-down was found to be directly related to both the polymer concentration in the coating solution and the nanofibre substrate areal density. The water vapour and oxygen permeation rates of the materials were measured using a custom counter-flow permeation apparatus. This apparatus simulates the operating conditions and geometry of actual devices and overcomes some of the well-known issues associated with measuring water vapour transport in highly permeable materials.

These nano-fibrous materials demonstrate improved water vapour permeation rates over current commercial materials with comparable selectively of water vapour over oxygen. Our ongoing research seeks to optimize the nano-fibrous and dense coating layering process to better improve permeation performance of these materials.

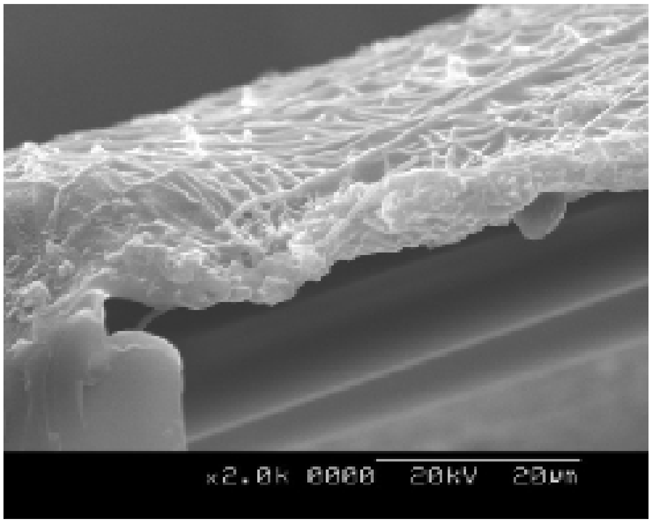


Figure 1: SEM image of coated nano-fibrous membrane cross-section.

CO2 capture 2

ICOM1786

A critical overview of membranes processes in a post-combustion carbon dioxide capture framework

FAVRE Eric
Nancy-Université, LRGP-CNRS, ENSIC, FR

Membrane processes have been initially seldom considered within a post-combustion carbon dioxide capture framework. Arguments such as a too high energy requirement, the impossibility to develop highly selective materials, too expensive capital costs characteristics (i.e. no economy of scale due to a scale up strategy based on numbering up) have been alternatively proposed in order to justify their inadequacy. Consequently, more traditional processes, particularly gas-liquid absorption in chemical solvents, are often considered as the most appropriate solution for the first generation of technologies. This presentation intends to re-examine the situation based on an overview of the different strategies which have been proposed up to now in order to use membrane processes for post-combustion carbon capture. Scientific and technological challenges will be addressed, with a particular emphasis on the industrial context and the associated constraints.

The state of the art of gas separation membranes for CO_2 capture, based on polymeric or inorganic materials, will first be exposed. The major targets of the capture process in terms of selectivity, energy requirement and productivity will be detailed and compared to the most recently reported membrane performances (selectivity / permeance). At this stage, two basic strategies can be identified in order to achieve the targets:

- A single stage approach, which most often requires a high CO_2/N_2 selectivity material (typically 100 or more),

- A multistage approach based on membrane materials which show a moderate CO_2/N_2 selectivity (classically 50 to 70)

The different possibilities based on these two major approaches, and the key process options (feed compression or vacuum) will be presented and discussed.

In the second part, the possibilities and limitations of alternative approaches, more specifically hybrid processes based on a combination of a membrane step with another unit operation, will be critically analyzed. Important remaining challenges of membrane processes for carbon capture, such as the sensitivity to particles or the fate of "minor" flue gas components (oxygen, water, NOx, SOx ..) will also be listed.

Finally, tentative guidelines on the best place and role of the “membrane separation box” within a post-combustion carbon capture framework will be proposed.

ICOM649

Hybrid absorber-membrane CO_2 capture

Martijn Huibers[1], Paul Raats[1], Nick ten Asbroek[2], Koen Broess[1]
[1]KEMA, New Energy Technologies, Arnhem, NL, [2]Procédé, Enschede, NL

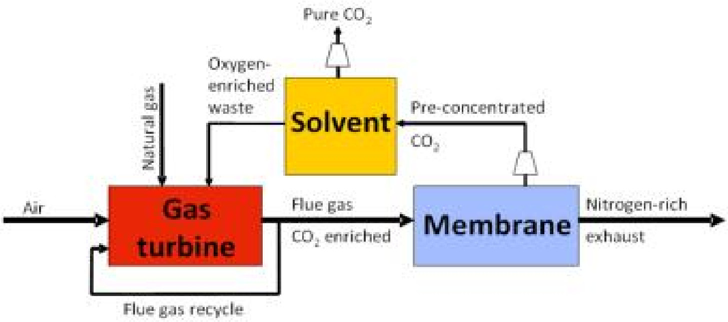
While R&D in post-combustion CO_2 capture from coal-fired power plants delivers ever improving low energy solvents and process enhancements, current research into post-combustion capture from gas-fired power plants is however not so forthcoming. Still, gas-fired power generation is a major source of CO_2: 23% of total emissions in 2006 of the EU-27.[i] The impact and need for a gas-fired CCS solution is clear.

In this paper, an original (patent pending) solution for post-combustion CO_2 capture from gas-fired CO_2 sources is presented. In the scheme displayed below its three key elements are highlighted:

· Recycling: looping back a fraction of the flue gas to the gas turbine to roughly double the CO_2-concentration;

· Membrane preconcentration: applying CO_2-selective membranes sequentially N2 leading to a CO_2-concentration of e.g. 50%;

· Absorber final capture: compressing this carbon dioxide rich flow and feed to a pressurized absorber where the CO_2 will be absorbed using a low energy consuming sorbent.



The three elements together offer an exciting new approach very suitable for their application. The low CO_2 concentration in the flue gas is raised by recycling, to such a point that membranes further concentration becomes feasible. Low contaminant content (e.g. SO_2 and particles) presents an excellent relatively mild environment for CO_2-selective membranes to operate in, which are elsewhere (e.g. coal-fired power plant flue gas) often troubled by durability issues. The absorber section, fed here with a preconcentrated CO_2 stream, is scaled down and less energy intensive.

This paper describes the first R&D towards concretizing the novel concept. Identification and analysis of interfacial parameters led to preliminary designs. Operating conditions were established as much as possible. Based on this, crude solvent selection has started. Membrane performance and operation optimisation tests have yielded base values for modeling, which in turn focused on characterising the tradeoff between the various system parameters: purity and recovery of the membrane step, and the same for the absorber section. Gas turbine analysis provided insight in how (not) to operate and alter the gas turbine in the proposed system design. The main open issues are water vapour management and the detailed manner of compression and vacuum application. Also, experimental verification and fine-tuning has current focus.

[i] Source: Eurostat

ICOM353

Membrane-cryogenic hybrid processes for CO_2 capture from power plants

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A variety of separation technologies are under investigation for post combustion CO_2 capture from coal fired power plants. Each potential technology features specific advantages and drawbacks. Membrane processes appear particularly suitable for efficient CO_2 bulk removal and initial CO_2 enrichment. In contrast, conventional separation technologies such as chemical and physical absorption, physical adsorption or cryogenic processing seem more attractive for the purification of CO_2 enriched streams. Hybrid processes have the potential of combining the advantages of its component processes by reducing their individual shortcomings. Different unit operations may work together in a synergetic manner and accomplish higher efficiencies and better separation results than the respective stand alone unit operations.
Unlike in natural gas processing, membrane hybrid configurations have not received much attention for post combustion CO_2 capture yet. It is the objective of this contribution to close this gap. Subsequent to a brief discussion of potential hybrid configurations, the most promising process – membranes in conjunction with cryogenic fractioning – will be examined in detail. The authors discuss the conceptual design of the hybrid process and the interactions among the component processes. Extensive parameter studies performed with ASPEN PLUS yield the CO_2 recovery, the energy requirements and the CO_2 composition for a wide range of operation parameters. To derive the potential of membrane cryogenic hybrid systems for post combustion CO_2 capture, the results will be compared to competing CO_2 capture technologies such as amine absorption. Besides technical aspects, also process economics are taken into account.

ICOM295

Membrane Contactors for Carbon Dioxide Capture from pre-combustion and post-combustion flue gases

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There is a continuing need to develop new carbon dioxide separation technologies, which have the potential to be applied to a wide range of carbon intense industries. Membrane gas-solvent contactors are a hybrid technology that utilize solvent absorption to make the process highly CO_2 selective, while utilizing the well defined membrane area to provide interfacial contact between gas and solvent. This hybrid approach takes advantage of both solvent and membrane technologies, and has shown potential for carbon capture.

Here, the performance of porous polypropylene and polytetrafluoroethylene based contactors for carbon dioxide separation is presented for a number of CO_2 selective solvents, specifically, 30 wt% Monoethanolamine, 30 wt% Potassium Carbonate and a commercial solvent PuraTreat (BASF). Furthermore, the performance of silicone contactors is also reported, where the high permeability of CO_2 through the non-porous membrane is utilized for separation. The lack of pores in the silicone configuration prevents pore wetting and loss in performance, an issue for porous membrane contactors. The overall mass transfer coefficient, as well as solvent loading, as a function of solvent flowrate and Reynolds number is reported for these combinations of membrane material and solvent based on laboratory performance. In addition, the performance of the porous membrane contactors in two pilot
plant trials of separation of CO_2 from syngas (pre-combustion capture) and flue gas (post-combustion capture) are reported, as part of the CO2CRC Mulgrave and H3 projects and compared to existing CO_2 capture technologies.

ICOM554

Membrane operations for CO_2 separation in post combustion capture: a comparison with conventional technologies

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To provide people interested in the use of membranes in CO_2 separation a useful strategy to follow with respect to the other separation ones, some important design parameter are proposed, based on specific considerations related to the output to be obtained as the product purity and the final destination of the product and to the feed conditions. The main technologies for CO_2 separation in post-combustion capture are adsorption, absorption, cryogenic and membranes. Each of these technologies is based on different separation principles and, as a consequence, the project characteristics differ significantly [1]. The membrane systems show very high flexibility and instantaneous response to the variation. Moreover, due to their easy modularity it is not necessary to foresee the possible expansion during the design phase. They are highly capable of maintaining product purity even though the capacity is reduced down to 10% of the initial design; they are extremely reliable with respect to the on-stream factor and show very low control requirements. Nevertheless, the composition of the feed and the product target are best considered together when selecting a CO_2 separation process because the three processes have economies of scale drastically different and these parameters strongly influence the performance, reliability and pre-treatment required by the three upgrading processes (Table 1).

	Absorption	Adsorption	Cryogenic	Membrane System
CO_2 in the feed, (% molar)	>5	>10	>5	>15
CO_2 purity, %	>95	75-90	99.99	80-95(*)
CO_2 recovery, %	80-95	80-95	99.99	60- 80(*)
Energy requirement, MJ/kg_{CO2}	4-6 [2]	5-8 [1]	6-10 [3]	0.5-6 [4]

(*)Considering a CO_2/N_2 selectivity of 50 in one stage process

Even if membrane operations are more suitable for CO_2 from streams containing more than 15-20% of CO_2, however, pursuing a retrofit strategy, it is very interesting to analyse the application of membrane gas separation in the treatment of the flue gas coming out from a power plant (CO_2 concentration is around 15%). In this work, some general maps of CO_2 purity versus CO_2 recovery, useful for analysing different design solutions in post combustion capture in terms of membrane area and compression/vacuum load ratio to be installed and comparison of different systems for having the same performances, have been proposed. Different membrane selectivities ranging from 30/50 (commercial membranes) up to 150 and 300 and different feed pressure ratios were considered. The results showed that, with currently available membranes it is not possible to get, simultaneously, high CO_2 recovery and purity (80% CO_2 in permeate stream). In order to fit this target, a fundamental role is played by the operating pressure ratio more than selectivity. In fact, with a selectivity of 100 (value showed by some lab-developed membranes), shifting the pressure ratio from 10 to 20 or 50, the CO_2 recovery passes from 22% to more than 60% or 80%, respectively.

Acknowledgements

The EU-FP6 project NANOGLOWA – Nanostructured membranes against global warming - is gratefully acknowledged for co-funding this work.

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Electromembrane processes 1

ICOM1836

Electrochemical characterization of ion-exchange membranes: theory and experiment

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Recently, the interest to ion-exchange membranes and, more generally, to nanoporous charged membranes is strongly increased due to their actual and especially perspective applications in green chemistry, clean energy and medicine. The understanding of membrane behaviour in electrochemical cells is one of the most important tasks aimed at harnessing membrane applications.

The main electrochemical methods used in membrane electrochemical characterization are voltammetry, chronopotentiometry and electrochemical impedance spectroscopy. The basic theory of all three methods is based on the Nernst-Planck equations applied to the ion transport in the membrane and two adjoining diffusion boundary layers (DBL).

In the case where the electroneutrality assumption is applied, the integration between two points relating to the positions of the capillary tips of pd measuring electrodes yields:

$$U_{tot} = -\frac{RT}{F}\left[(2t_1-1)\left(\ln\frac{c_s^I}{c_0}+\ln\frac{c_0}{c_s^{II}}\right)+\ln\frac{c_s^{II}}{c_s^I}\right]-i\left[\frac{RT}{(D_1+D_2)F^2}\left(\int_0^{\delta^I}\frac{dx}{c}+\int_0^{\delta^{II}}\frac{dx}{c}\right)+R_{s+mb}\right] \qquad (1)$$

where *i* is the current density, c_s the electrolyte surface concentration, *d* the DBL thickness, 1 and 2 relate to the counterion and co-ion, I and II, to the left and the right membrane interfaces, respectively, R_{s+mb} is the sum of the ohmic resistance of the membrane and the non-stirred solution layers.

Eq. (1) can be applied to steady-state as well as to transient processes: the matter is what concentration profile *c(x, t)* should be applied for the integration. In the case of voltammetry, only a steady state is considered, the profile is linear. In the case of chronopotentiometry, a non steady-state problem should be solved. There are two ways to calculate the membrane impedance spectre. The first one goes through the chronopotentiometric calculations by setting the current density as a small sinusoidal signal superimposed on DC bias. Another way passes through the use of phasors.

As the theory of all three methods is based on the same equations, the results of measurements are interconnected: when knowing one of the characteristics, it is possible to reproduce some parameters of two other ones. Thus, the differential resistance of the system may be obtained by differentiation of the voltamperogram or as the difference of impedances at zero and sufficiently high frequencies. All three methods allow determination of $d^I(d^{II})$.

It is found that d^I is not only a function of the cell size, its design and the flow rate. d^I depends as well on *i* and the membrane surface properties: its hydrophobicity and morphology (electrical heterogeneity, relief).

Different membranes are studied. The mechanisms of overlimiting transfer (which is mainly electroconvection) are discussed. It is found that in the case of Nafion, in a certain range of current densities the differential resistance of the system becomes negative: an increase in *i* is followed by a decrease in pd. This special behaviour is registered by voltammetry, chronopotentiometry and impedance spectroscopy.

Generalisations of Eq. (1) are considered: the use of Poisson equation instead of the electroneutrality assumption, and the Kedem-Katchalsky equations instead of the Nernst-Planck ones.

Acknowledgments
The study was realized within French-Russian laboratory “Ion-exchange membranes and related processes”. We are grateful to CNRS, France, and to RFBR (grants **09-08-96523 and 09-08-96529**) and RFTP (**contract 02.740.11.0861**), Russia, for financial support.

ICOM962

High Temperature Electrodialysis with Newly Developed Bipolar Membrane

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A bipolar membrane composed of a cation exchange layer and an anion exchange layer has a unique electrochemical property which results in the accelerated dissociation of water, i.e. generation of proton and hydroxyl ion, when electric current is applied to the membrane. This water splitting function of the bipolar membrane can be utilized for the production of an acid and a base from a corresponding salt in combination with conventional monopolar ion exchange membranes. Many applications of the bipolar membrane has been proposed and put to practical use up to date [1,2].

In this study, high temperature electrodialysis with the bipolar membrane was investigated. Applying high temperature to the bipolar membrane electrodialysis system gives some advantages of,

1) Joulean heat generated at the electrodialysis operation can be effectively used as a part of the heat source for an increase in the temperature of solutions. The bipolar membrane electrodialysis is usually operated with much higher current density compared with a conventional electrodialysis, which gives more heat generation.
2) Energy power consumption can be reduced because of a reduction of an electrical resistance of solutions, membranes and so on.
3) For an application in the field of fermentation and food industries, a bacteria growth in the electrodialysis stack is effectively inhibited, results in keeping a stable operation and a good sanitary condition.

A bipolar membrane with high temperature resistance was newly prepared and characterized in comparison with a conventional bipolar membrane NEOSEPTA BP-1E produced by ASTOM Corporation. As a result, the newly developed bipolar membrane shows a stable performance at high temperature up to around 80 C degree. Figure shows the water splitting voltage across the bipolar membrane as a function of temperature. BP-1E bipolar membrane increases in the voltage over 60 C degree. In contrast, the new bipolar membrane shows a stable behavior without any increase in the voltage at high temperature.

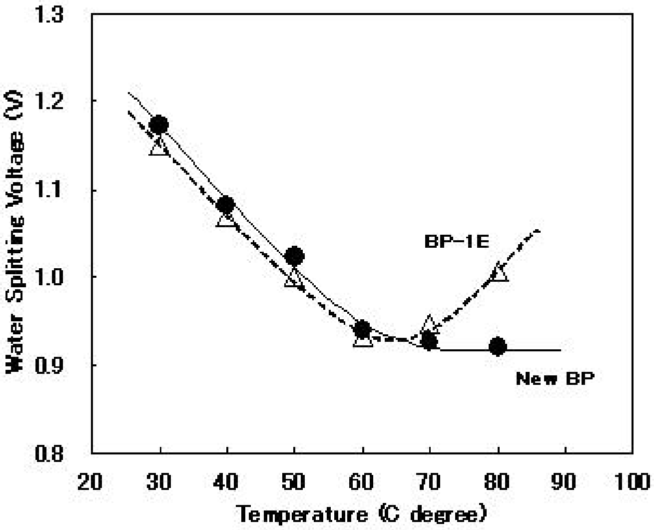

Figure. Effect of Temperature on Water Splitting Voltage
+) 1M-NaOH/BP/1M-HCl (-, 100mA/cm^2, 25 C degree

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ICOM1163

Optimizing water transport in bipolar electrodialysis membranes

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1. Background

The bipolar membrane process produces acids and bases from their corresponding salts by dissociating water at the interface within the bipolar membranes. However, EDBM (bipolar membrane electrodialysis) so far has been applied only in niche markets due to limitations of the current state of membrane and process development. Major drawbacks of the classic EDBM process are low product purity, limited current density and formation of metal hydroxides at or in the bipolar membrane. The low product purity results from ion-leakages through the membranes. Normally, minimizing the ion-leakage will also minimize the water transport through the membrane which decreases the limiting current density, e.g. the maximum productivity of the membrane.

The objective of the research was to overcome these limitations by developing a new bipolar membrane and membrane module with a new water transport concept into the inner layer of the bipolar membranes. This way ion leakage can be minimized and water transport maximized.

2. Results

Several promising membrane configurations have been developed and tested. The microstructured cation exchange membranes were cast on silicon moulds that were prepared from wafers using clean room technology:

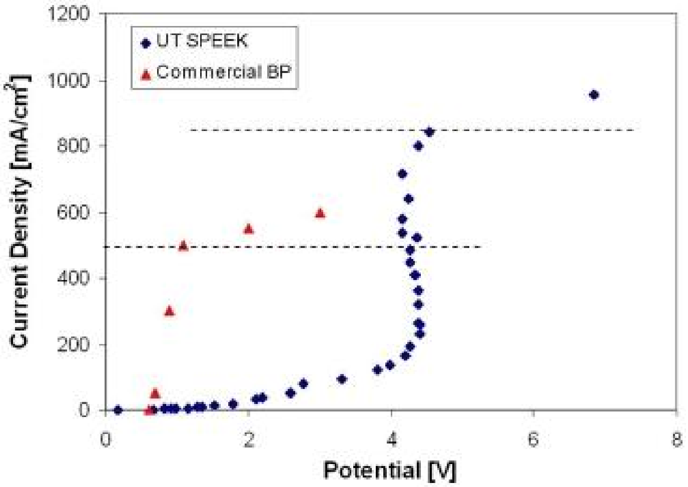

Figure 1A: Silicon mould for the preparation of corrugated electrodialysis membranes. **B:** corrugated sPEEK membrane.

The membranes that were produced were characterized on permselectivity for ions and resistance. With and without corrugations they performed up to the standard specifications for current commercial membranes.

Application of the cation membranes to produce the initial bipolar membranes showed that the water transport has been increased resulting in higher current densities than the state of the art commercial bipolar electrodialysis membranes:

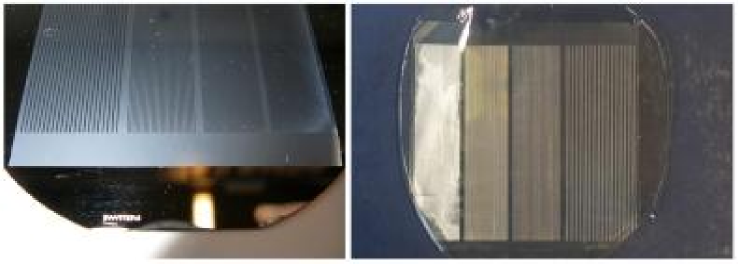

Figure 2: Comparison of the initial bipolar membranes (without catalysts and non-corrugated) with commercial bipolar membranes[1]. The thinner membranes allow for higher water transport resulting in a higher limiting current density.

Currently the project is continued with focus on the characterization of the corrugated membranes, crosslinking of the ion exchange polymers and upscaling to industrial size (50x60 cm) [2]. It is expected that the structured membranes will allow for higher current densities increasing the maximum productivity of a bipolar electrodialysis process. This will decrease the needed membrane area and hence capital costs. Using optimized ion exchange polymers decreases the salt leakage which increases product purity and allows for higher concentrations of the produced acid and base. This will make EDBM an attractive technology to produce acid and base and remediate highly saline waste streams.

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ICOM1180

Transport Mechanisms of Small Organic Ions with Mixed Salts in Electrodialysis

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Electrodialysis can be applied in the food and fermentation industry for separating inorganic salts and organic ions from other fractions. However, the separation efficiency for small organic ions should be understood in detail and the transport mechanisms are still to be investigated and systematically discussed. In this work, membrane selectivity and transport mechanism of small organic ions from mixed salts by ion-exchange membranes are theoretically and experimentally investigated. Furthermore, an experimental and modeling approach to provide a fundamental understanding of separation of organic ions with ED.

The results indicate that, on the one hand, it is observed that ionic size of butyrate can significantly affects the transport competition to the inorganic ions, which means that butyrate ionic size is close to free volume (cavity) size of PC-SA membrane. On the other hand, by comparing the separation efficiency of sulfate/chloride, the results imply that binary organic anions with a larger molar mass (>100, i.e. aspartate and tartarate) can be adsorbed into the membrane surface and the free volume and hence form a charged double layer, which affects membrane selectivity, i.e. permeability of sulfate becomes relatively lower, resulting in an increase of the separation efficiency between sulfate and chloride. Finally, competition between the small organic ions and inorganic ions was discussed using a comparison of concentration profiles and current efficiency of the different anions. Due to the hydrophilic functional groups of tartarate, the migration through the anion exchange membrane is the fastest of all organic anions considered, and the permeability is close to that of the inorganic anions. This indicates that an organic ion with a higher hydrophilicity (as tartarate ion) is easier to pass through the free volume of PC-SA membrane. It is thus more difficult to separate tartarate than any other of the compounds considered, from organic anions by electrodialysis.

	Relative Mobility*	Dominant Factor	CE Trend
Formate	,	Size	Increased up to 30% with peak
Acetate	,,	Size	Increased up to 30% with peak
Propionate	,,	Size	Increased up to 26%, no peak
Butyrate	,,	Size	Increased up to 12%, no peak
Aspartate	,	Size, Functional group	Increased up to 30%, no peak
Tartarate	±	Charge, Functional group	From 22% decreased to zero

* From weak to strong, the relative mobility between organic ion and inorganic ion is represented by ",," (very weak), "," (weak), "±" (equal).

Table 1 summarizes the relative mobility, the current efficiency of the organic ion (which reflects the organic ion and inorganic ions transport competition), and the organic ion characters (size, charge and functional group) that probably affect the separation.

ICOM1575

ENERGY EFFICIENT SEPARATIONS FOR THE PRODUCTION OF BUILDING BLOCKS FOR CHEMICALS FROM CHEAP PROTEIN SOURCES

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The depletion of fossil fuels and the increasing oil prices and emissions of CO_2, urge the chemical industry to find alternative routes for the production of functionalized chemicals. When isolated, amino acids obtained from cheap protein sources (e.g. side streams from the production of biotransportation fuels from rapeseed oil) can be used in a biorefinery to produce chemicals, fuels and power from biomass as they already have the required functionalities, resulting in a cheaper process with less energy consumption and less CO_2 emissions. The aim of the present work is to develop an energy efficient separation method for the isolation of the different amino acids using electrodialysis (ED) (Figure 1). Once separated, the amino acids can be used for further enzymatic conversion into chemicals.

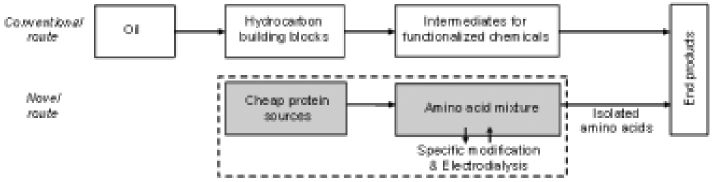

Figure 1. Conventional and novel route for the production of functionalized chemical intermediates.

Electrodialysis (ED) can be used for the selective extraction of ions from solutions but also to separate amino acids (zwitterions) based on differences in their iso-electric points (pI's). Amino acids are positive, neutral or negative depending on the surrounding pH. ED should be able to isolate every single amino acid as long as there is a difference in their corresponding iso-electric points. To enhance the successful fractionation of each amino acid, enzymatic modification thereof to obtain pronounced differences in their pI's is required.

The isolation of L-Glutamic Acid (Glu) and L-Aspartic Acid (Asp) with ED, based on the differences in their iso-electric points, using commercially available ion exchange membranes, is studied. Glu and Asp are negatively charged at neutral pH. This enables their separation from neutral and basic amino acids. Outstanding recoveries for Glu and Asp of around 90% and 83%, respectively, were obtained. However, their further separation with electrodialysis is not possible due to their similar charge behavior. In an enzymatic modification step, Glu can be converted into γ-aminobutyric acid (GABA) with the enzyme glutamic acid α-decarboxylase (GAD) as the catalyst. GABA is not only interesting as intermediate for various chemicals such as N-vinylpyrrolidone, but has no charge at neutral pH, enabling its isolation from Asp with electrodialysis at a pH of 6.0 (Figure 2a). The results of the ED of Asp and GABA at neutral conditions are presented in Figure 2b, showing that with time, negatively charged Asp migrates towards the receiving stream, with a current efficiency of around 70% and a recovery of 90%, while uncharged GABA is completely retained in the feed.

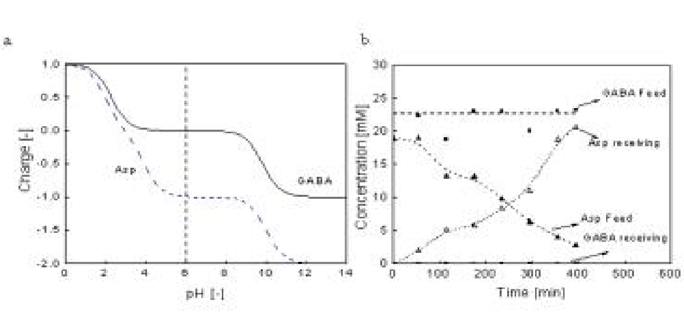

Figure 2. a) Charge behavior with pH of Asp and GABA; b) ED results of the separation of Asp and GABA.

Similar results have been obtained for the ED experiments of the basic amino acids. This opens the route to successful isolation of amino acids using an integrated process of enzymatic conversion and separation with electrodialysis.

Acknowledgements

This work is a close collaboration with Wageningen University (NL), which investigates the specific modification of the amino acids. The Dutch Technology Foundation STW, applied science division NWO and FUMA-Tech GmbH, ECN, CCL and Huntsman are acknowledged for their support.

Mixed matrix membranes 1

ICOM1837

Perspectives on Mixed Matrix Membranes

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Mixed matrix membranes are normally defined as the incorporation of a solid (dispersed) phase into a continuous polymer matrix. The objective is to use the solid phase in a composite structure to provide a means to overcome the upper bound on the Robeson plot for gas separations. The approach is to use existing materials and their processing capabilities while gaining an advantage in performance over each component used separately. Solids can be porous (zeolites, MOFs, etc), solid nanoparticles, and catalysts. Rationale is to obtain a higher selectivity due to the selective nature of the solid phase. It is possible to obtain a higher permeability if the preferred solute has a higher diffusion coefficient in the solid phase than the membrane. With catalyst incorporation, the objective is to get a higher yield and/or selectivity than one would obtain in a bulk phase. This approach was driven by the use of Maxwell's equation for the conductance of a mixed system containing a homogeneous and dispersed phase. This equation theoretically allows one to match the relevant physical and chemical properties of each phase to obtain the needed enhancement.

There are issues that need to be addressed in a manner that provides a significant improvement in membrane processing and resulting gas separation performance. A critical issue is the lack of complete adhesion between the solid and polymer phase. A recent approach to use a nonvolatile liquid such as an ionic liquid show promise but more work is needed to fully demonstrate the viability. But, this is an area where some novel chemistry and materials strategies can make advances since this is the most critical issue needing resolution. Next is the issue of particle size and distribution. Clearly, nanoscale particles would allow for the formation of very thin membrane layers. For a 100 nm film (typical gas separation membrane thickness), the particles would need to be on the order of 10 nm. Preparing particles of this size as a uniform mixture is non-trivial. One factor that is not often discussed is the fact that the shape and morphology of a particle can change significantly as the size is reduced to these levels. The result could be a change in properties that impacts the membrane performance. Also, general strategies to match the various phases for a given application are needed. One application area that has not been addressed in many studies is reactive separations. The ability to incorporate a solid phase that can provide catalytic as well as separative capabilities has significant potential that needs further study. This is actually an application where a larger particle and membrane thickness could be tolerated since it is the balance of reaction and diffusion times (Damkohler number) that will influence performance. Finally, but also very important, is the processing ability and economic cost. There are many polymers shown on a Robeson plot for a given separation but the number that are economically processed as membranes is much smaller. The same issue is true for mixed matrix membranes.

ICOM1253

Floatcasting of composite membranes - let' make a non-brittle and selective membrane from a brittle and a non selective compound

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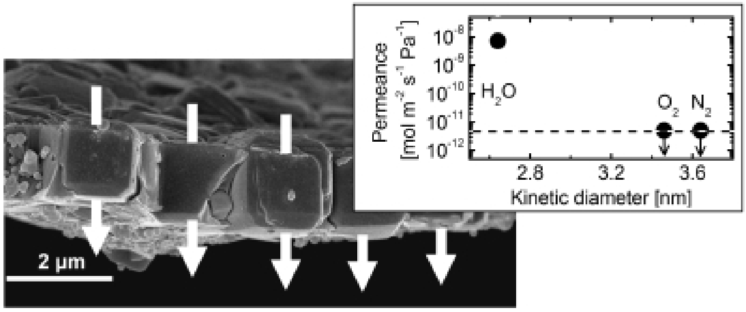
We prepared composite membranes composed of zeolite 4A particles forming a dense monolayer which is embedded in a polymer sheet in such a way that each particle penetrates both, the top and the bottom surface of the sheet.
Preparation was done via 'particle assisted wetting': A mixture of hydrophobized zeolite 4A particles and an appropriate volume of a non-volatile liquid acrylic monomer was applied to a water surface where a monolayer of the particles embedded within a film of the monomer formed spontaneously. The monomer was polymerized photochemically to form the above mentioned membrane.



This membrane is permeable for water vapor (permeance = 7* 10^{-9} mol $m^{-2}s^{-1}Pa^{-1}$, permeability = 1.6*10^{-14} mol m $m^{-2}s^{-1}Pa^{-1}$= 49 barrer), but impermeable for nitrogen (permeance < 5*10^{-12} mol $m^{-2}s^{-1}Pa^{-1}$, permeability < 1*10^{-17} mol m $m^{-2}s^{-1}Pa^{-1}$=0,03 barrer). The permeability for water indicates that the molecules are transported through the zeolite channels. The impermeability for nitrogen indicates a low amount of defects. Furthermore, the composite nature of the membrane reduces brittleness thus rendering it a promising candidate for separation technology.

ICOM1391

Incorporation of gold nanoparticles in membranes to improve fluxes by light irradiation

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The influence of the operating temperature on membrane performances has been studied in literature abundantly. For liquid filtrations, there are reports of an increased membrane flux when the feed temperature is increased. But in upscaled set-ups, large volumes are filtrated and heating the entire feed is not energetically efficient nor realistic. It may even be undesirable, in the case of products transforming or destabilizing at higher temperatures. A ***local heating of only the membrane*** could be sufficient ***to increase membrane fluxes*** and may in fact be much more efficient.

In this work, a strategy is presented to achieve local heating of a membrane during a separation process. By incorporating ***gold nanoparticles*** (GNPs) into the membrane structure, using the concept of ***photothermal heating***, the membrane can simply be heated by light irradiation. Photothermal heating has already been applied in imaging and sensing, drug release and tumor destruction but has up until now never been applied in membrane separation technology for the purpose of increasing fluxes.

GNP containing cellulose acetate (CA) and polyimide (PI) membranes were prepared and characterized by dynamic light scattering,
UV-VIS and diffuse reflection spectroscopy, scanning electron microscopy and transmission electron microscopy. For PI membranes, ***two synthesis methods*** to obtain GNPs inside the membrane matrix (using preformed GNPs or in-situ synthesis) were compared. Their influence on the membrane structure and the GNP size and aggregation in the membrane were analyzed. The photothermal effect of the GNPs on the temperature of the membrane was investigated by irradiating the membrane with continuous green laser light. A dead-end filtration cell was built to allow the ***laser light irradiation*** of the membrane during a liquid separation process.

It was shown that the permeance increase depended on the density of the membrane, the permeating solvent and the gold concentration. For PI membranes with a higher intrinsic flux, pure solvent fluxes were increased by up to 50%, while this augmented to >200% for PI membranes with intrinsically lower fluxes. For the even denser CA membranes, there was an ***improvement***
as high as 400% in isopropanol and 500% in ethanol. The results indicated that the solvent heat capacity, thermal conductivity and flow rate through the membrane determine the efficiency of the process. The two synthesis methods for GNPs in PI membranes yielded GNPs similar in size. However, to avoid extensive aggregation of GNPs in the membrane matrix, the in-situ synthesis of GNPs by reduction inside the membrane was preferred. Based on the collected data, a hypothesis was formulated on the ***mechanism leading to the flux increase***.

ICOM1725

Small-Molecule Stimulus Responsive Membrane with Reversible Gating Function

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Approaches to creating stimulus-responsive membranes have been explored for decades for liquid separations or controlled release applications yielding materials whose permeability varies, triggered by a change of pH, temperature, or ionic strength of the adjacent liquid, or the exposure to light, an electrical or a magnetic field. Approaches to creating stimuli-responsive materials known

hitherto rely mainly on responses such as a volume change of a bulk polymer or a polymer confined in the pores of a support structure, or the contraction/expansion of polymer chains at the edge of pores on a porous membrane surface resembling the function of a “gate-keeper” and with the result being an opening or closing of a porous structure. While some of the materials available nowadays may perform impeccably in defined applications, they do rely on stimuli that are non-specific and that might under non-ideal conditions either adversely affect the environment in which these membrane barriers are employed, or limit their range of applicability. In biomedical applications, for example, pH, temperature and ionic strength of the contacting liquid must not change beyond physiological conditions. On the other hand, light and magnetic field strength are less invasive stimuli and may well be specific, but the former requires optical transparency of the medium and the latter prefers proximity between the magnets and the stimuli-responsive barrier as the magnetic field strength changes with the square-distance. It therefore remains a challenge to mimic the specific and locally acting molecular recognition mechanism found in Nature for triggering a change of permeability in cell membranes, where a specific target-receptor interaction triggers a conformational change of a membrane transporter protein resulting in turn in a variation of the effective diameter of the cell membrane pores.

While the incorporation of such transporter proteins is one route to creating artificial molecular stimuli-responsive membranes, a possibly more robust and simpler one is the surface modification of a porous membrane structure with simpler molecules but likewise capable of a conformational change upon recognition of a molecular stimulus, such as aptamers. The capacity of aptamers to reversibly and specifically bind to target molecules of different molecular size while undergoing a conformational change is being explored since very recently for the surface modification of nanoparticless or biosensors. The challenge for membrane barriers, however, lies in the application of the molecular recognition principle of aptamers on a larger substrate area, and most of all achieve reversibility in its conformational changes for repeated applications.

We here report for the first time on a self-assembled stimuli-responsive membrane barrier which is capable of reversibly changing its permeability upon the molecular recognition of a small target molecule, rather than respond to a bulk stimulus.

ICOM366

The role of carbon nanotube tip functionalization on fluid transport in CNT membranes

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This work examines the role of carbon nanotube tip functionalization on the transport of water, ions and gases through carbon nanotube membranes. Single-walled carbon nanotubes, SWNTs, were purified, cut and functionalized with octadecylammonium - carboxylate zwitterion and carboxybetaine zwitterion groups. Vertically oriented carbon nanotube membranes were prepared by hydro-dynamically driven self-assembly of the functionalized SWNTs on a microporous filter and coating with an ultra-thin polyamide layer prepared by interfacial polymerization. The SWNT pore size distribution ranged from 8 to 15 Å. The enhanced interaction between water and zwitterions increased H2O permeability through the membrane. The zwitterions also reduced the adsorption of ions in the membrane, thereby decreasing concentration polarization and fouling. Permeability of gases through the SWNT membrane was also affected by the presence of the zwitterionic groups at the SWNT pore openings resulting in enhanced size-exclusion.

Membrane characterization 2

ICOM1855

Recent developments in characterization of ultrafiltration and virus filtration membranes

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Recent developments in membrane formation technology have led to significant advances in our ability to design and control the underlying pore structure, chemistry, and morphology of high performance ultrafiltration and virus filtration membranes. There is thus an increased need for characterization methods that can effectively probe the critical structural and chemical properties of these membranes. This talk will review some of the recent developments in characterizing ultrafiltration and virus filtration membranes, including new efforts in the use of dextran retention tests, confocal microscopy with fluorescently-labeled bacteriophage, and binary gas diffusion integrity tests. Emphasis will be placed on the fundamental insights that these techniques can provide into the underlying membrane properties and how this information can be used to develop new insights into the critical factors that control membrane performance.

ICOM1355

Transport and equilibrium properties of ion-exchange membranes with sulfonic groups of different polarity

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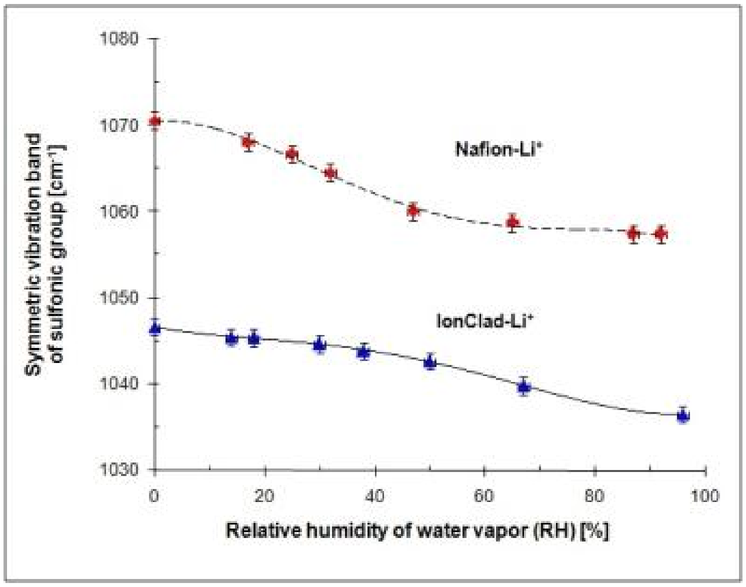
Ion-exchange membranes found various practical applications, e.g. in electrodialysis, diffusion dialysis, fuel cells or pervaporation. The properties of ion-exchange membranes depend on the type of ion-exchange group, its ionic strength as well as the type of counterion.

The contribution presents the equilibrium and transport properties of sulfonic membranes in lithium form in contact with solvents and/or liquid mixtures of different polarity. Two membranes possessing the perfluorinated backbone and sulfonic groups (Nafion 117-Li^+ and IonClad-Li^+) were chosen for the investigation.

The following experiments were performed: water vapours and methanol vapours sorption as a function of partial pressures, swelling in water and several organic solvents, water vapour transport and liquid water transport across the membranes, pervaporation of water-methanol and water-ethyl acetate mixtures.

It was found that despite the similar backbone, the same sulfonic ion-exchange group and the same lithium ion, the equilibrium and transport properties of both membranes were quite different. Swelling of IonClad-Li^+ membrane was much smaller than that of Nafion-Li^+ one. Moreover, IonClad-Li^+ membrane was much more selective in the pervaporation of water-methanol and water-ethyl acetate mixtures comparing to the selectivity of Nafion membrane.

To explain these differences in terms of interaction between sulfonic groups, lithium counter ions and solvent molecules, IR spectra were made of dry membranes, membranes equilibrated with different solvents (methanol, ethyl acetate, cyclohexane, water) as well as with water vapours of different relative humidity (0-95%). It was found that in the IonClad-Li^+ membrane, sulfonic groups, which are bound to the benzene ring, the ionic pairs sulfonic group-lithium counterion was not dissociated in the presence of methanol molecules. The position of symmetric vibration band of sulfonic group in the dry membrane is the same as in the membrane equilibrated with methanol. In the Nafion-Li+ membrane sulfonic groups are attached to the fluorocarbon vinyl ether chains and the dissociation of the ion-pairs occurs even in the presence of molecules of much lower polarity. It was found that position of symmetric vibration band of sulfonic group for the Nafion-Li^+ membrane equilibrated in methanol is much lower than that for dry membrane and close to that in the membrane equilibrated in water.



Moreover, the differences between investigated membranes were observed in the IR spectra of membranes equilibrated with water vapours of different relative humidities (RH) - Fig. 1. It is clearly seen in Fig. 1 that the total dissociation of ion pairs in Nafion-Li^+ membrane occurs in the RH of 50%, whereas for IonClad-Li^+ there is no dissociation until the RH is equal to 40-45%.

ICOM245

Characterizations of 3D structure of hollow fibre membrane using X-ray tomography and their links with spinning conditions

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Polymeric membranes are widely used in filtration processes. These applications require well-controlled porous structures. Most of the organic membranes are usually obtained by the well-known phase inversion process. The obtained porous structure is highly dependent on both the phase separation kinetics and thermodynamical equilibrium. Some process conditions promote the macrovoids formation, particularly detrimental in hollow fibre membranes. Their initiation and growth processes are still under debate. Recently, hollow fibres were imaged by synchrotron X-ray microtomography [1]. Using this technique, the 3D pores structure was revealed, as well as the distribution of the pore location in the membrane thickness. Besides, the observed morphologies were linked to the phase inversion phenomena. In this contribution, a standard bench X-ray tomograph was used to characterize the 3D structure of laboratory spun hollow fibre made under different conditions. The objectives are to correlate the 3D characterization to the spinning conditions and to show the interest of X-ray tomography.

X-ray tomography was performed using the nanofocus computed tomography system NANOTOM® (Phoenix). The observed hollow fibre was a cylinder of 5 mm in length and 0.8 mm in diameter, held vertically inserting one end in a glass tube. During data acquisition an X-ray beam irradiates the sample. Radiographs of the X-ray beam passing through the sample are recorded for 2000 different angular positions. A voxel size of 1.07 µm was reached. A filtered back projection algorithm was applied to reconstruct the 3D structure of the sample using scanned radiographs. The reconstructed 3D volume (421 x 950 x 950 voxels) represents a 3D map of the absorption coefficients (Beer Lambert law) coded in 16 bits. These absorption coefficients are directly linked to the polymer phase or to the void phase. To obtain quantitative descriptors of the sample structure, the 3D image was filtered using an "Edge-Preserving Smoothing" filter and segmented to distinguish porous and solid phases using the AMIRA® software. Figure 1 exhibits a volume extracted from the segmented 3D image. Only pores with diameter higher than the voxel size can be distinguished. It appears that the observed macrovoids have similar 3D shapes. As a result, they can be well discriminated by their diameter ø and their depth *p*. Besides, macrovoids are regularly arranged along the $\underline{\mathbf{e}}_\theta$ and $\underline{\mathbf{e}}_z$ directions. This arrangement can be quantified by measuring the mean spacing between the macrovoid initiation points in the two directions. In the presented volume, these parameters, noted λ_θ and λ_z, reach 60 (±10) µm and 45 (±11) µm respectively. By changing the spinning conditions, the pore diameter, the pore depth, the mean spacing as well as the total porosity or the number of macrovoids significantly evolve.

[1] J.C. Remigy, M. Meireles & X. Thibault "Morphological characterization of a polymeric microfiltration membrane by synchrotron radiation computed microtomography" *Journal of membrane science*, 2007, 305, pp. 27-35

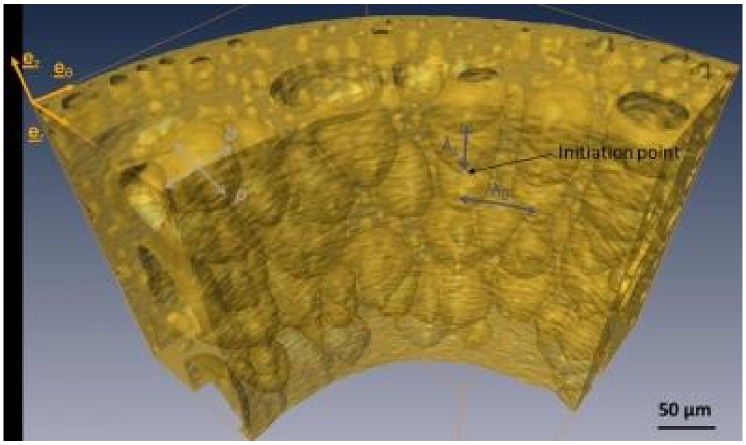

Figure 1: Volume extracted from a 3D image of a hollow fibre membrane imaged by X-ray tomography

ICOM397

Monodispersions of gold nanoparticles as a new tool for studying UF membrane pore size

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Ultrafiltration (UF) is a low-pressure membrane process widely implemented in bioseparation processes. The separation is achieved primarily by size rejection where solutes smaller than the pore size in the membrane are passing through and those bigger than the pore size are rejected. The pore size and its determination are, therefore, of primary importance in UF membrane processes.

The pore size distribution of Ultrafiltration membranes can be determined by several different techniques such as bubble point method, liquid displacement, thermoporometry and visual observation (scanning electron microscopy (SEM), transmission electron microscopy (TEM) or atomic force microscopy (AFM)), and more. Generally, the methods are providing information on average pore size or largest pore size, and not on pore size distribution. A more accurate method is to measure rejection of inert solutes. Polyethylene glycol (PEG) or Dextrans are usually used. The test measures molecular weight cut-off (MWCO) value that reflects the molecular weight of a solute molecule that is being rejected by 90%. The use of water-soluble molecules accounts for two major deficiencies: a weak link between the MW, the pore size and membrane performance, and a rather small diapason of available PEGs and Dextrans.

We are proposing to apply monodispersions of inert nanoparticles instead of the organic molecules. The nanoparticles offer the ability to estimate pore size distribution in a wide diapason of MF and UF membranes by a relatively simple method, to model filtration of viruses and for the first time to accurately predict absolute retention values.

The approach was exemplified by synthesis of a set of 7 monodispersions of gold nanoparticles (AuNPs) that were filtered through ceramic and polymer membranes. Size of the particles was evaluated by transmission electron microscopy and dynamic light scattering. Filtration experiments were performed in a standard dead-end cell. The retention ratio was calculated as , where and are the AuNPs concentration in the filtrate and in the permeate respectively. Concentrations of gold in feed and permeate solutions were determined by atomic absorption spectrometer (Perkin Elmer Analyst200, Waltham, MA, USA). *Figure 1* shows the retention percentage and the pore size distribution for PVDF-30 and C-50 membranes. The pore size distribution was determined using a log-normal probability density function.

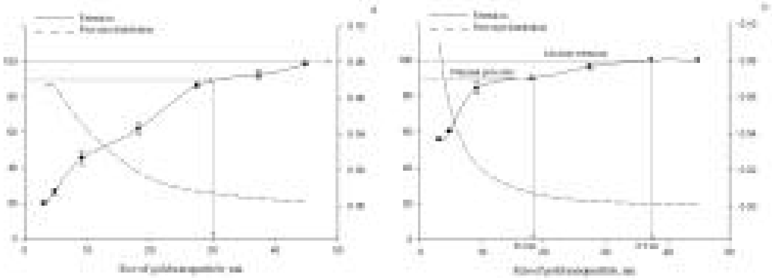

Figure 1. Retention and pore size distribution curves of **a.** PVDF 30 kDa membrane and **b.** C50 membrane.

The results were compared with standard tests performed with PEGs. The both tests displayed a unique sigmoidal rejection curve for each membrane. The pore size cut-off measured by two methods was higher in PVDF-30. The absolute pore size of C-50 was 37.4 nm and of PVDF30 slightly bigger than 50 nm. In addition, C-50 obtains a narrower pore size distribution, which indicates a smaller range of pore sizes. We are assuming that the proposed method is a valuable addition to the currently available research tool for pore size determination. The ability to accurately predict the absolute pore size may provide an advantage to confirm compliance of membrane systems with the stringent regulatory requirements of the drinking water industry.

ICOM431

Characterisation of Nafion Membranes Modified with Ionic Liquids Using Proton NMR Spectroscopy

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Nafion membranes are widely used as a reference material in polymer electrolyte membrane fuel cells (PEMFCs), due to their high proton conductivity, mechanical, thermal and chemical stability at temperatures up to 80 ºC. Several models have been proposed in the literature regarding its molecular structure and organization, stating that the ionic groups are aggregated in the perfluorinated polymer matrix to form a network of clusters which allow the transport of ions. However, there is still no generalized agreement regarding the size, the geometry and the spatial resolution of the clusters. The level of confinement of these ionic clusters has an important effect on the degree of water structuring within the membrane matrix, which is expected to directly influence the mechanisms of proton transport through these membranes. While seeking to understand the structure of Nafion membranes, there are still some problems in the performance of these materials that need to be investigated when used in PEMFCs.Their high proton conductivity is affected at temperatures above 80 ºC due to a decrease in the membrane water content. Additionally, a relatively high methanol and gas crossover is observed for Nafion, which affects the membrane performance when used in Direct Methanol Fuel Cells.

In order to overcome the problem of water loss observed at high temperatures and crossover, the solution proposed in this work was to incorporate different ionic liquid (IL) cations in Nafion membranes. ILs are compounds consisting entirely of ionic species comprising an organic cation and an inorganic or organic anion. Through an ion-exchange process between the counter cation of the Nafion membrane and the IL cation, it is possible to incorporate different amounts of ILs cations inside the membrane. The IL cations tested were phenyltrimethylammonium ($TMPA^+$), n-dodecyltrimethylammonium (DTA^+), and 1-*n*-butyl-3-methylimidazolium ($BMIM^+$), which were incorporated into a Nafion-112 membrane.

Proton nuclear magnetic resonance relaxometry was used in this work as a characterisation technique to study the ion mobility and water structuring degree within Nafion membranes modified by incorporation of IL cations. The frequency dependence of the proton spin-lattice relaxation rate for the modified Nafion/IL cation membranes was compared with that obtained for an unmodified Nafion membrane, allowing for distinguishing different contributions of the motions of the molecules. The translational self-diffusion coefficient of the moving molecular species in the modified membranes was also estimated, allowing understanding which were the modified membranes that presented a more confined and structured environment.

The effect of increasing temperature on the stability of the modified Nafion/IL cation membranes was also assessed through NMR relaxometry, making possible a qualitative correlation of the transient behaviour of the relaxation rate with water content, and the results were compared with those obtained by thermogravimetry. Both results point to a strong reduction of the proton mobility at high temperatures for the unmodified Nafion membranes, while for the modified Nafion membranes the ion mobility presented a small variation with increasing temperature, allowing to obtain membranes with an improved proton mobility at high temperatures.

NF/RO 2

ICOM1853

Membrane Desalination - History, Current Status and Research Needs

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Water desalination technologies are rapidly gaining momentum for potable water production from seawater and water reuse application including municipal wastewater and agricultural drainage (AD) water. This presentation will first provide a brief history of the major milestones in the development of water technology. Subsequently, an overview will be presented of the common desalination processes used for treatment of seawater, brackish water, and wastewater, as well as an outline of operating and performance issues. While a range of desalination technologies will be mentioned, the focus of the presentation will be on reverse osmosis (RO) membrane and thermal desalination (primarily for seawater) systems, as these two approaches are the dominant commercial processes. The major operational (e.g., fouling and scaling) and environmental issues will be discussed with respect to water sustainability an environmental compatibility of desalination technologies. Considerations of energy consumptions and possible paths to reducing energy consumption and integration of desalination technology with alternative energy sources will be discussed as well as an assessment of the potential role of alternative desalination processes currently at various research and demonstration stages, in addition to assessment of research needs aimed at reducing the overall cost and environmental impact of water desalination.

ICOM257

Hydration of Fluoride, Nitrate and Nitrite during Pore Transport in Nanofiltration

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A fundamental mechanistic understanding is required in order to optimize desalination processes such as nanofiltration. Traditional nanofiltration models account for mechanisms such as convection, diffusion, charge and size exclusion [1]. However, hydration is neglected even though it has been theoretically shown that ions demonstrate difference behaviour in confined channels (such as a membrane pore) than in bulk solution [2] and experimentally shown that bare ion size alone is not sufficient to describe size exclusion [3]. The objectives of this work are to (1) determine the hydration structure of fluoride, nitrate, and nitrite and (2) determine the change in hydration structure of the ions as they are moved into a pore and the associated energy cost of dehydration.

A method has been developed to assess ionic hydration structure in pores using simulations based upon classical molecular dynamics. The program NAMD [4] was used with solute parameters based upon literature studies or developed when not available. Model inputs such as pore size and concentration were selected to be representative of experimental conditions. Results show the likelihood of ion dehydration (partial or complete) to occur depending on ion type (F-, NO3-, NO2-), membrane pore size (0.34 and 0.42 nm) and pore size distribution.

Further, a method has been developed to directly compare modelling results with experimental outputs based on the Arrhenius relationship. Increasing temperature provides a driving force for ion transport across the pores and a measurement of solute flux under various conditions leads to the calculation of an “activation energy” representative of the energetic expense of pore transport. These experimental values are compared directly with model outputs.

The results highlight the importance of considering ion hydration in nanofiltration, both from a modelling and an experimental perspective.

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ICOM436

Process Intensification with Membranes

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Process intensification consists of the development of novel apparatuses and processing techniques that, compared to those commonly in use, are resulting in tremendous improvements in manufacturing. /1/ As an example, replacing or combining conventional separation processes with a low energy consuming membrane separation unit can further simplify the separation process. This will help to decrease equipment sizes and will ultimately result in cheaper and more sustainable process solutions.

Membrane filtration processes like reverse osmosis are well established in the production of drinking water or in the dairy industry. They are especially attractive due to low energy consumption as there is no phase change and no requirement to thermally expose the product. An example of this is the state-of-the art process for pre-concentrating sugar syrup which consists of reverse osmosis and evaporation.

The acceptance of membrane processes in the chemical and pharmaceutical process industry is continuously growing. The wide acceptance of reverse osmosis and the availability of various types of suitable membranes supports its implementation.

The following example shows the potential of process intensification for a conventional liquid-liquid extraction process. Highly diluted acetic acid waste streams are produced in large quantities in the chemical industry, for example in the synthesis of acetic acid, terephthalic acid or polyvinyl alcohol. The volumes are high, however, the acid content is up to 2 wt% only. Still, a recovery of this acetic acid for in-process recycling would reduce waste and save valuable resources. There are several options for the treatment of these waste streams:
- Sewage for biological treatment or chemical neutralisation
- Incineration of the waste stream
- Distillation
- Liquid-liquid extraction.

Liquid-liquid extraction is the extraction of a substance from one liquid phase into another liquid phase (extract). The process consists of an extraction column, followed by a (steam) stripper to further remove components from the aqueous phase, plus a conventional solvent distillation unit to generate a high concentration acid stream as well as regenerate the extracting solvent for recycle. The energy demand of both distillation and stripping is remarkably high, however, whereas the economic value of the recovered acetic acid often only marginally contributes to the operating expenses.

Reverse osmosis applied to preconcentrate the acid stream is an attractive process extension: a relatively small concentration factor reduces the volumes to be treated in the extraction unit by a significant factor, resulting in reduced loads, smaller equipment sizes and lower energy demand.

This presentation compares the stand-alone liquid-liquid extraction unit for recovery and concentration of acetic acid with a combined process including reverse osmosis.

/1/ Process Intensification: Transforming Chemical Engineering, A. I. Stankiewicz, Chemical Engineering Progress, January 2000, pp. 22-34

ICOM381

A new interpretation of “critical flux” for shear-enhanced nanofiltration process

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The critical flux hypothesis, first proposed for microfiltration (MF), is that there exists a flux below which flux does not decline with time; above it, flux decline by fouling is observed. It corresponds to a critical solute concentration for transition between concentration polarization and cake formation. The critical value is defined as the point at which the flux deviates from a linear variation with transmembrane pressure (TMP). The critical flux concept is very useful for understanding and improving the operation of membrane filtration, and widely adopted in research work and industrial productions, not only for MF, but also for ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). However, this concept was based on the mechanism of cake or gel formation in MF, not fully considering the resistance of concentration polarization layer and the osmotic pressure difference across the membrane. For a shear-enhanced NF process, a cake layer may not form due to a high shear rate, and concentration polarization, adsorption fouling and pore plugging are the dominant mechanisms for flux decline.

In this study, the flux variation with increasing TMP of a rotating disk module was investigated using a NF270 membrane, and test fluids were deionized water and diluted skim milk. As seen in

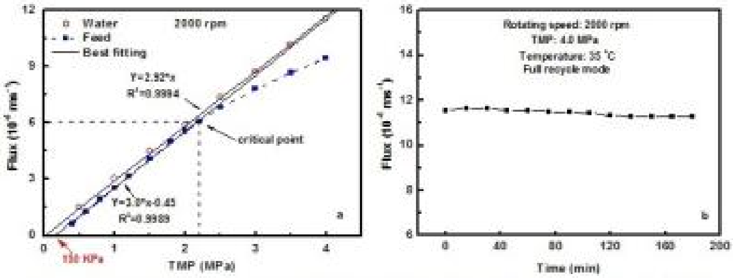

Fig. 1 Flux variation with TMP and time at a rotating speed of 2000 rpm (shear rate $_{max}$= 3.22×10^5 s^{-1}). TMP increases in steps and each TMP operation lasts 10 min for stabilization.

a, the form of critical flux is neither strong nor weak due to the presence of osmotic pressure (150 KPa); the critical flux (6.09×10^{-5} ms^{-1}) occurs at a TMP of 2.2 MPa, much higher than that for a crossflow module; and even if TMP rose to 4.0 MPa, no limiting flux was found. Moreover, operating at a constant TMP of 4.0 MPa for 3 h (

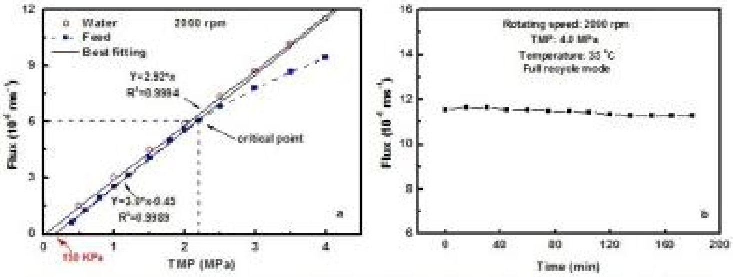

Fig. 1 Flux variation with TMP and time at a rotating speed of 2000 rpm (shear rate $_{max}$= 3.22×10^5 s^{-1}). TMP increases in steps and each TMP operation lasts 10 min for stabilization.

b), flux decline was small for this shear-enhanced NF process, even though the flux (11.55×10^{-5} ms^{-1}) was much higher than “critical flux”, indicating that a gel or cake layer did not really form due to a high shear rate. Therefore, the “threshold” of flux slope variation with TMP in

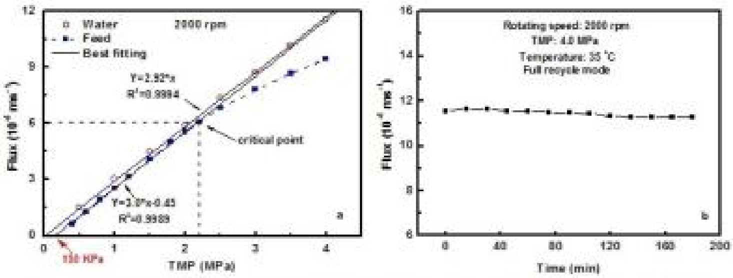

Fig. 1 Flux variation with TMP and time at a rotating speed of 2000 rpm (shear rate $_{max}$= 3.22 ×10^5 s^{-1}). TMP increases in steps and each TMP operation lasts 10 min for stabilization.

a was not caused by fouling, because whether the foulant adsorption and pore plugging occur mainly depends on the properties of membrane and solutes, not on solutes concentration at membrane surface.

According to the resistance model (considering the osmotic pressure difference, $\triangle\Pi_b$), filtration resistances for water and feed were calculated, showing that below the critical point, the total filtration resistance for feed (0.37×10^{14} m^{-1}) was almost the same as the membrane resistance (0.38×10^{14} m^{-1}). Thus, a new concept of “critical flux” for a shear-enhanced NF process, can be defined as a flux below which the resistance of concentration polarization is negligible; above it filtration resistance will be increasing. This new concept indicates that high flux does not result in membrane fouling when cake fouling does not occur, and it also provides a new approach to optimize shear-enhanced membrane systems.

ICOM546

High Recovery in Reverse Osmosis

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Introduction

Membrane technology is an efficient way of producing drinking water, but the recovery is often limited by scaling or biofouling, and sometimes by the formation of concentrate.

When the concentrate cannot be disposed of easily by discharging, the volume of the concentrate stream needs to be minimized. This can make further treatment of the concentrate more feasible. However, at the necessary high recoveries the risk of formation of scaling on the membrane is high. Hence, pretreatment of the feed water becomes necessary. For the removal of bivalent cations, cation exchange (CIEX) can be applied. After CIEX treatment the risk of silica scaling remains, for which additional measures have to probably be taken. This can either be the addition of a dedicated silica antiscalant, or to design and implement a crystallizer to remove the silica. With a combination of CIEX and silica antiscalant/crystallizer a very high recovery (96-99%) might be achieved. The purpose of this study was to investigate the performance of a pilot unit at these very high recoveries in terms of fluxes, pressure drops and scaling behaviour.

Materials and Methods

A pilot plant has been constructed to carry out this research (figure 1). As a first step a CIEX resin is used to remove Ca^{2+}(aq) and Mg^{2+}(aq) to prevent the deposition of salts containing these ions. CIEX is followed by nanofiltration (NF) at high recovery (80-90%) and subsequently the NF concentrate is treated with reverse osmosis (RO) at high recovery (80-90%). The membrane system recovery (NF+RO) is 96-99%. This recovery value neglects water losses due to regeneration of the CIEX, which in practice lowers the total recovery by 1-2%.

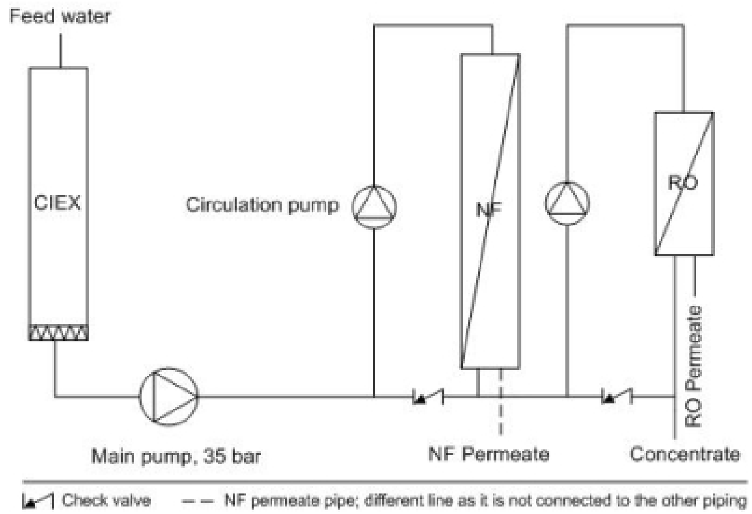

Figure 1 Scheme of the pilot plant used in this research.

The mass transfer coefficient (MTC) and (feed – concentrate) pressure drop are monitored for both membranes in order to investigate the occurrence of scaling and other types of fouling. Once scaling occurs, membrane autopsy combined with scanning electron microscopy energy dispersive X-ray spectroscopy (SEM EDX) will be used to determine the type of scaling.

Additionally, all the different water streams (raw water, feed water, the two permeates, concentrates, and water in the membrane loops) are analyzed to determine the concentration of scaling salts and retention behavior of the membranes. The elements present in the streams are measured with ICP-MS and further analyses are carried out to determine the DOC and the concentrations of HCO_3^-(aq), Cl^-(aq) and SO_4^{2-}(aq).

Results
In this study the first tests with the pilot plant are reported. Experiments at high recoveries (96-99%) have been performed in order to cause scaling in the membrane and to prove that silica scaling is actually the limiting problem.

Parallel Sessions

Tuesday, July 26th 2011

Afternoon Session 2, 15.50 – 17.40

Modelling 2

ICOM1856

Molecular simulations of transport in polymer membranes

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This talk will review the applications of classical simulation methods of molecular dynamics (MD) and Monte Carlo (MC) to problems associated with polymer membranes as barrier or separation materials. Providing that appropriate models can be built, such simulations can be used to characterize the structures and dynamics at the molecular level. The common procedure is to build bulk amorphous systems that are representative of the membrane core. However, these models cannot take into account the skin effects, and as such, recent advances have been made in the preparation of inhomogeneous atomistic films containing actual surfaces. It will be shown that the permeation of polymer matrices by small molecules can either be measured indirectly via diffusion and solubility coefficients in the bulk systems or directly in the case of the actual membranes models.

Amorphous polymer systems present a challenge for the simulator because of their relaxation times, which are usually much larger than the current MD timescales (~10^{-9}-10^{-8} s for fully-atomistic models). The starting structures for amorphous polymer chains must thus be already fairly relaxed. Various computational methods have attempted to solve this problem and a particularly robust technique is the hybrid pivot Monte Carlo-molecular dynamics (PMC-MD) single-chain sampling procedure, in which MC pivot moves of rotatable torsions are regularly attempted and the change in local energy is evaluated based on the Flory's hypothesis. The strength of this technique is that it has been systematically validated for a large variety of chain lengths and structures by comparing the PMC-MD results with those of bulk melts decorrelated using MD on its own.

Once the pure polymer model is prepared, small penetrants are inserted into the matrices. Issues associated with solubility such as the sorption and desorption isotherms, volume changes and plasticization, void spaces or preferential interactions can be characterized and compared to both experimental data and gas sorption theories. The basic mechanisms underlying gas motion can also be studied. The self-diffusion coefficient is usually evaluated from the penetrant mean-square displacements (MSD), but this is only valid within the framework of a long-time Fickian diffusive limit. It is now possible to extend the MSD timescale by orders of magnitudes with techniques such as the "Trajectory-Extending Kinetic Monte Carlo" (TEKMC) and predict the self-diffusion coefficient for systems where the Fickian regime is difficult to reach with MD simulations.

Probing possible skin effects requires the introduction of a planar interface into an amorphous long-chain polymer system, but it is still far from being trivial. Removing boundaries in one direction requires significant mobility in order for the polymer to relax, which is impossible in the case of long and/or rigid chains. It is also possible to mimic the experimental solvent-casting process by preparing a low-density solution and densifying the membrane with a wall. The application of such techniques to 50-150 Å thick film models will be illustrated. The insertion of penetrants on either side of the model membrane then leads to the characterization of sorption, solubility and diffusion at the polymer interface.

ICOM874

Molecular simulations of electrolyte solutions confined in nanopores

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[1]*University of Rennes 1, Sciences Chimiques de Rennes UMR CNRS 6226, Rennes, FR,* [2]*University of Rennes 1, Institut de Physique de Rennes (UMR CNRS 6251), Rennes, FR*

The events leading to rejection by nanofiltration (NF) membranes take place on a length scale of one nanometer and no significant progress in the understanding of NF could be done without learning more about the properties of nanoconfined solutions.

Molecular simulations are attractive tools to get insight into the physical properties of nanoconfined. However, for meaningful computer simulations, it is important to use force fields that are as accurate and realistic as possible. In particular, accounting for electronic polarization in force fields has been shown to be critical to the study of interfacial phenomena in heterogeneous systems [1] and it should be taken into account in NF for which interfacial phenomena are of great concern.

In this work, dynamic and dielectric properties of nanoconfined electrolyte solutions have been investigated by means of molecular dynamics simulations with a polarizable force field based on a core-shell approach [2]. Current limitations in terms of simulation time scales and knowledge about the molecular structure of NF membranes make impossible the use of all-atom simulations for real NF membranes. Nevertheless, significant progress can be done by investigating model nanopores since these latter can help to clarify the physics at play at the nanoscale. MCM 41 silica nanopores (diameter: 2.4 nm [3]) have been considered as ideal systems in this work.

The effect of confinement on the dielectric constant inside pores (the so-called Born effect) is currently a matter of debate in the membrane community. The dielectric constant inside pores of NF membranes is usually used as a fitting parameter in NF models and contradictory results can be found in the literature [4]. In this work, special attention has been paid to the determination of the dipole moment of water molecules inside nanopores, which has been further used to compute the effective dielectric constant of the pore-filling solution. Besides, the self-diffusion coefficients of ions inside nanopores have been determined from their mean square displacements and compared to the hindered diffusion coefficients computed from the hydrodynamic theory which is usually employed in NF models [5]. Various electrolytes have been considered (NaCl, NaI, $MgCl_2$…) so as to investigate the effect of ion polarizability, charge and size. The surface properties of the nanopore have been modified so as to investigate the effect of the surface charge density and the hydrophilic/hydrophobic nature of the surface on the physical properties of confined solutions. It was done by considering silica nanopores with different surface sites: protonated silanols, deprotonated silanols (i.e. negatively
charged nanopore), and trimetylsilanes (in order to get a hydrophobic surface).

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ICOM1593

Propane/propylene plasticization in polyimide membranes via molecular simulation methods

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Propane (C_3H_8)/propylene (C_3H_6) mixtures is an important but difficult and energy intensive separation. Propylene is largely a byproduct of ethylene production, which is the largest volume organic produced in the petrochemical industry. Propylene is also produced by dehydrogenation of propane and methanol-to-olefins conversion processes. These processes yield mixtures of propane/propylene which require further separation. The permeation properties of propane/propylene gases through polymeric membranes are of interest for the development of membranes for their separation. However, a major issue in the industrial application is the plasticization of polymer membranes during the permeation of these condensable hydrocarbons which causes significant reduction in selectivity of the membranes. Plasticization occurs due to high solubility of such components, increasing the mobility of polymer chains, fractional free volume (FFV), and hence permeability in the presence of penetrant molecules.

6FDA (4,4-hexafluoro isopropylidene diphthalicanhydride) based polyimides are promising membrane materials for gas separations because they exhibit low chain packing density and high separation performance for different gases in comparison with other conventional polymers. Furthermore, membranes with commercially attractive selectivities may be obtained by changing the diamine structure. In this work, 2,4,6-trimethyl-m-phenylene diamine (DAM) and 4,4-oxydianiline (ODA) were selected as the diamine moieties, since 6FDA-DAM and 6FDA-ODA polyimides have a strong potential for C_3H_6/C_3H_8 separation. DAM monomer includes three methyl groups which are believed to act as spacers to prevent close packing, and thus help open up the matrix but ODA monomer includes –O– linkage in the backbone which is believed to give flexibility to the polyimide structure to facilitate close packing, and thus help to close the matrix. In this work, C_3H_6/C_3H_8 plasticization effect in 6FDA-DAM and 6FDA-ODA polyimides is investigated via molecular simulation.

All simulations were carried out using the Accelrys Materials Studio software, with all molecular interactions being modeled using the COMPASS force field. The polymer simulation cells were constructed from 80 repeat units. Sorption simulations were carried out in the Grand Canonical Monte Carlo (GCMC) ensemble. To reproduce the hydrocarbon-induced plasticization effect, sorption-relaxation cycles were applied until the C_3H_6 or C_3H_8 concentration converges; i.e. at each cycle, the polymer matrix was loaded with sorbate molecules corresponding to its equilibrium capacity at the considered pressure, and then *NPT*-MD simulation runs were applied for 40 to 200 ps to obtain an equilibrated matrix. Next, the sorbate molecules were removed and the cycle was repeated. The increase in the FFV of the resulting polymer structure was considered as the extent of plasticization. This procedure was also applied to investigate the change in the sorption selectivity throughout the simulations of C_3H_6/C_3H_8 binary mixtures at different partial pressures. The convergence of hydrocarbon concentrations in 6FDA-ODA is illustrated in Figure 1 for pure C_3H_6 and C_3H_8 and their equimolar mixtures.

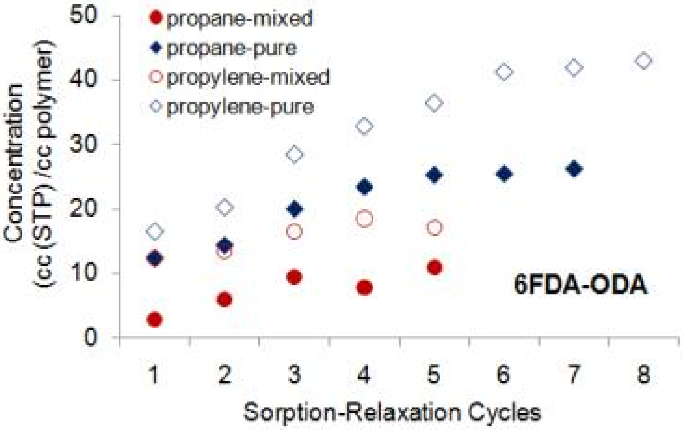

Figure 1. Increase in the propane and propylene sorption capacity in 6FDA-ODA due to plasticization for pure gases and an equimolar mixture at 25°C and 1 atm.

ICOM1486

Modeling combined fouling in reverse osmosis membrane devices: biofouling and scaling

Andrea Radu[1,2], Hans Vrouwenvelder[1,2], Mark van Loosdrecht[1], Cristian Picioreanu[1]
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Background

Membrane installations are crucial for water production all over the world. A major problem related to membrane applications is fouling. Membrane fouling affects negatively the performance of the installation. Several forms of fouling can occur, depending on feed water quality, pretreatment and membrane installation design and operation: (i) mineral scaling, (ii) colloidal fouling, (iii) organic fouling and (iv) biofouling.

Methods

A two-dimensional numerical model was developed to study the dynamics of local and global impact of fouling (biofouling and scaling) in a reverse osmosis membrane device. The micro-scale model includes hydrodynamics and the mass transport of solutes (salts and substrate). For biofouling, biofilm development is modeled including biomass attachment, growth and detachment due to mechanical stress induced by flow in the feed channel. For scaling, crystal formation and growth are considered based on local degrees of saturation for salts. Three fouling scenarios are studied numerically (biofouling, scaling and biofouling coupled with scaling) in respect to membrane process performance indicators.

Results

Simulation results for biofouling explained several experimental observations, most importantly the loss of permeate flux and the increase of salt passage in time due to biofilm formation. Three mechanisms were identified by which biofilms on reverse osmosis (RO) membranes contribute to performance loss: (i) biofilm enhanced concentration polarization (see Figure 1); (ii) increased hydraulic resistance to trans-membrane flow; and (iii) increased feed channel pressure drop. The evaluation of the relative contribution of these mechanisms showed that the biofilm enhanced concentration polarization has the most severe effect on flux decline, at least for treatment of brackish and sea water.

Numerical simulations for scaling suggested the critical places where precipitation could occur and that a non-uniform scale pattern is obtained for several feed spacer configurations. Surface coverage/blockage due to scale formation and the consequent flux decline were evaluated for different process conditions (cross-flow velocities, feed pressures, feed salt content, pH) and compared well with data from literature.

Model results indicate that scaling is accelerated in the presence of biofilms due to at least two reasons: (i) enhanced concentration polarization, which may lead to salt concentrations above the solubility product next to the membrane (ii) existence of biofilm, which can promote an increased surface for nucleation of crystals. Moreover, the biofilm removal (detachment) is more difficult in the presence of salt deposits, as its strength is increased.

Impact

The numerical modeling approach combining computational fluid dynamics (CFD) with fouling models (biofouling and scaling) contributes to a better understanding of combined fouling mechanisms. In addition, the model could suggest ways to improve spacer design and allows theoretical studies of operational conditions to reduce fouling effects in reverse osmosis and nanofiltration (NF) membrane devices.

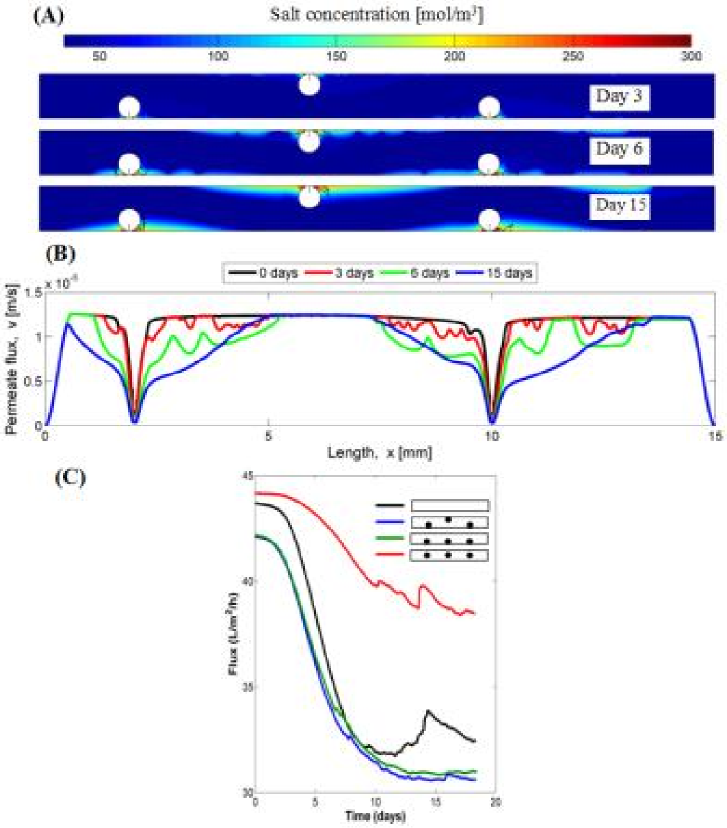

Figure1- Effect of biofilm development on: (A) 2-d salt concentration distribution in the channel; (B)the local permeate flux through the lower membrane. High salt concentration near the zigzag spacers and within biofilm colonies corresponds to very low permeate flux. (C) Comparative average flux decline for different channel geometries.

ICOM1179

A multiscale method for the prediction of the volumetric and gas solubility behavior of high-Tg polyimides

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The description of gas and vapor solubility in glassy polymers is relevant for many practical applications, from membrane separations to packaging and from sensors development to medical instrumentation. In the last decade, a new macroscopic model has been developed based on thermodynamic analysis of non-equilibrium polymeric glasses [1], the NET-GP theory. This approach, combined with an equation of state (EoS) theory, such as the Lattice Fluid or SAFT, gives rise to the corresponding non-equilibrium models named NELF and NE-SAFT [2], respectively, able to predict solubility of gases and vapors in glassy polymers, with negligible consumption of CPU time.

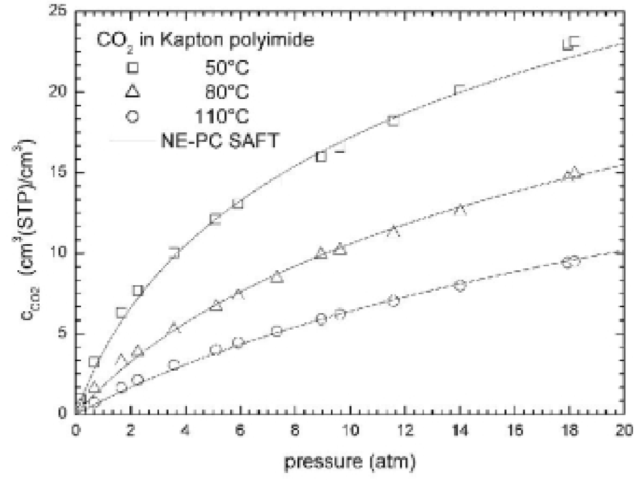
EoS characteristic parameters for the penetrants are normally retrieved fitting liquid-vapor equilibrium data for penetrants; for polymers, pressure-volume-temperature (pvT) data above T_g are required. Such data are available in the literature for low-T_g polymers [3], whereas for high-T_g glassy polymers, such as polyacetylenes and many polyimides of extreme importance for membrane separation, these data are practically impossible to be measured, and the NET-GP model faces a serious limitation.

In this work, an atomistic approach is employed to simulate pvT data of polymers at high temperature (in the rubbery region), by using a molecular dynamics tool. Data are then regressed with the desired EoS to obtain the polymer characteristic parameters, which are used to evaluate the gas solubility in the polymer with NET-GP model.

Two different polyimides, Polyetherimide (Ultem® 1000) and poly(4,4'-oxydiphenylenepyromellitimide) (Kapton® H), were selected to test the method feasibility: for Ultem®, experimental pvT data are available [3] and can be used to validate the method.

For both polymers, three independent atomistic models (a single chain of 70-80 repeat units, about 5000 atoms, for methodology see e.g. [4]) were created with Materials Studio software by Accelrys. Isobaric curves at different pressure have been simulated in a NpT ensemble ranging from 200 K up to 900 K with a COMPASS force field.

For Ultem®, MD simulations are in good agreement with experimental pVT data, especially at the higher temperatures. Hence, experimental and simulated data yield almost equivalent sets of characteristic parameters for the thermodynamic modeling. In the case of Kapton, pVT data are not experimentally available and the results from simulations allowed the calculation of the characteristic parameters of both LF and PC-SAFT EoS models. NELF and NE-SAFT models were then employed to predict rather accurately the sorption isotherms of different penetrants, as reported in Figure 1 for CO_2 sorption in Kapton at different temperatures.



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Membrane bioreactors 2

ICOM1860

Fluid dynamics – the poor cousin of MBR research

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Fouling in MBR has been a major research interest for the past decade but is still poorly understood. Due to the vast array of influencing parameters, most studies have focused on the quest for potential foulants, have applied a limited number of methods or had to neglect/eliminate certain phenomena in order to access others experimentally or numerically. The importance of the three phase fluid dynamics has been widely acknowledged with air scour having been applied commercially for about 20 years (Cui 2009), but a reliable and generally valid optimisation of aeration parameters and filtration cycles is still pending. Operation currently purely relies on manufacturers' recommendations and operators' experience. E.g., it has been observed that aeration does not yield an additional benefit above a threshold value or can be even detrimental (Drews 2010, Prieske et al. 2010), but exactly how all components or forces interact and how such knowledge can be used to optimise efficiency is still unclear – nor is it clear which parameters are the most relevant and need to be optimised in order to mitigate fouling: shear rate or crossflow velocity, their magnitude (maximum or average) or frequency, etc.

Difficulties arise from the complex and changing nature of the three phase system which consists of solutes, colloids and particles of different sizes, exhibits non-Newtonian behaviour and is subject to properties changes along the length of the membrane during module passage (MLSS concentration increases due to permeate extraction, flocs might rupture due to shear, compounds are preferentially deposited etc.). This greatly hampers theoretical approaches and also makes the application of certain experimental methods which, e.g., require transparent systems impossible. Measurement techniques such as PIV or the electrochemical method necessitate the use of model fluids and cannot fully capture effects in the micron region near the membrane surface. Model fluids normally do not show realistic rheological properties or contain a range of foulants.

The hydrodynamic flow field in the vicinity of a membrane results from very complex interactions of orthogonal and parallel flows as well as turbulent eddies created by bubbling. Both in turn affect biocake architecture and its hydraulic resistance, i.e. particle size or molecular weight distribution within the biocake (e.g. Metzger et al. 2007), its thickness, porosity etc. Besides these physical phenomena, biological reactions within the biocake and thus the occurrence of potential fouling conditions in the bottom layers (e.g. oxygen stress or lysis) are also affected by fluid dynamics since substrate, nutrient and oxygen supply depend on flux (Hwang et al. 2009).

In addition to multiphase flow in the vicinity of the membrane, flow should also be studied on the larger tank scale. The superficial air velocity inside the module relates to wall shear stress but also governs the circulating liquid velocity and thus the overall shear stress exerted (Prieske et al. 2010) turning fluid dynamics optimisation into a global optimisation problem where effects cannot be regarded independent of each other.

This talk will review these and other results of MBR fluid dynamics research.

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ICOM924

Computational Fluid Dynamics modelling of shear stress induced by aeration in a submerged hollow fibre membrane bioreactor: impact on biological media and consequences on membrane fouling

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Membrane fouling still limits a wider development of the Membrane BioReactor (MBR) process. A widespread solution to enhance membrane performance is the use of air sparging to remove fouling. However aeration is the main operational cost (Gil *et al.*, 2010) that should be improved to enhance the process. Its effect upon membrane filtration remains incompletely understood. Several local mechanisms were identified to explain the effect of bubbling on fouling: turbulences, fibre movement and shear stresses.

Recently shear stresses were calculated on hollow fibres membrane surface thanks to Computational Fluid Dynamics (CFD) and related to membrane fouling (Martinelli *et al.*, 2010). To further improve MBRs operation, studies should be led at this local scale but with more general conditions (wastewater as effluent, higher suspended solids concentration, higher packing density) to provide global trends that would be useful for full scale operation. Gathering these conditions, our work integrates the biological dimension to the study with the assessment of aeration impact on biological media through shear stresses.

A CFD model was developed to simulate the two-phase flow induced by aeration with the CFD code Fluent. Experimental values of bubbles size and velocity obtained in Braak *et al.* (2011) were used to calibrate it. This model enabled to evaluate the shear stresses imposed on the activated sludge in the module during filtration.

A hollow fibre SMBR pilot was run in semi external configuration (Lorain *et al.*, 2010). Instantaneous SAD_m (Specific Aeration Demand per membrane unit area) and filtration fluxes were the studied operational parameters. Different filtration/relaxation ratios were tested for sequences of 5mn. The average filtration flux was set to $6L.h^{-1}.m^{-2}$ and the mean SAD_m to $0,5m^3.h^{-1}.m^{-2}$. The instantaneous values of filtration fluxes and airflow rate were adapted in each sequence to match these mean values. Mixed liquor was characterized by the Extracellular Polymeric Substances (EPS) concentrations (both bound and soluble) and Particule Size Distribution (PSD). Fouling was monitored by TransMembrane Pressure (TMP) increase rate.

Our study explained the influence of aeration on permeability loss through biological media stability influenced by shear stresses. Providing shear stress values, CFD model aims to define a suitable shear stress range to balance fouling removal and mixed liquor integrity.

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ICOM1418

An alternative to chemical cleaning in MBRs: investigation of the mechanical action of the ultrasounds on membrane fouling

Adrien Moreau, Line Fournier, Thomas Thouvenot, Sébastien Logette
Veolia Environnement Recherche et Innovation, Maisons Laffitte, FR

Introduction and objectives

The membrane bioreactor process (MBR) is now a well-established technology which allows biological flexibility combined with an effluent quality suitable for potential reuse [1]. Chemical cleanings, mostly based on sodium hypochlorite solutions, are currently implemented on weekly or monthly bases in order to maintain cost effective membrane performances. However, the use of sodium hypochlorite in municipal applications is becoming an important issue due to the by-product formation and the lack of tolerance of the RO membranes to free chlorine (for the Reuse applications). Ultrasounds are widely used for commercial cleaning processes [2].Some publications [2-3] also reported the use of ultrasounds for flux enhancement during membrane filtration, mostly at laboratory-scale. However, there is still many unknown on the effect of the ultrasounds in this field.

The aim of the study was to figure out if the mechanical effect of the ultrasounds could improve the membrane cleaning and the membrane performances of an MBR, and therefore be considered as an alternative to the conventional chemical cleanings. The effects of the ultrasounds were investigated under three configurations in this study. Ultrasounds were implemented firstly as Cleaning In Place (CIP) replacement, then as maintenance cleaning replacement and finally as backwash replacement.

Materials and Methods

The study was performed with an MBR equipped with hollow fibre membrane (GE-Zenon Zeeweed 500d) with a membrane area of 63.3m^2. The study was performed with two industrial ultrasonic transducers. Details of the set up and the experiments will be available in the full paper.

Results and discussions

The effects of ultrasounds were investigated as a replacement for the CIP, the maintenance cleaning and the backwash. No significant effect, identical behaviour than with sodium hypochlorite and a slight improvement in membrane performances were observed for the CIP, the maintenance cleaning and the backwash replacement, respectively. These results are interesting especially for the maintenance cleaning replacement. An irreversible fouling prevention equivalent to the one obtained with chemical cleanings on weekly bases can be obtained for an OPEX significantly inferior and a free chemical process. With regards to the fact that the ultrasounds implementation was not fully optimised, this pilot-scale study can be considered successful.

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ICOM267

Characterization of shear influence on fouling of rotating ceramic membranes in a high shear Membrane Bioreactor using the TMP-step method

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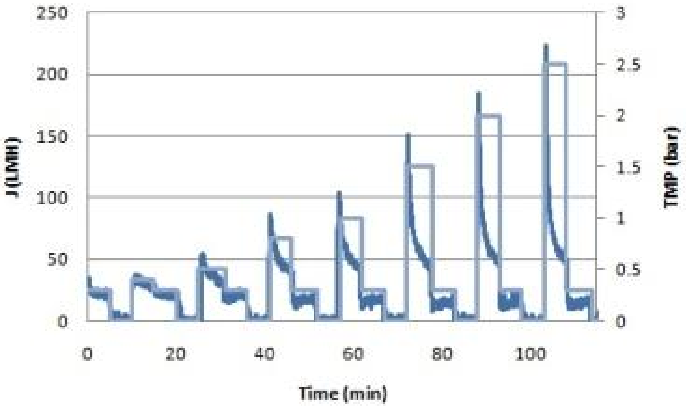
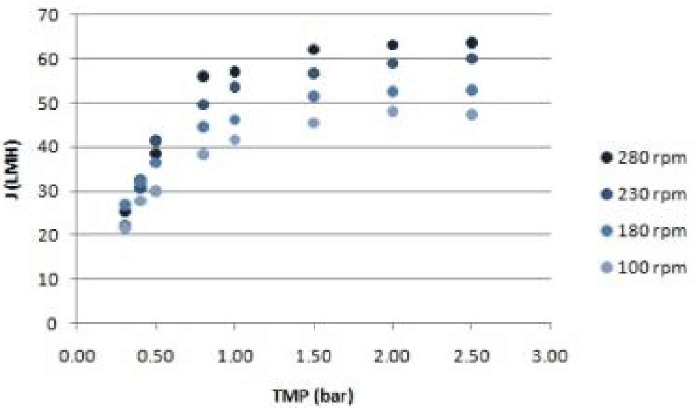
Membrane BioReactors (MBR) is believed to be the dominating technology for treating both domestic and industrial waste water in the future. The technology is a combination of a conventional activated sludge wastewater treatment plant and membrane filtration. Therefore, an MBR plant consists of both a bioreactor and a membrane unit, either submerged into the bioreactor or in a sidestream configuration. However, MBR systems have a major limitation to distribution due to fouling of the membranes. Fouling gives lower process efficiency and thus higher operational costs. One of the objects to control fouling is to create a shear along the membrane, preventing accumulation of foulants. Therefore Grundfos Biobooster has developed a unique MBR system, using rotating ceramic membranes. This enables treatment of concentrated sludge (MLSS up to 40 g/L) at high pressures (TMP up to 2.5 bar). To characterize fouling of a high shear MBR, the following mass balance is used, based on the transport of foulant to membrane (N):

$$N = J \cdot C - D \cdot dC/dx + p(\zeta) + q(\tau)$$

In the mass balance $J \cdot C$ denotes foulant transport to membrane from permeation drag, $D \cdot dC/dx$ is brownian diffusion of foulant away from membrane, $p(\zeta)$ is membrane-foulant and foulant-foulant interactions while $q(\tau)$ is the impact from shear induced diffusion. When $N=0$ there is a steady state in flux, but at $N>0$ the transport of foulant to the membrane exceeds the transport away from the membrane resulting in fouling. To study the influence of shear induced diffusion on fouling this model is used to interpret data from TMP-step experiments. The flux is measured in 5 minute intervals at different TMP from 0.3 - 2.5 bar to determine the decline in flux at different TMP, as shown in the following figure.



Between each step there is relaxation at 0.3 and 0 bar to restore permeability. TMP-step sequences were carried out at different rotation speeds at a lab-scale MBR inspired by the Grundfos BioBooster. The following figure shows the flux measured after 5 minutes of filtration at the different TMP-steps and rotation speed.



At TMP above 1 bar lower process efficiency is observed, as the flux at the end of the step does not increase with increasing TMP, but remain constant, i.e. a steady state in flux is obtained. However, the steady state flux increases with rotation speed as a result of enhanced shear. According to this, a linear relationship between steady state flux and roations speed is observed: $J = 0.0932 \cdot v_{rotation} + 35.590$, $R^2 = 0.9922$. These data are used to characterize the parameters in the mass balance.

Based on the results of the present study, it was possible to characterize shear influence on fouling and find optimal operation parameters for a high pressure and high shear membrane bioreactor using TMP-step experiments and describing the development in flux with a mass balance consisting of key parameters for membrane fouling.

ICOM668

Flat Sheet MBRs with Slug Bubbling: An Industrial Application in Xiamen

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Aeration in MBRs mitigates membrane fouling but the energy consumption for aeration is still one of the major operating cost for all MBRs in industrial application. Slug bubble was proved to be an effective to release membrane fouling and enhance flux in various membrane processes. But the information of industrial application of MBR to treat wastewater treatment is still limited. This paper investigates the performance of an industrial-scale flat sheet MBR treating municipal wastewater at very low aeration rates.

A flat sheet MBR contains of 75 pieces of flat sheet membranes and the total membrane area of 60m^2 was connected with a slug bubbling aeration system. Compared with the recommended aeration intensity (10-15 L/min/piece) by the supplier, a very low aeration intensity (1.5-3 L/min/piece) with slug bubble was provided to release membrane fouling. The MBR was running for 6 months at the local municipal wastewater treatment plant in Xiamen. It was found that slug bubbles show excellent antifouling performance under an averaged flux of 6-10 $Lm^{-2}h^{-1}$. The wastewater contains of 200-300 mg/L COD and 40-50 mg/L NH_4-N and the permeate contains less than 50 mg/L $COD_{averaged}$ and 5 mg/L NH_4-$N_{averaged}$ during 6 months operation.

The result shows that slug bubble gave an excellent performance not only to limit the reversible fouling during the bubbling period but also to release the fouling that had occurred during the non-bubbling period, And the energy consumption was analysis with the published free bubble data. The result indicates slug bubbling in flat sheet MBRs might be an attractive alternative method to achieve low-carbon MBR.

Desalination 2

ICOM1784

An Overview of the Global Desalination Situation

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According to the International Water Management Institute (IWMI), one in three people globally endures some form of water scarcity, one-quarter of the world's population lives in areas where water is physically scarce, and over a billion people live where water is economically scarce. Existing water supplies may be limited in quantity or quality for meeting the increasing demands from population growth and industry expansion. In many arid and semi-arid areas, providing the large volume of water required for industrial, agricultural, recreational and potable applications is especially difficult. The United Nations declared 2005-2015 the “Water for Life” Decade because water is crucial for sustainable development. The goals of the “Water for Life” Decade are to reduce by half the proportion of people without access to safe drinking water, to stop unsustainable exploitation of water resources, to aim to develop integrated water resource management and water efficiency plans, and to halve the proportion of people who do not have access to basic sanitation.

Membrane processes are now a proven and reliable method of providing high-quality, cost-effective water. Membrane technologies have immediate applications to treatment of fresh, brackish and seawaters, as well as wastewater reclamation. With innovative module design and engineering, micro- and ultra-filtrations have become effective and economical for drinking water production, particularly for removal of microorganisms. Desalination is becoming more and more a commodity to satisfy the growing demand for water.

ICOM357

Limitations, Improvements and Alternatives for the Silt Density Index

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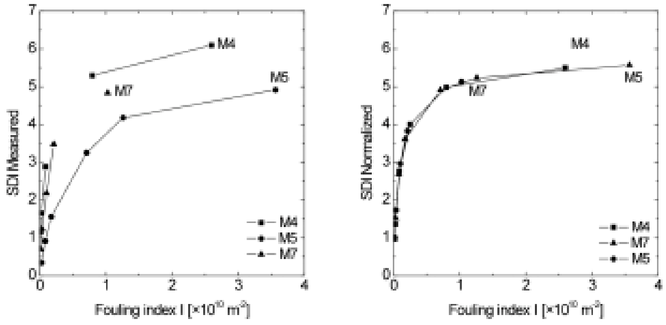
RO membrane systems are widely used in the desalination of water. However, flux decline due to fouling phenomena in RO remains a challenge. To minimize fouling, a reliable index is necessary to predict the fouling potential of the RO feed water. The ASTM introduced the Silt Density Index (SDI) as a standard fouling index to measure the fouling potential due to colloidal and suspended particles. For decades, the SDI is world wide accepted and applied. However there are growing doubts about the predictive value of this parameter. In addition there are several deficiencies observed, affecting the accuracy and reproducibility e.g. no correction factor for temperature, nor for variations in membrane resistance, and no linear correlation with the concentration of colloidal/suspended particles.

This paper gives an overview of our work on limitations, improvements and alternatives for the SDI. Firstly, the influence of the applied 0.45 µm test membrane on the SDI will be investigated. Variations in SDI values can be attributed to differences in properties of these membranes. In order to quantify the influence of pressure, temperature, and membrane resistance on the SDI a mathematical relation was developed between the SDI and the MFI0.45, assuming cake filtration. In addition, also other fouling mechanisms were incorporated in the model using the well known blocking laws.

Based on a cake filtration fouling mechanism and assuming 100% particle retention, the models were used to normalize the experimental SDI values for temperature, pressure and membrane resistance to the SDI+. By applying this normalization, the results of SDI tests carried out under different conditions and/or with different membranes can be compared easily (Figure 1) as was proven experimentally in the lab and at a seawater desalination plant.

Finally, an alternative filtration index will be introduced, the volume based SDI_v. The SDI_v compares the initial flow rate to the flow rate after filtering a standard volume of feed water using MF membranes with an average pore size of 0.45 µm. SDI_v has a linear relationship to the particle concentration if complete blocking is the dominant fouling mechanism during the test. Our mathematical model shows that SDI_v is independent of the testing parameters and membrane resistance. In that way it eliminates most of the before mentioned disadvantages of the SDI and has great potential to replace the SDI in the field.



(a) (b)

Figure 1. a: Measured SDI values b: SDI normalized for membrane resistance and testing condition parameters T=10 °C and =53600 µS/cm (SDI^+).

ICOM578

Real-time monitoring of mineral scaling in RO membrane desalination – fundamentals of surface crystallization, process optimization and RO plant control

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A novel approach was developed for real-time monitoring of mineral scale formation on RO membranes in order to detect the onset of scaling, determine recovery limits, quantify the antiscalant effectiveness and other scale mitigation strategies, and enable optimal control of RO plant operation. The approach is based on direct observations of mineral crystal growth on the membrane surface in an optically transparent high pressure a plate-and-frame RO (PFRO) cell. Mineral scaling in this membrane monitoring (MeMo) system is followed by real-time comparison of consecutive membrane surface images via specialized image analysis software (operating either on-line, or in a post-processing mode), developed specifically for the MeMo system, enabling real-time detection of the onset and development of mineral scaling. The MeMo system can be used for stand-alone studies or for online RO plant monitoring and control. In the latter application, operating conditions in the MeMo RO cell (i.e., cross flow velocity and transmembrane pressure) can be adjusted to match conditions in the monitored membrane plant (e.g., in the tail RO element) in order to mimic the surface scaling processes taking place within the monitored RO plant element. In the present work, the MeMo monitoring system was applied to: (a) fundamental analysis of membrane scaling with and without antiscalants, and (b) as a detector for early warning of the onset of mineral scaling and control of RO plant operation so as to avoid scale formation under challenging operating conditions. RO mineral scaling tests (using gypsum as a model scalant) were carried out with the stand-alone MeMo system, under identical operating conditions (i.e., with respect to the initial flux and crossflow velocity) to ensure essentially identical initial concentration fields within the MeMo PFRO channel. The kinetics of gypsum scaling were determined, over a reasonably wide range of solution saturation conditions of practical interest, from a single mineral scaling run. This part of the study demonstrated that, through direct surface analysis of crystal nucleation and growth, along with numerical CFD model simulations of the detailed concentration polarization field, it is possible to determine the effectiveness of antiscalant scale suppression (e.g., with respect to both retardation of crystal nucleation and growth) as a function of solution supersaturation conditions at the membrane surface. Accordingly, antiscalant crystal nucleation and growth retardation factors were derived to aid in the development, selection and dose optimization of antiscalants for use in RO desalination as well as for assessing the limits on product water recovery imposed by mineral scaling. In the second part of the study, the MeMo system was field deployed with our RO pilot facility and demonstrated to enable rapid determination of the optimal desalination operating conditions (for a scale-free and sustained operation) in a field study with brackish feed water of high mineral scaling propensity and diurnal salinity fluctuations. In addition, feed flow reversal mode of operation of the RO plant was shown to be effective for mitigating mineral scaling, without the use of antiscalants, where triggering of feed flow reversal was facilitated by the MeMo scale detector.

ICOM500

Diagnostic analysis and fault detection of RO membrane desalination via machine learning

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Optimal control and optimization of reverse osmosis water desalination plants under conditions of changing water feed salinity, temperature and pH require accurate RO process models that are specific to the plant under consideration. In this regard, the use of data-driven RO plant operation models, based on machine-learning, can be particularly useful for developing and deploying process optimization and control strategies, streamlining pilot plant studies, forecasting of plant performance, and assessing operational deterioration (e.g., due to membrane fouling and mineral scaling, as well as failure of plant components and membrane performance degradation). Accordingly, the present study presents a systematic approach for the development of data-driven models of RO membrane plant operation based on real-time data generated from a novel fully-automated and remotely controlled mini-mobile-modular (M3) RO pilot plant designed and built at UCLA. Laboratory and field studies with the M3 plant were over a wide range of process conditions (e.g., product water recovery, feed salinity, temperature, pH, feed pressure and cross flow velocity). The M3 RO plant was operated in a closed-loop configuration (i.e., RO brine and permeate recycled to the feed tank) in the laboratory and in a once-through operation in the field. The M3 RO plant was programmed to autonomously and rapidly generate, via the M3 embedded computer controlled system, random and prescribed cyclical process conditions (including the effect of process perturbations) under both dynamic (trajectory toward control set points) and steady state operations. With the above system, membrane characterization and fault detection were achieved in real-time. In addition, plant data (recorded at high frequency) was utilized to develop data-driven models based on Self-Organizing-Maps (SOM) and Support Vector Machines (SVM) to characterize the different operating regimes and identify the transition paths between different RO plant states. Identification and quantification of the characteristic operating trajectories served as a basis for arriving at specific optimal operational criteria (e.g. energy savings and permeate productivity) while meeting with operational restrictions (e.g., avoidance of membrane fouling and mineral scaling). The use of machine-learning for the development of virtual-plant model was also explored with the goal of providing a unique tool for the design of control schemes and fault detection. The present study demonstrated that data-driven RO plant models can be developed with a reasonable level of accuracy, and can be used in tandem with deterministic models to describe the complete domain of plant operability under both steady and unsteady state conditions.

ICOM505

Biofouling detection using flow cytometry and other analyses: Experiences from the Adelaide Desalination Pilot Plant

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Biofouling detection using flow cytometry and other analyses: Experiences from the Adelaide Desalination Pilot Plant

Membrane desalination technology is expanding worldwide, but in particular the technology in Australia has grown rapidly in response to drought and climate change. Six large municipal seawater reverse osmosis plants are being constructed or have been commissioned in Australia. The 300ML/day Adelaide Desalination Plant in South Australia is currently under construction and will commence operation in late 2011. Minimising energy and chemical usage are key to optimising the operation of desalination plants. Control of biofouling is critical to achieving this objective. Various methods for the control of biofouling have been proposed including ultrafiltration pre-treatment, dosing of biocides, phosphorus limitation and membrane modification. However, rapid detection of biofouling in spiral wound reverse osmosis modules remains important for optimal biofouling control.

At the Adelaide Desalination Pilot Plant, several detection methods were evaluated and used simultaneously to maximise information on the biofouling of membranes. One potential method for in-situ biofouling detection is Flow Cytometry (FCM), a technique used for accurately counting bacterial cells. The technique can perform detailed light scattering and fluorescent signal measurements on single bacterial cells at a rate in excess of 1000 cells/sec. Hence, bacterial data from a water sample can be acquired and processed rapidly and, if necessary, corrective action can be taken sooner when compared with samples processed using conventional culture-based techniques. FCM was used in conjunction with the fluorescent dyes from the LIVE/DEAD® BacLight™ bacterial viability kit for detection of live and dead cells. In addition to FCM, seawater culture media and 16S RNA profiling were used to identify the bacterial species on the membrane surface. Feed and process waters were analysed using Size Exclusion Chromatography with a fluorescence detector and Liquid Chromatography using an organic carbon detector to identify the presence of Extracellular Polymeric Substances (EPS), which are considered to be the conditioning contaminant responsible for biological adhesion to membrane surfaces. Autopsies were performed on several elements and Fluorescent In-Situ Hybridisation (FISH), Fluorescent Excitation Emission Microscopy (FEEM), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS) analyses were performed to provide further information on the EPS adhered to the membranes.

Results showed varied log removals of bacteria by the reverse osmosis membranes using FCM. This change in removal may indicate either an increase in biofouling as bacteria become bound to the surface of the membrane, or sloughing of bacteria as the biofilm on the membrane surface matured (Figure 1). 16S RNA analysis identified the exact bacterial species (Figure 2) within the biofilm which allowed or identification of problem bacteria in the feedwater. This may assist in further investigations for developing in-situ biofouling detection methods.

FCM has the potential to enhance in-situ detection of biofouling in reverse osmosis modules, in conjunction with other complimentary analytical methods.

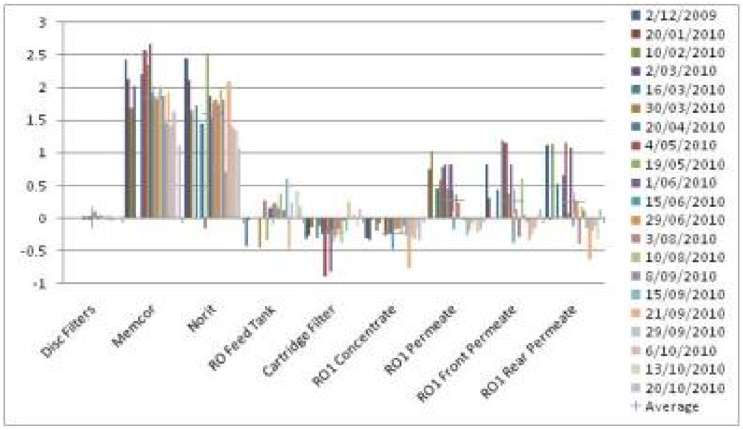
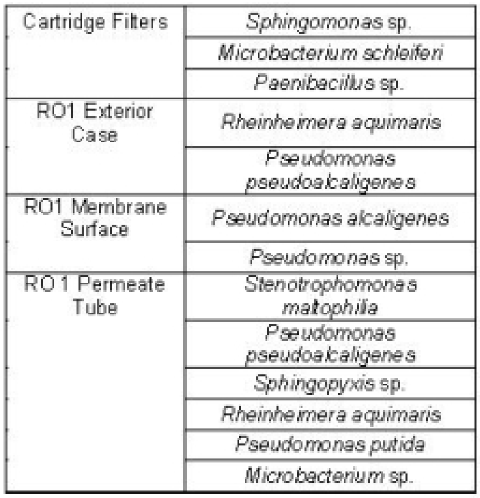


Figure 1 Log removal of active bacteria using FCM



Cartridge Filters	*Sphingomonas* sp.
	Microbacterium schleiferi
	Paenibacillus sp.
RO1 Exterior Case	*Rheinheimera aquimaris*
	Pseudomonas pseudoalcaligenes
RO1 Membrane Surface	*Pseudomonas alcaligenes*
	Pseudomonas sp.
RO 1 Permeate Tube	*Stenotrophomonas maltophilia*
	Pseudomonas pseudoalcaligenes
	Sphingopyxis sp.
	Rheinheimera aquimaris
	Pseudomonas putida
	Microbacterium sp.

Figure 2 Bacteria identified by 16S RNA

Facilitated transport membranes 1

ICOM1852

Facilitated Transport in the Solid State and Its Applications for Olefin Separation Membranes Using Activated Metallic Nanoparticles as a Carrier

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Olefin/paraffin such as propylene/propane and ethylene/ethane mixtures have been commonly separated by cryogenic distillation process requiring intensive-energy consumption and large space. Therefore, novel energy-saving process has been ever demanding. Facilitated transport membranes in the solid state have been attracted as an alternative process because they can increase the selectivity and the permeability simultaneously. In facilitated transport membranes, carrier mediated transport occurs in addition to a normal Fickian transport because of the reversible interactions between the carrier and specific solute. The facilitated transport therefore depends on the carrier activity significantly, which is commonly characterized by reversible interactions with a specific solute in mixtures, and consequently plays a major role in determining the separation performance.

Metallic silver nanoparticles show small interactions with olefin according to *ab initio* quantum mechanical calculations, suggesting a weak carrier activity for facilitated olefin transport. The carrier activity of silver nanoparticles may be further enhanced by inducing partial positive charge on the surface of the metallic nanoparticles by electron acceptors or polarizers such as *p*-benzoquinone (*p*-BQ), tetracyanoquinodimethane (TCNQ) or ionic liquids, resulting in much higher separation performance of olefin/paraffin mixtures [1-4]. Furthermore, activated silver nanoparticles have shown much longer long-term stability than the cationic silver ions as an olefin carrier. In these regards, metallic nanomaterials as an olefin carrier could be much more plausible than silver cations for the facilitated olefin transport. Here, recent studies on metallic nanomaterials as a novel olefin carrier will be introduced. (Ag, Au and Cu).

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ICOM1102

Dynameric membranes: toward an adaptive constitutional transport

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Numerous artificial transport systems utilizing carriers, channel-forming or self-organized polymeric and hybrid superstructures able to orient, to select and to pump the ionic transport across membranes have been developed in the last decades. Artificial membrane materials are the subject of various investigations, offering great potentialities as well on the level of their chemical composition or organization as to that of the concerned applications. Of special interest is the structure-directed function of biomimetic and bioinspired membrane materials and control of their build-up from suitable units by self-organisation. The main interest focus on functional biomimetic membranes in which the recognition-driven transport properties could be ensured by a well-defined incorporation of receptors of specific molecular recognition and self-organization functions, incorporated in a hybrid dense or mesopourous materials. We are therefore proposing to review the membrane transport properties of such supramolecular membrane materials.

The first part begins with a survey of different methods and processes which can be used for the generation of molecular recognition-based hybrid materials.

Then basic working principles of self-organized membranes are provided in order to better understand the requirements in material design for the generation of functional membrane materials.

These results describe the simple synthetic hybrid biomaterials which successfully formed molecular recognition devices, transport patterns so as to enable efficient translocation events.

Finally actual and potential applications of such self-organized systems presenting combined features of structural adaptation in a specific nanospace will be presented. From the conceptual point of view these membranes express a synergistic adaptative behaviour: the addition of the fittest solute (ions, molecules and gaz, etc) drives a constitutional evolution of the membrane toward the selection and amplification of a specific transporting superstructure in the presence of the solute that promoted its generation in a first time. This is the interesting example of dynamic evolutive membranes “**dynameric membranes**” where a solute induces the upregulation of (prepares itself) its own selective membrane.

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ICOM1235

Modelling of facilitated transport in solid membranes containing active AgNP stabilized by PVP for the separation of propane/propylene gas mixtures

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Separation of olefins from their paraffins is of primary importance in the chemical industry. Traditional separation processes, like low-temperature distillation, are energy-consuming and voluminous due to the similarity in the boiling point of olefin and their corresponding paraffin. Therefore, alternative, energy-saving separation processes are required. Facilitated transport membranes in the solid state containing fixed site carriers dispersed in solid polymer matrix offer advantages over conventional membranes, such as high selectivity and high permeability, resulting in low energy consumption, and compact and modular design.

Olefin/paraffin separation through facilitated transport membranes in the solid state containing metallic silver nanoparticles (AgNP) dispersed in a polymeric matrix has attracted interest due to the good stability and high separation performance [1]. The separation performance is mostly associated with the large surface area and partial positive charge of the silver nanoparticles. The large surface area was obtained by using nanoparticles and the partial positive charge on the metallic silver surface was induced by an electron acceptor such as TCNQ. Silver nanoparticles can also be stabilized by crosslinked poly(vinyl pyrrolidone) (PVP).

This work provides a simple mathematical model of propylene/propane separation through facilitated transport membrane, which assumes Henry´s law gas solubility, reversible complexation of olefin with positively polarized AgNP and hopping of propylene from one fixed AgNP carrier to the next one. Physico-chemical parameters, namely propylene and propane diffusion coefficients, Henry's law and equilibrium constants in the membrane, necessary to predict the gas fluxes, have been experimentally determined. Finally, the unknown parameters, facilitated transport and kinetic constant of the reversible reaction, are obtained by comparing the data estimated by the software Aspen Custom Modeller with the experimental data series. Consequently, the facilitated transport process in the solid state was understood more precisely.

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ICOM1067

Stable ionic liquid polymer gel membranes for gas separation

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In spite of their high cost, ionic liquids (IL) offer interesting perspectives for use in membranes for gas and vapour separations [1]. In this study we discuss the preparation and characterization of stable polymer gel membranes based on the room temperature ionic liquid 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) in poly(vinylidene fluoride-*co*-hexafluoropropylene) (p(VDF-HFP)). Due to their gel structure, these membranes show excellent stability compared to traditional supported liquid membranes in which the IL is physically sorbed inside the pores of a porous membrane and which often suffer from leakage of the IL under the applied pressure difference.

Membranes containing from 20 wt.% to 80 wt.% of the IL were prepared by solvent casting from a solution in acetone [2]. The gel properties were studied by Differential Scanning Calorimetry (DSC), X-Ray diffraction, tensile tests and density measurements. DSC analysis shows a gradual decrease of the melting point of the gel and a decrease in the overall melting enthalpy with increasing IL content (Figure 1). The IL also reduces the elastic modulus and break strength dramatically, while the maximum deformation first increases due to higher flexibility of the plasticized polymer and then rapidly decreases above 40 wt.% of IL, as a consequence of the progressive decrease of the number of entanglements. At 80 wt.% of IL the Young's modulus is three orders of magnitude lower than that of neat p(VDF-HFP).

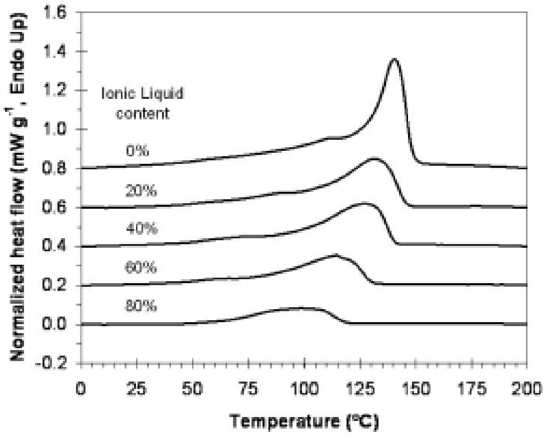

Figure 1. Melting peak in the second DSC heating run of the polymer gel as a function of the IL content [2].

The IL improves the gas transport properties significantly. The effective solubility and diffusion coefficients and the permeability of six permanent gases show that the membrane changes from a barrier material for pure p(VDF-HFP) to a highly permeable membrane at 80 wt.% of IL. The dramatic increase in permeability is mostly due to a higher diffusion coefficient. This is related to the strong plasticization effect of the IL and to the reduction of polymer crystallinity with increasing IL content.

For most gases the increase of permeability is coupled with a moderate selectivity reduction and the data move parallel to or in the direction of the Robeson upper bound. The opposite behaviour is observed for the CO_2/H_2 pair, for which the IL enhances the selectivity (Figure 2). This makes such membranes potentially interesting for applications where CO_2 should be removed from a H_2 rich stream. A detailed discussion on the preparation and the performance of these membranes will be presented.

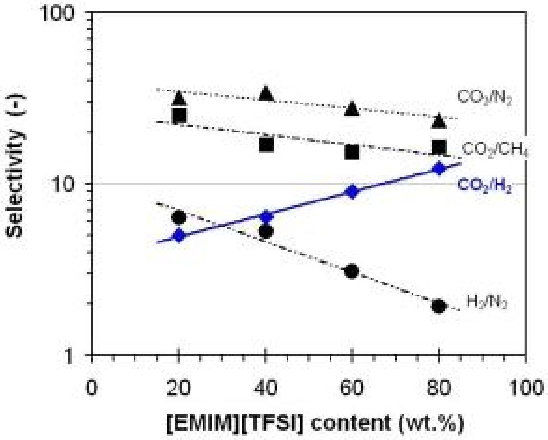

Figure 2. Selectivity of selected gas pairs as a function of the IL content [2].

Acknowledgements: This research was financially supported by the CNR-CAS bilateral agreement 2010-2012, by the Czech Ministry of Education, Sports and Youth MSM (Grant No. 6046137307), by the Czech Science Foundation (Grant No. P106/10/1194) and by the Grant Agency of the Czech Republic (grant no. 203/08/0465).

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ICOM478

CO_2-selective facilitated transport membranes for hydrogen purification for fuel cells

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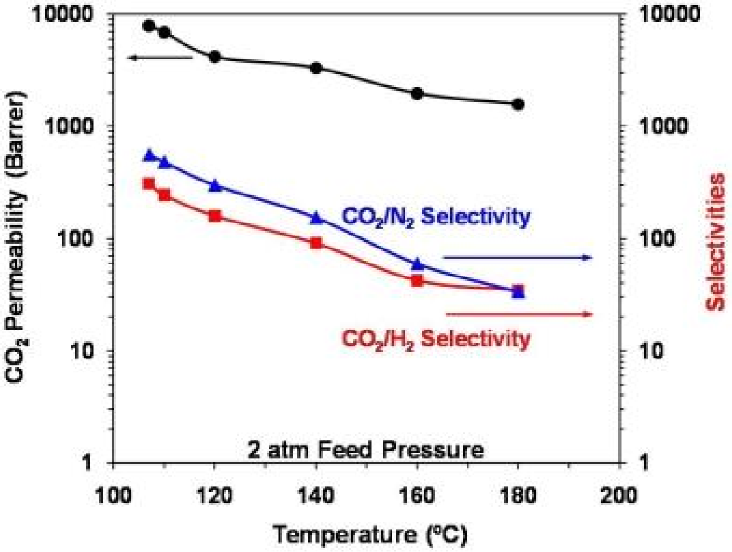
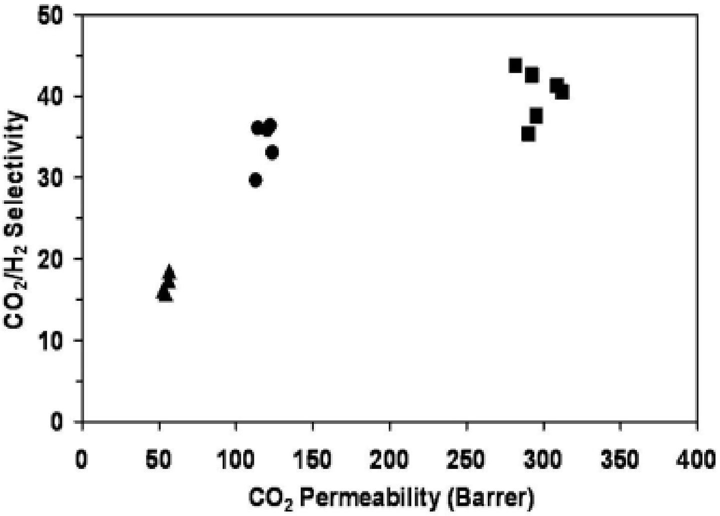
CO_2-selective facilitated transport membranes have been synthesized by incorporating amino groups into polymer networks for hydrogen fuel processing for fuel cells. These membranes are selective to CO_2 and H_2S preferentially versus H_2 since the acid gases permeate through the amine-containing membranes via the facilitated transport mechanism due to their reversible reactions with the amine. But, H_2, CO and N_2 are rejected by the membrane due to their absence of reaction. The membranes synthesized have shown high CO_2 permeability and selectivities vs. H_2 and N_2 up to 180°C.



The CO_2 permeability was greater than 3000 Barrers, the CO_2/H_2 selectivity was at least 90, and the CO_2/N_2 selectivity was higher than 150 at 100 – 140°C. However, the permeability reduced to about 1800 Barrers, which is still quite high, as the temperature increased to 180°C. This was due to the reduction of water retention in the membrane as the temperature increased. At 180°C, both CO_2/H_2 and CO_2/N_2 selectivities reduced to about 34, which is considered to be reasonably high as it is still good enough to give a high H_2 recovery of ~95%. In addition, the CO_2/CO selectivity obtained was at least 2000, which is very high. These results indicate that the membrane should be well suited at 100 – 120°C for H_2 purification and CO_2 capture, in which the membrane has the best performance with a CO_2 permeability of 5000 – 6500 Barrers, a CO_2/H_2 selectivity of about 170 and a CO_2/N_2 selectivity of about 400.

Since H_2S has much higher reaction rate with the amine than CO_2, H_2S permeates through the membrane much faster than CO_2. This allows the complete removal of H_2S in the treated synthesis gas before water-gas-shift (WGS) reaction. Our initial experiments have shown a nearly complete removal of H_2S from 50 ppm in the synthesis gas feed to about 10 ppb in the hydrogen product. Using the membrane, we have obtained <10 ppm CO in the hydrogen product in WGS membrane reactor experiments via CO_2 removal. The data have been in good agreement with our modeling predictions. CO_2 was also removed from a syngas containing 17% CO_2 to <30 ppm, resulting in >98% CO_2 in the acid gas stream for sequestration.

Moreover, sterically hindered secondary amines, e.g., poly-N-isopropylallylamine and poly-N-tert-butylallylamine, have been synthesized from the unhindered primary amine, polyallylamine, and incorporated as the improved fixed carriers into membranes. FTIR spectra revealed that the primary amino groups of polyallylamine were successfully converted to the secondary amino groups. In side-by-side comparisons, the CO_2 permeability obtained from membranes containing 70 wt.% of the sterically hindered amine was at least two times that from membranes containing the same amount of polyallylamine.



The average CO$_2$ permeabilities for moderately sterically hindered poly-N-isopropylallylamine **(■)** and severely sterically hindered poly-N-tert-butylallylamine (●) were 5.4 and 2.2 times that for polyallylamine (▲), respectively. The CO$_2$/H$_2$ selectivities for poly-N-isopropylallylamine and poly-N-tert-butylallylamine were 2.4 and 2 times that for polyallylamine, respectively. These results showed that CO$_2$ transport capability of the fixed carrier was enhanced significantly by steric hindrance.

Richard W. Baker session

ICOM1821

Do the right thing and keep it simple

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I have learned many things from Richard Baker, but the most important one I have chosen as title for this presentation. "Do the right thing and keep it simple", I will not discuss this here as a general motto for a decent life, but I will relate it to membrane research. During the last years I was involved in two interesting projects: 1. Carbon capture from flue gas and 2. Manufacturing membranes by molecular self-assembly. Let me start with carbon capture. Is this the right thing to do? Will it be beneficial for the environment? The right starting point to find the answer to this question is not to ask what techniques are available or what could be the best membrane to do the job, but to look at the process as a whole and here thermodynamic is a good adviser. Thermodynamic teaches us that a theoretical minimum of about 11 % of the output energy of the power plant is required to capture and compress 90 % of the carbon dioxide. Under no circumstances you can beat this number. Looking at the efficiency of the blowers, compressors, vacuum pumps etc. the real energy consumption will be at least twice as high, so we can assume that about a quarter of the power plants energy is required for the carbon capture. This result already diminishes the enthusiasm for the process. Now let us look into the membrane process. Even with the best available experimental membranes at least a million square meters of membrane area are necessary to recover the CO2 of a 600 MW coal fired power plant. This is not very encouraging, but it is possible. So we still don't know if carbon capture is the right thing to do, but we know now, what is the wrong thing to do. It makes no sense to investigate in sophisticated systems like low flux facilitated transport membranes for this application or to put expensive enzymes into the process. We have to keep the process as simple as possible. The last question I often ask myself when analyzing a new process is: would I invest my own money into this technique? In the case of carbon capture I leave the answer till you hear the lecture, but if the answer is no, should we risk taxpayers money?

The second example I will examine under the light of the title motto is one of the current activities of my group: membrane preparation by molecular self-assembly. This seems to be a quite sophisticated process, but I will show you, how it can be kept simple. In this context another advice of Richard Baker will be discussed, which is "Be honest" /1/.

/1/ Richard Baker, Doing the Right Thing, Guest Viewpoint in Membrane Quarterly (NAMS), July 2006

ICOM1816

Commercial Potential of Microporous Polymers for Membrane-Based Gas Separation Applications

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[1]King Abdullah University of Science and Technology, Advanced Membranes and Porous Materials Center, SA, [2]Membrane Technology and Research, Inc., US, [3]National Research Council of Canada, CA

Membrane-based gas separation has been practiced as an economically viable separation technology during the past 30 years. Progress in this field resulted from significant improvements in materials science, development of high-performance membranes/modules, and optimization in process design. This presentation will focus on novel, intrinsically microporous glassy polymers, which may find applications in a wide variety of commercially important applications. The first generation of microporous glassy polymers was based on ultra-high free-volume glassy polyacetylene-based polymers, which exhibit the highest organic vapor/permanent gas selectivties coupled with the highest organic vapor permeabilities of all known polymers. However, a significant disadvantage of this class of materials is their inherent poor physical and chemical instability when operated under industrial conditions. Recently, Budd et al. reported that a new class of rigid, glassy ladder polymers, so called 'polymers with intrinsic microporosity' (PIM) may offer advantages over microporous polyacetylene-based polymers for membrane separations. This presentation will compare the transport properties of these two classes of microporous polymers for membrane separations. This study includes long-term gas permeability data of PTMSP and PIM-based materials. We studied the pure-gas permeation properties of PIM for over four years and the polymer's properties are exceptional. The initial oxygen permeability dropped from 1,535 Barrer to 523 Barrer; on the other hand, the initial oxygen/nitrogen selectivity increased from 3.7 to 5.3. These are unmatched permeation properties for air separation, which lie far beyond the typical Robeson permeability/selectivity trade-off. In addition, PIM is stable in hydrocarbon environment with very high mixed-gas selectivity and permeability. For example, PIM-1 has a mixed-gas *n*-butane/hydrogen selectivity of 30-50 depending on the feed composition. In summary, microporous glassy polymers exhibit properties, which are unmatched by conventional polymers and provide a window to broaden possible applications for membranes used for gas separations.

ICOM1822

On electro-chemical membrane reactors

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Ion exchange membranes find frequently use in electro-chemical conversion processes, the largest one being the chlor-alkaline electrolysis. They are also used in acid and base productions, in particular to convert organic salts into acids.
In fuel cell applications, membrane electrode assemblies convert fuel such as hydrogen and methanol into electricity. Also here, the membrane plays a crucial role in together with the catalysts.
Within the scenarios of a society based on renewable energy, demand increases on energy storage systems that can decouple natural cycles based on radiation and wind from power usage. Such energy storage systems are introduced in this presentation: redox flow batteries. In particular, this presentation focusses on the principles of the redox flow batteries and the various dimensions influencing the performance of this electro-chemical membrane reactor for energy storage.

ICOM1819

A View of Richard Baker's Contributions to Membrane Science From an Academic Perspective

Benny D. Freeman
University of Texas at Austin, Department of Chemical Engineering, Texas Materials Institute, and Center for Energy and Environmental Resources, US

Richard Baker is unique in the field of membrane science: (1) having studied under both Richard Barrer and Alan Michaels, (2) having produced two of the best fundamental textbooks for teaching membrane science[i] and controlled drug delivery[ii] while working in industry, (3) having co-authored highly cited journal articles surveying both the fundamental scientific foundations underpinning the transport mechanism operative in all solution/diffusion membranes[iii] as well as technological applications of membranes[iv], and (4) having created a unique culture of innovation at Membrane Technology and Research, Inc. which has given many leading membrane scientists their start and continues to serve as an incubator of innovative ideas for applying membranes in technologically important applications while having grown into a significant commercial supplier of membranes. His accomplishments serve as an example of the power of sustained, systematic application of fundamental science and engineering principles to real-world problems in separations. This presentation will survey Richard's accomplishments as they have influenced my research and teaching as well as my perception of Richard's influence on the field of membrane science.

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ICOM1857

A Career in Membrane Technology

Richard W. Baker
Membrane Technology and Research, Inc, US

Almost 50 years ago, I noticed a flyer on my college bulletin board: Professor R.M. Barrer of Imperial College had a British Gas Council Fellowship in his gift and was looking for a graduate student applicant to work on gas permeation in membranes. I knew nothing about Barrer or membranes, but becoming a graduate student was clearly better than getting a job and having to work. Barrer must have been short of applicants, since he gave me the slot after a ten-minute interview, and my career in membranes began.

Fifty years later, I am still a student of membranes, and for me it has always been better than work. When I entered the field, the total membrane industry had sales of only a few million dollars per year, and the study of membrane permeation was a sub-study of materials science. Since then, the membrane industry has grown a thousand-fold. I was fortunate to be present during this transformation and will describe how this industry was created, and the people who were involved.

Membrane formation 2

ICOM1834

The Fabrication Technologies of Polymeric Hollow Fiber Membranes: Past, Present and Future

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Abstract

Energy, water, affordable healthcare and global warming are four major concerns globally resulting from resource depletion, record high oil prices, clean water shortages, high costs of pharmaceuticals, and changing climate conditions. Among many potential solutions, advance in membrane technology is one of the most direct, effective and feasible approaches to solve these sophisticated issues. So far, polymeric hollow fiber membranes made from non-solvent induced phase inversion are the dominant products because polymers offer a broad spectrum of materials chemistry and result in membranes with a variety of physicochemical properties for various applications. The low cost and easy fabrication characteristics also make polymeric membrane superior to inorganic membranes. Therefore, this review not only highlights the state-of-the-art polymeric hollow fiber membranes made from non-solvent induced phase inversion, but also emphasizes on the membrane R & D as sustainable technologies for water and energy productions. We will cover several applications such as: (i) The basic principle of hollow fiber membrane formation and phase inversion process; (ii) Membranes for energy (natural gas, H_2, and biofuel) production; (iii) Membranes for CO_2 capture; and (iv) Emerging desalination technologies (forward osmosis and membrane distillation) for water production. In addition, the opportunities and challenges from the past and present developments in hollow fiber fabrication for future research direction will be elaborated.

Websites: http://www.chee.nus.edu.sg/membrane/ http://www.chee.nus.edu.sg/people/faculty_chungneal.html

ICOM1512

Solvent-Free Synthesis of Alkaline Anion Exchange Membrane for Fuel Cells via In-situ polymerization

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University of Science and Technology of China, Chemistry, Hefei, Anhui, CN

Traditional synthesis of AAEMs focuses on attachment of chloromethyl groups to polymer backbones and followed by quaternization. Although this method is convenient, the chloromethyl methyl ether, used as the chloromethylation reagent in most cases, is a carcinogen [1]. Hence, a lot of approaches towards avoidance of it, including post-polymerization modification and direct polymerization, have been developed [2-4]. However, they all require excess reagents and a large excess of solvent maintaining polymer solubility in the reaction medium will carries toxic risk to the environment during membrane formation.

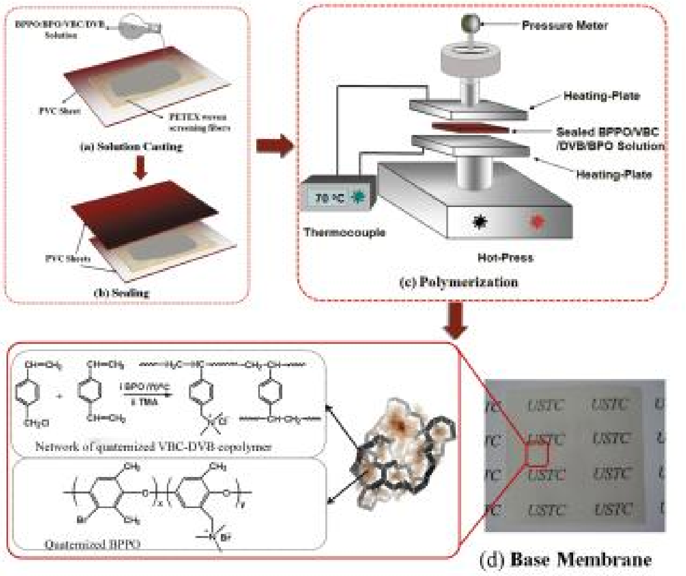

Figure 1 Schematic of the strategy to prepare base membrane

In this study, we described a solvent-free strategy for alkaline anion exchange membranes synthesis by in-situ polymerization. Different from the available modifications, this non-solvent strategy was performed by dissolving brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) in monomers mixture of vinylbenzyl chloride (VBC) and divinylbenzene (DVB), then in-situ polymerizing to incorporate BPPO into the network of poly(VBC-DVB) (Figure 1a, b, c). After quaternization, a translucent, flexible and robust anion exchange membrane was obtained (Figure 1d). The optimized membranes exhibited favorable water uptakes (ranging from 19.9% to 29.3%) and hydrated hydroxyl conductivities (ranging from 0.017-0.028 S cm^{-1}) at room temperature, excellent mechanical and alkaline stability (tensile strength of 41.7 MPa and stable in 2 mol L^{-1} KOH solution at 60℃ for 192 h). Those excellent properties allow its application in alkaline anion exchange membrane fuel cells (AAEMFCs). Moreover, this solvent-free strategy is not limited to the above BPPO/VBC/DVB system. It can be applied to other compatible systems of (aromatic) polymers and (aromatic) monomers as long as homogeneous cast solution of the monomers and polymers can be formed. Thus this research will provide a versatile environmentally friendly route to prepare anion exchange membranes with tailored properties for alkaline fuel cells.

Acknowledgements. This project was supported in part by the Natural Science Foundation of China (nos. 21025626, 20974106), the National Basic Research Program of China (No. 2009CB623403), the China Postdoctoral Science Foundation (no. 20090460060) and the Fundamental Research Funds for the Central Universities.

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ICOM1196

The use of FT-NIR spectroscopy for the online determination of the composition of casting solutions and cast films during industrial membrane manufacture

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Casting solutions used for the industrial manufacture of membranes usually have complex chemical compositions and often consist of a polymer, a solvent, one or more nonsolvents and additives. Fluctuations of composition in casting solutions may have a great influence on membrane properties (bubble point, throughput, retention, flow rate etc…). It is, therefore, crucial to accurately determine this composition during the casting process.

Due to the complex chemical nature of industrial casting solutions, it is common practice to combine several analytical techniques in order to achieve the full determination of the chemical composition. The conventional analysis of such casting solutions is mostly performed by combining chromatographic, coulombmetric and gravimetric methods. These lab techniques are known to be time consuming and high maintenance demanding. They often require particular sample preparation steps and are, therefore, not very suitable for online measurements. The online analysis of the composition of casting solutions is an essential step for the implementation of online adjustment of solvent and nonsolvent contents during casting.

New generation of FT-NIR spectrometers offer a way to circumvent this bottleneck. Near infrared radiations can typically penetrate much farther into a sample than mid infrared radiations. FT-NIR spectroscopy is thus a well established and robust technique for the online analysis of bulk material with no sample preparation. Due to the incorporation of state-of-the-art optics during the last decade, sensitivity and precision of FT-NIR instruments have been considerably improved.

This contribution demonstrates how FT-NIR spectroscopy may be calibrated and implemented in a casting line as an all in one solution for the rapid and precise determination of the full composition of industrial casting solutions (via transmission measurements) and cast films (via reflection measurements). The investigated casting solutions and cast films consisted of a polymer, a solvent, two nonsolvents and additives. It shows furthermore that the disturbing effects of temperature fluctuations and additives may be eliminated by considering them during the calibration of the system.

ICOM390

Macrovoids in membranes - Flux enhancers or integrity disturbers?

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Norit X-Flow B.V., Research and Development, Enschede, NL

Introduction

The development of new, innovative bio-mass based polymeric membranes is of strategic importance. Decreasing oil resources, the increase of the global warming and the awareness of need of more eco-friendly products from renewable sources are the major driving forces.
Anyways, it is of major interest to produce a membrane which is a) producible and b) chemically and physically resistant. Therefore Cellulose Acetate derivatives, which are produced from up to 70% of renewable sources, are chosen as membrane material [1]. Flat sheets and hollow fibre membranes are researched to show the influence of phase separation parameters on the transition phenomena of the material. Furthermore, the correlation between macrovoids and integrity of the membranes is investigated.

Experimental

Several dope solutions with different compositions are evaluated in this research to investigate the best composition forming macrovoid free, high flux membranes. The initial tests are performed on flat sheets whereas proof of principle is always performed at the lab spinning machine. The influence of temperature and casting thickness is researched to investigate the influence of the afore mentioned parameters on the structure of the membrane.

Results and discussion

The results show that the thickness of the membrane has an enormous influence on the formation of macrovoids. Furthermore, the experimental results show major differences in membrane formation between test flat sheet membranes and spun membranes as shown in Figure 1 and 2.

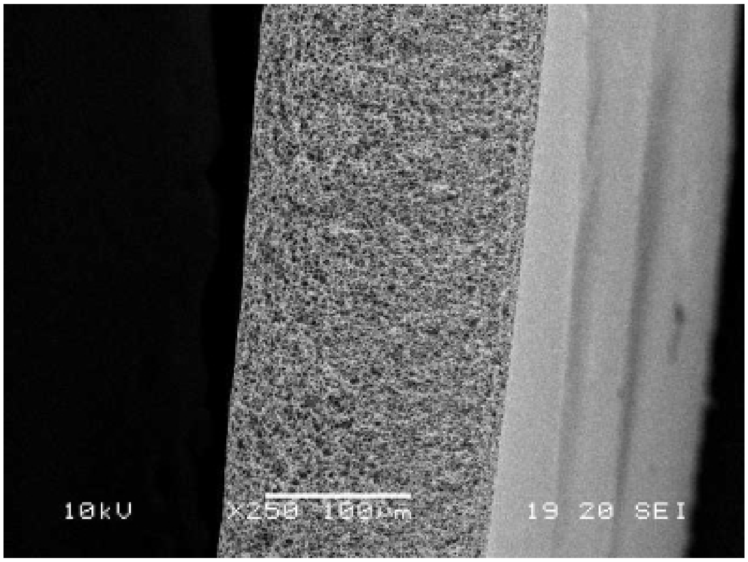

Figure 1: Flat sheet membrane.

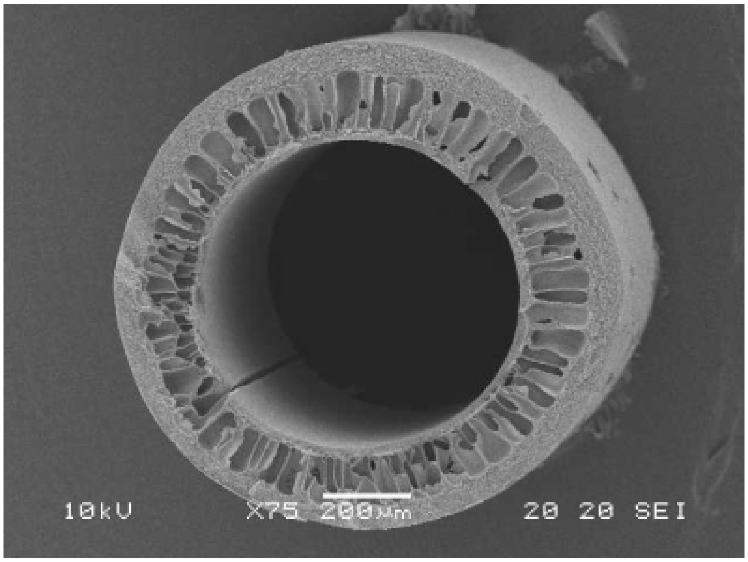

Figure 2: Spun membrane from the same dope solution.

Although the dope solution showed no tendency to form macrovoids in the flat sheet, spun membranes under the same circumstances show extreme macrovoid formation. These spun membranes are hardly producible, because of their fragility. This fragility is mainly introduced by the macrovoids in the structure.

Further investigation shows that tuning the phase separation parameters during the membrane formation leads to perfect sponge structured, macrovoid free membranes. A transition from brittle to ductile behaviour is observed when switching towards a macro void free sponge structure.

This investigation gives an overview on the possibilities of producing qualitatively high membranes from renewable sources. This research shows that the integrity of macrovoid free membranes is higher than that of membranes with voids. It is shown that by understanding phase separation phenomena and by translating it to full size production, a membrane with excellent mechanical and separation properties can be produced.

Acknowledgments

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 214653.

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ICOM571

Analysis of Solidification Rate of Polymer Solution during Membrane Preparation by Nonsolvent Induced Phase Separation

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Water purification process using polymeric membrane has been attracting a lot of attention as one of possible solutions for worldwide water problem. Although many studies were devoted to enhance membrane characteristics such as antifouling property, rejection and water permeability which determine the process performance, few studies were carried out for solidification of membrane during membrane preparation process which largely affects the production cost. In this study, membrane solidification process in nonsolvent induced phase separation (NIPS) method was investigated for effective membrane fabrication. The investigation of solidification process was carried out by measuring the repulsive force of polymer solution during the phase separation process.

Poly(vinylidene difluoride) (PVDF; Mw = 136,000) and dimethylacetamide (DMAc) were used as polymer and solvent, respectively. Water and mixture of water and DMAc was used as coagulation bath. The schematic diagram of strength measurement apparatus is shown in Fig. 1. 20–30 wt% PVDF solution with a frame was set on the movable stage. The stage moved upward at 50 μm/s and the surface of polymer solution contacted with a sphere set to the edge of needle. The membrane strength was measured by contacting polymer solution surface and the needle at arbitrary timing during phase separation by adjusting the start time of phase separation and stage movement. The displacement of blade spring measured by a laser displacement sensor was converted to surface repulsive force of the polymer solution.

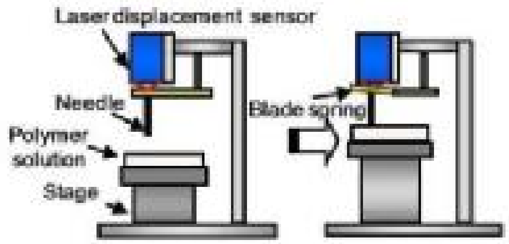

Fig. 1 Schematic diagram of strength measurement apparatus.

In the membrane strength evaluation, needle displacement x is plotted against the displacement of sample stage l. The slope of this plot represents the stress of the sample. After the plot is differentiated, $\mathrm{d}x/\mathrm{d}l$ at the contact of solution surface with the needle is adopted as the strength of the sample. $\mathrm{d}x/\mathrm{d}l$ lower than 1.0 means that the needle is partly sticked into the sample as a result of elastic or plastic deformation. The measurement with elastic deformation of the sample surface was adopted as a plot of the membrane strength.

The effect of polymer concentration in the solution on the membrane strength was investigated. Fig. 2 shows the plot of obtained slope $\mathrm{d}x/\mathrm{d}l$ against time. Solidification of polymer solution rapidly proceeded at the beginning of the phase separation, and it gradually reached saturation value for each membrane. Higher concentrations of PVDF solution resulted in faster and higher membrane strength.

The effect of coagulation bath composition was examined. Coagulation bath with the ratios of water to DMAc of 10:0, 8:2 and 5:5 were used for NIPS process. Solidification with the coagulation bath of 10:0 was the fastest system in the three compositions. The condition of water coagulation bath resulted in instantaneous phase separation and that of mixture of water and DMAc changed the process to delayed phase separation. The instantaneous phase separation brought about the faster membrane solidification during the membrane preparation.

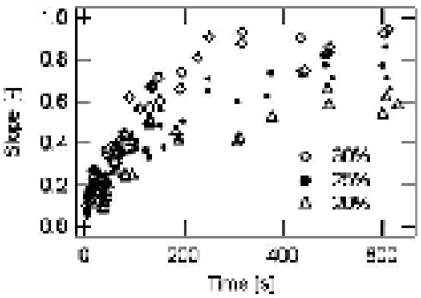

Fig. 2 Effect of polymer concentration on the solidification behavior.

ICOM 2011

Wednesday, July 27th 2011

Parallel Sessions

Wednesday, July 27th 2011

Morning Session 1, 8.30 – 10.20

Gas and vapor separation 4

ICOM1835

TRANSPORT BEHAVIOR OF POLYMER MEMBRANES FOR FLUE GAS TREATMENT

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Polymer membranes are a viable alternative for carbon capture processes. Two distinctively different classes of polymer materials have been recognized as potentially interesting, i.e. glassy and rubbery polymers. This work reflects extensively on the transport of CO_2 through two representatives of these classes for post combustion capture: the segmented block-copolymer PEBAX®1074 and the sulfonated polymer S-PEEK. The understanding of gas and water vapor transport phenomena through these membrane materials is particularly interesting because both materials differ in their chemistry and physical state:

- PEBAX shows molecular transport of gases and vapors through a soft rubbery, polyethylene oxide based phase.

- S-PEEK shows gas and vapor transport through an amorphous glassy phase containing ionic groups that will preferentially hydrate over the apolar matrix.

This work aims at understanding the molecular transport properties through these two types of polymers by investigating their sorption, diffusion and separation behavior. Little data is reported on multi-component mass transport through these polymers. Here we investigate the transport of single components, binary (water vapor/N_2 or water vapor/CO_2) as well as ternary (water vapor/CO_2/N_2) gas mixtures. Both the effect of water vapor activity and temperature is addressed.

Results show that water vapor sorption in both polymers increases with increasing water vapor activity, showing Flory-Huggins type sorption for the rubbery material PEBAX and Dual Mode sorption for SPEEK at low activities followed by Flory-Huggins sorption at higher activities. Kinetic diffusion coefficients of water vapor through the polymer membranes assuming constant frame of reference show a maximum as function of activity. However, after correction of these values for the extensive swelling of the materials, the kinetic diffusion coefficients increase with increasing water vapor activity and show equal behavior for both materials. Analysis of the state of the water molecules in the polymer matrix reveled that sorbed water molecules in PEBAX®1074 have a significant tendency to form water clusters in the polymer at each water vapor activity. This effect of water clustering in polymers is attributed to self-hydrogen bonding of water molecules due to strong penetrant–penetrant interactions. A profound thermodynamic analysis of water vapor sorption in PEBAX®1074 shows that enthalpically penetrant-penetrant interactions are indeed more favorable than polymer-penetrant interactions in PEBAX®1074. In S-PEEK, water molecules do not tend to cluster and remain isolated at almost all water vapor concentrations.

Permeation data for both binary and ternary mixtures show that extremely high water vapor/gas selectivities can be obtained at high water vapor fluxes. When comparing the binary and ternary systems, the presence of N_2 does not change the transport behavior of CO_2 through both membrane types, as is the case for the effect of the presence of CO_2 on the N_2 permeability in the rubbery material PEBAX. The presence of CO_2 does however significantly increase the transport of N_2 through the glassy polymer membrane SPEEK due to the occurrence of plasticization and relaxational phenomena (figure1A), resulting in considerably lower CO_2/N_2 selectivities for ternary systems when compared to binary systems in the case of such glassy polymer membranes (figure1B).

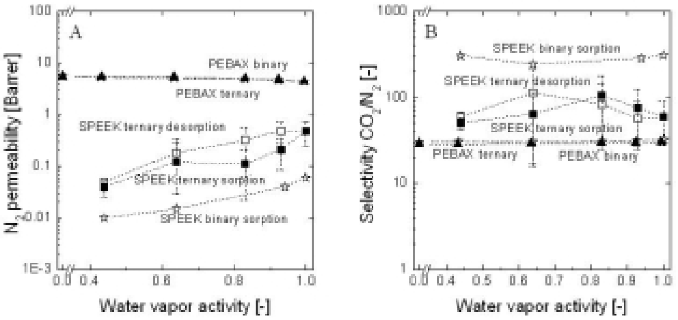

Figure 1: Separation performance of the rubbery material PEBAX and the glassy polymer SPEEK for both binary (CO_2/N_2) and ternary (CO_2/N_2/water vapor) systems during sorption and desorption. A) N_2 permeability and B) CO_2/N_2 selectivity.

ICOM1190

High Temperature Stable Supported Ionic Liquid Membranes for Gas and Vapour Separations

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Absorption of gaseous effluents from high temperature sources is an important area of investigation, from the environmental point of view. The aim of this work is the design of high temperature stable supported ionic liquid membranes (SILMs) for different applications, namely removal of dioxins from gaseous streams, separation of CO_2 from flue gas streams, and purification of natural gas.

Due to the ability of RTILs to absorb dangerous dioxin compounds from a vapour phase above room temperature, and due to their negligible vapour pressure, the concept of immobilizing RTILs in porous supports is expected to be an efficient process for recovering toxic compounds from effluents by vapour permeation at high temperatures (above 200 ºC). In order to evaluate the efficiency of this concept, a new procedure of immobilising RTILs in the porous structure of ceramic membranes with different pore size was developed. The RTILs selected were stable at high temperatures (higher than 250ºC) and presented a high solubility towards different dioxins. Stability studies were performed and it was demonstrated that the tested ceramic membranes effectively retain the immobilized RTIL at high temperatures (up to 150 ºC), resulting in a very stable membrane. Experimentally different conditions were tested: flow rate, membrane pore size, type of RTIL, and type of dioxin . The results show that a significant amount of dioxins is captured by the SILM at high temperatures (between 50 % and 70 %), which validate the potential of using ceramic membranes immobilized with RTILs in separation of dioxins from high temperature sources.

In order to study the application of SILMs for separation of gaseous mixtures (CO_2/N_2 and CO_2/CH_4), one RTIL ([BMIM][Tf_2N]) and one organic solvent (PEG) were immobilized inside the porous structure of different polymeric membranes. Stability studies were also performed and it is demonstrated that these SILMs effectively retain both the immobilized RTIL and PEG, in a very stable mode. Solubility and diffusivity values of pure gases in the RTIL and PEG were determined at high temperatures. The permeability towards different pure gases, such as N_2, CH_4, and CO_2 was measured at different temperatures, between 30 ºC and 100 ºC. It was observed that the selectivity of Supported Ionic Liquid Membranes towards CO_2 was high when compared to that of N_2 (selectivity values in the range of 7-48), and when compared to CH_4 (selectivity values in the range of 15-46), with no loss of liquid immobilised. These high selectivity values obtained for CO_2 open good perspectives for these SILMs to be used for CO_2 separation processes.

ICOM1099

Nanocomposite PIM membranes for gas separation

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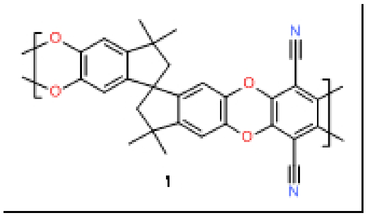
Gas separation membranes are attracting great interest as they offer cost effective, lower environmental impact and energy efficient processes compared to current technologies. They are increasingly being used for applications such as hydrogen recovery, nitrogen generation and carbon dioxide separation.[1] However, current high free volume polymer membranes struggle to compete with existing methods used in gas separation processes, so further progress is required to overcome the limitations of the permeability-selectivity trade off.

Recently, attention has turned to preparing so called "mixed-matrix membranes" to further enhance the separation performance of high free volume polymers. These composite materials consist of a high free volume polymer (e.g PIM-1, **1**)[2] matrix incorporating inorganic, carbonaceous or organic fillers such as zeolites, metal organic frameworks or carbon nanotubes. This potentially enhances mass transport through increased sorption or diffusion, resulting in greater permeability.



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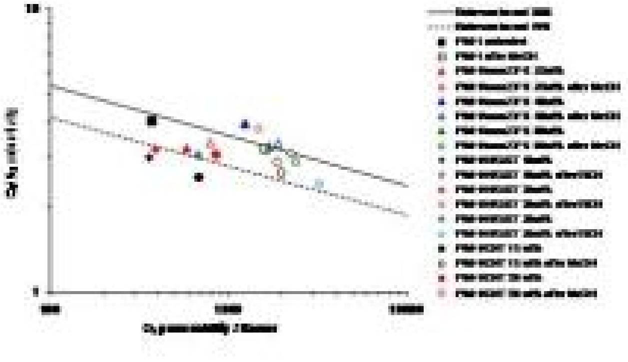
In this presentation we will report the incorporation of several fillers (e.g. zeolitic imidazole framework ZIF-8, metal organic framework HKUST-1 and carbon nanotubes), of varying weight percentages, into a PIM-1 matrix and discuss the gas transport properties. It has been found that increasing the filler content results in an increased permeability whilst maintaining good selectivity, with some composites lying above Robeson's 2008 upper bound[3] for several important gas pairs. For example, Figure 2 shows the O_2/N_2 Robeson plot for PIM-1 incorporating differing weight percentages of fillers. Treatment with small chain alcohols is shown to increase the permeability further.



The work leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. NMP3-SL-2009-228631, project DoubleNanoMem.

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ICOM929

New polymers for gas separation membranes with enhanced resistance to plasticization

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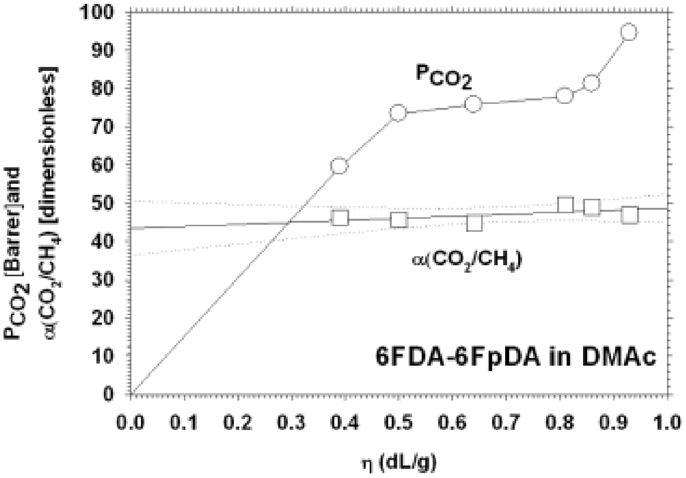
Many polymeric compounds show excellent processability, good mechanical properties and high thermal stability, and that many aromatic polymers, mainly polyheterocycles, having high fractional free volume are excellent candidates for gas separation applications.

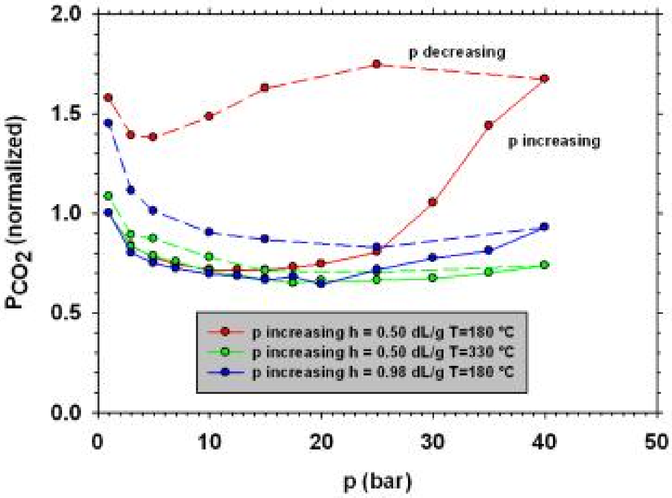
However, all polymeric membranes are very prone to suffer plasticization leading to a lost selectivity when the feeding pressures are high mostly when the fluid processed includes a highly soluble gas as for example CO_2 [1]. Plasticization is detected because a minimum appears in the perrmeabilty *vs* applied pressure plot. The subsequent increase in permeability is paired with a steeply decrease in selectivity [2]. Thus, the search of new materials with a lower tendency to go through plasticization is a hot topic in this field.

Our approach includes the use of polymers with good separation properties and tries to increase the length of the chain, rising its molecular weight. Here, specifically, 6FDA-6FpDA, which features outstanding gas separation results for various pairs of gases but showing a non negligible plasticization for high enough pressures [3]. Other polymers have been tested too as for example Matrimid® and P84®.

Properly, on using a specific method of synthesis, polymers of high or very high molecular weights have been obtained in a controlled way [4]. These polymers were cast on films and evaluated for CO_2 and other gases at different pressures, giving a dazzling ability to resist plasticization processes permeabilities that increase with molecular weight cut off (equivalently inherent viscosity) as shown in Figure 1 for the 6FDA-6FpDA membranes.



The corresponding hysteresis for different molecular weights and different thermal treatments are shown in Figure 2 where it is seen that for high enough molecular weights an increase in the temperature of treatment leads to lower plasticization than ulterior increases in molecular weight. Adequate thermal treatment parameters and high enough molecular weight can be reached for all the polymers tested.



These procedures are a good alternative to others treatments as crosslinking, for
example, that is the main procedure proposed up to now in the literature achieve some protection against plasticization of gas separation membranes.

Aknowledgements

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ICOM1058

An adaptive anhydrous ionic liquid nano-composite membrane for olefin-paraffin separations

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The separation of olefin-paraffin gas mixtures by low-temperature distillation is one of the most important but at the same time one of the most energy-consuming separation processes in petrochemical industry[1]. Therefore, the development of alternative separation methods such as membrane processes is required. Especially liquid membranes can be high-permeable and high-selective as diffusion in liquids is much faster than that in solids and as it is possible to functionalise liquid membranes with selectivity-enhancing carriers[2]. However, the industrial application is limited, mainly due to their poor mechanical stability and evaporation of solvent which in turn leads to a lacking stability and long-term performance. In this regard, functionalised ionic liquids provide the opportunity to develop high-permeable and high-selective liquid membranes without solvent loss due to their inherent characteristic properties, especially due to their negligible vapour pressure.

Ionic liquids are liquids that are comprised entirely of ions. They represent a new class of solvents that offer a huge potential for industrial applications due to their remarkable properties including high thermal stability, negligible vapour pressure and nonflammability[3],[4],[5]. These properties make ILs potential solvent replacements for volatile organics traditionally used in organic synthesis and separation processes. Owing to the quasi-infinite numbers of possible cations and anions combinations that can be envisioned, ionic liquids are considered as designer solvents[5] and are therefore considered here as membrane phase for olefin-paraffin separation. For the separation of olefins and paraffins selectivities can be tremendously increased by dissolving olefin complexing salts of silver or copper(I) in the liquid. They effect a higher solubility of the olefins and open the possibility of a facilitated transport through the membrane.

At the Chair of Chemical Process Engineering, RWTH Aachen University, a new carrier-mediated ionic liquid membrane system based on the neat silver salt $AgNTf_2$ is developed and characterised for olefin-paraffin separations as it has a much higher silver and therefore carrier content than systems with dissolved silver salts. The here presented high-permeable flat-sheet immobilised liquid membranes (figure 1) for olefin-paraffin separation show promising separation properties. Due to the application of a silver-functionalised ionic liquid, high permeances and high selectivities are achieved, in particular at small olefin feed concentrations[6].

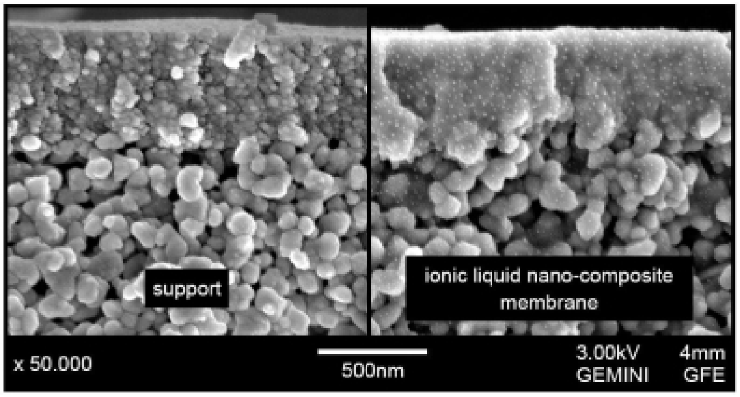

Figure 1: Adaptive anhydrous ionic liquid nano-composite membrane

Acknowledgements

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Alan S. Michaels Award session

ICOM1815

My Membrane Research

Norman N. Li
NL Chemical Technology, Inc., US

The speaker will review the highlights of his industrial research in the last 20 years. His membrane research includes gas separation membranes, facilitated membranes, mix-matrix membranes, ultra filtration membrane, and reverse osmosis membranes. He will discuss not only the highlights of his R&D experience, but also the recent advancement as well as future directions.

ICOM1813

Why Membranes and Membrane Systems are becoming dominant?

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Our modern Society has to solve and overcome various severe problems from the global water stress, to the CO2 capture, from energy production, to environmental pollution, for maintaining and increasing the quality of our life.

Process intensification in process engineering, regenerative medicine, new advanced smart materials, molecular engineering are all discipline which might contribute to find solutions. The progress in the understanding of the biological processes and of how nature has been developing in the past years is offering interesting opportunities.

Membrane systems in particular are playing already a central role in a large variety of chemical transformations, of separations, of energy devices, in Nature and in the biological systems.

The possibility for scientists and engineers to reproduce artificially and to utilise some of these systems in our life and in our industries world is becoming an interesting reality. Reverse osmosis , hybrid artificial organs, fuel cells and other membrane operations are important case studied.

ICOM1806

Improving the Efficiency of Membranes in the Water Industry.

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Membrane technology is a key separations domain for the water industry. In countries like Singapore more than 50% of the water used passes through membranes in processes for water treatment, desalination and reclamation. There are strong incentives to improve the efficiency of membranes by reducing energy demand and chemical usage, minimizing wastes and improving water quality. This presentation reviews activities in a programme at the Singapore Membrane Technology Centre on strategies to improve membrane process efficiency. The programme aims to innovate and optimize, via three synergistic tracks, novel concentration polarization control, biofouling control and monitoring and process control.

Concentration polarization is an inefficiency that not only affects existing membranes but also seriously limits the potential of new generation 'high permeability' membranes. Our approach is to evaluate a range of 'flux enhancing' techniques based on unsteady shear stress and fluid flow. Techniques of interest are two-phase flow (bubbling), vibrations and ultrasound, applied to both low pressure processes (MF, UF as in MBRs) and high pressure processes (RO in desalination and recalamation). Some results of this track will be presented.

The second track is focused on biofouling control in both RO and MBRs. Our approach is to apply concepts of biomimicry to control biofilm development, interfering with quorum sensing and biofilm dispersal mechanisms. These processes require trace levels of signaling molecules and could obviate use of significant disinfection and cleaning chemicals. Preliminary findings will be discussed.

The third element of the programme involves monitoring parameters related to loss of membrane performance. A range of sensors are being evaluated that either characterize the fouling propensity of the feed or monitor the 'state' of the membrane module (incipient fouling or blockage). Our techniques include a novel membrane-based integrity sensor, a bundle blockage sensor using CTA probes, and 'canary cells' operating in parallel with the main plant and based on either ultrasonic miscroscopy of electrical impedance spectrometry of 'canary' membrane surface deposits. Data obtained by these various sensors will be presented. The overall aim of the programme is to link the sensor information to dynamic process control methods that optimally adjust the novel hydrodynamics and biofouling controls to deliver improved membrane process efficiency.

ICOM1814

Facilitated-Transport Supported Liquid Membranes for Antibiotic Recovery

Michael E. Vilt, W.S. Winston Ho
The Ohio State University, William G. Lowrie Department of Chemical and Biomolecular Engineering, US

This presentation covers facilitated-transport supported liquid membranes (SLMs) with strip dispersion for the extraction and recovery of antibiotics from aqueous solutions. The membrane stability has been ensured by a modified SLM with strip dispersion, where the aqueous strip solution is dispersed in the organic membrane solution. With the SLM, Cephalexin has been extracted and concentrated significantly with a very high recovery; typical results have shown > 99% extraction and recovery rates of 96 – 98%. A mass transfer analysis has shown that the resistance from the extraction reaction is dominant. Initial results from a 4-component feed mixture derived from its enzymatic synthesis have shown selective Cephalexin recovery possible. This allows Cephalexin recovery from the mixture in conjunction with complexation without enzyme deactivation, which commonly occurs when complexation is conducted in enzymatic reaction mixtures.

ICOM1817

Microstructured hollow fiber membranes

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Hollow fiber membranes with an undulated circumference offer the possibility of packing more membrane surface area into a module for the same number and outer diameter of the fiber. This presentation reviews the achievements made so far for the development of the fibers as well as for the applications. Gas separation as well as water filtration will be addressed. In the area of water filtration, the presentation reviews recent results in colloidal filtration (humic acid and silica) as well as submerged ultrafiltration. For the later, bubble aeration is only effective when the microstructured hollow fibers are twisted causing the bubbles and the hydrodynamic flow to deviate from the parallel direction with respect to the fiber grooves.

Membranes for extreme conditions 2

ICOM1828

ORGANIC SOLVENT NANOFILTRATION: AN EMERGING MOLECULAR SEPARATION TECHNOLOGY

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Organic Solvent Nanofiltration (OSN) separates molecules present in solutions of organic solvents. In OSN, a pressure gradient is applied across a solvent stable nanoporous film, inducing transport of liquid across the film. Depending on relative permeation rates, molecular species in a feed liquid stream can be concentrated and separated. Typically OSN will use a small fraction of the energy of thermal methods such as evaporation and distillation, and can work at temperatures around ambient. These advantages have led to a huge surge in interest in OSN technology in the past few years, and a rapidly increasing number of commercial applications.

This presentation will firstly briefly describe recent research and development leading to a new class of OSN membranes and modules. The DuraMem^{TM} series OSN membranes are made through post-formation processing including crosslinking of polymer membranes, which makes them stable in polar solvents such as acetone, DMF and THF. These membranes are commercially available from Evonik MET as spiral elements. Some of the key challenges overcome in developing a membrane from lab bench discovery to a commercially available product will be described.

The presentation will then move on to describe OSN research at Imperial College in the areas of membrane formation, membrane characterisation, prediction and processes, and applications. New membranes include thin film composites, based on interfacial polymerisation (TFC-IP). By using inert supports, including crosslinked polyimide and poly ether ether ketone (PEEK), the first reported TFC-IP membranes having good flux and rejection in solvents including DMF and THF have been developed. A further innovation is the development of OSN membranes that can withstand highly basic and acidic environments. To characterise OSN membranes, impregnation with nanometer size particles of osmium followed by imaging under TEM has provided images of the separating layer; the high resolution allows the differences in pore sizes in polyimide membranes to be visualised. Crucially, this correlates strongly with the membrane performance in terms of flux and rejection.

Membrane transport models, and process models for designing OSN operations will be described. The relationship between the alternative transport models and the final predictions of the process model will be described. Finally some new applications of OSN in organic liquids processing will be presented. These will include production of speciality polymers, application to continuous processing for organic synthesis, and manufacture of peptides and oligonucleotides.

ICOM842

Polyimide/Polybenzimidazole (PI/PBI) blends for solvent resistant nanofiltration

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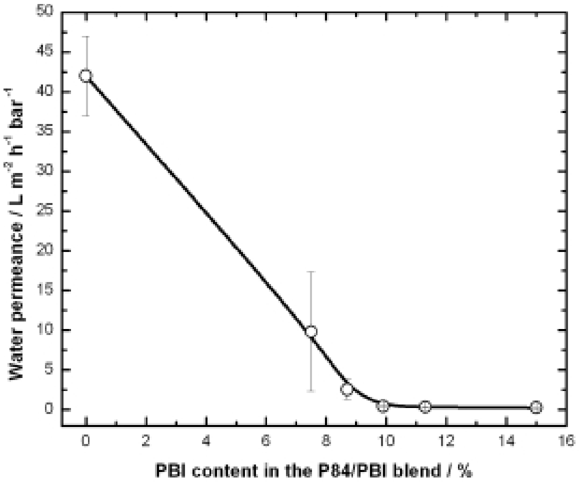
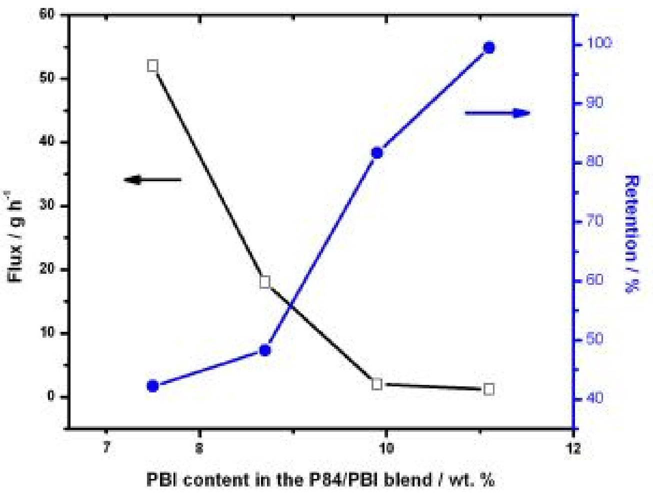
Solvent resistant nanofiltration (SRNF) is attracting considerable attention as potential enabling technology for various industrial processes. The state-of-the-art membranes for SRNF are derived from a limited number of technical polymers, such as polydimethylsiloxane (PDMS) and polyimides (PIs). The current work aims at preparation of SRNF membranes *via* polymer blending, more specifically, P84 polyimide and Polybenzimidazole. The objective of incorporating PBI into P84 is to enhance membrane stability and concurrently decrease the molecular weight cut-off.

Flat sheet polymer blend membranes were fabricated by the conventional dry-wet phase inversion technique. SEM micrographs indicate that, as compared to their pure P84 analogue, P84/PBI blend membranes have a tighter and thicker top-layer and less macro-voids in the sub-layer, as compared to the pure P84 membrane. In aqueous nanofiltration, membranes with increased PBI content show a decline in pure water permeance, combined with significant increase in rejection





. A water filled, wet blend membrane with PBI content of 11.1 % shows a water permeance of 0.33 L m^{-2} h^{-1} bar^{-1} combined and rejection of 99.5 % towards brilliant blue FCF (*Mw* 792.84). After filling the pores with glycerol, in ethanol nanofiltration similar membranes showed a permeance in the range 0.1 to 0.3 L m^{-2} h^{-1} bar^{-1} combined with a very high rejection towards brilliant blue FCF, 98.9 % to 99.6 %. These results imply that the P84/PBI blend membranes can be promising candidates for SRNF.

ICOM472

Preparation of membranes for organophilic nanofiltration based on photo-crosslinkable polyimide

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In this work new organophilic nanofiltration (NF) membranes based on commercial polyimides are developed. The polyimide Lenzing P84 is used as first starting point. By applying N,N-dimethylethylenediamine (DMEDA) or N,N-diisopropylethylenediamine (DIPEDA), the polyimide is modified so that new side groups are added. These groups should promote a selective UV-induced cross-linking based on the intrinsic photoreactivity of the benzophenone units in the polymer main chain (Fig. 1) [1]. The aim is to obtain in a simple way a polymer which is able to cross-link during the membrane formation by non-solvent induced phase separation (NIPS). Due to the cross-linking swelling of the selective layer of the membrane could be controlled or, at best, the membrane will become solvent resistant. These options lead to NF membranes with tuneable separation properties.

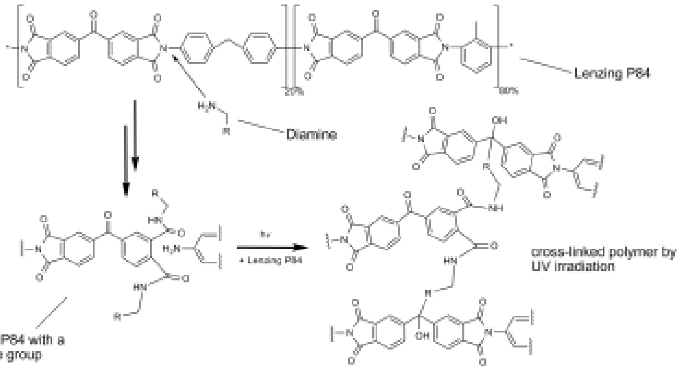

Fig. 1: Scheme of the cross-linking reaction of Lenzing P84-based polymer blends induced by UV irradiation.

After reactions of Lenzing P84 with the amines DMEDA and DIPEDA, size exclusion chromatography data for the product indicate that the modification is so efficient that chain scission of the polyimide can also occur. All results with such degraded polymers demonstrate that the modified polymers have too small chain lengths for membrane preparation. Therefore, polymer blends of modified and unmodified Lenzing P84 were used to obtain stable membranes and to investigate the selective UV reaction. Conditions have been established to obtain via NIPS in water membranes which are free of defects. All membranes have an asymmetric cross-section structure (Fig. 2a).

Swelling experiments of dense films, prepared from the same polymer blends with and without UV irradiation, show with increasing size of crosslinking group and increasing UV irradiation time a reduction of swelling. Trends of the swelling experiments can be verified by permeance and rejection measurements with membranes. Also, the selective layer of membranes, composed of polymer blends with modified Lenzing P84, become more dense after UV irradiation (Fig. 2b vs. 2c). The DIPEDA modified polyimide led to a more pronounced effect, i.e. decrease of flux and increase of rejection, than the DMEDA modified one. However, for some modification conditions the selective layer was so dense, that no filtrate flux could be measured (Fig. 2d). These results support that the cross-linking was successful. Without added modified polyimide the UV irradiation had little or a negative effect on density of the selective layer and NF performance of the membranes.

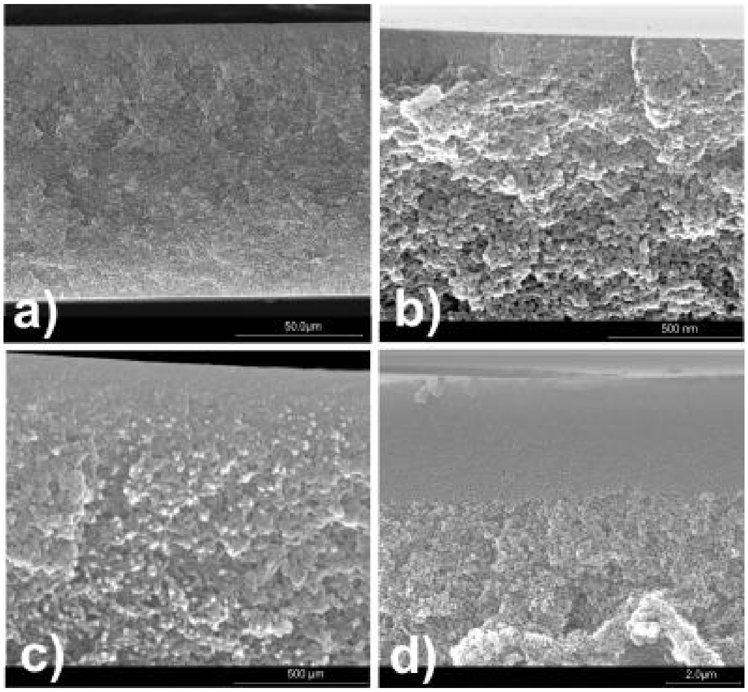

Fig. 2: Scanning electron micrographs of NF membranes from Lenzing P84: a) overview on typical cross-section, b, c) selective layer of membrane from blend of unmodified with DMEDA modified polyimide b) before and c) after UV irradiation, d) selective layer of same membrane but after longer UV time which had negligible filtrate flux.

Currently the preparation process of membranes is varied by choosing different moments during NIPS for the UV irradiation. The results indicate that this is a promising concept to tailor the selectivity and permeability of the membranes.

Acknowledgements: Financial support of the project in the frame of the program "Chek.NRW" is gratefully acknowledged.

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ICOM1043

Investigation of the separation behaviour of a material class of linear organic molecules in organic solvent nanofiltration with special focus on the influence of their functional groups

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The majority of the speciality chemicals produced at Merck have an elongated molecular structure, consisting of two, three or four ring-type core molecules (e.g. aromatic rings, cyclohexyl rings etc.), which are either attached directly or via linking groups.

In the core structure further groups like alkyl-, fluoro- or carboxyl may be added. Several of these molecules are very temperature-sensitive and tend to decompose at high temperatures. Therefore, an implementation of new membrane technologies in the production process offers a great potential due to their moderate operation conditions, e.g. in comparison to distillation. With the current development of stable solvent-resistant nanofiltration membranes (polymer and inorganic), the integration of membrane technology in chemical production becomes feasible.

First experiments show that the performance of organic solvent nanofiltration (OSN) for the separation of this material class differs a lot from the given membrane specifications, e.g. the molecular weight cut-off. This is due to their linear molecular structure as well as to the different end and intermediate groups.

A prediction of the separation behaviour is up to now not possible. Consequently, it is necessary to perform extensive systematic studies in order to gain a deeper insight into the separation behaviour in OSN.

In this work, experimental investigations concerning the influence of functional groups on the flux and rejection in OSN separations are presented. The solvents used in the experiments are methanol, heptane and THF which are similar to the various synthesis steps in the production of these speciality chemicals. The influence of functional groups was investigated by direct comparison of the separation behaviour of two substances, which differ only in one functional group (see figure 1a and b). By incorporating these into a complete Design of Experiments (DoE), using two, three and four ring-type core substances with different end- and side groups, a qualitative separation model could be defined.

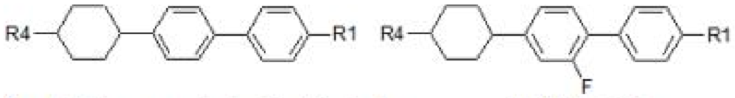

Figure 1: a) three core molecule without fluorination b) with fluorination

ICOM1432

Characterization of commercial reverse osmosis membranes and evaluation of their performance under supercritical CO_2 processing conditions

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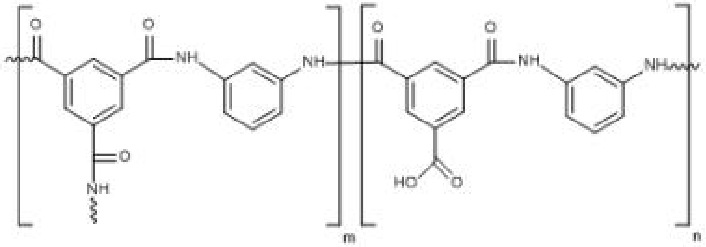
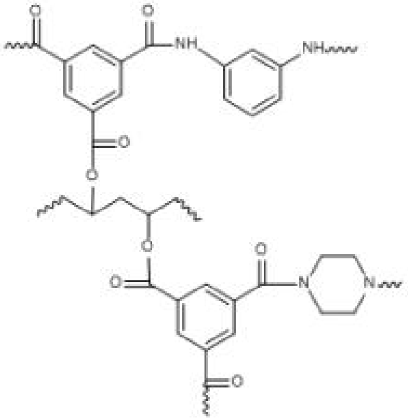
Coupling supercritical CO_2 (SC-CO_2) extraction with membrane separation is a novel technology, which aims to provide energy savings by recycling CO_2 at supercritical state in addition to the separation of extract components. Commercial polymer reverse osmosis (RO) membranes are commonly used due to acceptable retention rates and lower prices compared to inorganic membranes. However, high pressure operating conditions may cause physicochemical and morphological changes in polymer membranes, which in turn can adversely affect membrane performance. In order to reveal these effects, membrane chemical structure must be well characterized; however, most of the information on commercial RO membranes is proprietary. The objectives of this study were to: a) characterize two commercially available RO membranes, AK and SG, using contact angle, FE-SEM, AFM, XPS and ATR-FTIR measurements, b) investigate the effect of SC-CO_2 processing at different flux (50 and 200 kg/m^{2}h), temperature (40 and 80 °C) and time (0-8 h) levels at 120 bar on the membranes using contact angle, ATR-FTIR and FE-SEM measurements, and c) assess the performance of the membranes by measuring the change in flux and oleic acid retention under specified conditions.

AK membrane exhibited the characteristic properties of PA membranes formed via interfacial polymerization of m-PDA and TMC monomers. For the SG membrane, piperazine and m-PDA blend was most likely used as monomers, which underwent esterification with PVA during thin film formation.



AK - Interfacially formed fully aromatic polyamide



SG - Polyesteramide

Figure 1. The suggested chemical structures of AK and SG membranes

Consistent with the AFM and XPS results, high contact angle of AK was due to extensive intermolecular hydrogen bonding as a result of close proximity of chains. SG membrane was lacking most of the amide hydrogen and carboxyl groups due to the different protocols employed during its fabrication.

After SC-CO_2 processing, contact angle of AK increased substantially at high flux and high temperature conditions unlike SG. The peaks assigned to N-H and carbonyl groups at 1541, 1609 and 1663 cm^{-1} showed the highest decrease in absorbance with high flux processing while high temperature was more effective on O-H groups between 2700-3700 cm^{-1} for both membranes.

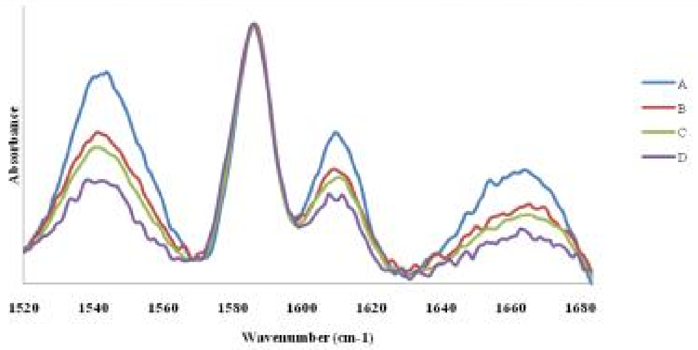


Figure 2. Normalized spectra for the change of absorbance of amide and carbonyl groups of AK membranes processed at different flux and temperature conditions under 120 bar (A) virgin, (B) 50 kg/m²h, 40 °C, (C) 200 kg/m²h, 40 °C, (D) 50 kg/m²h, 80

AK membrane exhibited the formation of bead-like structures at different processing times and conditions and showed prominent changes both chemically and morphologically due to the presence of excess amount of hydrogen-bonded groups in its structure. SG membrane did not show any substantial difference in its hydrophobicity, regardless of processing conditions. Bead-like structures were formed out of polymer strands of AK membrane due to strong self interactions of carbonyl and tertiary amide functional groups.

In terms of membrane performance, the greatest increase in flux was observed with high temperature processing for both membranes. The polymer chain distributions were altered upon cooling where the oleic acid retention of both membranes was susbstantially increased due to contraction. Repressurization affected the flux of AK while SG did not show a substantial difference unless processed for more than 2 h at high temperature. Efficiency of AK membrane was found to be more sensitive to SC-CO_2 processing conditions most probably due to extensive hydrogen bonding in its structure unlike SG.

Membrane and surface modification 3

ICOM1867

Membrane and surface modification

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This work discusses the process of fabrication of 3D topography membranes and their characterisation using complementary techniques such as atomic force microscopy (AFM), small-angle light scattering (SALS), scanning electron microscopy (SEM) and polarizing optical microscopy (POM).

In particular, this work illustrates how the design of three-dimensional relief microstructures at the membrane surface, with topographic modulation of features with characteristic dimensions, may lead to improved momentum and mass transport conditions at the membrane surface through promotion of local micro-turbulence.

The impact of membrane topography on the interaction of complex biomolecules such as proteins will be also addressed aiming at interpreting how surface features induce conformational changes in proteins' structure and, ultimately, in their activity and function. Non-invasive fluorescence techniques using internal reporters will be employed to access proteins' alterations of conformation.

ICOM600

Taylor-made Enzyme-catalyzed Modification of Poly(ethersulfone) Membranes aimed at Prevention of Adhesion

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The robustness of a membrane is determined by the properties of the base polymer and the functionality of its surface. One of the most popular polymers used for membrane preparation is polyethersulfone (PES), which has excellent thermo-physical properties, but the surface properties are in need of improvement to reduce membrane fouling by protein adsorption that may cause sever flux decline during filtration. Therefore, it is not strange that a wide range of modification methods has been published to reduce surface hydrophobicity of PES membranes. However, the methods that are currently suggested are all rather harsh and not environmentally friendly; in contrast, in this work, we use the enzyme laccase from *Trametes versicolor* that can catalyse reactions under ambient conditions. This enzyme is able to oxidize phenol compounds to their corresponding free radical forms that are subsequently grafted onto PES membranes creating free hydrogen acceptor sites (OH, COOH) on the membrane surface. During the reaction, which can take place at ambient conditions, oxygen is used and water is formed; therefore, we label this an eco-friendly modification method.

In this project, we use 4-hydroxybenzoic acid and gallic acid as substrates, and depending on the reaction conditions, they may for covalently bound layer on the PES membrane, or mainly form homopolymer in solution, which may subsequently attach to the membrane. The extent of modification (length of the grafted polymer) can be adjusted through the reaction conditions.

The grafting yield was measured and linked to membrane flux and prevention of protein adsorption. Protein adsorption was significantly reduced in all cases, and sometimes even thus low that it was within the measurement error, while the flux was at most reduced by 10% compared to the base membrane. Protein adsorption behaviour was investigated in detail by reflectometry and AFM, and it was found that the surface structure or shape, which can be tuned through the reaction conditions, has a decisive role in prevention of protein adsorption rather than surface hydrophilicity as is often assumed. Besides, the mechanical properties were measured, and it was found that modification did not adversely affect the membrane properties.

When comparing 4-hydroxybenzoic acid and gallic acid, it is clear that the first substrate is more effective in protein repellence, although also with gallic acid considerable reduction in protein adsorption can be achieved even at very short reaction times, there is room for improvement.

In conclusion, the suggested enzyme-catalyzed modification method shows remarkable flexibility, and allows careful tuning of the membrane properties in such a way the protein adsorption can be suppressed. Besides, the modification method does not influence the mechanical properties of the membrane adversely, and the modified layer is resistant to low and high pH, which makes this modification method an interesting eco-friendly alternative to currently used methods.

We would like to thank DSTI and their project partners Norit X-Flow and Friesland Campina for financial support of this research.

ICOM1414

Efficiency of surface grafted ceramic membranes in hydrophobic pervaporation and membrane distillation. I. Grafting of Al_2O_3, TiO_2 and ZrO_2 powders by perfluoroalkylsilanes

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Ceramic membranes show many important advantages over polymeric ones, however the hydrophilic nature of the ceramic limits the wider range of applications. Changing the hydrophilic character of ceramic membranes into hydrophobic one is nowadays of particular interest. The hydrophilic character of the ceramic membrane can be modified by surface grafting with perfluoroalkylsilane compounds. During grafting process the reaction occurs between hydroxyl (-OH) groups presented on the active surface and the ethoxy groups (O-Et) of organosilane compound. Grafting results in the creation of hydrophobic monolayer on the membrane surface and in the membrane pores what changes the separation and transport properties of modified membrane.

The aim of this study was to determine the optimal grafting conditions of perfluoroalkylsilanes (PFAS) on powders of the chosen metal oxides. PFASs are the group of compounds with a general formula of $R\text{-}C_2H_4\text{-}Si\text{-}(R_1)_3$, where R represents the fluorocarbon chain ($-C_nF_{2n+1}$) and R_1 can be methyl-, ethyl-, methoxy- and ethoxy- group or chlorine atom.

Powders of γ-Al_2O_3, ZrO_2, TiO_2 were used in this work. The specific areas of powders used in the research were 102.6, 82.9 and 38.4 $m^2\ g^{-1}$ for γ-Al_2O_3, ZrO_2, TiO_2, respectively. Prior to the grafting process, powders were pre-conditioned in the identical temperature and humidity. Two types of PFAS with a different length of fluorocarbon chain were used: 1H,1H,2H,2H-perfluorooctyltriethoxysilane and 1H,1H,2H,2H-perfluorotetradecyltriethohysilane, denoted as C6 and C12, respectively.

To find the optimal conditions of the grafting process the following parameters influencing the grafting yield were investigated: i) amount of PFAS (in moles) per active surface of powder (in m^2), ii) time of grafting and iii) temperature of the grafting process. The infrared spectroscopy (IR) was used to characterize the modified powders. The efficiency of grafting was determined by using thermo-gravimetric analysis (TGA). The yield of grafting was calculated from the mass loss of grafted powder compared to the mass loss of pristine material.

It was found that grafting efficiency was dependent on the time of grafting, temperature, type and concentration of PFAS. Generally, yield of grafting was increasing with a grafting time however for the grafting times longer than 70 hours the yield improvement was not substantial. Grafting was more efficient for C12 molecules compared to C6 ones. The best grafting efficiency was obtained for the PFAS molecules in contact with γ-Al_2O_3 powders. These results will be used to foreseen the grafting efficiency of ceramic membranes with a selective layer made of γ-Al_2O_3, ZrO_2, TiO_2 and applied in pervaporation and membrane distillation.

ICOM1485

Novel salt tolerant membrane adsorber for contaminant removal

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Contaminant removal in the manufacture of therapeutics is dominated by traditional anion exchange chromatography (AEX), which typically is based on strong quaternary amine (Q) ligands. AEX chromatography is performed in flow through mode to bind remaining traces of contaminants such as DNA, Host cell proteins, virus and endotoxins, while the target therapeutic molecule passes through the media. Due to the fact that membrane based media are convective media and, because flow-through applications are driven by volume rather than mass, membrane chromatography has become a robust alternative to diffusion limited AEX columns.

However, Q membranes have not addressed any intrinsic limitations of the ligand chemistry. The binding capacity of Q ligands is reduced at high conductivities, so concentrated feed streams must be diluted to remove contaminants efficiently. To overcome this limitation, we have developed a novel salt tolerant membrane adsorber based on a new generation cellulose membrane combined with a weak anion exchange chemistry that features a high charge density.

The newly developed supporting membrane is a cross-linked, regenerated cellulose membrane, that exhibits a double porous structure. This structure consists of 2 classes of pores: pores with an average diameter around 1 µm and a second class of ultrapores that completely excludes a dextran blue based exclusion marker.

Within this work, Localization of binding sites using confocal laser scanning microscopy (CLSM) and labeling of the membrane and adsorbed solute was performed on membrane adsorbers based on the new double porous structure and compared with established surface grafted membrane adsorbers. The obtained results combined to a further characterization of the pore size distribution show how this new structure can dramatically impact the binding capacity of the resulting membrane adsorber. Furthermore, new insights into the structure and ligand related mechanisms governing salt tolerance are presented. Additionally, performance characteristics in regard to contaminant removal at a large variety of pH and conductivities are presented.

ICOM592

Direct observation of particle deposition on the surface of micro-fabricated membrane during crossflow micro-filtration

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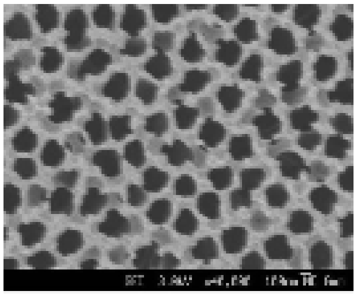
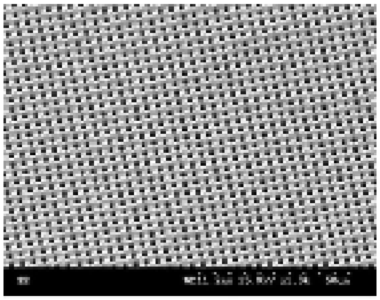
Tangential flow/crossflow micro-filtration is a widely used technique for processing particulate suspensions in different areas such as wastewater treatment, microorganism removal, and mineral processing. In crossflow micro-filtration, a deposit cake layer (i.e. fouling) tends to form on the membrane which usually controls the performance of the filtration process. The concept of 'critical flux' and idea of hindering fouling by low flux operation was suggested by some researchers in the 1980s. A common non-invasive, in situ, technique that can identify the critical flux is direct observation through the membrane (DOTM) to view particle deposition on a transparent membrane. Using this method with well-controlled crossflow hydrodynamics, it is possible to see the cake formation on the membrane surface as the flux transits across the critical flux. A famous transparent membrane which normally used for DOTM micro-filtration was the Anopore^{TM} inorganic membrane (Anodisc, Whatman, UK) with a nominal pore size of 0.2µm. This kind of membrane has a high porosity and narrow pore size distribution, and is visually transparent when it is wet because of the capillary honeycomb pore structure which allows light transmission. However, this membrane has two major drawbacks. Firstly, the pore size distribution is limited due to the nature of the fabrication process (i.e. Anodization). Secondly, this membrane is so fragile and required extreme cares during handling and characterization.



Micro-fabricated filters, that normally made with MEMS techniques, contain pores with the same size and can thoroughly overcome these micro-structural defects. The fabrication process allows enough flexibility to control the microfilter characteristics such as pore size, pore shape and density. In addition, variety of optically transparent polymers (like SU-8 and Polyurethane) can be employed during fabrication in order to make a robust and flexible membrane for micro-filtration process. In recent years, different methods have been proposed to create membranes with cylindrical pores like laser interference lithography, aperture array lithography, phase separation micromolding, and more recently dissolving mold technique. In this study, we used polymeric micro-fabricated membranes, which mainly made by dissolving mold technique to study the mechanism of particle deposition on membrane surfaces using DOTM technique.



We employed membranes with different pore density and pore shape (i.e. circular and rectangular) in order to study their effect on the critical flux. In general, the critical flux data determined from the observation of the particle deposition confirm the previously described trends using the flux and transmembrane pressure observations. Furthermore, the initial results reveal that under equal conditions, micro-fabricated membrane presents higher critical flux in comparison to the commercial membranes which can be attributed to the smooth surface of them.

Membrane fouling 3

ICOM1790

A Review of the Impact of Fouling and Scaling on Flux Performance in Membrane Processes

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Fouling and scaling of membrane processes has been studied for decades, yet the mechanisms by which they lead to flux decline are still being elucidated. This lecture will look at fouling in general and biofouling and mineral scaling in particular and provide a historical overview of studies of the mechanisms by which these phenomena have lead to flux decline. The lecture will highlight the importance of mapping the location and structure of fouling deposits on and in the membrane to elucidate mechanism. Examples will be provided from ultrafiltration, NF/RO and membrane distillation. Mechanisms surveyed will include: cake resistance, pore blockage, surface blockage, and concentration polarization enhanced osmotic pressure effects. These effects can be divided into those that relate to flow parallel to the membrane and flow perpendicular to the membrane, as will be illustrated for the case of biofouling.

A particular focus will be provided on the interaction between biofouling and mineral scaling where biofouling is shown to exacerbate and accelerate the process of scaling via biofilm enhanced concentration polarization.

ICOM895

Fouling control using backpulse systems

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Introduction

One of the main challenges in micro- and ultrafiltration operations is reducing the effects of fouling formation. Fouling can occur in different mechanisms, such as cake layer formation or pore blocking. Backwashing has been used for some years as a method to overcome internal pore blocking. It consists of the flushing of permeate to the feed at regular intervals in order to reopen the pores by removing the deposited material back to the feed side of the membrane. Backpulsing follows a similar approach, but both the time interval between backwashing steps, the time and the volume of backwashing are reduced. This technique focuses instead on disturbing the cake layer and thus maintaining a lower resistance.

Experimental approach and results

In the Hi-Fre project, various prototypes of a novel valveless backpulse system were developed and tested by mounting it on the permeate side of tubular ceramic and polymeric membranes. The backpulse system consists of a mechanically driven piston capable of flushing permeate back to the membrane. The system can be adjusted in terms of backpulse frequency, backflushing volume and time.
The impact of backpulsing and various backpulsing and filtration parameters on fouling was investigated during experiments with different media such as milk powder, surface water and digestate from biogas production. The presentation will focus on the different parameters to adjust and the underlying mechanisms.

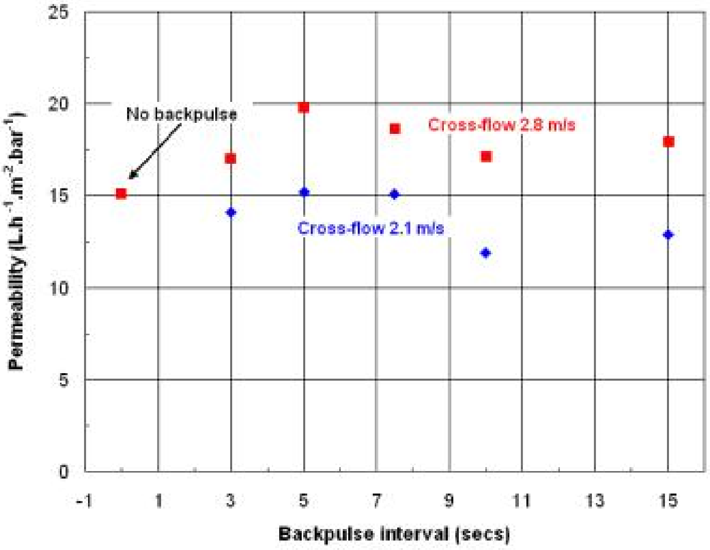

Figure 1. Influence of backpulse interval and cross-flow speed on the filtration of digestate from biogas production using ceramic membranes.

The results (see Figure 1 for an example) showed a distinct advantage in using the developed backpulse system. Positive effects were observed both for micro- and ultrafiltration tests and both for ceramic and polymeric membranes. The use of backpulse strongly reduced the flux decline and could increase the net permeability by up to 50%. Flux improvements were obtained by adjusting the backpulse shape (□ 20%) and cross-flow speed (□ 30%), thus demonstrating the potential of backpulsing when combined with other fouling control strategies.

Conclusions

The backpulse prototypes developed, proved to be powerful tools for fouling control during microfiltration of different media. The advantages mainly lie in the removal of deposited particles from the membrane surface and in the disturbance of the cake layer.

Acknowledgments

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Technological Development under Grant Agreement No 232086 The project is part of the Sub-Programme Capacities - Research for SME's.

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ICOM395

Structure of Milk-protein Deposits on Micro-sieves

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Microfiltration is used to separate caseins from whey proteins in milk. The caseins are organized in spherical micelles, approx. 150 nm in diameter. Beta-lactoglobulin is a globular whey protein, approx. 3 nm in size.

The study of the molecular structure of casein deposits on membranes is important to precisely understand the separation process during the microfiltration of milk. We report on those structure study using static and dynamic light scattering (SLS/DLS), grazing incidence small angle X-ray scattering (GISAXS) and atomic force microscopy (AFM). GISAXS as an advanced scattering technique offers the unique possibility to investigate the molecular structure of deposits as occurred during fouling on membranes. Especially, GISAXS allows resolving shape changes of casein micelles occurring first on the contact area between casein micelles and the membrane, and second on the contact areas between casein micelles lying upon another. Such changes cannot be seen by methods looking from the top on the deposit such as AFM or electron-microscopy. However, the method demands the use of smooth membrane surfaces as provided by Si_XN_Y-micro-sieves.

We observed structured GISAXS pattern from size-fractionated casein micelles indicating highly ordered structures. Corresponding AFM pictures showed a partially hexagonal ordering of casein micelles on the micro-sieves .Single casein micelles within such ordered clusters appeared as compact, homogeneous spheres. We observed two processes of the deposit formation during simple filtration, which we assigned to internal and external fouling processes. Using static and dynamic light scattering, size and size distribution were measured in the permeat and compared with those of the feed solution. Hence, we could determine indirectly the sizes of the casein micelles deposited in dependence of the filtration time. We could show that there was a tendency for the deposition of those micelles which would lead to more dense layers. In detail, we observed the deposition of large and small particles whose size ratio allowed a formation of mixed hexagonal lattices.

Using GISAXS, we observed deviations from an ideal spherical shape of deposited casein micelles. GISAXS pattern of casein micelles deposited on the micro-sieves by simple filtration differed significantly from those obtained from solution cast casein micelles. From the experimental results a more oblate shape of the micelles caused by filtration forces could be derived. Smaller sizes of casein micelles in the deposit layer were observed when filtrated in the presence of high beta-lactoglobulin contents.

ICOM512

Biofouling-resistant polymer hydrogel coatings for desalination membranes

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Applying a hydrophilic coating to the membrane surface is one common strategy to control membrane fouling. More specifically, it had been demonstrated that the anti-fouling properties of ultrathin grafted layers of polymeric hydrogels on ultrafiltration membranes are improved with increasing degree of hydrogel swelling in water [1]. Our current work focuses on hydrophilic membrane coating materials synthesized from poly(ethylene glycol) (PEG)-based hydrogels and application of these thin gel layers on the surface of composite membranes for reverse osmosis and nanofiltration. The aim of this work is to explore fundamental relationships between synthesis conditions, polymer structure and hydrogel properties in fouling-resistant coating materials. Hydrogels were synthesized from poly(ethylene glycol) methyl ether methacrylate with three different PEG molar masses, in combination with varied cross-linking degree. For characterization of the bulk hydrogels, rheological measurements were employed to examine gelation time as well as the mechanical strength and mesh size of the gels as a function of synthesis conditions. These data were correlated with degree of swelling. Sorption experiments using proteins of three different sizes were performed to identify the relationship between the microstructure of the hydrogels and protein adsorption on the surface and its penetration into the hydrogel network. Bacterial deposition kinetics and biofouling were also examined using gels anchored to glass substrates and correlated with synthesis conditions and gel structure.
For preparation of tightly anchored hydrogel coatings on polyamide composite membranes via *in situ* graft and cross-linking photopolymerization, adsorbed cationic macroinitiators based on poly(2-dimethylamino-ethylmethacrylate-*co*-2-hydroxyethyl methacrylate) and comprising photoinitiator side groups were used. The modified desalination membranes were characterized with respect to hydrogel layer thickness, water permeability and salt rejection as well as propensity to fouling.

Acknowledgements. Financial support by the German-Israeli Foundation for Scientific Research and Development (GIF, #953-25. 10/2007) is gratefully acknowledged.

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ICOM1111

Fouling of RO membrane by hydrocarbonated and fluorinated surfactants contained in firefighting water: measure and characterisation

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Extinguishments of large scale solvent fires produce large amounts of water that may contain various hydrocarbonated and fluorinated surfactants depending on the type of firefighting foam used. Due to their chemical nature, fluorinated parts of fluorinated compounds are highly resistant to biochemical and advanced oxidation processes. Therefore the current treatment for the degradation of fluorinated surfactant from water used in fire extinguishment is high temperature incineration of the water in halogen resistant incinerators. A previous paper [1] aimed to propose a process for purifying firefighting water containing fluorinated surfactants. Experimental results indicated that electrocoagulation and cake filtration followed by reverse osmosis efficiently treated fire extinguishment water.

Several papers on filtration of real industrial solutions containing surfactants were already published and noticed important fouling but few of them tried to understand the behaviour of surfactants on membrane interface [2-6]. The aggregation of amphiphilic polymer molecules in water solutions is a very common phenomenon. Surfactants and more specifically fluorinated surfactants are able to aggregate themselves into micelles in solution but also in double layers, vesicles, or cylinders[7, 8]. Their organisation at the membrane surface in the polarisation layer is unknown at the moment. Isolated compounds, thin film, hemi-micelles or hemi cylinders could occur depending on conditions [9]: surfactants and salts concentration at the membrane interface, pH of the solution, roughness, hydrophilicity of the membrane, hydrodynamic etc. The objective of this paper is to better understand surfactants organisation in order to, in fine, identify better operating conditions limiting fouling.

In this paper, laboratory-scale fouling tests on a plan SEPA CFII cell (GE osmonics), comparing the fouling behavior of cellulose acetate and several aromatic polyamide thin-film reverse osmosis membranes, are reported. AFM, ellipsometry and contact angles measurements were used to characterise the membrane surface. The model solution contained sodium octyl sulfate and an amphoteric fluorinated surfactant. Laboratory scale flux measurements were compared to pilote scale measurements on spiral modules (Millipore Proscale pilot 12*1.85in and Polymem 40*2.4in) in similar conditions.

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Modelling 3

ICOM1789

Membrane Modeling: Overview and Challenges

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Models are widely used today in membrane science and are an important part of engineering using membranes and membrane development. Membrane transport, fouling phenomena, and membrane formation have been the most active areas of model development. These efforts are intimately connected to development of advanced characterization and simulation tools that help to independently evaluate relevant characteristics of membranes and solutes and verify proposed mechanisms.

This presentation reviews the current state-of-the-art in membrane modelling and its relation to developed characterization methods focusing on pressure-driven transport in dense and nanoporous membranes. The main challenges are discussed in detail for the case of transport of salts and organic molecules in nanofiltration and reverse osmosis. The models currently in use are discussed within the following hierarchy:

1. Phenomenological models that played a pivotal role in establishing important fundamental concepts of membrane transport a few decades ago (solution-diffusion mechanism, flux coupling etc.). Transport coefficients linearly connecting fluxes to driving forces were first defined within these models and still remain widely popular in engineering calculations and useful in analysis of complex cases.

2. Physical models, which essentially attempt to “open up the black box” and split the phenomenological coefficients to 3 distinct contributions: pore geometry, molecular frictions or mobilities within the membrane, and partitioning of permeants between membrane and solution. The set of phenomenological coefficients is then replaced with a set of characteristics with transparent physical meaning, such as pore size, fixed charge, dielectric constant etc. Perhaps the largest challenge is to establish physical mechanisms and corresponding relations between these characteristics and solute transport that will be reasonably simple, physically sound and consistent with experiment. The presently used relations still do not fully meet these criteria. This aspect and recently proposed improvements will be discussed in more detail.

3. Molecular simulations, e.g., MD, which are the most recent and advanced models based on unified first-principle concepts. Despite very large computational effort such calculations have a great potential for providing input for simpler models (e.g., estimating partitioning and mobilities of permeants), verifying mechanisms and analyzing novel membrane materials.

ICOM256

Ion rejections in nanofiltration are essentially controlled by spontaneously arising trans-membrane electric fields

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Nanofiltration is carried out under conditions of zero electric current. Therefore, the trans-membrane flows of cations and anions (in solutions of single salts) must be stoichiometric. If the intrinsic membrane permeabilities to cations and anions are different the stoichiometry of trans-membrane ion transfer can be assured only due to the appearance of trans-membrane electric fields. These fields increase the flux of “slower” ions and reduce that of more “rapid” ones.

In electrolyte mixtures, the effect of these fields is especially visible. In particular, they give rise to negative rejections of “rapidly-permeating” ions present as relatively small additions to well-rejected dominant salts. This is most pronounced in the limiting case of trace feed concentrations of “rapid” ions.

The phenomena of electrical coupling of trans-membrane flows of various ions have been studied theoretically and experimentally. The theoretical analysis has been carried out within the scope of solution-diffusion-film model recently extended to electrolyte mixtures [1].

Experimental data have been obtained with a commercial NF membrane (NF270, Dow Chemical) in a cross-flow test cell with a spacer-filled feed channel. Several combinations of dominant salts ($MgCl_2$, $MgSO_4$, Na_2SO_4, NaCl) and trace ions (Na^+, Cl^-, Mg^{2+}) have been used. The rejection of ions crucially depended on their “environment” namely the nature of dominant salt. Fig. 1 shows the rejections of Na^+ as a part of dominant NaCl, as the trace added to $MgCl_2$ and as the trace added to $MgSO_4$. The dramatic differences in the rejections can be explained by the spontaneously arising electric fields. The intrinsic membrane permeability to sulfates is very low and, thus, lower than to Mg^{2+}. Therefore, in dominant $MgSO_4$ the electric field retards cations and makes the rejection of Na^+ relatively high. In dominant NaCl the direction of electric field is the same but its magnitude is essentially smaller because of the much higher membrane permeability to Cl^-. In dominant $MgCl_2$ the membrane permeability to Mg^{2+} is lower than to Cl^-. Therefore, the electric field accelerates cations, which makes the rejection of Na^+ negative.

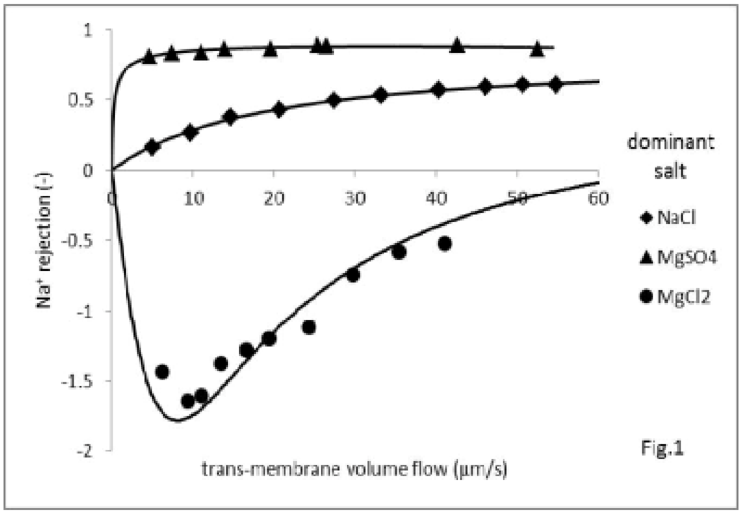

Fig.1 Rejectionof Na^+ against trans-membrane volume flow; cross-flow rate 1 m/s, concentrations of dominant salts 100 mM; relative concentrations of traces ca. 0.5%; lines are theoretical fits.

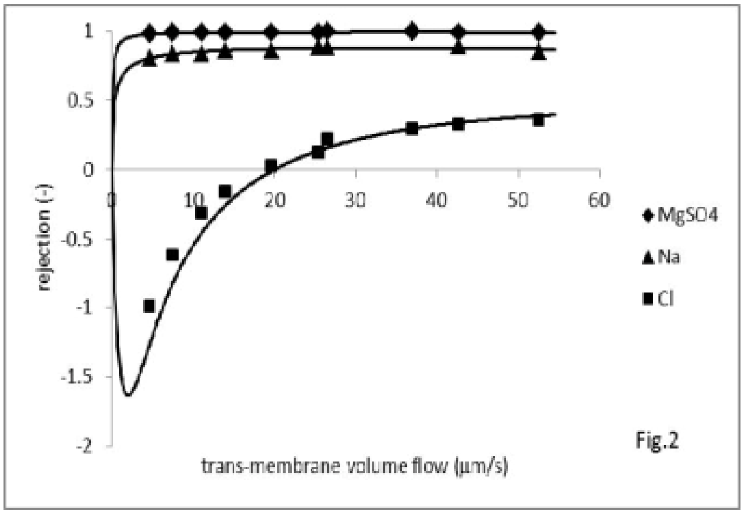

Fig.2 Rejection of $MgSO_4$ (dominant salt) and traces of NaCl against trans-membrane volume flow; cross-flow rate 1 m/s, concentrations of dominant salts 100 mM; relative concentrations of traces ca. 0.5%; lines are theoretical fits.

From Fig.2 it is seen that the rejection of trace Na^+ is much higher than that of trace Cl^- (both simultaneously added to dominant $MgSO_4$) despite the higher intrinsic membrane permeability to Na^+. This again can be explained by the electric field, which retards Na^+ but accelerated Cl^-.

As a result of theoretical interpretation the intrinsic membrane permeabilities to ions have been estimated for various solution chemistries. Information on the ionic permeabilities is useful for the optimization of membrane performance in electrolyte mixtures.

[1] A. Yaroshchuk, et al. (2010) J.Membr.Sci., 368 (2011) 192-201

ICOM405

A multi-ionic transport model to fully predict rejection of mineral salts by nanofiltration.

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Nanofiltration (NF) is the most recent membrane separation process which allows selectivity between charged solutes according to their size as well as their electrical charge. NF processes are frequently used in many industrial applications such as chemical, pharmaceutical, food industries or water treatment. This process has recently aroused much scientific interest on account of the numerous functions it serves for environmental purposes since it presents many advantages compared to other processes because of its easy control, lower energy consumption, and its environmental respect.

Within the framework of these potential applications, the contribution of transport modeling is of the primary importance not only for the understanding of physical mechanisms governing selectivity between ions but also regarding the performances prediction of a given separation. Such a model could be a very useful tool for diagnostic (in-situ for supervision or optimisation of desalination processes) and for process development.

Although much research has been devoted to the modeling of transport through NF membranes, a fully predictable model is not achieved yet. Indeed, the key point lies in the parameters assessment. In the model used in this paper, the two main parameters are the membrane charge density Xd and the dielectric constant of the solution inside pores ε_p. It has been shown that an infinity of couples (ε_p, X_d) can describe the rejection curves of a single salt solution. On the contrary, selectivity between three ions in ionic mixtures can be described only by a unique couple (ε_p, X_d).

The aim of this paper is to show the possibility of fully predict rejection of salts (NaCl and $CaCl_2$) from couples numerically identified with ionic mixtures at various proportions. Evolutions of ε_p and X_d with divalent (Ca^{2+}) proportion are drawn for a given concentration of Cl^- (100 mol m^{-3}) in Fig.1 and the trends are thus extrapolated to 0 and 100 % corresponding respectively to pure NaCl and $CaCl_2$ solutions. Fig. 1 shows that when Ca^{2+} proportion increases, both ε_p and X_d are decreasing monotonously which is coherent with the physical meaning of these parameters. These trends are accurately discussed in this paper.

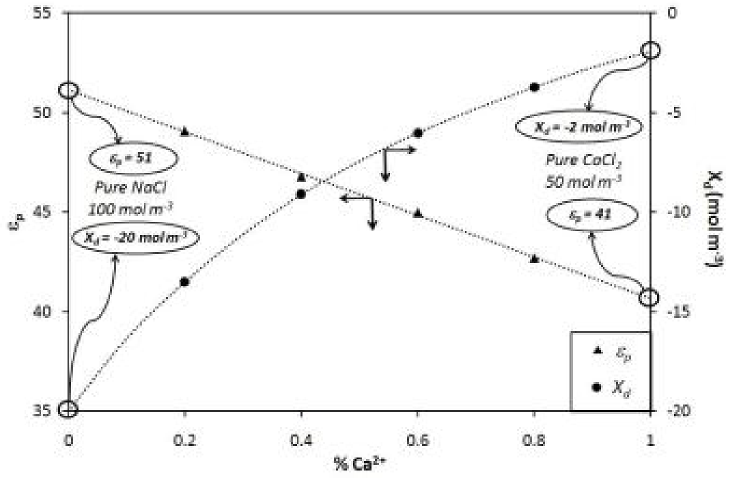

Fig. 1: Evolution of dielectric constant inside pores εp and membrane charge density X_d with proportion of divalent ion (Ca^{2+}) for mixtures with a constant chloride concentration of 100 mol m^{-3} and extrapolated values for single salt solutions.

The parameters extrapolated from mixtures were thus used to predict rejection curves of the two salts at two concentrations and results presented in Fig.2 (for 100 mol m^{-3} of Cl^-) prove that this procedure allows a well-prediction of single salt rejections. Finally, the rejection of these salts at an intermediate concentration (for which parameters were not identified) has been investigated. This study shows that it is conceivable that a model can predict any salt rejection, knowing the couple (ε_p, X_d) describing six mixtures (3 proportions at two different concentrations of the common ion).

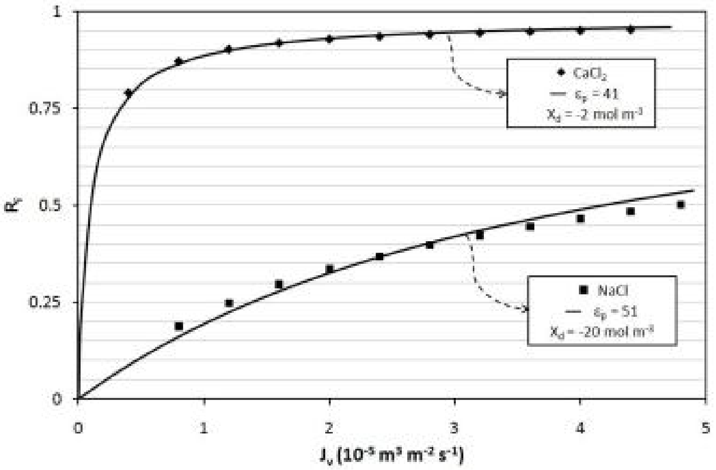

Fig. 2: Experimental and predicted real rejection curves obtained for NaCl and $CaCl_2$ solutions for a constant chloride concentration of 100 mol m^{-3}.

ICOM430

Colloidal interactions in the deposition of casein micelles on membranes: Modelling the surface energies by contact angle measurements to understand the fractionation of milk proteins

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Fouling is the major drawback in membrane (micro-)filtration of milk and other protein containing solutions. It reduces the flux and alters the retention characteristics of the filtration unit. Apart from the hydrodynamic conditions in the membrane channel colloidal substrate-membrane and protein-protein interaction influence the formation and the characteristics of a deposit layer.

Models exist explaining the deposition of proteins on the membrane as a function of hydrodynamic forces. However, the description of the deposit layer structure (porosity, thickness) as a concurrence of intermolecular interactions between the deposit layer forming proteins and the compression force of filtrate flow is often not possible.
The lack of understanding of colloidal interactions between complex protein structures and the use of oversimplified models lead often to results, which are inconsistent with experimental observations. Formally, electrostatic interactions and Van-der-Waals-forces (classical DLVO modelling) were used to explain the colloidal behaviour of casein micelles, which are the major constituent of deposit layers formed during membrane fouling at the MF of milk.

In this paper it will be shown that due to the high ion strength of milk serum the DLVO-forces can not be used as an explanation for milk deposit layer structure e.g. as a function of pH. A new interaction model for casein micelles based on the measurement of surface energies of milk proteins is presented which integrates van-der-Waals and electrostatic forces as well as hydrophilic and hydrophobic interactions. With this model, the influence of colloidal interactions on deposit layer build-up, structure, flux and whey protein permeation along ceramic MF membranes can be explained. The model is experimentally validated by a variation of environmental conditions (pH). By measuring the length-dependent distribution of flux and protein permeation, the influence of the inhomogeneous filtration conditions along a membrane on deposit-layer characteristics could be assessed

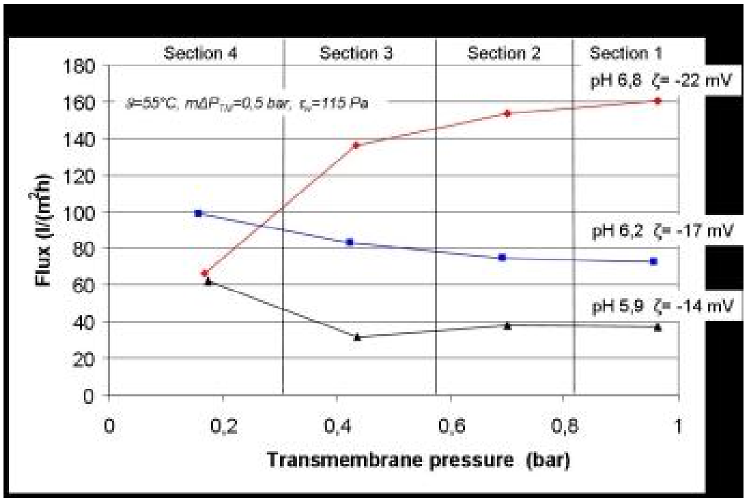

Fig. 1: Flux as a function of TMP, which corresponds to the static pressure along the membrane tube, for 3 different pH values

It could be shown that the effect of pH can be explained by hydrophilic repulsion of the protein particles rather than by their electrostatic repulsion. Fig. 2 shows the interaction energy as a function of particle distance, which is mostly influenced hydrophilic interactions.

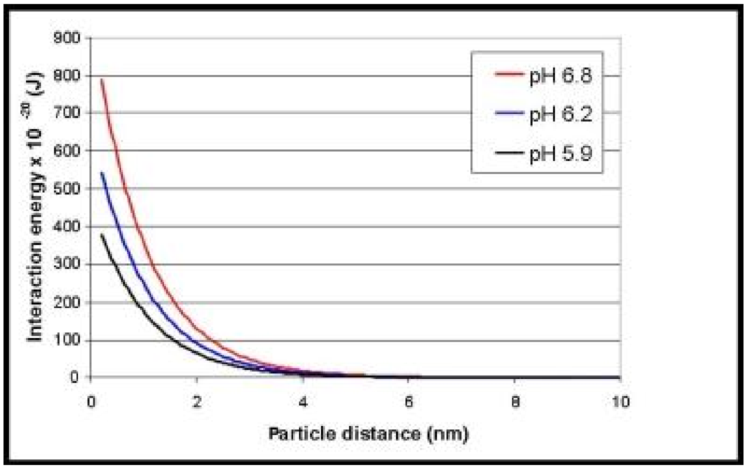

Fig. 2: Interaction energy between particles as a function of pH and particle distance

The integration of surface energies of proteins into an interaction model can be transferred to other proteins besides casein to reveal valuable information about colloidal interactions during filtrations of protein solutions. This knowledge facilitates the optimal alignment of process and membrane properties to the filtration task.

Parts of this paper are based on the thesis of co-author W. Kuehnl whose work received the Julius-Maggi-Award of the European Federation of Chemical Engineering (EFCE) in 2010.

ICOM1205

A simple physics-based transport model for electrodialysis with non-perfect membranes

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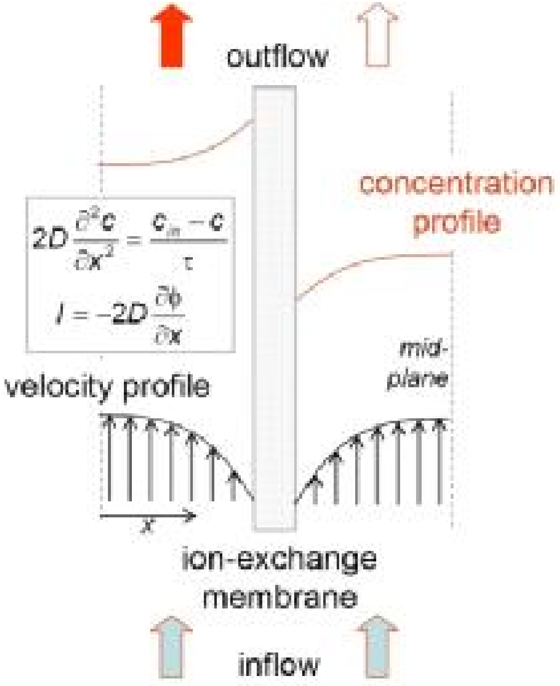
For energy-efficient water desalination, electrodialysis (ED) is an important technology [1]. Ion transport models for ED make use of the theoretical concept of the mass transfer film located on each side of the membrane, in which ion transport is assumed to be directed only towards the membrane. Other words for the mass transfer film are the Nernst layer, or the (stagnant) diffusion layer (SDL). A typical estimated thickness of the SDL is of the order of 200 µm. Current developments in ED are towards decreasing the spacer channel thickness. When the spacer thickness is less than ~1000 µm, the SDLs no longer have a negligible thickness compared to the spacer channel, and the theoretial concept of the SDL becomes less appropriate for ED-modeling.

Therefore, we develop a simple steady-state ED-model which does not require the assumption of SDLs. Instead we describe the fluid flow in each spacer channel using a Poisseuilli velocity distribution, combined with the Nernst-Planck (NP) equation for ion transport, as well as local electroneutrality. We combine this description with the exact steady-state solution of the NP-equation for non-perfect membranes, i.e., including non-perfect membrane permselectivity [2,3]. The complete model can be used for arbitrary values of the spacer thickness, flow rates, concentrations, etc., and does not require as input the ion transport number or membrane permselectivity.

We present results of the mathematical model and compare with experimental data from a small-scale ED test-stack. We show how the membrane permselectivity is not constant but depends on various process conditions, such as ionic strength [4]. The model we present is one-dimensional, but can be extended to multiple dimensions, corrugated membranes, and the case of continuous electrodeionization.



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4. P. Dlugolecki, B. Anet, S.J. Metz, K. Nijmeijer, and M. Wessling, *J. Membrane Sci.* **346** 163 (2010).

Parallel Sessions

Wednesday, July 27th 2011

Morning Session 2, 10.50 – 12.40

Membrane characterization 3

ICOM1793

Characterization of Membranes and Membrane Processes: Overview and Future Needs

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There is a continuing and critical need for improved methods to characterize membranes and membrane processes in a wide range of applications including water desalination, industrial gas separations, renal dialysis, membrane lung oxygenators, and controlled-release drug delivery devices. For example, one of the most fundamental properties of semi-permeable membranes is pore size, but there remain issues with such measurement. Pore-size distribution determines the ability of a membrane to retain colloidal particulates, bacteria, macromolecules and/or molecular aggregates, but no one technique can characterize membranes over the full spectrum of pore sizes typically encountered. In addition, recent work has highlighted the advantages of real-time, non-invasive measurements for characterization of membrane module hydrodynamics, fouling and cleaning, but significant improvements are required for commercial implementation. Further, there is a growing recognition regarding the importance of understanding changes in membrane properties that may occur after extended use.

Currently, a variety of analytical tools are available for characterizing the morphology of membranes including scanning electron and atomic force microscopy, which are used to quantify properties such as surface roughness, asymmetry, and pore-size distribution. However, these techniques typically require expensive instrumentation and cannot easily provide values reflecting an entire sample. Many of the most recent techniques used for membrane characterization have been adopted from other scientific disciplines such as vertical scanning interferometry for characterizing membrane surface topography, three-dimensional morphological analysis using x-ray synchrotron radiation-computed microtomography, and ellipsometry of angle-resolved scattering to more accurately characterize membrane structure. In contrast, other techniques have evolved from direct consideration of membrane-based needs such as evapoporometry, a novel methodology for accurate characterization of membrane pore-size distribution based on the evaporative mass loss.

There is also great benefit in the ability to characterize membrane processes in real time. For example, seawater desalination is rapidly becoming even more important because of the need to provide sustainable quantities of potable water to ever-growing populations, but scaling of inorganic salts on the membrane surface presents a significant challenge for improving process efficiency. Studies employing ultrasonic time-domain reflectometry as well as optical observation and modeling for real-time monitoring of scaling have demonstrated that these techniques could be used for active process control to optimize the use of back-flushing, chemical antiscalants, and flow reversal. More recent work has described the use of integrated electrolytic sensors for measuring the concentration polarization boundary layer. In gas separations as well, characterization of membrane behavior during operation has proven useful. For example, changes in membrane mechanical properties can provide better understanding of fundamental phenomena such as plasticization during CO_2 exposure.

Looking ahead, suitable characterization methodology is needed for improved understanding regarding the structural factors that affect the performance of new membrane materials, lifetime predictions of membrane behavior over long time scales, and analysis of membranes that have failed prematurely. Although all of these important aspects cannot be discussed in a brief presentation, we will highlight recent representative developments that utilize novel and advanced characterization techniques and we will provide a perspective regarding future characterization needs.

ICOM609

New microscopic characterization methods for porous polymeric membranes

Herbert Reingruber

Graz University of Technology, Institute for electron microscopy and fine structure research, Graz, Steiermark, AT

In modern variable pressure scanning electron microscopes different *in situ* tests for various kinds of porous membranes can be performed. They provide, in contrast to other characterization methods, information about the fluid transport in membranes on a µm-scale. In this abstract two new microscopic methods for the space-resolved characterization of polymeric membranes will be presented: wetting and drying experiments and automated *in situ* ultramicrotomy. The respective results enable a correlation between the membrane structure and the membrane behavior during the dynamic wetting and drying experiments.

In the low pressure range of an environmental scanning electron microscope (ESEM) wet specimens can be investigated. The onset and progression of the respective processes can be observed with high magnification and great depth of focus. For example, the investigation of the wetting and drying of porous membranes can be studied on a µm-scale. It provides information about the dependence of both the number of dry pores and their size at the membrane surface on the time elapsed. This information cannot be gained by conventional test procedures. For the experiments a Peltier cooling system is used for cooling down the membrane to a temperature of 3°C. At this temperature and at a pressure of 6 torr the water vapor inside the ESEM chamber condenses at the cooled surfaces and wets the membrane. The wetting and drying process can be controlled by changing the pressure between values above (wetting) and below (drying) the dew point. By successive recording of images of the membrane surface the number, size and size distribution of dry pores as a function of time can be determined.

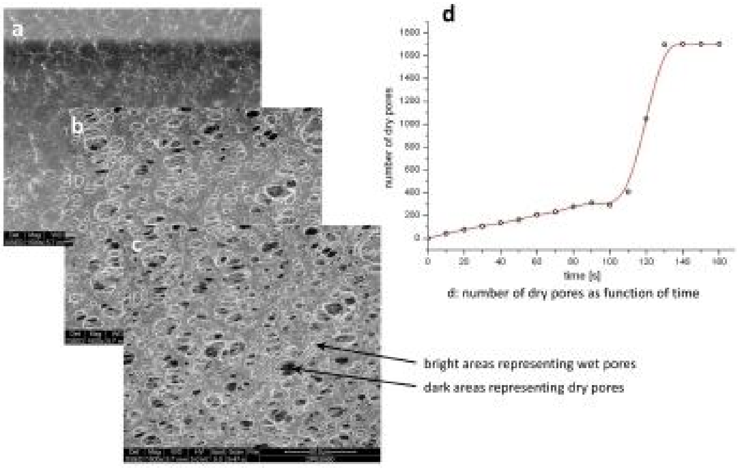

Figure 1: a: wet membrane at the beginning of the dry process ; b-c: partly dry membrane after 30 and 110 seconds

Conventional scanning electron microscopy is a powerful tool for the characterization of porous membranes. However, a single image of the surface or the cross-section of the membrane provides only information of the surface topography and the pore size. But the pore volume, connectivity of the pores and the area of the inner membrane surface cannot be determined from such images. *In situ* ultramicrotomy is a new method to get a stack of already aligned images from which a three-dimensional model of the complex membrane structure can be reconstructed with nm resolution. For this purpose an ultramicrotome was mounted inside the ESEM. The membranes to be investigated were embedded in resin and mounted at the microtome holder. Subsequently automated serial sectioning and block face imaging of the cross-section of the membrane were performed (slice thickness: 50 nm). The stack of images was used to create 3D models by using special computer software. The software allows the calculation of a tube network model (red) representing the pores. The 3D model can also be used for further fluid simulations.

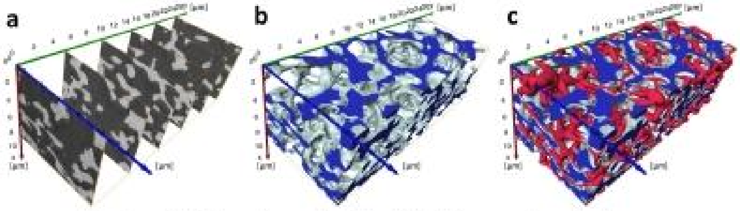

Figure 2: a: stack of images; b: reconstructed model of the inner membrane structure;
c: tube network model (red) representing the pores

ICOM1001

Characterization of the nanostructure of isolated polyamide films of RO and NF membranes

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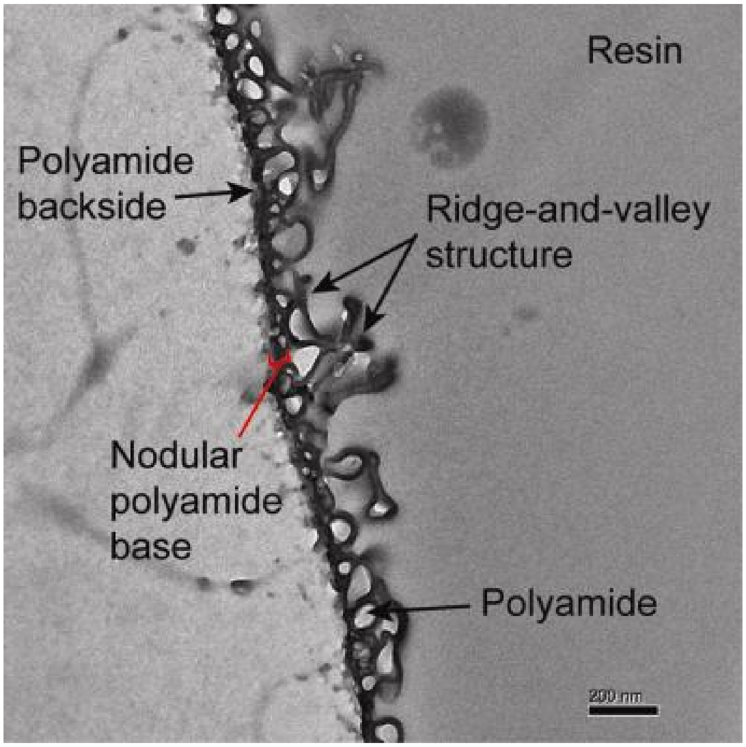
Achieving a better understanding of transport and rejection mechanisms in RO and NF membranes requires more detailed information of the nanostructure of polyamide thin films. The active layer in state of the art RO membranes consists of cross-linked networks of fully aromatic polyamide, with an overall average thickness of approximately 200 nm and a heterogeneous structure that confers the membrane a relatively rough surface (RMS roughness about 100 nm), also described in the field as the peak-and-valley structure. The ability to separate these polyamide films from the underlying polysulfone support was used in combination with advanced microscopy methods to investigate the nanostructure of the films. Cross-sectional and projected area TEM (PA–TEM) images of isolated films revealed the existence of a 30–60 nm compact base of nodular polyamide that forms the interface with the polysulfone support and from which the more open ridge-and-valley structure extends outward. AFM measurements showed that the backside of the nodular base (i.e., the polyamide surface facing the polysulfone support) is relatively smooth with RMS roughness values approximately 5 times lower than the film surface. In SEM images of the backside, the polyamide nodules are clearly visible giving it the appearance of a "granular" surface.

In contrast, the semi-aromatic polyamide active film in NF membranes is approximately 40 nm thick with an extremely smooth surface (RMS roughness of about 7 nm). The peak-and-valley structure is absent in these films. A detailed analysis of the nanostructure showed that the entire film consists of a nodular polyamide layer similar to those observed in the RO films. Our characterization results suggest that these nodular polyamide structures are most likely responsible for the separation and transport properties of RO and NF membranes. To further examine which sections of the film are actively involved in the transport and rejection mechanisms (i.e., to look for specific areas of higher water permeability that could be more sensitive to initial fouling), cross-flow filtration experiments with 10 nm gold nanoparticles were performed. PA–TEM was used to image and analyze the spatial distribution of the nanoparticles.



ICOM363

Positron annihilation lifetime spectroscopy (PALS) characterization of polymeric membrane materials for desalination applications

Geoffrey Geise[1], Anita Hill[2], Hao Ju[1], Wei Xie[1], Alyson Sagle[1], Cara Doherty[2], James Mardel[2], James McGrath[3], Benny Freeman[1], Donald Paul[1]
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The fractional free volume of dense, non-porous polymeric membrane materials, such as those used in desalination applications, is a key determinant of the material's separation performance. Positron annihilation lifetime spectroscopy (PALS) is well suited for analyzing the free volume characteristics of these materials. It is important to understand how polymeric free volume responds to water sorption in order to design improved desalination membrane polymers. Combining and correlating free volume data, measured using PALS, with water and salt transport properties is critical to building a fundamental understanding of these materials.

This study interprets transport results from three polymer platforms of increasing complexity in terms of PALS observations. First, a series of cross-linked poly(ethylene glycol) (PEG) hydrogels were studied to confirm that hydrated-state PALS data correlates with water and salt transport properties as expected from free volume theory. The results show that as water sorption increases, the free volume element size decreases and the concentration of free volume elements increases in agreement with a simple water-polymer mixing model. The overall fractional free volume of the system increases with increasing water sorption. Next, a series of directly copolymerized sulfonated poly(arylene ether sulfone) random copolymers were studied. Unlike the rubbery PEG hydrogels, water sorption in these glassy copolymers has an effect on free volume that cannot be explained by the simple water-polymer mixing model. As water sorption increases, the state of sorbed water, degree of copolymer sulfonation, and plasticization of the material appear to influence the copolymer's free volume. Finally, a sulfonated styrenic pentablock copolymer was studied. Transport data for this highly micro-phase separated material correlated with free volume data obtained by PALS. Furthermore, the effect of water sorption on the block copolymer's free volume was found to be very similar to the result observed for the random copolymer system; this behavior suggests a general similarity between the latter two polymers and distinct from the PEG hydrogels. In addition, o-Ps inhibition implications for PALS studies on polymers containing electron-withdrawing moieties, such as sulfonated polymers, will be discussed.

ICOM1592

Method for measuring local fluxes and localizing defects in zeolite membranes

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The selectivity of zeolite membranes is often limited by the presence of non-selective defects that are larger than the separation pores. The defects may form during membrane preparation or as a result of thermal stresses. Most defect characterization techniques use integral methods to estimate average sizes and total defect fluxes, but they do not determine the defect locations. A common integral approach is to measure the flux of molecules that are larger than the zeolite pores and therefore can only pass through the defects. Another technique is permporometry, where the pores are selectively blocked by adsorption or capillary condensation of a vapor and the remaining flux of an inert gas is used to estimate the size and quantity of the defects. A method recently reported by Kumakiri et al. [Micro. Meso. Mater., 115 (2008) 33] measures local fluxes by scanning the surface of a membrane with a mass spectrometer probe. A membrane was automatically moved along the stationary probe, and a small amount of helium was fed on the opposite side of the membrane. Near defects, the helium signal increased and a surface map was obtained that showed the location of the defects.
We adapted this technique to determine both defect locations and local permeances for tubular SAPO-34 zeolite membranes. The SAPO-34 pores are approximately 0.4 nm in size. The probe used a coaxial design so that the permeating gas was sampled with a capillary that connected to a mass spectrometer. This capillary was centered inside a second capillary that provided a purge gas. The Teflon tip of the probe was spring loaded and it slided across the membrane surface. The purge gas locally diluted the permeate, so that the concentration measured by the mass spectrometer was a measure of the permeance. In contrast to the design by Kumakiri et al., the membranes were stationary, and the probe scanned the inside surface of the tube. The locations of the defects were detected by feeding i-butane or CF$_4$ to the shell side of the membranes. Because i-butane and CF$_4$ are larger than the zeolite pores, they only permeate through defects, and spatial defect maps, as shown for i-butane in Figure 1, were obtained. The probe was sufficiently sensitive to identify few small defects, even though macroscopically, no flow was detectable with flow meters.

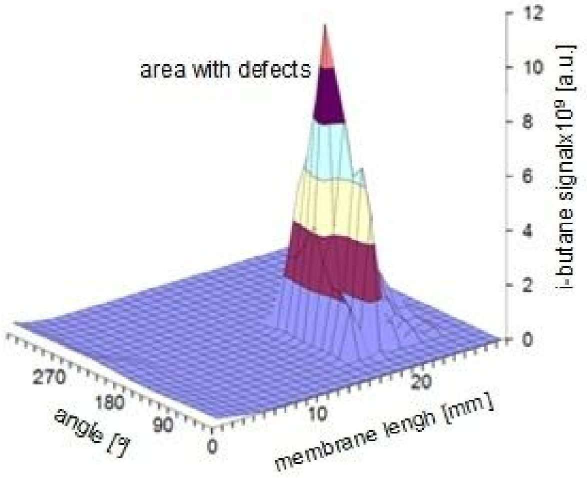


Figure 1: Iso-butane MS-signal as function of spatial location on a SAPO-34 membrane

A map of the overall permeance of the membranes was obtained by feeding CO$_2$ on the shell side; CO$_2$ is smaller than the SAPO-34 pores. Figure 2 shows a spatial map of the CO$_2$ signal for a SAPO-34 membranes that indicates that this membrane has regions near the center where permeances are close to zero (low fluxes near the ends indicate glazed areas). The cause of the impermeable sections is not known. Not all membranes show such behavior, and detailed knowledge of local permeances and defect distributions will help improve membrane preparation.

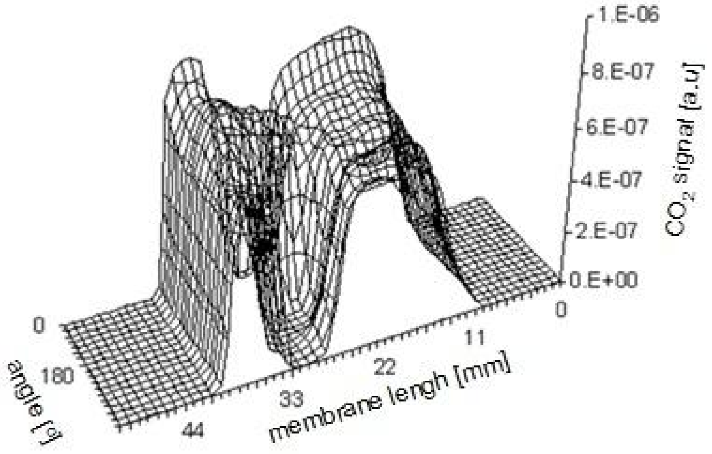


Figure 2: Profile of the CO_2 MS-signal for a SAPO-34 membrane

Membrane formation 3

ICOM1792

The formation of membranes with uniform pores

Werner A. Goedel
Chemnitz University of Technology, Physical Chemistry, DE

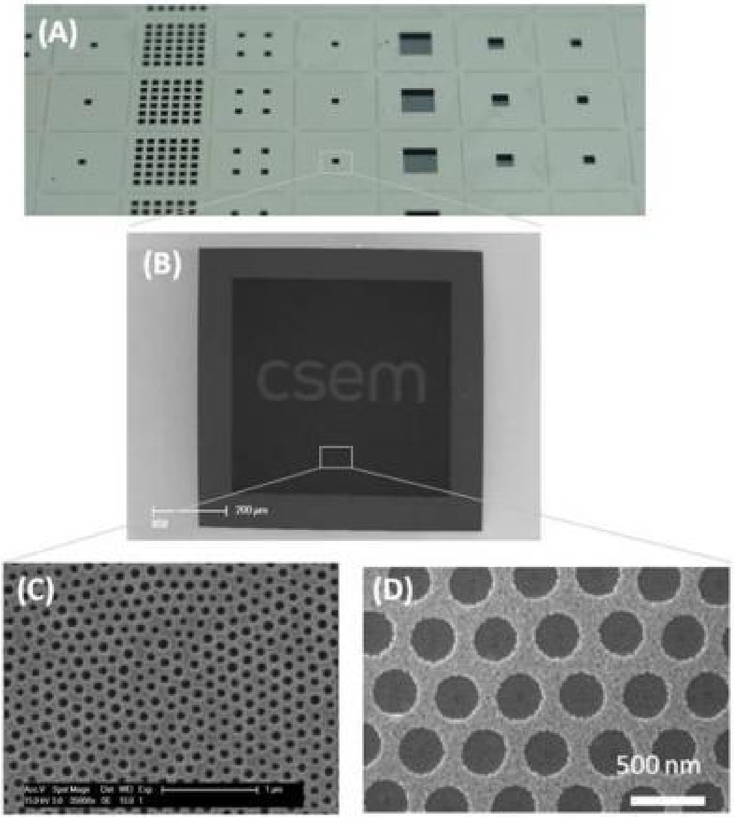
Most methods used to produce porous membranes give rise to pores of non-uniform diameter and membranes bearing such non uniform pores are without problems used in most filtration applications. These membranes fulfil their function either because most of their non uniforms pores are way smaller than the particles that shall be retained or because the particles to be retained build up a filter cake in an initial (and inefficient) phase which subsequently act as the 'real' filtration medium. Although such membranes are working quite well and often offer the best balance between performance and price, there are quite a few application worth investing the effort to prepare membranes of uniform pore size. For example uniform pore size is desirable if the membrane is intended to let objects pass that have a size not drastically smaller than the objects to be retained, membranes with uniform pore size have a lower flow resistance than membranes having the same size cut-off and porosity but non-uniform pores and membranes with uniform pores may work not only without a filter cake they may as well facilitate removal of a filter cake by cross flow or back flushing and thus allow higher filtration speeds. The talk will focus on ways to prepare such membranes by top down approaches such as machining, printing or photolithography, embedding of sacrificial objects that act as template for pores and self-organization.

ICOM283

Ultrathin Nanoporous Silicon Membranes

Franck Montagne, Mona Klein, Nicolas Blondiaux, Harry Heinzelmann, Raphael Pugin
Swiss Center for Electronics and Microtechnology, Nanotechnology and Life Science, Neuchâtel, CH

Nanoporous membranes fabricated from silicon materials have recently emerged as a new class of inorganic nanosieves offering a relevant technological alternative to commercially available ultra- and microfiltration polymer membranes for (bio)separations. Here, we present a new fabrication process based on polymer self-assembly for producing arrays of ultrathin nanoporous silicon membranes (NSiMs) at wafer scale. The process utilizes either self-assembled monolayers of block copolymer micelles or nanospheres to create a nanopatterned metallic mask, which is then used to produce nanopores in low stress silicon nitride layer by deep reactive ion etching. The membrane released is achieved via a combination of dry and wet etching, thus leading to a free-standing nanoporous film. A key aspect of this process is the ability to tune independently the size and density of the nanopores, as well as the membrane thickness and dimension. Typically, NSiMs as thin as 100 nm can be produced with various lateral dimensions (up to few cm^2) and homogeneous pore sizes in the range of 30 to 500 nanometers. The pore density is comprised between 10^{10}-10^{11} pores/cm^2, which is superior by two orders of magnitude to commercial track etch membranes.



We will show that such membranes exhibit outstanding mechanical properties as they can withstand up to few bar differential pressure. These unique specifications enable fast transport of molecules with high selectivities, making NSiMs ideal sieving materials for applications in biotechnology. In particular, they can be considered as new structural elements of (Bio)-Micro-Electro-Mechanical Systems (BioMEMS) because of their facile integration in microfluidic devices, as will be discussed.

ICOM747

The development of membranes for nanofiltration based on pre-assembled nanoparticles.

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Organic solvent nanofiltration (OSN) is a technique for economic and efficient separation of molecules in the range of 200-1000 g.mol^{-1} which are dissolved in organic solvents. The most widely studied OSN membranes are asymmetric polymeric membranes prepared by the phase inversion technique. It is believed that the separation performance of these membranes is determined by the dense top layer formed during phase inversion. The separation performance (flux and rejection) can be varied by changing the solvent/co solvent ratio and polymer weight % in the dope solution [1]; however achieving wide range of molecular weight cut-offs using this technology is still difficult. This paper reports first findings from new work at Imperial College into preparing membranes using controlled building blocks to form permeation passages in a manipulated way. By creating a controlled nanostructure in the top layer of a nanofiltration membrane we seek the power to tune molecular permeation properties.

A new class of OSN membranes have been fabricated by assembling nano-sized particles with methacrylate moieties onto the surface of crosslinked polyimide ultrafiltration support membrane. Multiple layers of these nanoparticles create a separation film functionally similar to the top layer of asymmetric polymeric OSN membranes. Nanoscale interstitial spaces formed between the particles serve as permeation channels. In principle, manipulating the size of the nanoparticles can be used to control the dimensions of the interstitial spaces through which permeation occurs. Two different sizes nanoparticles - 120 and 300nm - were used. As expected, membrane separation performance changed with the size of nanoparticles employed due to the changes in interstitial dimensions. Crosslinked polyimide ultrafiltration membranes prepared by phase inversion were coated with successive layers of nanoparticles by spin coating. The nanoparticles were crosslinked by photoinitiated free radical polymerization using ultraviolet light (365nm wavelength). In addition to the size of the nanoparticles, the separation performance was also manipulated by changing the thickness of nanoparticle layer.

Membranes were characterized using scanning electron microscopy (Figure 1a). The nanofiltration performance of these membranes was evaluated in solvents such as dimethylformamide, acetone and toluene. The molecular weight cut-off of the membranes was from 300-1000 g.mol^{-1} depending upon the nanoparticle building block size and thickness of nanoparticle layer (Figure 1b).

Thus membranes with the graded nanoscale porosities were successfully fabricated from interconnected nanoparticles providing control over membrane permeation performance.

Table1: Thickness calculation of the membranes coated with 120nm nanoparticles

Entry no	Membrane code	No of layers	Thickness calculated (µm)	Thickness increase guage(µm)	Thickness SEM (µm)
1	Thickness 3	20	1.7	.9	.76
2	Thickness 2	113	9.0	7.5	6.9
3	Thickness 1	282	22.5	17.5	15.3

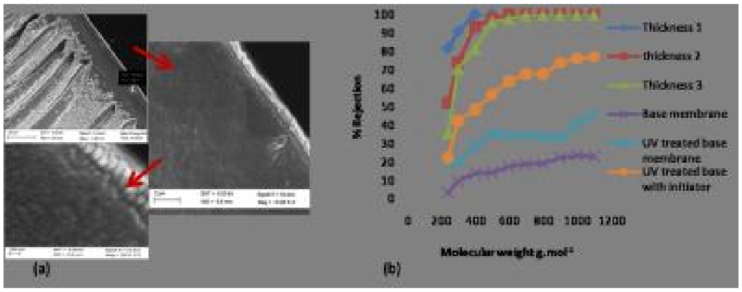

Figure 1: (a) SEM image (b) Separation performance of nanoparticles coated membranes. (Tested in toluene at 10 bar)

Acknowledgement
Author wish to acknowledge FP7 GA-CP-FP 214095-2 HiCat project and Prof. Vamvakaki (Foundation for Research and Technology HELLAS) for assistance.

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ICOM479

Fabrication and characterization of novel nonwoven nano-structured thin film composite membrane for engineered osmosis applications

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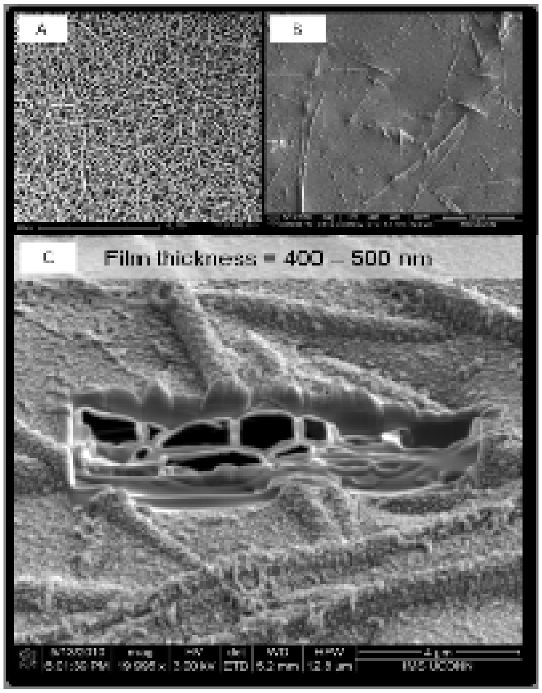
The shortage of energy and water resources is a grand challenge facing humanity in the 21st century. Engineered osmosis (EO) technologies have been increasingly investigated as alternative means of sustainable water and energy production. These membrane technologies exploit the gradient of osmotic pressure between a dilute feed solution and a concentrated draw solution as a driving force for water treatment (forward osmosis) and electricity generation (pressure retarded osmosis). However, EO development has been hindered by the lack of well-designed membrane that exhibits high water flux, superior selectivity, chemical stability, and adequate mechanical strength.

Thin film composite (TFC) membranes comprised of an ultrathin dense selective layer formed over porous support membranes have been broadly used in reverse osmosis. However, the thick support layers of traditional TFC-RO membranes are unsuitable for EO because they hinder salt diffusion internally, which is referred to as internal concentration polarization. In order to mitigate this problem, composite membranes are needed with thinner and highly porous support layers. The support layer also needs to be more hydrophilic than traditional TFC-RO membranes, while retaining appropriate physical, chemical, and thermal stability.

In this study, nanostructured nonwoven mats with high porosity and well-interconnected pores were fabricated by electrospinning technique and applied as supports for TFC membranes for EO. Polysulfone (PSf) and polyethersulfone (PES) were selected as membrane support materials. The surface morphology, size distribution, mechanical strength and thermal stability of the electrospun nanofibers were optimized by changing polymeric solutions properties during electrospinning, *i.e.*, polymer concentration and solvent ratio in mixtures.

A thin RO-type polyamide layer supported by this electrospun nanofiber nonwoven mid-layer and PET nonwoven substrate was finally formed using an in-situ interfacial poly-condensation reaction between *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) monomers. The performances of these thin film composite membranes were tested in direct osmosis system and found to

exhibit high water flux and relatively low reverse salt flux. Early results show that this nanostructured TFC membrane appears to be a promising candidate as a next generation membrane for engineered osmosis.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Film thickness = 400 – 500 nm
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ICOM778

Metal-organic framework membrane derived from a LBL self-assembly seeding procedure

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Current interest in metal-organic framework (MOF) membranes is rapidly expanding because of their potential applications in separation science.[1-4] An integrated MOF membrane supported on a porous substrate is required for high permeation flux and selectivity. For the preparation of MOF membranes, secondary growth has been proved to be a feasible and effective method. The key steps for this method are the synthesis of seeds and uniform seeding. However, for many MOF materials, the formation of uniformly distributed crystals served as seeds on the surface of the supports is very difficult. Thus, besides the commonly used dip coating and wiping, some new seeding routes based on the chemical features of MOFs were also developed, such as thermal seeding and reactive seeding. [3]

In this paper, we reported a novel seeding method to prepare HKUST-1 (known as $Cu_3(btc)_2$) membranes on porous α-alumina supports. Uniformly distributed seeds were produced by *in situ* layer-by-layer (LBL) self-assembly through the coordination of H_3btc (1,3,5-benzenetricarboxylic acid) and Cu^{2+} on α-alumina support. Therefore, an integrated $Cu_3(btc)_2$ membrane can be synthesized by the secondary hydrothermal growth on the seeded support. The formation process of the seeding layer was investigated by ultraviolet-visible (UV-Vis) absorption spectroscopy and atomic force microscopy (AFM)(Figure 1). The morphology of the membrane was characterized by the scanning electronic microscopy (SEM)(Figure 2). The gas permeation performance of the $Cu_3(btc)_2$ membrane was also evaluated.

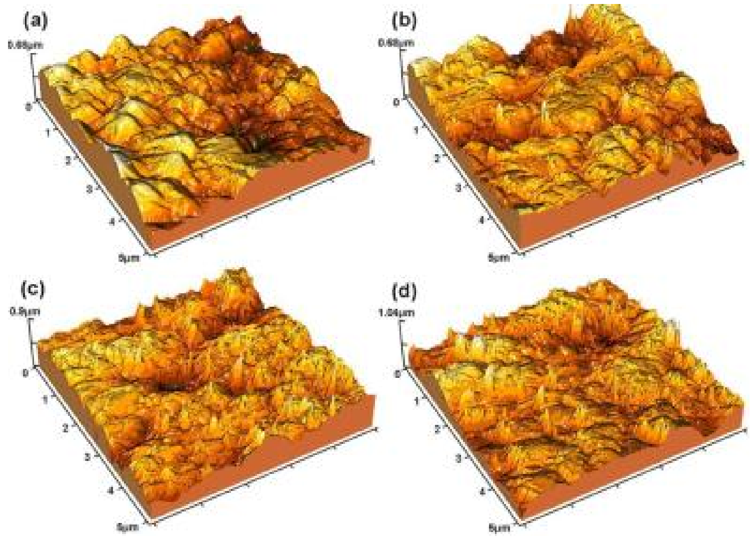

Figure 1. AFM images of bare (a) and LBL self-assembly seeded support after two cycles (b), four cycles (c) and eight cycles (d).

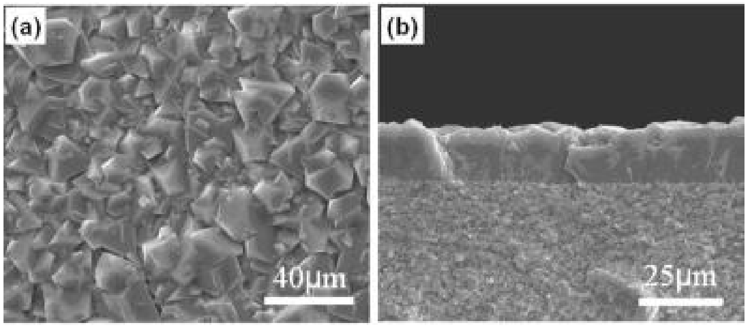

Figure 2. SEM images: (a) surface and (b) cross-section of HKUST-1 membrane.

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Inorganic membranes 2

ICOM1811

Ceramic-Carbonate Dual-Phase Membranes for High Temperature Dioxide Separation

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High temperature CO_2 perm-selective inorganic membranes offer potentials for post-combustion and pre-combustion CO_2 capture by means of membrane separators or membrane reactors. These membranes can also be used for many chemical reactions involving carbon dioxide reactant or product for process intensification. Extensive work conducted by researchers in the past two decades resulted in many microporous inorganic membranes with high CO_2 permeance and selectivity at low temperature (around room temperature). However, all these membranes loss CO_2 selectivity over other gases at temperatures above 300°C. This paper reports on the synthesis and carbon dioxide transport properties of novel ceramic-carbonate dual-phase membranes which are CO_2 permeable with theoretically infinite CO_2/N_2 selectivity at high temperatures. The carbonate-ceramic dual-phase membranes are composed of a solid ceramic phase that acts as a support for the eutectic molten carbonate phase (such as Li-K-Na carbonate). Mixed oxygen ionic-electronic conducting ceramic, such as $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-d}$, or oxygen ionic conducting ceramics such as yttria stabilized doped zirconia, was chosen as the support material to take advantage of its high oxygen ionic conductivities and excellent oxidation resistance. The oxygen-ionic and electronic conductivity of the ceramic support allows for CO_2 to be separated by two distinct separation mechanisms – one with and the other without the need for oxygen. In the presence of oxygen, CO_2 is reacts with O_2 in the feed gas and electrons provided by the support to form a carbonate ion, $CO_3^{=}$. In the absence of oxygen, CO_2 reacts with oxygen ions ($O^{=}$) provided by the support to form $CO_3^{=}$. The carbonate ion can then be transported through the molten carbonate phase. Upon reaching the downstream side of the membrane, the reverse reactions occur. Several ceramic-dual phase membranes have been prepared in our laboratory. The membranes are perm-selective to CO_2, with CO_2 permeance of about $1x10^{-7}$ mol/m.^{2}.Pa.s at high temperature above 600°C. The effects of the membrane thickness, temperature and CO_2 partial pressure on the CO_2 permeation through the dual-phase membranes were experimentally studied to elucidate the CO_2 transport mechanism. The application of the new ceramic-carbonate dual-phase membrane will be demonstrated by use of the membrane in a membrane reactor packed with a reforming catatlyst for simultaneous CO_2 capture from flue gas and dry-reforming of methane to produce syngas at high temperatures.

ICOM838

Newly developed zeolite membranes for dehydration under higher water contents and acidic conditions; MOR/MFI hybrid membrane and high-silica chabazite membrane.

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Two types of zeolite membranes were synthesized for dehydration under sever feed conditions of higher water contents and acidity; 1) MOR/MFI hybrid zeolite membrane and 2) high-silica chabazite membrane.

The MOR/MFI hybrid zeolite membrane was fabricated by a seeded growth method using ZSM-5 seed crystals with a chemical composition of $10Na_2O:0.15Al_2O_3:36SiO_2:960H_2O$ for synthetic solution to be composed by two zeolitic phases of mordenite and ZSM-5 [1]. The grazing incidence X-ray diffraction (GIXRD) observation on the vertical structure of the membrane showed that the most upper surface layer was composed mainly by mordenite phase. The relative abundance of mordenite to ZSM-5 phase was increased in the upper surface layer of the membrane. These implied that ZSM-5 phase was mainly crystallized in the early stage and then mordenite phase was tend to be increasingly precipitated in the latter stage. The membrane exhibited higher membrane performance for dehydration of acetic acid (AAc) aqueous solution in vapor permeation (VP) at higher temperatures up to 160℃. The permeate fluxes are 5.7 kgm^{-2}h^{-1} at 120℃ and 13.7 kgm^{-2}h^{-1} at 160℃ at a feed vapor composition of ca. water(60wt.%)/AAc(40wt.%). The leakage of AAc concentrations into the permeate were 0.2 wt.% at 120℃ and 160℃, or separation factors α were 300, indicating that sufficient separation ability for industrial utilization.

The high-silica chabazite membrane (***MSM-1***; **M**itsubishi High-**S**ilica **M**embrane-**1**) was synthesized using a template material [2]. The higher permeate fluxes up to 25.9 kgm^{-2}h^{-1} at 130℃ from 7.6 kgm^{-2}h^{-1} at 90℃ were observed in pervaporation at a feed mixture of water(50wt.%)/IPA(50wt.%). The separation factors α were changed from 320 at 90℃ to 120 at 130℃, or the IPA leakages into the permeate were 0.34 wt.% at 90℃ and 0.86 wt.% at 130℃. In VP experiments, higher performance was also observed that the permeate fluxes increased from 9.2 kgm^{-2}h^{-1} at 90℃ (water content in the feed vapor [Xw] was 25wt.%) to 25.9 kgm^{-2}h^{-1} at 130℃ (Xw=25wt.%). Membrane samples with 40cm long for commercial purpose can be fabricated to be applied in dehydration solvents with higher water contents.

The membranes with acid-proof and with resistance to high-water feed contents can dehydrate solvents under the sever conditions that cannot be covered by the conventional commercialized A-type zeolite membranes.

Acknowledgmenet; This study is supported by NEDO (New Energy and Industrial Technology Development Organization, JAPAN).

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ICOM1715

Highly selective separation of p-xylene in xylene isomers with tubular silicalite-1 membrane

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Since the boiling points of xylene isomers are close (*m*-xylene, 412 K; *o*-xylene, 417.6 K; *p*-xylene, 411.5 K), separation of these isomers remain a problem. Membrane separation is anticipated to be a less energy intensive process. Silicalite-1 is a sort of medium pore, silicious zeolite. The micropore size of silicalite-1 is close to the kinetic diameter of *p*-xylene (0.58 nm) and its bulkier *m*- and *o*-isomers (kinetic diameter = 0.68 nm) are difficult to enter into the micropore. Tapatsis *et al*. have synthesized a *b*-oriented silicalite-1 membrane grown from a well aligned, thin, *b*-oriented seed layer from on a flat mesoporous support disk surface with a specially-designed organic structure-directing agent[1]. They reported their silicalite-1 membrane gave a high selectivity with a high permeance of *p*-xylene (separation factor of p-xylene/m-xylene >1000). In this report, we propose alternative method to prepare a randomly-oriented silicalite membrane prepared on a porous tubular support for p-xylene separation.

Silicalite-1 membrane was prepared on a tubular alumina support (Noritake Co. Ltd., outer diameter = 10 mm, average pore diameter = 0.17 mm, length 3 cm). Silicalite-1 seed having a diameter of ca. 200 nm was dip-coated on the outer surface of the support. Hydrothermal treatment of the dip-coated support was performed at 403-453 K in a hydrogel having a composition of $25SiO_2$:3TPAOH:$1500H_2O$:100ethanol where TPAOH is tetrapropylammonium hydroxide. After the crystallization, the membrane was washed in boiling water and calcined at 773 K for 6 h.

At 453 K of crystallization, the permporometry measurements implied that mesopores formed between crystals remained after prolonged crystallization up to 122 h. The FE-SEM observations suggested that the aspect ratio of crystals composing the membrane is rather high, possibly leading to a difficulty to fill the voids between crystals. With these membranes no separation was observed for a mixture of *p*- and *m*-xylene.

When the crystallization was carried out for longer than 12 h membrane became compact. Fig. 1 shows the typical FE-SEM views of these membranes crystallized at 403 K. Crystals having a small aspect ratio were densely formed after 12 h of crystallization. Figure 2 shows the separation results for a mixture of *p*- and *m*-xylene at different temperatures. The membrane crystallized for 18 h was used. It should be noted that *p*-xylene was selectively permeated at above 473 K and the permeance of bulkier *m*-xylene was below the detection limit (the separation factor > 3000), while at 423 K *m*-xylene permeated possibly owing to the condensation of xylene isomers in slightly-remaining voids between crystals in size of ca. 1 nm.

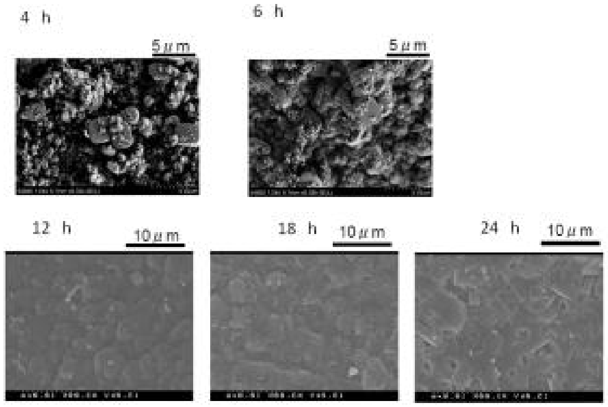

Fig. 1 FE-SEM views of the top surface of silicalite-1 membrane at 403 K crystallized for difference period.

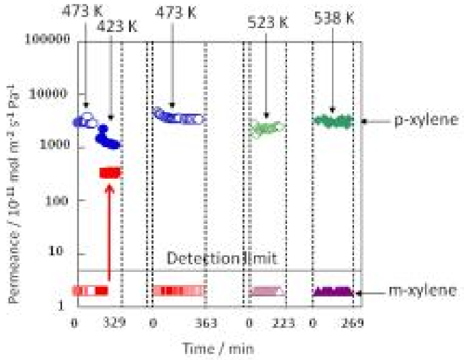

Fig. 2 Time courses of the permeances of *p*- and *m*-xylene at different temperature. Partial pressure on the feed side: *p*-xylene, 0.4 kPa; *m*-xylene, 0.4 kPa. Total pressure, atmospheric. Carrier, nitrogen. Sweep gas, helium (100 ml(STP) min^{-1}).

In conclusion, we successfully prepared p-xylene selective silicalite-1 membranes on the tubular support. The synthesis temperature is a key factor governing the morphological feature of silicalite-1 crystals, resulting in governing the compactness of membrane.

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ICOM1310

Fast Preparation of High-flux Zeolite T Membranes in Fluoride Media

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Zeolite T membranes were prepared rapidly by secondary hydrothermal synthesis on the outer surface of porous mullite tubes in fluoride media. Effects of fluoride source and content, gel composition, synthesis temperature and time were investigated on microstructure and pervaporation performance of membrane. Zeolite T and zeolite T membranes were characterized by XRD, FE-SEM, IR, elemental analysis and ^{29}Si and ^{19}F MAS NMR. Zeolite T crystal formed in fluoride media showed different crystal morphology, surface area and crystallinity from that obtained in fluoride-free media. A high-quality zeolite T membrane could be formed on seeded mullite tubes for only 4 h at 433 K, which displayed a high flux of 4.40 and 3.60 kg·m^{-2}·h^{-1} together with a high separation factor of 8200 and 2900 for water/isopropanol and water/ethanol mixtures with a 10 wt% water concentration at 348 K, respectively. The membrane showed a good hydrothermal and acidic stability for feeds of 30 wt% ethanol solution at 348 K or of acidic solution of pH=3 for one week. It suggested that zeolite T membrane prepared in fluoride media has great potential applications in pervaporation and membrane reactor in acidic conditions.

ICOM785

High Performance Zeolite T Membranes Supported on Porous YSZ Hollow Fibers

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Zeolite T membrane shows great potential for separating water from organics in acidic environment. Several groups have been working on the preparation of zeolite T membrane. However, the membrane flux still needs to be advanced for commercial utilization. For pervaporation process, the membrane flux is strongly related to the structure of substrate facing to vacuum side. In this work, we used a thin yttria-stabilized zirconia (YSZ) hollow fiber substrate to prepare zeolite T membrane for reducing transportation resistance. The membrane was synthesized by secondary growth method. The outer surface of YSZ hollow fiber was rubbed with water slurry of zeolite T crystals (PS ~1.6 μm) prior to membrane synthesis. Hydrothermal crystallization was carried out at 373 K for 40 h using milk-like aluminosilicate gel (SiO_2:Al_2O_3:Na_2O:K_2O:H_2O=1:0.05:0.26:0.09:17 in mol) as a precursor. Well-intergrown zeolite T film with thickness of about 10 μm was formed on substrate surface. The membranes showed high performance of pervaporation (PV) for dehydration of organic liquids. For the feed of 90 wt.% isopropanol solution, the membrane had a water flux of 7.36 $Kg{\cdot}m^{-2}{\cdot}h^{-1}$ with separation factor of >10000 at 348K.

Waste water treatment 2

ICOM1801

Market prospects of low pressure membrane filtration systems for wastewater treatment

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The last decade has witnessed a market boom of low pressure membrane filtration systems for wastewater treatment. With the development of more efficient and more reliable membrane technologies and process schemes, the high tech membrane separation processes historically used for high value added products (energy, health, food industry etc) could enter the low cost global water market. Today, membrane systems have become competitive to conventional water treatment processes, and low pressure membrane filtration technologies have become one key element in the portfolio separation technologies for water treatment.

Market analysts report that the recent annual market growth of the low pressure membrane technologies for water purification is about +15% per year, compared to around +10% per year for high pressure membrane systems driven by reverse osmosis, today the most mature and largest market for water applications.

The main applications of membrane technologies for wastewater treatment are primarily tertiary treatment of municipal wastewater with micro- or ultrafiltration followed by membrane activated sludge process (commonly referred to as 'membrane bioreactor') for municipal and industrial wastewaters. The commercial drivers for these applications are often the advanced and constant water quality required for bathing water, sensitive receiving water bodies or water reuse, sometimes as pretreatment for reverse osmosis, but also restricted footprint, and plant refurbishment in the case of membrane activated sludge systems.

The future of membrane technologies for wastewater treatment is bright, and will be increasingly prompted by water scarcity and the needs of environmental protection following up global changes such as demographic growth, trade and wealth increase, urbanisation and climate change. However, in the context of the global energy crisis and climate change, the future process schemes are expected to show a reduced carbon and energy footprint while remaining affordable. This will come with further technological improvement through out the entire value chain of membrane processes: membrane formulation and production, module optimisation, process scheme integration, and process operation. Such development will need to be evaluated by rigorous and normalised methods for environmental footprinting (Life Cycle Assessment).

In addition, future membrane schemes for wastewater treatment should support the development of novel concepts considering wastewater as a valuable source of energy and other resources. In addition to enabling water reuse, future membrane based wastewater treatment schemes will enable the extensive recovery of energy from the wastewater (organic fraction) and of other essential resources such as the nutrients.

The presentation will include some examples of approaches and research initiatives aiming at improving the energy efficiency of membrane systems for wastewater treatment and future membrane based wastewater treatment schemes.

ICOM880

The effects of addition of PVDF-g-POEM and spinning parameters on PVDF hollow fibre filtration performance

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Waste water treatment by membrane technologies has increased significantly in the last decades as a result of the demand for wastewater reuse [1]. Amongst all the polymer membrane materials, PVDF has a great thermal stability as well and good mechanical strength; furthermore, it shows excellent resistance to most chemicals such as corrosive materials including oxidants, inorganic acids (except fuming acid), halogens, aromatic, aliphatic and chlorinated solvents which makes it suitable for wastewater treatment [2]. Despite all those advantages, PVDF membrane has a significant flux decline in the application of ultrafiltration which is mainly due to its hydrophobic nature which causes fouling. In this study, amphiphilic PVDF-g-POEM was used as an additive to the spinning dope in order to improve the hydrophilicity, flux and decrease the fouling problem.

PVDF-g-POEM was synthesised using newly developed method of ATRP [3, 4]. A simpler and more environmental friendly method for purification and drying the synthesised copolymer was introduced in which water was used to wash and purify the copolymer instead of methanol/petroleum ether. The purified copolymer was characterised using XRF, DSC, CHN analysis, FTIR, GPC, density and NMR, and the results showed the purity of the copolymer was greater than 99.26%.

Hydrophilic PVDF hollow fibre was successfully prepared by using different amounts of the copolymer as the additive in the spinning dopes. The effects of several spinning parameters such as internal coagulant composition, extrusion rate and air gap on the prepared hollow fibres were also studied. The morphology of the hollow fibre was studied by SEM and the hydrophilicity of the membranes was studied by measuring contact angle. Mechanical strength of the fibres was also measured. In order to determine the filtration performance of the hollow fibres, pure water flux as well as dextran rejection was obtained.

Results showed that the hydrophilicity and water flux were significantly improved by adding the synthesised amphiphiic copolymer. By changing the dope composition and spinning parameters, different sets of hollow fibres were produced with a wide range of flux and rejection.

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ICOM1417

Numerical simulation of porous membrane impregnation with carbon nanotubes for water treatment applications

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FORTH/ICE-HT, Patras, GR

The observation that water molecules travel in carbon nanotubes (CNT) at a significantly higher speed than that predicted by fluid flow theory for pores or tubes of similar diameter using molecular dynamics [1], in combination with their high pollutant rejection efficiency, has stimulated numerous attempts to incorporate CNTs in water treatment applications. In this work, the flow of a suspension of CNTs in the vicinity and across a porous membrane is investigated numerically using a combination of lattice-Boltzmann and finite elements techniques. Asymmetric polymeric membranes can be used to offer a gradually decreasing permeability as the water entrance face is approached but also lend themselves to the easier impregnation with CNTs from the exit face.

The simulation proceeds at three steps. First, the structural details of the membrane are simulated on the computer using either pore size and connectivity data from the membrane manufacturer or microscopy images that serve for the computer-aided reconstruction of the membrane. Subsequently, the flow field of the CNT suspension is calculated using the single phase lattice-Boltzmann method or the finite elements with immersed elongated particles technique. Finally, the motion and potential deposition of the suspended CNTs are numerically monitored taking into account the hydrodynamic interactions of the CNTs with the pore walls.

The simulator is dynamic and is capable of producing the temporal evolution of the internal microstructure of the membrane as the suspension flow and deposition of CNTs progress. The effects of various parameters on the CNT deposition rate profile and on the eventual morphology of the pore space of the membrane are investigated, including the diameter and length of the CNTs, the number density of the CNTs in the suspension, the pore size distribution, the connectivity of the membrane, the pressure drop that drives the flow through the membrane, and the thickness of the membrane. It is found that depending on the magnitude of the pressure drop or, equivalently, the mean flow velocity of the suspension, microflow details at pore mouths may affect the straining process during CNT filtration and the spatial distribution of CNT attachment sites.

Reference
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Acknowledgement
Financial support was provided by the FP7 European Project BioNexGen (Contract Number 246039-2).

ICOM1093

Removal of pharmaceutical compounds in the Ultrafiltration / Reverse Osmosis treatment of the secondary effluent of a WWTP. Pilot scale monitoring.

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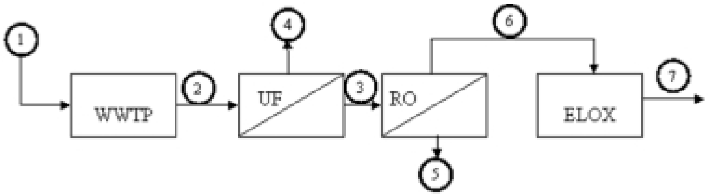
Water reuse is finding a rapid implantation in countries with unbalanced water demand and supply, and membrane processes have become the primary technology for water reclamation purposes. Ultrafiltration permits the removal of turbidity/suspended solids and microorganisms, the main quality parameters for agricultural and urban reuse, while reverse osmosis allows the reduction of salinity when required for industrial reuse. Despite the rapid implementation of water reclamation facilities, as it is the case of the Mediterranean region, there are some issues that still require further research in order to increase the knowledge and/ or the cost effectiveness of the membrane processes, such as the membrane fouling and cleaning, the treatment of RO concentrates and the removal of emerging micro-contaminants.

In this work, the presence of a group of 123 emerging contaminants including pharmaceutical compounds, personal care products, priority pollutants and heavy metals was monitored in the influent and effluent of a municipal wastewater treatment plant. Furthermore, a group 12 most prevalent compounds, all of them classified as pharmaceuticals and stimulants were analysed along the different stages of an advanced tertiary treatment facility composed of ultrafiltration and reverse osmosis and including an advanced oxidation process for the treatment of the reverse osmosis concentrate.

Real wastewaters, without any addition or spiking were used in the experimental work, performed on site in the WWTP of Vueltra Ostrera (Northern Spain) in a pilot plant facility with a capacity of 3 m^3/hour. Dead-end UF was performed using two parallel hollow fiber modules (AquaFlex, Norit), 40 m^2 of membrane area each one. Reverse osmosis was implemented in a series / recirculation flowsheet, using LFC1-4040 membranes supplied by Hydranautics. Seven different sampling points were defined, as described in Figure 1. An analytical procedure, based on preconcentration of the water samples by solid-phase extraction and HPLC – Qtrap MS/MS was applied.

This work identified those pharmaceutical compounds that were recalcitrant to the conventional secondary treatment, and the efficiency of the UF and RO stages were quantified. Rejection values of the UF stage were between 90 % for nicotine and hydrochlorotiazide, 70 % for gemfibrozil, and less than 20 % for the majority of the prevalent compounds. Reverse osmosis allowed to reduced the permeate concentration of all of the investigated compounds below 30 ng/L. However, the high concentrations found in the rejection stream recommended the application of a destructive treatment. The efficiency of electrooxidation on boron-doped diamond electrodes was higher than 90 %, allowing to reduce significantly the environmental impact of the reverse osmosis operation.

Reference: Perez et al., Water Research, 44, 2763-2772, (2010).



1. Municipal wastewater. Influent to the WWTP
2. Secondary effluent of the WWTP
3. Ultrafiltration permeate
4. UF backwash
5. Reverse osmosis permeate
6. RO concentrate
7. Treated RO concentrated after electrooxidation

ICOM1346

The role of solutes interaction during the nanofiltration of coke plant ammoniacal wastewaters

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This work addresses the treatment of coke plant wastewaters by nanofiltration (NF). Real wastewater and surrogate model solutions, containing NaCN, phenol and NH_4Cl, were used in several NF experiments. The NF experiments were carried out in a Lab-Unit equipped with 0.072 m^2 to 0.144m^2 of membrane surface area. NF-270 and HR-98-PP membranes were used for the nanofiltration experiments. The applied pressure was 30 bar.

The main objective of this work is the separation of the compounds NaCN, phenol and NH_4Cl and the optimization of this separation as a function of the pH and of the permeate recovery rate.

Membrane performance is highly dependent on solution composition, binary or multi-compound solutions, and characteristics, namely on pH. In fact, the rejections coefficients observed for the binary model solutions containing sodium cyanide, ammonium chloride and phenol present completely different behaviors from the ones observed for ternary and real wastewater experiments. For ternary solutions (cyanide/ammonium/water) it was observed that for pH values lower than 9 the rejection coefficients to ammonium are well above the ones observed for the cyanides, but for pH values higher than 9.5 there is a drastic decrease in the ammonium rejection coefficients with the increase of the pH. For the real wastewater, with the increase of the recovery rate there is also a change in pH solution and the cyanide/ammonium fractionation is greatly influenced by it. For recovery rates lower than 40% there is cyanide depletion from the ammonium concentrate stream and for higher recovery rates the cyanide rejection increases and the cyanides are also concentrated. These results take into account the changes that occur in solution, namely the solute species that are predominant, with the increase of the recovery rate and of the pH.

UF/MF 2

ICOM1787

Fouling in the context of an understanding of Critical Flux, Threshold Flux and Sustainable Flux

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For membrane filtration processes, fouling is the dominant limitation and so particular care should be taken with the vocabulary used to describe fouling and the terms that are linked to it. It is also recognized that excessive proscription will limit the adoption of fruitful ideas.

Over the last 15 years, large amounts of membrane filtration data have been assessed using the concept of critical flux [1,2]. This concept has been used in a number of different ways often without explicit redefinition and without reference to particular components in the feed. Originally there were two forms of the critical flux [1] and at least two more have emerged. Especially in constant flux operation, the concept of **Critical flux** represents an ideal and for most operations, it may be a guiding concept but is not a practical concept. If a distinct break-point exists in a rate-of-fouling *vs* flux curve then it is useful to define this point as a **Threshold flux.** Others might consider that this is the "sustainable" flux but a distinction will be made between boundaries which depend solely upon physical matters (e.g. hydrodynamics, feed conditions and process time) and those influenced by economics. It will be argued that the **sustainable flux** is not a member of the critical flux family as it does not represent a transition on the fouling curve. The selection of a sustainable flux will be influenced by the critical flux (if it exists), the threshold flux and costs.

Over more than 30 years, copious amounts of membrane filtration data have been assessed to determine modes of fouling and fouling rates. The fundamental fouling equations have been based upon four modes of fouling, with one or more acting sequential or simultaneously. Following Hermia [3], the four fouling mechanisms for porous membranes have been hypothesized as: (i) complete pore blocking; (ii) internal pore blocking; (iii) partial pore blocking; and (iv) cake filtration. The equations arising from these mechanisms were originally only for dead-end filtration and sometimes dead-end filtration analysis has been used inappropriately for the cross-flow mode of operation with no allowance being made for the lateral movement/removal of foulants. Some allowance for crossflow has been made, e.g. by Field et al [1]. The form of the removal term in the differential mass balance equation is re-assessed and the link to critical flux scrutinized. A re-evaluation suggests that the critical flux, J^*, maybe proportional, under certain circumstances to the square root of shear stress; a finding that is worthy of further investigation.

References

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ICOM1619

Harvesting of Micro-algae by Membrane Filtration

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Micro-algae have fast growth rate and high lipid content. Its potential oil productivity is projected to be one to two orders of magnitude higher than other crops. Harvesting of micro-algae from the culture solution is one critical process for mass production of the algae in an economical and sustainable way. The culture solution comprises very dilute suspension of micro-algae cells of a few µm sizes at a loading level of about 0.01 to 0.05 wt.%. The desired harvesting technology should have these performance attributes, (i) low energy consumption, (ii) complete recycling of water and nutrients, (iii) no addition of harmful chemicals/materials, (iv) compact and small-foot print.

In this presentation, we will discuss our recent research results about using membrane filtration technologies for micro-algae harvesting. Thin, porous metal sheets of mean pore size at 1.0 micrometer level at a thickness of 25 to 100 micrometer are effective membranes for the micro-algae harvesting. The membrane allows permeation of water and the nutrients at very high flux while blocking the algae cells. The membrane is resistant to algae adhesion and bio-fouling. The harvesting can be performed in either dead-end or cross-flow filtration mode. In the dead-end filtration, the algae layer collected on the membrane surface is readily removed by flushing with a little water or by vacuum. In the cross-flow filtration, deposition of the algae on the membrane surface can be avoided by operating filtration at certain cross-flow linear velocity so that a nearly steady-state water permeation flux is obtained. The water permeability under steady-state cross-flow filtration of an actual culture solution can be as high as 300 liter/m2/h/bar. The algae can be concentrated by 50 times with the cross-flow filtration.

The performances of the unique porous metal sheet membrane are further improved by modifying the pore structure and surface chemistry with ceramic coatings. The modified membrane minimizes penetration of the algae cell fragments into the pore and enhances anti-corrosion and biocidal attributes, which benefits long-term membrane operation.

Polymeric membranes obtained from commercial sources are evaluated for comparison. The algae readily adhere onto those materials. The water permeation flux is substantially lower than what is obtained with the porous metal sheet-based membrane.

ICOM687

Modeling the filtration of deformable and permeable colloidal particles: the case of casein micelles

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When filtrating a colloidal dispersion, colloids accumulate at the membrane surface, thus forming a polarized layer that can ultimately turns into a deposit (= a "gel") in some extreme cases. Modeling such a filtration has always been a challenge. In recent developments, Bacchin *et al.* propose a model based on the analogy between permeation in a deposit and diffusion in a polarized layer [1]. The permeation flux is then given by the following equation, which is the analog of the classical Darcy's law: $J = k(C)/\mu \, . \, d\Pi(C)/dx$ (eq.(1)), where x is the distance to the membrane, μ is the solvent viscosity, k(C) and Π(C) are the permeability and colloidal osmotic pressure at distance x, respectively.

As for now, the model of Bacchin *et al.* has been used successfully to describe the filtration of impermeable and "hard" spherical objects like latex particles [2]: the idea is to measure the osmotic pressures Π(C) of the latex dispersions through osmotic stress experiments and to estimate the permeability k(C) using the well-known theoretical expressions of Happel. Knowing Π(C) and k(C), eq.(1) is then used to obtain important information like permeation fluxes or concentration profiles in the accumulated layer.

The objective of our study is to adapt such a model to the filtration of more complex colloids, namely, deformable and permeable objects like colloidal microgels. Casein micelles, which represent 80% of the proteins in cow milk, are the perfect candidate for that since they are highly permeable and compressible protein aggregates [3]. Additionally, ultra- and microfiltration are widely used for the concentration of milk and there is a serious need for a model that is able to describe these operations.

The osmotic pressure of casein micelle dispersions is now perfectly known [3]. So the main difficulty lies in determining k(C) since no theoretical expression is currently available for deformable and permeable objects. Our presentation focus on the different strategies we used to overcome this difficulty and on the significance of the k(C) values we managed to estimate either indirectly from filtration experiments or directly from osmotic stress experiments (Figs. 1 and 2). We then discuss on the ability for the resulting model to predict filtrations conducted in different modes (dead-end/cross-flow, constant pressure/constant flux).

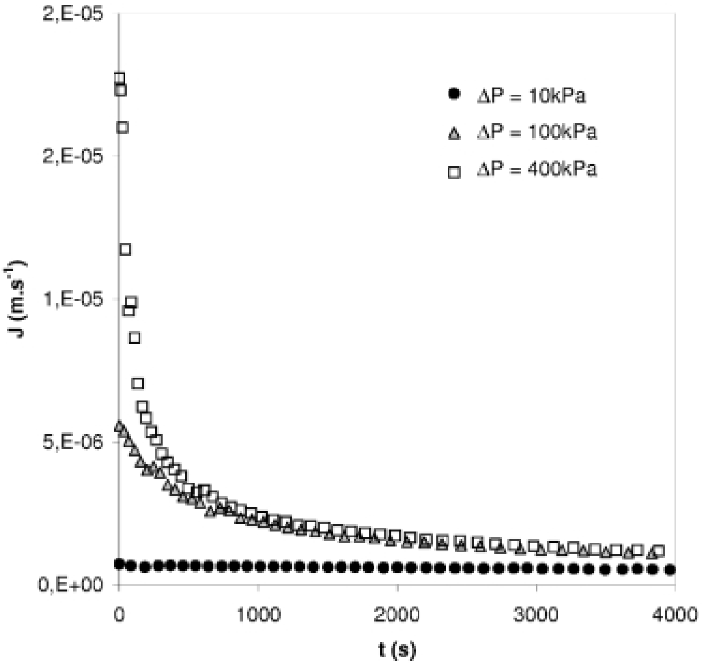

Figure 1: Permeate flux as a function of time in dead-end filtration of a casein micelle dispersion (1 g/L) under various transmembrane pressures.

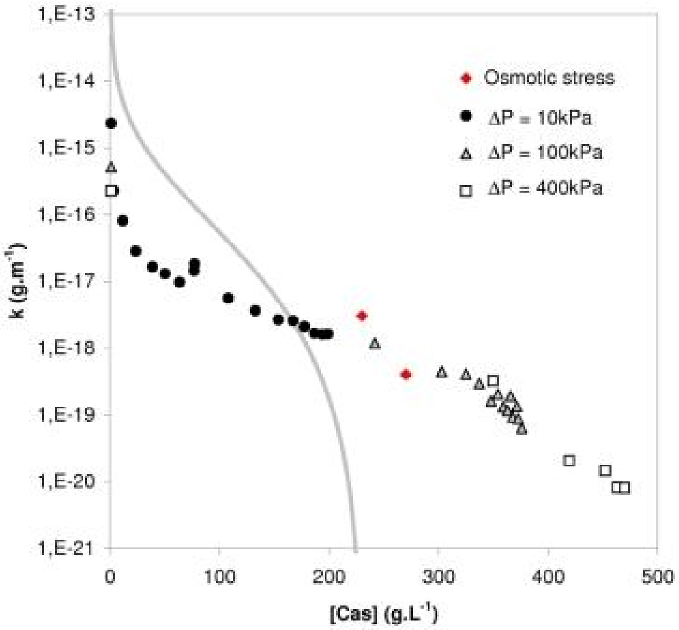

Figure 2: Permeability as a function of casein concentration as estimated through eq. (1) from the data of Fig. 1 and as determined through osmotic stress experiments. The grey line is the prediction from Happel's law for impermeable and hard particles with the dimensions of the casein micelle.

[1] P. Bacchin, M. Meireles, P. Aimar, *Desalination* 145 (2002), 139-146

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ICOM1409

Time-optimal diafiltration under gel polarization conditions

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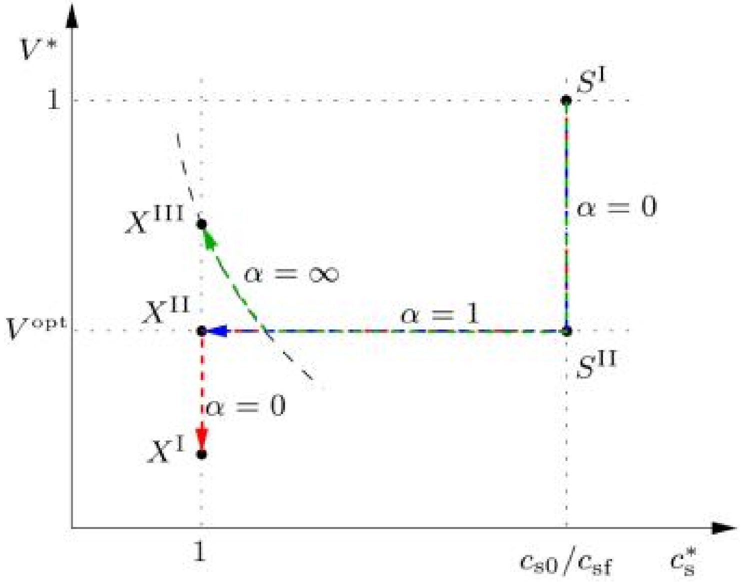
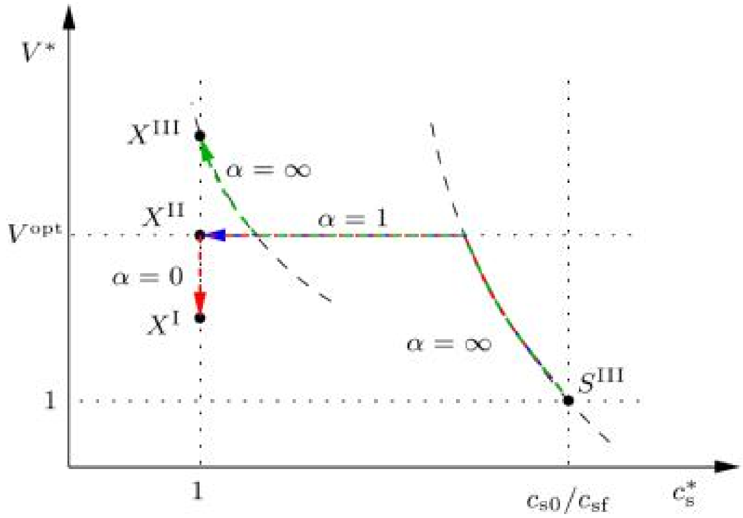
Diafiltration is widely used technique for separation of at least two components from a solution. These are separated employing separation (microfiltration, ultrafiltration, ...) membrane, exploiting a difference in their effective particle sizes. This process can be intensified in several ways. Minimum time of an overall process run can be considered to minimize certain expenses of this process (e.g., amount of electricity consumed during the process run). Another possibility is to minimize an amount of fresh solute-free stream (diluant) added to the feed tank throughout diafiltration. This study addresses a problem of minimization of overall running time of generalized diafiltration process.

An ultrafiltration/diafiltration process is considered for which a micro-solute (c_s) is to be decreased in concentration together with reducing initial liqueur volume (V). It is assumed that flow through the membrane is modeled under gel polarization conditions. We derive a dimensionless model in order to generalize the process evolution in time. This means that dimensionless process model (in dimensionless variables c^*_s and V^*) is only dependent on initial micro-solute concentration and final requirement on volume.

Minimization of overall process running time is a dynamic optimization problem. Dynamic optimization encompasses several theoretical and numerical techniques to find an optimal control of a dynamic processes. In this work we use both theoretical (Pontryagin Minimum Principle) and numerical (Control Vector Parametrization) approaches aiming to find optimal control of this process which is defined as a ratio between a flowrate of inflowing diluant and a flowrate of outflowing micro-solute/solvent stream passing through the membrane. Previous attempts on this optimization problem considered arbitrarily constructed schemes, which may be, but need not to be, optimal. Using previously mentioned dynamic optimization approaches, we found the optimal control of generalized diafiltration process which can be visualized in a state diagram considering different starting (S) and target (X) points.





The state diagrams in Figures 1 and 2 provide a practical procedure to evaluate the optimal strategy. The number and type of consecutive operational steps can be simply determined from the relative position of $V^*(0)$, V^{opt} and $V^*(t_f)$. These can be determined for a known macro-solute gel concentration. To summarize the results, the optimal minimum-time operation under gel polarization conditions can be stated as follows. The first (optional) step is either pure dilution ($\alpha=\infty$) or pure ultrafiltration ($\alpha=0$) until optimal normalized volume V^{opt} is obtained. The second step is diafiltration at constant volume ($\alpha=1$). This step finishes if either final concentration of micro-solute or final ratio of micro/macro-solute concentration is obtained. Finally, the third (optional) step is again either pure dilution ($\alpha=\infty$) or pure ultrafiltration ($\alpha=0$) until final requirements are satisfied.

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ICOM210

Antibacterial Property of PES Ultrafiltration Membrane containing Halloysite Nanotube Loaded with Ag Nanoparticles

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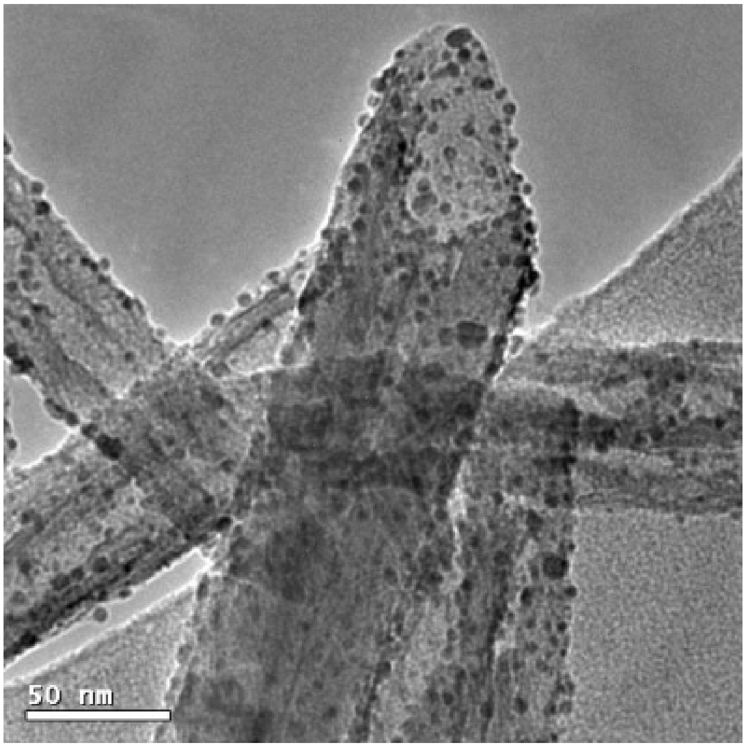
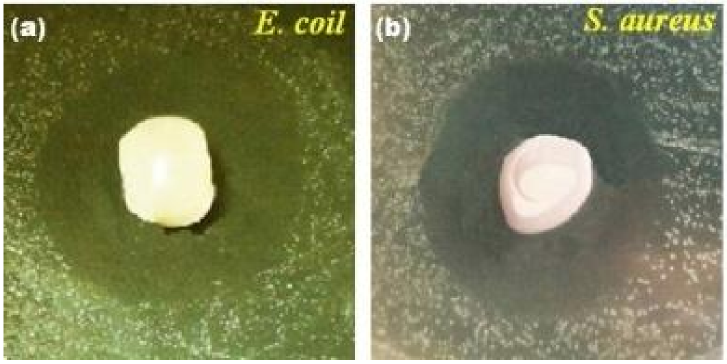
Halloysite nanotube (HNT) is a two-layered aluminosilicate clay mineral, consisting of one alumina octahedron sheet and one silica tetrahedron sheet in 1:1 stoichiometric ratio, which is available in abundance in China as well as other locations around the world. It is chemically similar to kaolin, differing mainly in the morphology of crystals. HNT possess hollow nanotubular structure in the submicrometer range and large specific surface area. Their novel physical and chemical properties derived from the structural versatility provide opportunities for advanced applications in the fields such as electronics, catalysis, biological systems and functional materials. In this paper, HNT with a 15 nm lumen and 50 nm external diameters was developed as a support for loading of antibacterial agents. Firstly, the amino groups were grafted onto the surface of HNT. Then, modified HNT was immersed in silver nitrate solution and a complex between the two amino groups of KH-792 and silver ions formed, leading to large clusters on the surface of HNT. These silver containing clusters were converted into silver nanoparticles (Ag NPs) with about 5 nm diameter, that is, Ag NPs supported halloysite nanotube (Ag NPs/HNT) was fabricated.



Finally, Ag NPs/HNT incorporated into polyethersulfone (PES) casting solutions and PES UF membranes containing Ag NPs/HNT was obtained via phase inversion method. The antibacterial property of resultant membranes was measured using inhibition zone method. The results indicated that PES UF membranes containing Ag NPs/HNT showed good antibacterial property against *E. coli* and *S. aureus.*


(a)
E. coil
(b)
S. aureus

Membranes for fuel cells 2

ICOM1823

New aspects in proton conductive membranes for polymer electrolyte membrane fuel cells

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The characteristic of the separator and the membrane-electrode-assembly defines the operation regime of a proton exchange membrane fuel cell. Vice versa, R&D on membranes should strongly follow the design requirements of future fuel cell systems. In the past, research was driven by cost reduction of the ionomer used for membrane fabrication. Therefore, most attention in research was dedicated to the development of hydrocarbon type membranes. Today, membrane development focuses on cost reduction by system simplification, reliability and durability.

For mobile application of hydrogen fuel cells in mid size passenger cars an operation temperature of maximum 105°C with anode gas recycling and well humidified cathode gas seems to be ideal. In order to assure good conductivities of the anode layer even at high current densities, thin reinforced membranes with low gas cross-over are needed. The durability of the membrane electrode assembly has been identified among the most relevant issues for fuel cell car commercialization. Therefore, improved ionomer dispersions for electrode fabrication and thin membranes preferably based on perfluorosulfonic acid polymers of different lengths of the side chain are used. More recent work is done on cross-linked of low equivalent weight PFSA as well as on mixed matrix membranes. High performing hydrocarbon membranes based on low cost ionomers are not yet visible. Highly sulfonated polysulfone seems to be an interesting future alternative to PFSA in both performance and durability. This polymer shows higher conductivity at low R.H. and improved hydrolytic and oxidative stability compared to PFSA polymers. Additional work has to be done, however, on ionomer dispersions for electrode preparation based on the same material.

For stationary application of reformate fuel cells in 1-5kW combined heat and power plants (CHP) or in auxiliary power plants for mobile applications (APU) an operation temperature of minimum 150°C seems to be ideal for heat coupling of the reformer with the fuel cell system. Such systems will work on dry cathode gas and wet reformate with moderate impurities from carbon monoxide. The expected life-time is minimum 40.000 hours. Today's most preferred membranes are prepared from phosphoric acid doped polybenzimidazole type polymers. Among others, conventional high molecular weight PBI and cross-linked ultra-high molecular weight ABPBI copolymers play the most important role. Differences in the amount of phosphoric acid per repeat unit as well as in the membrane thickness are relevant to the design and the performance of the membrane electrode assembly. More recently, new membrane materials with intrinsic proton conductivity in the absence of water have been published. Progress is made on the durability of these materials. Additional efforts are needed, however, to prepare a reliable membrane electrode assembly based on dry membranes.

In direct methanol fuel cells, alkaline fuel cells as well as in low power portable fuel cells hydrocarbon membranes play an important role. A lot of attention recently is attributed to the development of highly conductive anion-exchange resins for use in platinum-free alkaline fuel cells and alkaline electrolysers.

ICOM752

Ion-exchange membranes from side-chain sulfonated poly(arylene ether sulfone)s

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Fuel cells are considered as attractive and clean alternatives to the widely employed internal combustion engines for power production. Among the various types of fuel cells, polymer electrolyte membrane fuel cells (PEMFC) possess the broadest area of application. One key-component in PEMFC is the membrane, which enables the charge transport from anode to cathode side. Furthermore, the membrane should prevent the reactants from diffusing to the opposite electrode. Despite intensive research activities in the past, fuel cells are used to date only in niche-markets. The reasons for not having reached the breakthrough in mass-markets, are the costs for the membrane, the standard is still Nafion®, as well as for the catalyst and on the other hand an operation temperature below 100°C. However, an operation temperature well above 100°C is preferred, because the catalytic activity is increased with increasing temperature, the catalysts are less susceptible to poisoning, both allowing the use of less amounts of catalysts, and water management is much easier due to the absence of liquid water.
Nowadays research in materials for ion-exchange membranes is focused on sulfonated fully aromatic polymers like sulfonated poly(ether sulfone)s. Most often, the sulfonic acid groups are introduced into the polymer main chain, which might have an impact on the polymer stability (1). Furthermore, block copolymers have superior properties over random copolymers with similar chemical composition and ion-exchange capacities (2).
In this contribution, we report on novel poly(ether sulfone)s based on 2,5-diphenyl hydroquinone, which are sulfonated at the side-chain only. These polymers are mimicking on one hand poly(styrene sulfonic acid) (side chain sulfonation) but possessing on the other hand a thermally, chemically and mechanically stable polymer backbone. The degree of sulfonation and thus the ion-exchange capacities are determined by the amount of 2,5-diphenyl hydroquinone moieties in the polymer backbone. Two different types of polymers, namely random copolymers and multiblock copolymers, were synthesized and their structure and composition was evaluated by NMR spectroscopy. The effect of molecule architecture and ion-exchange capacity on thermal properties, water-uptake, dimensional stability and proton conductivity will be discussed.
Although having comparable ion-exchange capacities, the sulfonated multiblock copolymers showed higher proton conductivities than the sulfonated random copolymers and at high IEC (>= 1.95 mmol/g) even higher than Nafion® at 100% relative humidity, which was attributed to the relatively high water uptake of
the membranes prepared from the multiblock copolymers (fig. 1).

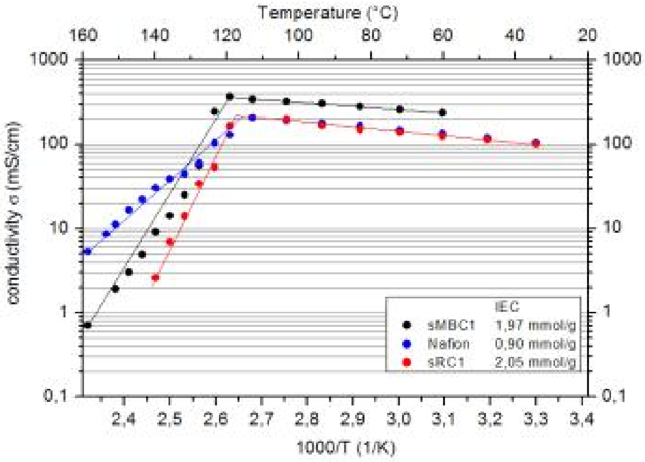

Figure 1: Comparison of proton conductivities of a random and a multiblock copolymer with Nafion as function of temperature

On the other hand, membranes prepared from random copolymers with an IEC ≥ 1.8
mmol/g tend to soften to a high extend in water at elevated temperatures.

Due to their high proton-conductivity and good dimensional stability at elevated temperatures sulfonated multiblock copolymers turned out to be promising candidates for membrane materials in PEM fuel cells operated at temperatures up to 120°C.

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ICOM1535

Nanostructured electrolyte membranes based on microporous materials, protic ionic liquids and porous PBI films for HT PEMFCs

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PEMFC operating at high temperatures has been recognized as a promising solution to meet the technical challenges stressed by the European Strategic Agenda on Energy Policy. Polybenzimidazole membranes doped with inorganic acids have been the mostly studied for this application [1]. However, one of the most serious drawbacks of acid-doped polybenzimidazolemembranes is the leaching of the proton conducting acid. Thus, protic ionic liquids (PIL) emerge as very promising in PEMFCs due to their particular properties such as excellent thermal stability, exceptional ionic conductivity and very low vapor pressure. Indeed the key property differentiating PILs from other ionic liquids (ILs) is the proton transfer from the acid to the base, leading to the presence of proton donor and acceptor sites [2]. In this work, porous PBI membranes have been deployed as imidazolium based protic ionic liquids containers. To avoid the release of the proton conductor, which may affect the long term stability of the membranes, the external surfaces of such proton-conducting porous PBI membranes were seeded with nanometric functionalized ETS-10 crystals by covalent linkage. Finally, to promote the proton conductivity of both microporous top layers, the as prepared nanostructured electrolyte membranes were immersed in phosphoric acid. “Through-plane” and “in-plane” conduction performance and H_2 and methanol permeation properties have been deeply investigated through the preparation process. As an example, through-plane conductivity values up to 170ºC of the nanostructured electrolyte membrane after each preparation step are depicted in Figure 1. As it can be observed, the final nanostructured electrolyte membrane outperforms acid doped porous PBI in agreement with the proton conductor loadings estimated by TGA analyses (see Table 1). However, the most distinguished feature is the exhibited methanol fuel cross over behaviour at different temperatures. Thus, the incorporation of the microporous top layers onto porous PBI containers allows to decrease the methanol permeability up to a 40% of the initial value at 150ºC. Durability test and MEAs performance from state of the art electrodes are being evaluated for H_2 HTPEMFCs.

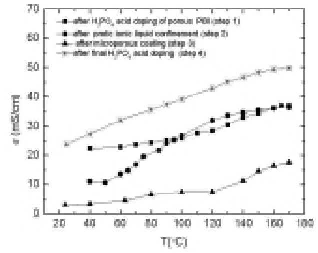

Figure 1. Proton conduction performance of porous PBI based membranes along the preparation process in presence of y_{H_2O}=0.05.

Mb.Preparation Step	PBI (%wt)	H_3PO_4 1st step (% wt)	PIL (% wt.)	ETS-10 (%wt.)	H_3PO_4 4th step(% wt.)
(1) Initial acid doping of porous PBI	21.0	79.0	---	---	–-
(2) PIL immobilization	11.1	40.4	48.5	-–	---
(3) ETS-10 coating on membrane external surfaces	10.0	37.7	49.8	2.5	–-
(4) Final acid doping	6.3	23.9	48.1	2.4	19.3

Acknowledgements:
The research leading of these results has received funding from the European Community's Seventh Framework Programme ([FP7/2007-2013]) under grant agreement nº 209481-ZEOCELL project (http://ina.unizar.es/zeocell).

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ICOM185

Development of hydroxide ion conducting pore filling membranes for a solid alkaline fuel cell and their cell performance

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Novel hydroxide ion conducting polymer electrolyte pore-filling membranes were prepared for the application of a solid alkaline fuel cell. In this research, an quarternary amine based electrolyte monomer and several UV curable crosslinkers were employed to prepare the pore-filling membranes. The highly quarternary-aminated electrolyte was introduced into porous hydrocarbon substrates and crosslinked by UV irradiation. Finally, film-like polymer electrolyte membranes were prepared. Because the porous substrate suppressed high swelling property of highly quarternary-aminated hydrocarbon polymers in water media, it is able to protect aqueous electrolytes such as aqueous KOH crossover from anode to cathode, thus, it enhances the cell performance in the operations of a solid alkaline fuel cell. The prepared membranes were analyzed in terms of hydroxide ion conductivity, ion exchange capacity, water content etc. Also the thermal and the structural property of the prepared pore-filling membranes were evaluated by TG-DTA and SEM. As the results, The prepared hidroxide conducting pore-filling membranes were thermally stable at least up to 150 ℃. Thus, it is considered that the membranes are reliable to be applied for solid alkaline fuel cells. The polymer electrolyte membranes prepared in this study showed extremely high hydroxide ion conductivity and chemical stability even though they were dependent on the composition ratio of the electrolyte monomer and crosslinking agent used for polymerization. However, the hydroxide ion conductivity of the membranes was relatively higher of the whole cases than those of commercial products. These pore-filling membranes have also excellent properties such as smaller dimensional affects when swollen in solvents, higher mechanical strength, lowest electrolyte crossover through the membranes, and easier preparation process compared of traditional cast membranes. The prepared membranes were then applied to a solid alkaline fuel cell, and had a good performance (260 mW/cm^2@50degree celsius with H_2/O_2)

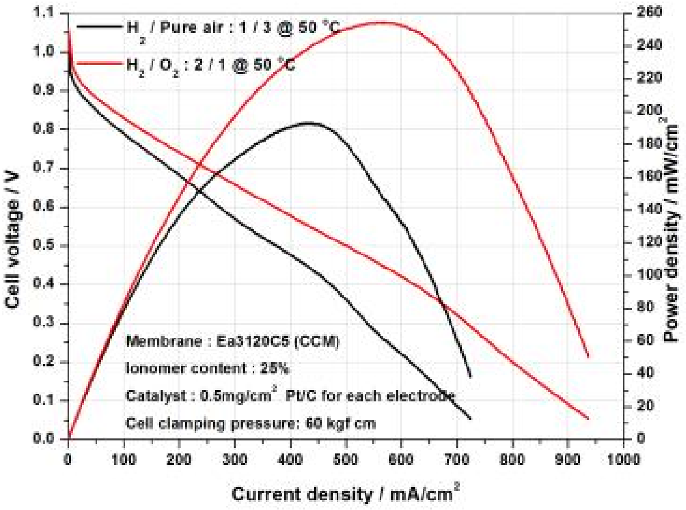

Fig. 1. SAFC performance by using a prepared hydroxide ion conducting pore filling membrane.

ICOM1662

Anomalous hydration and surface-induced micelle orientation in Nafion

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Properties of Nafion, a perflourinated ionomer and the benchmark membrane material in electrochemical applications, critically depend on the level of hydration. However, Nafion hydration is complicated by different hydration measured in contact with liquid and vapor (Schroeder's paradox). Moreover, we show that this anomalous behavior is not limited only to saturation conditions and two different isotherms, vapor and liquid, are obtained using isopiestic (vapor) and osmotic stress (liquid) techniques (1). On the basis of general thermodynamic considerations, we relate this behavior to the microphase-separated structure of Nafion and, specifically, to the balance between the interfacial and elastic forces in the regions adjacent to microscopic interface in conditions of incomplete relaxation of the matrix (2). The model predicts that the macroscopic surface of Nafion presents a special region that may undergo drastic structural re-arrangement ("macaroni-spaghetti" transition) and, subject to the environment, exert different "Laplace" pressures of a special type on the aqueous microphase within the polymer. Depending on the adjacent phase (vapor, liquid or a specific substrate), Nafion micelles may tend to adopt a variety of conformations and preferential orientations and align either parallel or perpendicular to the membrane surface (Figure 1) (3). Motivated by these predictions, we employed a number of surface-sensitive techniques (GISAXS, contact angle, and AFM) to examine the structure in the bulk and at the surface of thin films of Nafion on different substrates. The results appear to be consistent with the model and clarify the role of non-equilibrium microstructures in the hydration behavior of Nafion (Figure 2). In addition, the observed orientation of micelles within Nafion films induced by the external surface and substrate suggests attractive possibilities of enhancing membrane performance in the desired direction.

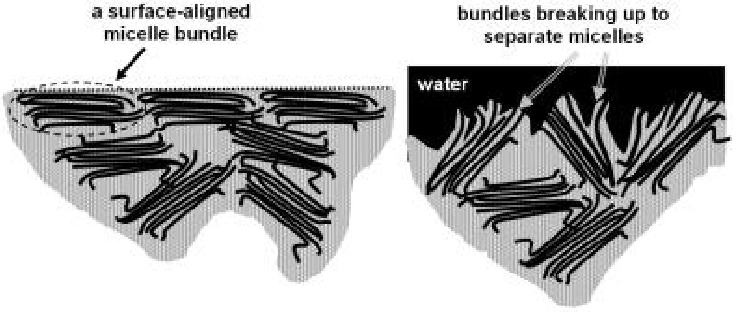

Figure 1. Schematic presentation of the proposed micelle orientation at the surface of Nafion

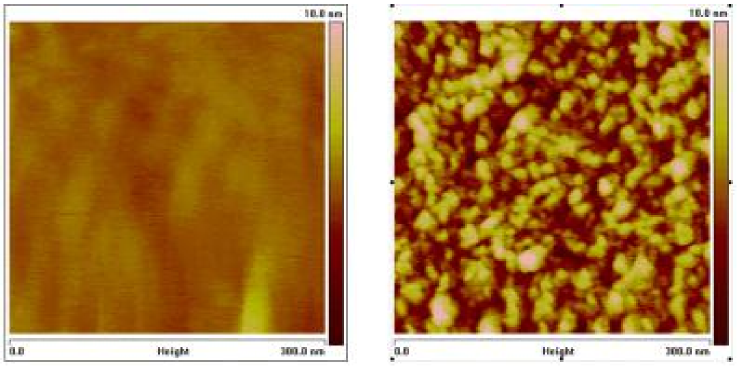

Figure 2. Topographic AFM images of the Nafion surface in vapor and under liquid.

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ICOM 2011

Thursday, July 28th 2011

Parallel Sessions

Thursday, July 28th 2011

Morning Session 1, 8.30 – 10.20

Membrane fouling 4

ICOM1866

Membrane fouling

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RWTH Aachen University, DE

With fouling being such a broad topic, including foulant characterization, foulant interaction with membranes, foulant removal by membranes or flocculation, influence of material, operating and module design parameters on fouling, and with the term fouling being used both for local and more global phenomena („clogging“), an all encompassing 25 min lecture on membrane fouling seems an impossible task.

Instead of tackling it, I would rather choose a pragmatic approach, looking mainly for individual solutions in innovative fields, some of which come from our own research and are centered around hydrodynamics, others seeming so promising that it would be foolish to overlook them.

The topics touched upon will include an introduction, substantiating my doubts about mechanistic fouling theories, an outline of pragmatic options for fouling abatement and an elaboration of some oft them. Examples are the influence of hydrodynamically optimized spacers and of intelligent module operation (back pulsing) for application in fermentation, options of coating membrane surfaces and of mimicking natures ways to protect pores from foulants and of a totally novel way of telling biofoulants to go away by introducing trace amounts of messenger substances.

ICOM1558

Online analysis of the nanoparticles to prevent membrane fouling by a secondary effluent

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Nanoparticles are removed from the water in Ultrafiltration (UF~0.001 – 0.1 µm) and Microfiltration (MF~0.1 – 2 µm) processes. Nanoparticles have sizes between 10 nm and 1000 nm and thus, they could be retained and potentially cause irreversible fouling not removed by backwash. One possible option to enhance the process understanding of MF/UF membrane fouling is to monitor the submicron particle size distribution (< 1 µm) in the water. Pre-treatments can decrease the irreversible fouling and increase the filtration performance. The whole process can be optimised if the pre-treatments mechanisms and their effects on nanoparticles are well understood. Therefore the goal of this study was to find an online monitoring device able to analyse the nanoparticles in the water in real time. The availability of such sensors will improve the operation of membrane filtration systems. The device used to carry out these experiments is the Nanosight LM10 from Schaefer Technologie. It uses a laser light source to illuminate nano-scale particles, moving under Brownian motion. The software allows the user to automatically track and size nanoparticles on an individual basis. 500 µl of sample of suitable viewing concentration (10^7 – 10^{10} particles/mL) is introduced into the viewing unit. The software then rapidly determines the particle size (10 – 1000 nm). A pre-filtration has to be optimised to remove all particles above 1 µm. The tests were carried out on representative secondary effluent. Table 1 presents the quality of the water used.

DOC (mg/L)	pH	Pt (mg/L)	UV254	COD (mg/L)	SS (mg/L)
10-13	7-7.3	0.15-0.5	22-30	30-40	3-6

Table 1.1 Water quality of the secondary effluent

Figure 1 presents results obtained with 4 different samples treated with combined ozonation and coagulation and 1 untreated sample, all filtered at 1.2 µm. The ozonation dose was 0, 2, 4 and 6 mg/L and the coagulation dose was constant at 4 mgFe/L. The Nanosight was used to determine which one of the pre-treatment is the best solution to reduce the content of nanoparticles compared to the secondary effluent.

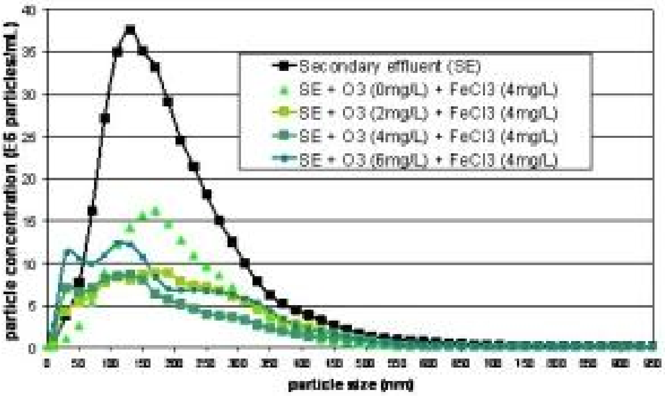

Figure 1 Nanoparticles size distribution comparison of 5 samples (mean of 4 measurements per sample) by the Nanosight

The results showed impact of pre-treatment: the higher is the ozone dose, the higher is the particle concentration (<100 nm). Without ozonation the amount of particles between 100 nm and 300 nm is higher which confirm the microflocculation effect of the ozone combined with coagulation. The combination ozonation and coagulation reduces the amount of particles below 1 µm by a factor 4. According to these experiments, the best combination was to treat the water with 2 mgO$_3$/L and 4 mgFe/L to get the fewer nanoparticles between 0 and 150 nm on the membrane. The global concentration of the nanoparticles was reduced and the nanoparticles critical for the fouling were shifted into larger particles or removed from the water.

Conclusion:
With the Nanosight the effect of ozonation and coagulation on size distribution and absolute concentration of nanoparticles can be observed within a few minutes. It must be related with the membrane fouling to see if an online monitoring is possible with this device.

ICOM967

Transverse vibration as a fouling limitation strategy in membrane bioreactors

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Fouling is a critical factor that determines the performance of membrane systems. Increasing shear rate at the membrane surface by cross flow velocity and air bubbling has been reported to decrease the fouling layer [1]. The shear rate can also be increased by using unconventional methods such as vibrating systems, which involves vibration or rotation of the membrane. These systems are known as the vibratory shear enhanced processes (VSEP) or vibrating membrane filter (VMF) and are generally based on flat sheet membranes [1]. However, the application of the vibration principle to hollow fibre systems is so far limited even at the lab scale. Beier et al. [1] and Genkin et al. [2] have investigated the effect of vertical vibration on fouling mitigation using yeast as the feed solution. Vertical vibration requires shifting the membrane module up and down which could result in potentially higher energy requirement than transverse vibration, which has not been investigated systematically to date. Wickasana et al. [3] showed that transverse mechanical displacement can reduce the transmembrane pressure increase in submerged hollow fibres systems using yeast as a model solute [3]. In this study, transverse vibration of hollow fibre membrane as a potential fouling limitation strategy has been investigated. Yeast suspension and anaerobic bioreactor supernatant were used as feed solution.

The results indicate that with the aid of low frequency transverse vibration (3.33Hz), the rate of increase in transmembrane pressure (TMP) was much lower compared to that observed without vibration. Compared to the traditional fouling limitation methods such as filtration with periodic backwash and relaxation, the continuous filtration with transverse vibration also shows lower final TMP value at the end of 16 hrs of operation. Critical flux experiment was also performed to evaluate the efficiency of fouling limitation by transverse vibration. Critical flux improvement of 250% was observed when continuous filtration with and without vibration were compared for 4g/L yeast solution at vibration frequency of 10 Hz (shear rate of 792.10 s^{-1}). A critical flux improvement of 181% was reported previously for membrane filtration of yeast suspensions using vertical vibration under similar operating conditions (yeast concentration of 5g/L and shear rate of 863 s^{-1}) [1].

The effect of vibration frequency and displacement on fouling limitation was also investigated to optimise the performance of the vibration system. Fouling layer observation and characterization was performed at the end of experiment to provide better understanding of fouling limitation mechanisms as a result of vibration.

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ICOM1528

Operation of Ultrafiltration at low pressures without flushing and cleaning: mechanisms and applications

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We have investigated a new approach to operate membrane processes in a dead-end mode at relatively low pressures obtained by gravity without any cleaning and flushing. Flat-sheet UF membranes with a MWCO 100 kD were operated at a pressure of 65 mbar. Decline of flux occurred due to membrane fouling and biofouling during the first days of operation. However, as shown in Figure 1-a, after several days of operation the membrane flux stabilizes at 4-10 L.m^{-2}.h^{-1} (Peter-Varbanets *et al*., 2010) and remains stable during at least one year (Fig. 1-b). Stable fluxes have been observed for all natural feed waters which have been tested so far and also with diluted wastewater, as long as the temperature is above 10ºC and the dissolved oxygen content of the feed water is above 3.5 mg/L.

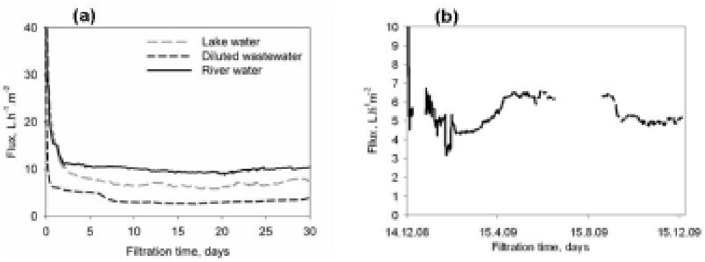

Figure 1: Flux stabilization with different types of feed water (left) and long-term flux operated with river water (right). Chriesbach River water turbidity was in the range of 0-2 NTU, with peaks up to 100 NTU, TOC content was 2.0-3.5 mg C/L; Lake Greifensee: TOC 3.5-3.9 mg C/L; 0.5-1 NTU; Diluted wastewater TOC 5.0-6.4 mg C/L; 3-8 NTU.

Characterization by Confocal Laser Scanning Microscopy (CLSM) and Optical Coherence Tomography (OCT) showed that a relatively porous fouling layer containing cavities and channels is formed on the membrane. It was found that the biofouling layer structure and resistance are influenced by the presence of predators, such as protozoa and metazoa (Derlon *et al*., 2010). With predation, an open and heterogeneous structure that partially covered the membrane surface was observed (Fig. 2a). This open structure is the reason for the fact that the membrane is not clogged, but that the flux remains on a constant level. Conversely, a flat and compact structure with a much higher hydraulic resistance was developed in absence of predation (Fig. 2b).

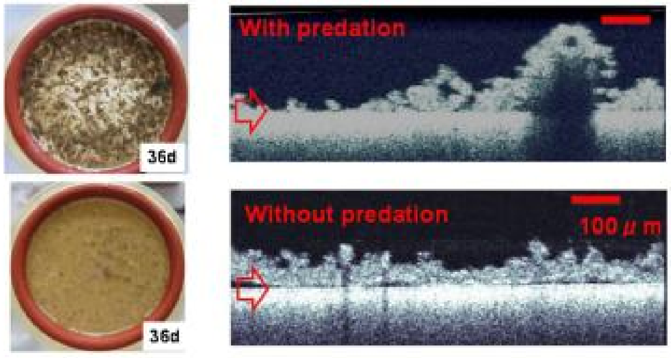

Figure 2: Top view of membrane surface (left) and optical cross-sections of the membrane with fouling layer (right) in presence (upper panels) and absence of predators (lower panels)

Pilot experiments have been carried out with a water treatment plant based on this principle in France and in South Africa. Furthermore, household systems based on gravity-driven UF are in development and will be evaluated in Kenya. Results on these tests and an outlook on application possibilities will be presented. Furthermore, the process provides interesting perspectives for membrane filtration at remote locations in industrial countries where no or only limited amounts of energy are available.

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ICOM273

DWP Botlek – 34 MLD Demin Water Plant with Air-Sparged Spiral Wound RO

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[1]*Evides Industriewater, Rotterdam, NL,* [2]*Logisticon Water Treatment, Groot-Ammers, NL*

1. Introduction

Evides Industriewater BV is the largest supplier of tailor-made water services to the industry in The Netherlands. In this work we describe the design, construction and operation of the DWP Botlek, the largest single demin water plant in The Netherlands (34 MLD). It is in operation since January 2010.

2. Membrane Biofouling Prevention & Control

During the design special consideration was given to the prevention and control of membrane biofouling. To combat the effects of fouling three different strategies were followed during the design of the treatment plant. Firstly the RO feed water is treated by ion exchange softening. Removal of bivalent ions from RO feed water has proven to greatly reduce the negative effects of biofouling, especially on feed channel pressure drop and membrane permeability.

Secondly all first position membrane elements from the first stage of the RO skids are isolated and positioned vertically. By orientating all first elements vertically it is possible to clean them periodically with an air & water mixture (Cornelissen et al, 2007). Finally the DWP Botlek is equipped with fully automated CIP installation to combat the effects of membrane fouling.

4. Plant Design

The plant was built on the site of Huntsman Holland BV at Rozenburg (The Netherlands). There are 8 identical demin trains of 200 m^3/h, with one demin train acting as a spare (redundancy N-1). The DWP Botlek will use surface water from the nearby Brielse Meer as soon as work on the pre-treatment plant is completed (second half of 2011). At this moment drinking water from the nearby Evides WTP Berenplaat at Spijkenisse is used as an alternative water source. The DAFF (Dissolved Air Flotation & Filtration) is not yet operational.

Evides is the first operator to use air/water cleaning on industry standard 8-inch spiral wound RO elements. Coarse air bubbles injected into a counter-current feed water flow provide gentle abrasion of particulate fouling and biofouling within the feed spacer channel, without damaging the membrane surface. No chemical cleanings of the RO were performed during the first year of operation.

Vertical RO skid.

5. Conclusions

In less than fifteen months, Evides designed and constructed its biggest multi-client demineralised water plant. Since January 2010 the plant has been supplying high-quality demineralised water to twelve chemical companies and three refineries in the Rijnmond area. At the Amsterdam conference we will present the highlights of the first 18 months of operational experiences since the start-up in 2010.

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Desalination 3

ICOM1827

Static Mixing Spacers For Spiral Wound Modules

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University of Toledo, ES

Membranes play a critical role in many separation processes ranging from nitrogen production to desalination. The membranes are used most commonly in the form of fine hollow fibers or sheets. The sheet form is used to produce spiral wound modules that permit the efficient contacting of process streams with the membrane in a compact form.

Spiral wound modules are the dominant form used in reverse osmosis and nanofiltration membrane processes. Spacers are used in spiral wound modules to create feed and permeate flow channels and to enhance mass transfer rates by reducing concentration polarization. Most spacers possess a ladder or mesh structure and rely on the generation of turbulence and eddies to enhance mass transfer. The literature contains numerous experimental and theoretical studies of how pressure drop and mass transfer rates depend on the geometry of these spacers.

Spacer design features that increase mass transfer rates also tend to increase pressure drop. The preferred spacer is determined by the tradeoff between the reduction in membrane area and concomitant increase in pumping costs. A review of previous spacer design studies is presented with emphasis on the proper basis for comparison of the results.

Following this review, we present a new spacer paradigm. The spacer acts as a static mixer for planar flow channels and mixes without generating turbulence and eddies. Simulations of flow and mass transfer with the new spacer were performed using computational fluid dynamics. The results indicate mass transfer rates are greater than that reported for other spacer designs. Flow visualizations clearly show how the spacer mixes fluid.

ICOM656

Scaling Mitigation in Reverse Osmosis Desalination via Flow Reversal Controlled by Ultrasonic Sensors

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Reverse osmosis (RO) desalination is a pressure-driven process that removes salt from seawater or brackish water sources. A major problem for RO utilization is that efficiency is compromised by the development of scaling that significantly degrades membrane performance and water quality, and hence increases desalination cost. Flow reversal (FR) enables the entry and exit points of the feed to be periodically reversed before the induction time for measureable scalant is exceeded. FR has been shown to mitigate scaling. This study tests the hypothesis that FR triggered in response to real-time signals from in-situ ultrasonic sensors (US) can signficantly delay the onset of scaling, and enable high-recovery RO.

A flat-sheet system with the ability to operate in FR mode was utilized. RO cross-flow cell permeate collection is divided into separate ports to obtain local permeate flow-rates. US for monitoring real-time scaling were mounted on the top plate of the cell above the permeate collection ports. A numerical model was utilized for predicting the supersaturation conditions. Optimal operating conditions were selected to achieve undersaturation at the upstream and supersaturation at the downstream locations, respectively.

Experiments were conducted with repeated forward-flow and reverse-flow cycles. Permeate flow-rates and conductivity from all permeation ports were monitored and US measured the membrane surface condition every 5 minutes. The real-time acoustic data were analyzed via a novel “dynamic window” methodology that utilizes: (1) upper and lower window boundaries that are adjusted in real time to reflect operating conditions during a particular flow cycle, and (2) a trend line such that the departure of the trend line from the window boundaries constitutes a “switch” signal to change the flow direction After each experiment, the membrane was sectioned for post-mortem analysis obtained via low-magnification light microscopy.

Results are presented for a FR experiment with a total of 34 forward-flow and reverse-flow cycles. The data were obtained during the last cycle such that the experiment was terminated when the switch signal was given. The overall permeate flow-rate decreased by 7% due to scaling over the 80-hr experiment as compared with a much greater decline over a shorter duration in the absence of FR. Post-mortem analysis indicated that the US responded as intended to accommodate light scaling at the downstream port (area coverage of 7%) while the corresponding midstream and upstream ports were kept no scalant.

Results confirmed that US-controlled FR can effectively delay scaling and thus lessen the permeate flow-rate decline caused by scaling. Real-time measurements in combination with post-mortem results provide an effective means to correlate local and overall cross-flow cell behavior to quantify FR effectiveness.

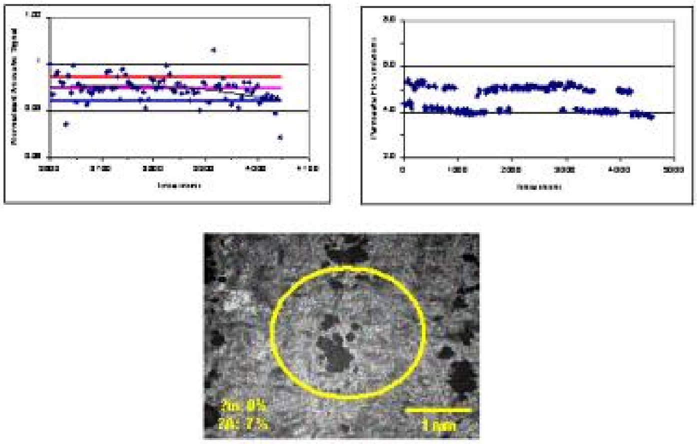

Figure 1. Representative flow-reversal test results showing the dynamic window and trend line from ultrasonic measurements during the final cycle (upper left), permeate flow-rate changes over 34 cycles (upper right), and post-mortem mass (Δm) and area coverage (ΔA) data for the downstream port with the sensor sampling area indicated by the circle (bottom).

ICOM474

Contribution of the EDBM technology to products recovery from RO concentrates generated in desalination plants.

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Seawater desalination is becoming increasingly popular for production or fresh potable water as limited availability of high quality fresh underwater and surface water sources and rapid population growth has led to greater consideration of alternative drinking water sources. As of 2005 more than 15,000 desalination facilities were operational in more than 120 countries worldwide [1]. However RO treatment produces concentrate brine equivalent to 5-25% of the influent flow. Concentrate disposal of RO/NF desalination facilities is an important concern due to several factors, such as loss of significant volume of feed water as waste, high concentration of salts and contaminants present in these streams, and regulations associated with concentrate disposal [2].

The feasibility of EDBM for the production of acids (HCl) and bases (NaOH) achieving industrial quality from seawater desalination concentrates is demonstrated in this research. The technological aspects, e.g. how to avoid divalent ions precipitation causing membrane fouling have been addressed and solved, the energy efficiency of the process is has been calculated and a mathematical model able to describe the kinetics of the acid and base recovery has been used.

Table 1 presents the water quality of RO concentrates used in this research simulating the composition of the concentrates generated in *Las Aguilas* desalination facility (Spain).

Compound	**Concentración (mg l^{-1})**
calcium	790
magnesium	2,479
sodium	**21,921**
potassium	742
strontium	8.86
chloride	**38,886**
sulphate	5,315
nitrate	1.78
bicarbonate	173.40
carbonate	154.80
fluoride(*)	2.00 (ng l^{-1})(*)
silica	0.50
total ion	70,487
pH	9.20

EDBM experiments were performed in a laboratory scale plant. Additional information related to the experimental set up can be found elsewhere [4]. All experiments were carried out in a batch mode working with current densities in the range 250 -100 A m^{-2}.

The results presented in Figure 1 indicate that salt reduction in feed stack is achieved down to values higher than 90% of the initial concentration under appropriate conditions thus allowing safe disposal of the treated water. Regarding the acid production concentrations up to 800 mol m^{-3} can be reached with a high degree in purity, trace concentrations of sulphuric acid were found. A Similar behaviour was observed in the base stack.

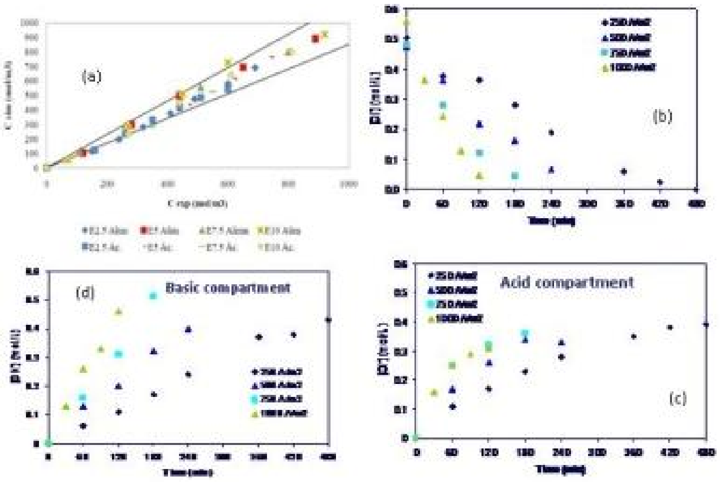

Figure 1. (a) Parity graph of [chloride]. Evolution of [chloride] with time as a function of applied current density (b) feed compartment (c) acid compartment. (d) Evolution of [OH$^-$] with time in basic compartment as a function of applied current density.

The current efficiency has been determined obtaining up to 80% efficiency for base production and 70% for acid production. Finally the model developed by Mier et al [3] has been used to describe the kinetic data obtained in the EDBM system. Ninety percent of the of the results of C_{sim} fall within the interval C_{exp} 15% C_{exp}, [figure 1], proving that the proposed model describes satisfactorily the ionic mass transport through the EDBM system applied to the treatment of RO concentrates obtained in marine water desalination plants with recovery of acid and base products.

Acknowledgements
Financial support of projects nº CTQ2008-03225/PPQ and CSD 2006-44 from the Spanish MICINN is acknowledged.

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ICOM1497

Salt transport characteristics of a sulfonated styrenic pentablock copolymer for desalination applications

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Sulfonated hydrocarbon polymers have shown promise as chlorine-tolerant desalination membrane materials. These polymers have sulfonate groups that can dissociate into a counter-ion and a negative fixed charge group. The presence of these fixed charge groups on the polymer backbone renders the material highly-charged. Salt sorption and permeability are affected by the presence of fixed charges on the polymer backbone. In order to better understand structure-property relationships for these materials and to guide development of new polymer materials, fundamental sorption and transport studies are needed. We have considered sodium chloride sorption and transport in a sulfonated styrenic pentablock copolymer. The ability of sulfonated polymers to undergo ion exchange results in unequal sorption of counter-ions (sodium) and co-ions (chloride); the content of sodium ions is much higher than that of chloride ions.

The sulfonated pentablock copolymer was equilibrated in sodium chloride solutions of varying concentration. The content of sodium ions was measured by analyzing the polymer's ash residue after the organic material had been burned off. The chloride ion content was measured by extracting salt from the equilibrated films into pure water and analyzing this water for chloride content. At equilibrium, for all external salt concentrations, there is a sodium ion associated with all accessible sulfonate groups. This will also be the case during a desalination process.

The chloride ion content in the polymer is equal to the mobile salt content in the membrane. We interpret the mobile salt sorption within the framework of the solution-diffusion model where the salt permeability is equal to the mobile salt sorption coefficient multiplied by the effective salt diffusion coefficient, $P_s = K_s D_s$. Mobile salt sorption measurements can be combined with salt permeability measurements to determine the effective salt diffusion coefficient. In these highly charged materials, salt sorption and permeability decrease with decreasing external salt concentration as Donnan theory suggests. Therefore the permeability, sorption, and diffusion coefficients are analyzed as a function of salt concentration.

This approach will be useful for analyzing the situation that results for multi-salt solutions characteristic of most desalination processes.

ICOM1655

Concentration polarization-enhanced surface modification of RO membranes and it use for improving boron removal in brackish water desalination

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Surface modification of membranes through graft polymerization is a versatile method for improving performance of RO and NF membranes, in particular, for reduced fouling and enhanced selectivity. Recently, we reported an facile modification approach whereby graft-polymerization is carried out under pressure while filtering the monomer solution, thus utilizing the concentration polarization effect that occurs during filtration (1, 2). It was shown that this method greatly enhances surface reaction and essentially prevents the undesired homopolymerization, which improves kinetics, substantially reduces the required amounts of reactants and broadens the range of usable monomers including sparingly soluble and slowly reacting ones.

The potential of the method for improving removal of boric acid by brackish water RO membrane (BWRO) was explored. Poor rejection of boric acid is a consequence of its neutrality and small size and is a major problem in sea and brackish water desalination. Commercial high flux RO membranes (ESPA1 and XLE) were modified using different hydrophlic, hydrophobic and charged monomer and the membrane performance – permeability, NaCl and boric acid rejection – were measured at a pH 7, i.e., below pK_a of boric acid. Improvement in B removal was achieved for monomers with the lowest affinity towards boric acid selected on the basis of suggested physico-chemical rationales. In particular, water/boric acid partitioning experiments in different organic liquids indicated that low polarity/polarizability, i.e., of the graft polymer could be beneficial for boric acid removal. Among the examined monomers glycidyl methacryalte having the lowest affinity towards boric acid showed the largest improvement in B removal along with a moderate loss of permeability and slightly improved salt rejection. Most of the improvement was attributed to sealing less selective areas ("defects") inherently present in the original LPRO membranes; however, the choice of monomer was crucial for maximizing selectivity.

The technique was also tested for *in situ* modification of commercial spiral-wound elements (XLE). ATR-FTIR spectra recorded at different location along the element revealed that the membrane was successfully and uniformly modified troughout the element. The performance of the modified element was superior to reported performance of most commercial BWRO elements (Fig. 1). Pilot tests employing the modified XLE element and a typical BWRO element BW30 confirmed that, despite 1.4 times higher permeability of modified XLE element, its salt rejection was 99.7 % vs. 99% for BW30 and its B rejection was 85% vs. only 65% for BW30.

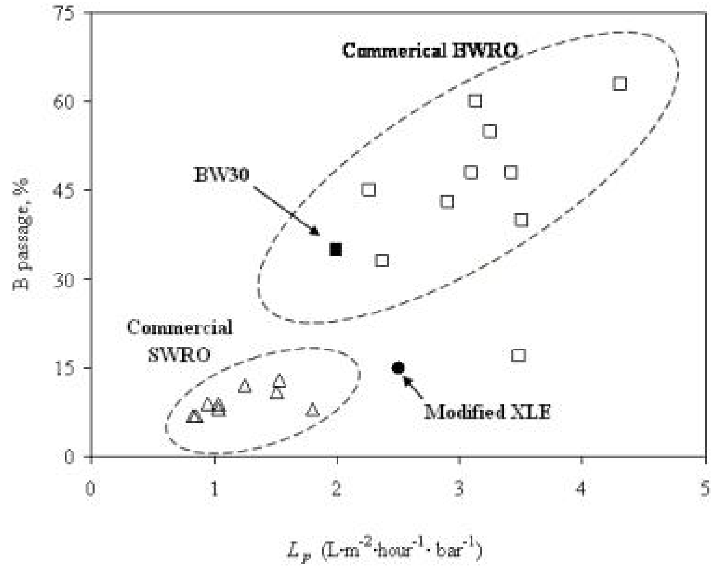

Figure 1. The B passage and permeability (Lp) of the modified membrane and commercial brackish (BWRO) and see water (SWRO) membranes. Solid symbols are present measurements and empty symbols are based on published data.

Acknowledgement. Financial support from the Water Authority of Israel is gratefully acknowledged.

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Membranes for drinking water 2

ICOM1799

Design of Low Fouling Membrane for Water Treatment: A Status Quo and Future Development

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Membrane fouling and flux decline are undesirable, albeit inevitable, problems in membrane filtration processes for water treatment. The development of low fouling membranes, the design of high efficiency modules, the selection of optimal operational strategies, and several improvements made in peripheral control, monitoring, and cleaning techniques have been adopted to deal with these formidable obstacles. One of the most efficient and elegant ways of alleviating this problem is the design of low fouling membranes. Regarding to the low fouling membrane design, learning from nature, *i.e.* biomimetics or bionics, is a concept of a relatively new branch of science. It has already led to a variety of innovative membrane design. In this presentation, the status quo and future development of low fouling membrane design for both of porous membrane (MF and UF) and dense membrane (NF and RO) for water treatment will be discussed.

ICOM1442

Rejection of trace organic solutes by FO and NF/RO membranes: influences of solute and membrane properties and membrane fouling

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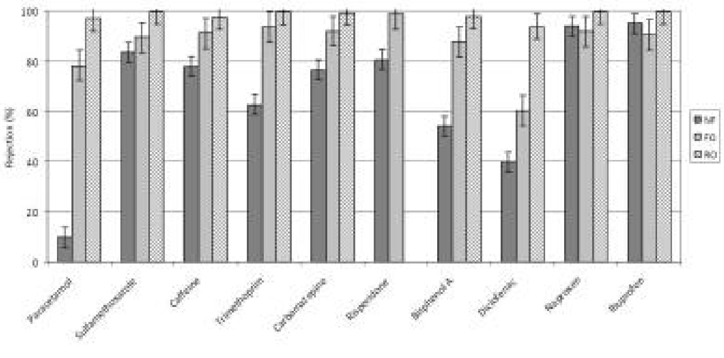
Forward osmosis (FO) has rapidly gained interest over the last years. FO is driven by an osmotic pressure difference, resulting in water transport across the membrane. Different salts and organic solutes can be used to generate the required osmotic pressure difference. Frequently cited advantages of FO are lower energy use and potential lower fouling propensity and higher rejection capabilities. These potential advantages have driven research towards use of FO in wastewater reuse applications. FO systems are normally combined with a secondary treatment step (often reverse osmosis (RO)) to recover the draw solution and produce clean water. Combination of FO with RO is usually regarded as a double barrier system.

One of the principal concerns in wastewater reuse, is the occurrence of elevated levels of trace organics. In contrast to transport mechanisms of salts, limited knowledge is available on transport of trace organics through FO membranes.

In order to investigate performance of FO-RO systems for wastewater reuse, this research focuses on removal of trace organics by FO membranes, and compares this to rejection by commercial nanofiltration (NF) and RO membranes. “Single pass” FO-RO (no recovery of draw solution) applications are compared to “multi-pass” (with recovery of draw solution) applications. In multi-pass applications, higher rejections of solutes (e.g., trace organics) by the RO than the FO will lead to increasing concentrations of these solutes in the draw solution, thus compromising the double barrier concept.

FO experiments were carried out in a counter-current cross-flow cell. NF/RO experiments were carried out at normal (20 l/m^2.h) and low fluxes (comparable to FO, 4-10 l/m^2.h), to obtain an objective comparison.



Rejection values of different pharmaceuticals by a commercial FO membrane (HTI) were in between rejections by NF (Dow-Filmtech) and RO (Dow-Filmtec) at similar fluxes (see Figure 1). Apparently, the FO membrane is more open than the RO membrane, but tighter than the NF membrane. Surprisingly, rejection of negatively charged solutes (ibuprofen, naproxen) by NF was higher than by FO, which was due to the higher surface charge of the NF.

Organic solute transport mechanisms in FO-mode were further investigated by dosing a wide range of model trace organics with different physico-chemical properties. An attempt was made to construct a predictive model for rejection of trace organics by FO, comparable to previously constructed predictive models for NF and RO.

The effects of membrane fouling on rejection by FO, compared to NF and RO were also studied. For NF and RO, membrane fouling is known to (often negatively) impact rejection. NF, RO and FO membranes were fouled with model organic foulants (BSA, alginate, humic acid) and model colloids (20nm silica colloids), but also with wastewater effluent. For the FO membranes, the influence of biofouling in the feed and draw solution spacer channels on rejection of trace organics was also determined and compared to the influence of biofouling on rejection by NF and RO. All membranes were extensively characterized before and after fouling to relate changes in membrane surface properties to temporal changes in rejection performance.

ICOM1060

Nanofluid Filtration using Electrospun Nanofibers

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Water pre-treatment as separation of micron to sub-micron particulate contaminants has gained increasing importance in water purification. Pre-treatment can minimize the risk of fouling of the downstream filter unit and maintain its performance for a much longer time before cleaning and/or replacement. Two conventional methods for water pre-treatment and elimination of such pollutants are adsorption and filtration.

Among the new membrane technologies, electrospun nanofibrous membranes (ENMs) are emerging as a distinct novel class possessing promising potentials for both the above mentioned separation mechanisms.

ENMs have been mainly used as a microfiltration (MF) membrane able to capture coarse particles from water streams. However the bigger pore size of ENM embarrass its application in the nanofluid filtration.

Here we show the first engineered ENM filter for separation of colloidal suspensions of nanoparticles from water fluid with nearly 100 % efficiency. The effect of the structural, surface and morphological properties on the membrane separation performance will be illustrated.

ICOM784

Synthesis and Characterization of Novel Forward Osmosis Membranes based on Layer-by-Layer Assembly

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Forward osmosis (FO) has received considerable interests for water and energy related applications in recent years. The current study investigated the synthesis of novel nanofiltration (NF)-like FO membranes using layer-by-layer (LbL) assembly. The membrane substrate was tailored (high porosity, finger-like pores, thin cross-section, and excellent hydrophilicity) to achieve a small structural parameter of 0.5 mm. Increasing the number of polyelectrolyte layers improved the selectivity of the LbL membranes while reducing their water permeability. The solute reverse transport was strongly affected by membrane selectivity, and the more selective membrane 6#LbL (with 6 polyelectrolyte layers) had much lower solute flux compared to 3#LbL and 1#LbL. Meanwhile, the FO water flux was found to be strongly affected by both membrane water permeability and solute reverse transport. Severe solute reverse transport was observed for the active-layer-facing-draw-solution (AL-DS) membrane orientation, likely due to the suppression of Donnan exclusion as a result of the high ionic strength of the draw solution. In contrast, the active-layer-facing-feed-solution (AL-FS) orientation showed remarkable FO performance (15, 20, and 28 $L/m^2.h$ at 0.1, 0.5, and 1.0 M $MgCl_2$, respectively, for membrane 3#LbL while maintaining very low solute flux), superior to other NF-like FO membranes reported in the literature. To the best of knowledge of the authors, this is the first study on the synthesis and characterization of LbL based FO membranes.

ICOM230

Removal of nanoparticles from ground and surface waters by coagulation and membrane process

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During the last decade, there has been extensive development of nanotechnologies. Nevertheless, research about the potential impacts of nanoparticles on human health and environment has barely started. Since drinking water is the main source to men exposure to the ingestion of nanoparticles, the efficiency of water treatment process for nanoparticles removal is crucial.

This study focuses on the achievement and the improvement of membrane filtration for the removal of nanoparticles in ground and surface waters or in industrial effluents. Nanoparticle filtration approach differs from classical filtration of particle suspensions because specific interactions between particles have to be considered.

Filtration was performed at laboratory scale with flat regenerated cellulose membranes. Silica dioxide nanoparticles ($SiO_{2,}$ 80 nm, 0.14 %wt), reported to be one of the most abundant nanoparticles used in industry, were chosen as model suspension. Characteristics of the filtration were studied first with SiO_2 in ultrapure water. The influence of the membrane molecular weight cut-off (MWCO) [10, 30 and 100 kDa] and the operating conditions were examined: stirring [0, 250 and 500 rpm], TMP [0-2.5 bar].

Different fouling phenomena were set into evidence for the selected MWCO. For the 10 kDa membrane, filtration is controlled by cake deposit, whereas pore clogging was observed for the 30 and 100 kDa membranes. Fouling resistance was indeed found proportional to permeate volume. Stirring close to the membrane surface was shown to significantly enhance the membrane permeability on the whole filtration time, similarly for 250 rpm or 500 rpm. From a process viewpoint, retention close to 100% associated to a sustainable permeate flux around 24 $L.h^{-1}.m^{-2}$ (TMP=0.8 bar) was achieved with the 10 kDa membrane, with mostly reversible fouling. Those results demonstrated the feasibility and the sustainability of membrane filtration process for concentrated nanoparticles suspension treatment.

Closer to real environmental conditions, the influence of ionic strength (NaCl [0-0.5] M) and natural organic matter content (NOM) (humic acid 1:100) on filtration performance (flux, retention and membrane cleanliness recovery) was investigated. Compared to experiments with nanoparticles in pure water, permeability decline was systematically accentuated (from 30 to 50% at identical process conditions), while permeate quality remained satisfying. Integration of a pre-treatment was experimented to recover the initial filtration performance. Optimal coagulation (determined by Jartests) was performed with $AlCl_3$ before filtration and enabled to obtain micrometric and monodisperse particles. The impact of particles size change on the characteristics of 10 and 100 kDa membrane filtrations was determined. Coagulation enabled to recover the initial performance of SiO_2 suspension filtration in ultrapure water obtained with the 10 kDa membrane. An optional decantation step before filtration was shown not to improve much filtration results. The same experiments are currently being performed with the 100 kDa membrane. Changes of fouling characteristics and permeate quality are being studied.

The results demonstrate that membrane filtration process is a sustainable, efficient and easy to perform process to ensure satisfactory performance of nanoparticle removal from various types of effluents and waters.

Microfluidic membrane applications 1

ICOM1808

Membranes and microfluidics; a strong combination

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The goal of this presentation is to highlight some applications of membranes in microfluidic and microreactor processes that illustrate the connectivity and opportunities between the two. Both fields can profit from each other and the approach here is to discuss both directions of expertise transfer respectively.

First, interesting applications are discussed where membrane technology can be applied in microscale processes. The small characteristic length scale is exceptionally compatible with membrane based processes, including separations, contacting, membrane reactors, and extractions. Within the field of microreactor technology, there is significant effort directed towards development of microreactor concepts, including those using membrane microreactors. Such reactors are characterized by high area to volume ratio and continuous flow operation. Much periphery equipment to support these microreactor processes, however, is still underdeveloped. Downstream processing, for instance, has to be made compatible with the typical small volume flows. Gravity based approaches, like sedimentation and distillation, simply become less effective at small length scales. Instead capillary forces and interfacial processes start playing dominant roles. The exploitation of membrane-based technologies has great potential for microscale processes.

Secondly, microfluidics research can forward understanding of membrane-based processes. The well-defined flow conditions are suitable for direct observations and allow one to study processes on a detailed scale. A striking example is the study of biofouling under controlled microfluidic flow conditions. Such studies elucidate the relation between biofilm growth and geometry by means of flow and concentration profiles. These well-defined methods can then be correlated to numerical models that aim to grasp the growth mechanics of biomass. Eventually, a better understanding can be applied to develop improved designs for fouling control. The fundamental study of interface related phenomena is also demonstrated in ion selective transport experimentation. The development of ion concentration polarization layers in microchannels was exploited for desalination purposes and strongly illustrates the benefit that microfluidics bring to membrane research. The local study of ion transport and fluid flow in microdevices provides much insight to design membrane based separation processes. Microfluidics based methods have proven to be powerful research tools to study membrane processes in great detail.

ICOM495

Selective removal of hydroxylamine using membrane microchannels

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Large effort has been put into the integration of unit operations on micro-fluidic devices like sample pre-treatment, mixing, reaction, and separation/purification of the products. The integration of membranes into chips has shown substantial growth over the last decades due to their versatile functionalities.

We aim to demonstrate that high reaction selectivity at high conversion is possible for reactions that traditionally do not give reasonable yields because of non-selective, consecutive reactions; by means of integrating repetitive mixing, conversion, and separation functionalities in a micro-reactor. The proposed system of study is the direct production of hydroxylamine from ammonia via partial oxidation. This reaction is known to occur and is selective at very low conversions. To achieve high reaction selectivity and high conversion, a multiplexed reactor comprising of reactant and product separation membranes is developed. The membrane functionalities must be able to selectively introduce oxygen into the reactant stream, while a second membrane removes hydroxylamine from each microchannel.

For the removal of hydroxylamine from the reaction medium, which is mainly composed of ammonia, appropriate separation methods based on charge differences between hydroxylamine and ammonia are investigated. Ion concentration polarization due to an electrical current through a partially ion-selective membrane (Nafion "Nanoslot") is a novel, fundamental transport mechanism for water desalination [1], and we suggest that it can be also an effective method for the separation of hydroxylamine from ammonia. To implement this approach, a simple microfluidic device is fabricated for the continuous separation of hydroxylamine. The challenge is to divide the reaction mixture into two streams, one with a high ionic conductivity mainly composing of ammonium, and the other one including neutral hydroxylamine. During operation, the charged ions will be pushed away from the ion exchange membrane, which is placed in a nanojunction. In order to investigate the separation and mass transfer mechanisms, this non-linear non-equilibrium process is also analyzed numerically. The full model including the Nafion nanoslot membrane is based on coupling the classical Poisson, Nernst-Planck, and Navier-Stokes equations.

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ICOM1514

Bacteria streamers formation during filtration in microfluidic devices mimicking filters

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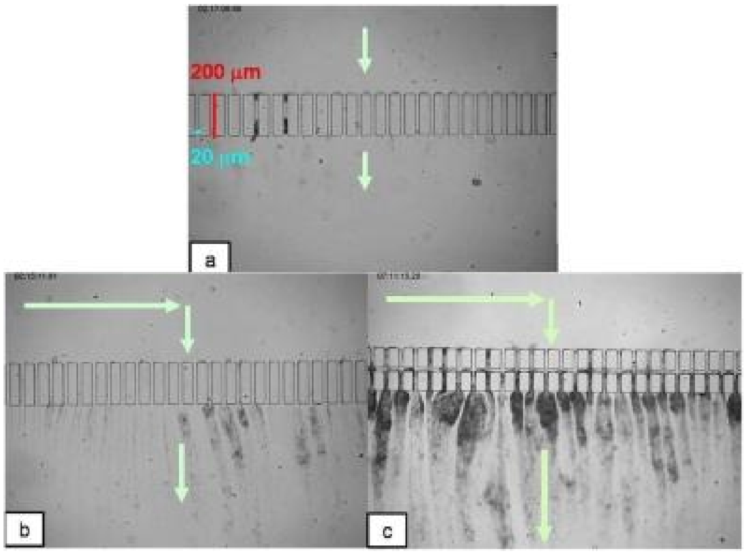
In natural and engineered systems bacteria colonizes surfaces and forms biofilms. In engineered systems, these biofilms can have a positive role by participating to the organic removal for example in waste water treatment by Membrane Bio-Reactor (MBR). On another hand, biofilms are a sanitary problem as they increase the bacteria antimicrobial agents' resistance and participate to the transmission of diseases. The formation of bacteria colonies is a complex process which is influenced by numerous factors. The aim of this work is to develop experimentin order to progress in the understanding of bacteria capture in filters and membranes. PDMS microsystems have been realized to allow for direct dynamic observation of bacteria transfer across different microchannels mimicking filtration processes. A first surprising observation is the behavior of bacteria when they are filtering in such devices : we found that Escherichia coli accumulate in the downstream zone of the filter and form large streamers oscillating in the flow. This result is very different from the one observed in same system with "inert" particles of equivalent size which are captured in the bottleneck zone and are accumulated in the upstream zone [1]. The bacteria streamer development is influenced by the flow configuration (dead end mode (a) or cross flow mode (b,c)) and the presence of connections between channels (c).



Confocal microscopy and 3D reconstruction of streamers show how these streamers are connected to the filter. The use of specific markers proves that these streamers are constituted of viable cell and exopolysaccharide. These results are discussed at the light of 3D flow simulations. In confined systems and in laminar flow there is secondary flow (z-velocities) surimposed to the streamwise motion (in xy plane) [2]. It has been recently shown [3] that the presence of the secondary flow in the microsystems could have an effect on the bacterial adhesion. Actually, we observe that streamers formation are promoted by cross flow mode and the presence of connection between channels which are flow configurations where secondary flows zones with positive and negative velocities along z are very close. We discuss these results by explaining how the streamers formation could be correlated to the proximity of these secondary flows.

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ICOM1566

An NF microfluidic device and its use for development of biomimetic membranes

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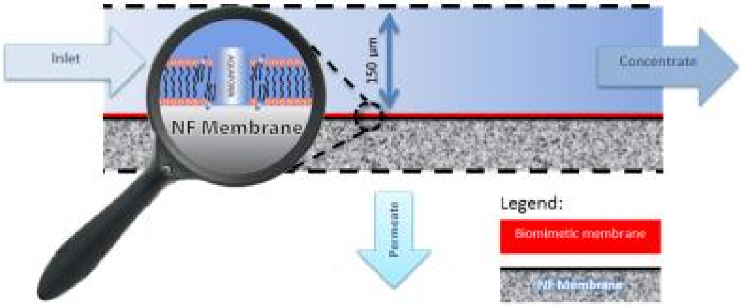
The field of membrane operations in microfluidics is still at early stages of development. Current state-of-the-art in manufacturing of filtration membrane for microfluidics, which is driven by hydraulic pressure, extends down to pore size of several nm, i.e., covers the range of micro and ultrafiltration (MF and UF). The ultimate goal of the presented study is to add nano-filtration (NF) applications to the arsenal of microfluidic operations.

As a preliminary step, the incorporation of commercial NF membrane in a microfluidic device will be presented. It has been shown that sealing micro-channels and concentration polarization in such devices may be challenging. A simple and cheap method for sealing the micro-channels has been developed and will be presented. In addition the concentration polarization phenomenon will be discussed.

The advantages of the new micro-NF setup are employed to develop and study highly selective bio-mimetic membranes based on bolaamphiphiles with incorporated aquaporins (water channel proteins) using minimal amounts of biomaterials. The setup is schematically illustrated in figure 1 and allows a facile preparation of bio-mimetic membranes and measuring their performance (permeability and rejection) and comparison with commercial NF/RO membranes.



ICOM1023

Emulsification: a comparison between membranes and microfluidic devices

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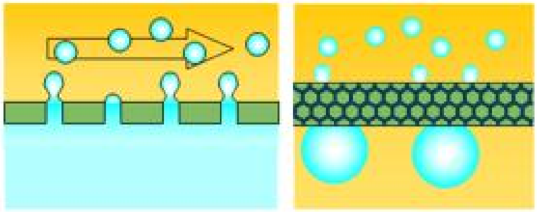
Currently, emulsification research is very lively with many different new emulsification technologies being published; all with their own pros and cons. Membranes are mostly applied either in cross-flow mode or in pre-mix mode. During cross-flow emulsification (see Figure 1 a), the to be dispersed phase is pressurized through the membrane where it forms small droplets on top of the membrane, that are consecutively sheared off by the cross-flowing continuous phase once they have grown to a certain size. During pre-mix emulsification, the big droplets of a pre-emulsion are broken up into smaller ones, as is the case in the classic emulsification techniques (see also Figure 1 b).Figure 1. Schematic representations of a. Cross-flow membrane emulsification, in which the cross-flowing continuous phase shears-off the droplets. b. Pre-mix emulsification; a coarse emulsion is broken up into smaller ones through passage through a membrane. □ □



When comparing membrane emulsification with the more classic techniques (Figure 2), it is clear that cross-flow emulsification is a much milder less energy consuming technique than e.g. high pressure homogenizers are. In some cases, the energy density is orders of magnitude less. Pre-mix emulsification, seems to be more in line with the traditional techniques, but may be useful in the production of relatively large droplets. Also, this technology is not that developed as cross-flow emulsification. In order to develop membrane emulsification further, it is necessary to understand the underlying mechanisms and for this, microfluidic devices are important tools.

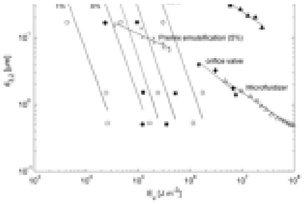


Figure 2. Energy efficiencies of various emulsification methods.

During cross-flow emulsification, it is hard to observe droplet formation, if not completely impossible. Therefore, various efforts were made to idealize a membrane or even a pore and learn from that. Pioneering work was done with so-called microsieves invented by Van Rijn, which are extremely flat porous plates, which have uniform pore size, and allow observation of droplet formation from the top. Besides, so-called T-junctions (and later Y-junctions) were used to investigate droplet snap-off from the side and compared to computational results. In a T-junction, the to-be-dispersed phase is pressurized into a channel with the cross-flowing continuous phase, where it slowly protrudes into the continuous phase channel. Due to the shear of the continuous phase, the to-be-dispersed phase the droplet(s) will snap off, and this process can be summarized in scaling relations. Besides shear based methods, also spontaneous droplet formation (due to Laplace pressure differences) is used for emulsification; these processes have been investigated in detail, and scaling relations are available. □ In the presentation, the various methods will be discussed and compared based on the energy density, and monodispersity of the emulsion. Further, options for up-scaling and improved designs will be presented based on the scaling relations obtained from our microfluidic investigations, and an outlook will be given for membrane and microfluidic emulsification.

Modelling 4

ICOM1796

Modeling and operation of dynamic membrane processes

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Membrane processes are very often influenced by the inherent drawbacks of concentration polarization and fouling of the membrane surface. With increasing performance of the membrane itself in terms of permeability and selectivity these drawbacks become even more severe. One way to reduce and uncouple these phenomena are to operate the membrane process under unsteady-state conditions: By changing the driving force direction before steady-state concentration profiles have been obtained it is possible to operate under conditions closer to the real performance of the membrane itself.

The “Back-shock” process (1) using reverse asymmetric microfiltration membranes is one such example using a dynamic pressure pulsation where the permeate is pressurized during very short time intervals (less than 1 s) and with a frequency around 0.2-1 s^{-1}.

The “Reverse Electro-Enhanced Dialysis (REED)” process (2) using an array of only anion exchange membranes (or cation exchange membranes) and switching the current direction at short intervals (around 5 minutes) is another example of such dynamic membrane process, where the frequent change of the conditions at the membrane surface diminish the fouling of the membranes even in strong fouling potential solutions like a fermentation broth (3).

Dynamic microfiltration using vibrating hollow fibers is another method to decouple the pressure loss in the bulk solution from the trans-membrane-pressure and thereby facilitate a higher permeability and selectivity of the MF process (4).

Another way to decouple the pressure loss in the bulk solution from the trans-membrane-pressure is to apply an electric field across the membrane during the normal operation of the UF/MF membranes, thereby increasing the permeate flux and/or the selectivity (5).

In the lecture the modeling of the dynamics of the concentration polarization and how it influences the membrane selectivity and productivity will be described. The build-up of the polarized highly concentrated layer at the surface of an ultrafiltration membrane typically takes 10-30 seconds why it is possible to obtain a dynamic layer with a substantially reduced surface concentration thereby increasing the selectivity of the membrane.

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ICOM607

Transient Simulation of Beer Microfiltration

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Pilsner beer is filtrated commercially to obtain a bright clear beer using hollow fiber membranes. Beer is a complex mixture, involving compounds each having a different mode of fouling, which interact each other quite strongly. Our interest in this problem is due to two objectives 1) to develop a novel model-based control algorithm, for significantly reduced consumption of energy and cleaning agents, and 2) to obtain insight in the complex physics, which involves shear induced diffusion. Beer is composed of three classes of compounds: 1) dissolved macromolecules, which lead to pore constriction inside the membrane, 2) protein-polyphenol aggregates leading to pore blocking of membrane, and 3) yeast cells which form a cake layer – which can act as a secondary membrane partly capturing the aggregates and thus prevents pore blocking. Aggregates and yeast lead to turbidity and need to be removed. The cake layer formation is governed by shear induced diffusion, for which we have recently formulated a predictive theory based on an effective temperature, a concept regularly used for driven soft matter [1]. This novel theory we have linked to standard blocking, pore blocking and secondary membrane fouling models, to which we have performed scale analysis, and subsequently obtained a reduced model. In the model reduction we partly use techniques already developed by Romero and Davis [2]

In this paper we describe the resulting reduced model, and validate the underlying hypotheses using literature data. Subsequently, we present parameter studies showing how strong the interaction is via the different modes of fouling. We end with some conclusions which are also of important to filtration of other complex biological media, as obtained from fermentation in biotechnological applications.

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ICOM579

Strategies for reducing the cost of RO water desalination via process integration and optimization

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Membrane RO desalination of both seawater and inland brackish water is currently being considered in various locations around the world, with a growing number of large-scale desalination plants in the planning and/or construction stages. In addition, desalination is being increasingly implemented in water reuse application. RO desalting of agricultural drainage (AD) water is also being evaluated for reclamation and reuse of irrigation water. The cost of water production in RO plants generally consists of the cost of energy consumption, equipment, membranes, labor, maintenance and financial charges. Considerable efforts, dating back to the initial days of RO development in the early 1960s, have been devoted to minimizing the specific energy consumption of water desalination and development of fouling resistant membranes. In order to reduce RO process energy consumption and decrease the volume of generated concentrate stream, product water recovery must be optimized while keeping the overall water production cost at a reasonable level. Accordingly, the present study introduces a formalized theoretical modeling framework to systematically evaluate options for minimization of energy consumption with and without energy recovery devices (ERDs), considering the impact of membrane cost and the cost of brine management. In this approach we compare single versus multi-stage and two-pass membrane desalting including considerations of stream mixing and recycling. In addition, the deployment of chemically enhanced seeded precipitation (CESP) is evaluated for high recovery desalination in order to reduce the cost of concentrate management in inland water desalination. Process analysis indicates that the use CESP for interstage concentrate demineralization (ICD) of primary RO concentrate to enable enhanced in a secondary RO stage, can be more effective and less costly than chemical-intensive than conventional precipitation softening. The present analysis demonstrates that, given that current RO membranes already allow operation nearly up to the thermodynamic limit and with the capability of ICD to enable high recovery RO desalination, RO cost reduction must consider the development of membranes of higher fouling and mineral scaling resistance, reduction in costs associated with membranes of low fouling and mineral scaling propensities, optimal dynamic process control to achieve lower energy consumption operation and reduction of concentrate management costs.

ICOM392

Dynamic Modeling of Ionic Mass Transport In Electrodialysis Processes

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In Electrodialysis (ED) ion-exchange membranes are used to separate ions of opposite charges in an electric field. The efficiency of the process is determined by the intensity of the mass transfer in the electrolyte-membrane system. The underlying coupled physico-chemical phenomena characterizing the mass transport in the membrane-electrolyte system are not completely understood although the process has been established in industry for several decades. The interactions of thermodynamics, the electric field, diffusive and migrative transport inside the membranes and complex hydrodynamics in the electrolyte flow channels are complex and of decisive impact [1].

There are only very few studies investigating the rigorous modeling of the coupled transport processes in the membrane-electrolyte system. Particularly, the development of models describing processes with complex electrolyte solutions is hardly covered in literature. In addition to semi-empiric model formulations [2], process models using a one-dimensional, quasi-stationary formulation are proposed [3, 4]. Thus, negligibly small concentration changes along the flow path in the electrolyte flow channels are assumed and transport processes are only considered in the direction of the electric field. However, due to these simplifying assumptions their application is restricted to batch processes with a high number of recirculations. In addition, the quasi-stationary formulation may be inadequate to describe processes operated in a dynamic mode such as pulsed current ED or ED reversal.

In this contribution, a dynamic process model for an electrodialysis process is presented. Its rigorous formulation aims at giving insight into the underlying coupled physico-chemical phenomena on a high scale of granularity. The model describes the temporal and spatial dynamics of the transport processes on a high level of detail, which is not encountered in previous works. In particular, the model covers the description of ionic mass transfer inside the ion-exchange membranes and the spacer filled flow channels in two spatial dimensions using the Nernst-Planck formulation of ionic mass transfer.

The model contains numerous model parameters which are subject to significant uncertainty. Particularly, diffusion coefficients for the membrane phases and parameters characterizing the membrane-electrolyte equilibrium are unknown for most commercial membranes. In this context, we present a methodology for the thorough identification of these parameters: First, equilibrium experiments are conducted for the identification of parameters characterizing the membrane-electrolyte equilibrium. Subsequently, the identification of diffusion coefficients is carried out using current-voltage curves at varying concentrations of the adjacent electrolyte solution. Finally, experimental data from desalination experiments are used to identify the parameters characterizing the hydrodynamic conditions in the spacer filled flow channels.

The proposed model gives a detailed insight into the coupled physico-chemical phenomena in the membrane-electrolyte system. Furthermore, it allows a model-based approach for process design and control, which will be the focus of future works.

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ICOM1156

Mass transfer in organic solvent nanofiltration membranes: Modeling and experimental investigation

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The development of solvent resistant membranes and membrane modules has established organic solvent nanofiltration (OSN) as a technically proven separation method in chemical and biochemical industry. The advantages of OSN, such as mild processing conditions and low energy consumption, have led to intensive research towards the development of new solvent stable membranes. However, for a given separation problem it is rather difficult to identify a suitable membrane due to complex interactions between the membrane, the solvent and solutes. In literature there are no generic models which are able to predict membrane performance.

The goal of this work is measuring and modeling of the flux and rejection in asymmetric integral polyimide nanofiltration membranes, by considering the thermodynamics of solvent/solute/polymer systems. Ethanol and 2-propanol, and paracetamol were chosen as solvents and solute, respectively, for investigation. Commercially available membranes STARMEM^{TM} as well as further polyimide membranes made of Lenzing P84 were investigated. The permeation experiments were conducted on a lab-scale nanofiltration plant LStA60LM (Sima-Tec). The experiments were performed in a pressure range from 5 - 35 bar, with a feed volume flow of 55 l/h, and at constant temperature of 25°C. The concentration of paracetamol was varied up to 4 weight percent.

Simulation is performed by using the solution diffusion theory, and by calculating diffusion and sorption separately. In order to determine the sorption of the solvent and solute in the polymer membrane, the PC-SAFT Equation of State [1] was applied. Independent sorption measurements were applied to determine the PC-SAFT pure component and interaction parameters. The calculated phase diagrams have shown that this equation of state is capable of describing the solvent/polyimide liquid liquid equilibrium. Stefan-Maxwell diffusion coefficients were estimated based on permeation measurements.

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UF/MF 3

ICOM1841

Microfiltration/ Ultrafiltration Membranes - Nearly a century old and still not "mature"?

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Synthetic membranes as we know them today trace their beginnings to the early years of the 20th century. With the microfiltration membranes' earliest "industrial" reference [1] dating back to 1917, this technology is now approaching a century of developments. Although ultrafiltration membranes are much younger [2], they too can hardly claim a label of a new or emerging technology. Despite of nearly a century of improvements and refinements, formidable challenges in the field remain and new developments are constantly expanding the frontiers of membrane technology to new areas.

The evolution of technologies leading to commercially significant microfiltration and ultrafiltration membranes will be described. Examples of key technological advances in the field will illustrate a steady progress of improvements in four generations of microfiltration membranes and three generations of ultrafiltration membranes. Key challenges in microfiltration and ultrafiltration membrane technologies awaiting future membrane innovators and membrane scientists will be illustrated on real life industrial examples of microfiltration and ultrafiltration membranes in life science applications.

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ICOM429

New views on process and membrane design to promote particle migration and improve membrane microfiltration

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Membrane microfiltration processes are important in several industries to separate or fractionate components on size, and popular due to their energy-efficiency and clean way of production [1]. A large drawback is fouling of the membrane because of particle deposition and accumulation, causing flux decrease and changing retention behavior as function of time. Fouling prevention is therefore of imminent importance to make membrane processes attractive in terms of separation behavior as well as in terms of economic feasibility. Therefore, there is a strong need to get insight in particle behavior and develop new ways to fractionate or separate components by membrane microfiltration in the absence of fouling.

In this study, we show how particle migration phenomena can positively affect membrane microfiltration and can enhance separation of particles without fouling occurring. We will elaborate on the possibilities of important migration phenomena in microfiltration, being inertial lift, shear-induced diffusion, and fluid-skimming, and support our claims with experimental and theoretical findings. The results for particle concentrations below 5% show that under certain process conditions and module designs, inertial lift and fluid skimming can be used to improve membrane microfiltration. More specifically, only the cross flow velocity and transmembrane pressure need to be controlled in order to get a constant separation characteristic as function of time; all experimental data converge into one master curve that describes transmission and particle size. Additionally, experimental results show that when concentrated suspensions are targeted (around 20%), process conditions can be used to induce shear-induced diffusion resulting in separation on particle size. This is illustrated for a bi-disperse suspension, and guidelines will be given on how these insights can be used in membrane microfiltration.

Additionally, a reflection is made on membrane design, which can positively improve migration behavior of particles. From our experiments we could conclude that not only pore size and shape are of importance (as is generally the case in membrane processes), but also the distance between the pores influences separation. When making good use of particle migration phenomena, we could typically use membranes with pore sizes five times bigger than the average particle size, thereby drastically decreasing the chance of fouling.

In conclusion, by combining specific process and membrane designs, we were able to influence particle migration and induce fractionation and separation of particles without membrane fouling. Based on this, we were able to derive guidelines for process and membrane designs, leading to new opportunities for separation of suspensions.

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ICOM1667

The preparation of microsieves via particle assisted wetting and colloidal templating

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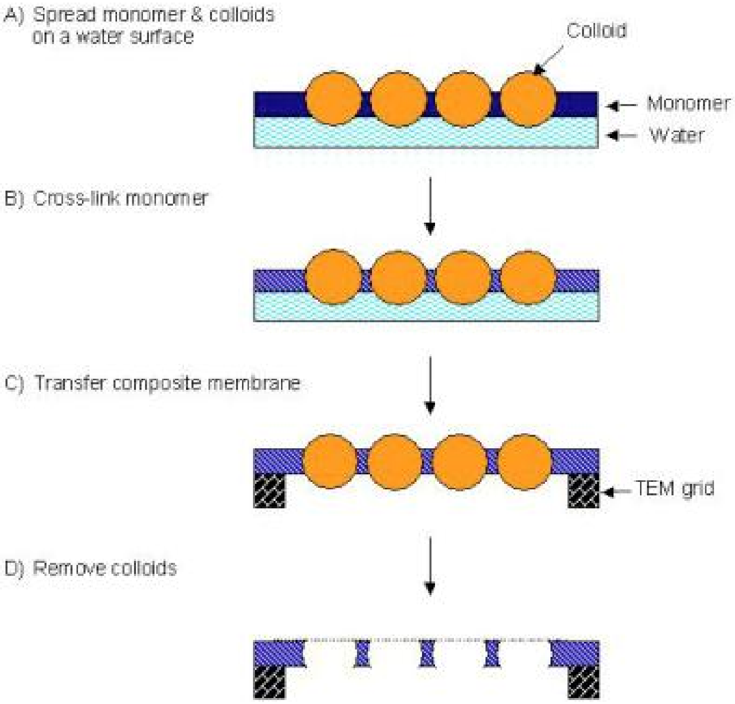
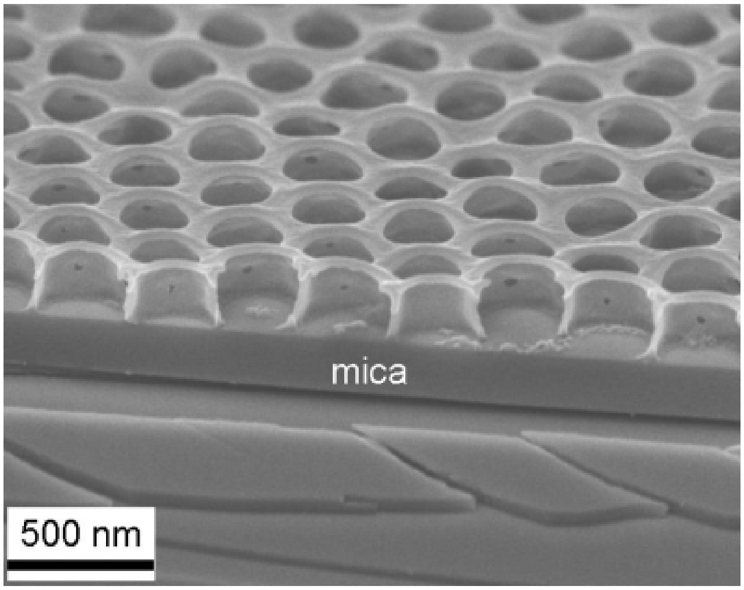
Microsieves - Filtration membranes bearing dense arrays of uniform pores of sub-micrometric diameter and having a thickness smaller than the pore size - were first introduced by Cees van Rijn. Compared to conventional filtration media they offer a lower flow resistance, a smaller tendency of fouling and a sharper size selectivity. Usually, microsieves are prepared from inorganic materials using photolithography. The use of inorganic material facilitates cleaning and provides rigidity, the use of photolithography allows precise control of the size and arrangement of the pores and the preparation of hierarchically structured microsieves.



Here we show an alternative route for the production of microsieves: a mixtures of particles and a non-volatile polymerisable organic liquid is applied to a water surface. The mixture spreads out, the particles forming a monolayer and dragging the polymerizable liquid (which would not spread in the absence of the particles) with them due to capillary forces. Subsequently the liquid is photo-polymerized and the particles removed – leaving behind a microsieve composed of an organic polymer. Thus, the particles have dual purpose. They are used as wetting agents and subsequently as porogens.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500 nm

ICOM1522

Reactive phase separation: A novel method for preparing low fouling ultrafiltration membranes

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Porous polymer ultrafiltration (UF) membrane has become promising separation process in a wide range of applications including water and waste water treatments, dairy, biotechnological and pharmaceutical industries, food and beverage processing, and medical applications. Nevertheless, along with those increasing demands, fouling is still a severe problem that reduces the membrane performance and hinders more widespread industrial applications. Many efforts including pretreatment and process condition have been developed to minimize the problem of fouling, but the heart of UF process is the membrane itself. Therefore,
preparation of low fouling membrane is gaining rapidly increasing importance. Common methods used to manufacture low fouling UF membrane is blending membrane polymer with hydrophilic additive during phase separation and membrane surface (post)modification. Polymer blending can increase the membrane hydrophilicity but the stability of the modifying agent in the membrane matrix can be a problem. On the other hand, membrane surface modification can increase the membrane hydrophilicity with high stability but such treatment needs another step after membrane formation via phase separation process.

In this works, low fouling PES UF membranes were prepared by reactive non-solvent induced phase separation. Redox initiators were used to promote radical polymerization during phase separation. Two hydrophilic additives, i.e. polyethylene glycol (PEG) and polyethylene glycol methacrylate (PEGMA) were used as modifying agent. Influences of casting solution composition (non-solvent, initiator and additive content) and coagulation time were investigated. The resulting membrane characteristics, which include hydraulic permeability, surface hydrophilicity, chemical composition and membrane morphology, were studied. The membrane performance was examined by investigation of adsorptive fouling and ultrafiltration using solutions of bovine serum albumin as the foulant model.

The results suggest that the hydrophilicity of the resulting membrane could significantly be increased and consequently the resistance towards fouling also increased. The presence of redox initiator in casting solution and coagulation bath qualitatively changed the membrane characteristics as indicated by the results of CA, ZP, and membrane morphology measurement. Coagulation time was also identified as important variable for determining the membrane performance. Further, addition of cross-linker resulted in membranes having different characteristics as well as performance.

ICOM1766

Solution Processing of Novel Microcapillary Film Membranes

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Fabrication of novel micro-capillary film (MCF) membranes by solution processing is reported. MCFs are films with embedded multiple hollow capillaries and can be considered as a hybrid geometry between flat sheet and hollow fibres. Compared to the conventional membrane geometries, MCFs potentially provide better mechanical integrity, ease of handling and more efficient module fabrication. MCF membranes were fabricated out of polyvinyledene flouride (PVDF) and ethylene vinyl alcohol (EVOH) copolymer through a solution extrusion followed by a nonsolvent induced phase separation process (NIPS). Fluid flow observations were carried out at different regions in the process in order to better understand the dynamics of extrusion and phase inversion. It was observed that polymer solution and bore fluid rheology as well as processing conditions including air-gap distance and take up rate have significant effects on the flow dynamics and consequently the macrostructure of the membranes. Furthermore, the flow observations led to the identification of an extrudate expansion phenomenon in the external coagulation bath which strongly influenced the membrane formation process. The micro-structure characterization of the fabricated membranes showed the formation of a highly porous, interconnected and macrovoid-free microstructure in the membranes. MCF membranes can be applied with a potentially promising performance in a variety of membrane applications such as micro and ultrafiltration, membrane bioreactors (MBR), porous microfluidic devices as well as membrane contactors for process intensifications.

Parallel Sessions

Thursday, July 28th 2011

Morning Session 2, 10.50 – 12.40

Gas and vapor separation 5

ICOM1805

A brief overview of material development

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The commercial applications of membranes for gas and vapor separation are still, after about 30 years, not overwhelmingly many. The work of Loeb and Sourirajan on RO membranes around 1960 [1], had also a major impact on the later development of gas separation membranes. The work of Henis and Tripodi about 20 years later made industrial gas separation membranes economically feasible. They developed further the technique of putting a very thin homogenous layer of a highly permeable polymer on top of a asymmetric membranes [2]. The first major industrial development was the Monsanto Prism membrane for hydrogen recovery from a gas stream at a petrochemical plant. Shortly after was the air separation membrane introduced for production of high purity nitrogen (Dow Chemical Company) and membrane systems for separation of carbon dioxide from natural gas (Cyanara NATCO Group and Separex UOP). These first membranes were basically composite membranes where the thin, nonporous layer usually was polysulfone or cellulose acetate.

So where are we today; almost 30 years later? The same applications are still out there – very few new have been added. The most important ones added which are now commercial, include membranes for solvent recovery, dehumidification, pervaporation and helium recovery [3].

The focus for our research on membranes for gas separation is: the challenge to develope a membrane with both high selectivity and flux; a material which also has the necessary toughness when exposed to industrial gas streams under challenging operating conditions, may be also a gas containing harmful components which may degrade your material. And last but not least – the membrane systems must be able to compete economically with the traditional separation processes. Having experienced how difficult it is to meet all these demands, we must admire the work of the pioneers within our field.

We have a job to do – because we know that our technology is the most environmental friendly separation process which can be offered to industry. The research activities on gas separation membranes have exploded the last 15 years – and there are many tracks on material and system development currently being followed: New polymers, combinations of inorganic and organic materials, nanocomposites, carbon membranes, inorganic membranes, facilitated transport materials, ion conducting membranes, metallic membranes… Even the design of the membrane is experimented on – the optimum design of a hollow fiber is for instance not necessarrily completely circular.. And for high temperature applications; we may have an oxide or a palladium membrane with beautiful separation properties, and then discover that the main problem in the end is actually the sealing of the module.

The presentation will try to focus on a selection of the many exciting new material under development around the world, and also the challenges being faced when we want to go from lab-scale to demonstration on industrial scale.

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ICOM650

P84® co-polyimide hollow fibre membrane module for the purification of H_2 from its mixture

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A membrane module containing 165 hollow fibres made of P84® co-polyimide, was used in the separation of H_2/N_2 and H_2/CO mixtures [1]. The measured permeance and separation factors showed relevant difference in comparison with that obtained feeding pure gases. The H_2 flux practically remained unchanged, whereas N_2 and CO fluxes showed significant increases. As a consequence, a separation factor in the range 9-18 and 6-12 was measured for the H_2/N_2 and H_2/CO mixtures, respectively, against an ideal selectivity of 78 and 60. A linear dependence of the H_2 recovery on the stage cut was observed in the whole feed pressure range investigated. At low stage cut, only a small part of the hydrogen fed is recovered in the permeate, since the feed flow rate is oversized with respect to the membrane area available and, thus, to the extractive capacity of the membrane module; the higher the stage cut the higher the H_2 fraction recovered in the permeate. No differences in the behaviour of the membrane versus the two different mixtures were observed. The hydrogen-rich stream recovered in the permeate achieved interesting values of H_2 concentration up to 90% molar hydrogen purity.

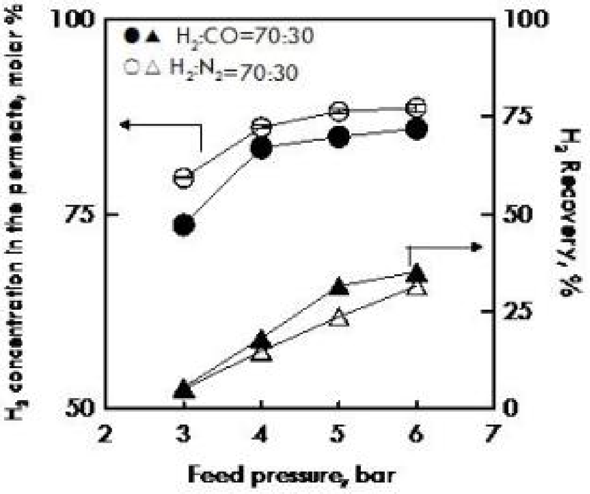

Figure 1 - H_2 concentration in the permeate and H_2 recovery as a function of Feed pressure for H_2:N_2=30:70 and H_2:CO=30:70 mixtures.

The performances of a membrane system showing the properties of the module realized in this work, were compared with that of the other separation operations actually used at industrial level such PSA and cryogenic, considering two metrics. In particular, the membrane systems showed a lower installation area with respect to the other two units, reaching interesting values of productivity-footprint ratio. This gain was much higher as the driving force was higher. However, the H_2 recovery and H_2 purity obtained with membrane operation were lower or comparable with the other two systems, even if the mass intensity was higher. It must be pointed out that the membrane systems considered in these evaluations operated at 50°C. However, at a higher temperature, the permeance of the membrane increased therefore higher recovery can be expected. Moreover, the results presented by [2] for PSA and cryogenic consider the treatment of a refinery off-gas, where the amount of hydrogen in the feed is higher (50-75%) [3] than that used in this work (30%).

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Acknowledgements

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ICOM773

Low-Energy Distillation Membrane Separation Process

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A low-energy separation process combining distillation and vapor permeation has been developed as an alternative to conventional distillation. The process can be applied to any liquid mixture for which appropriately selective membranes are available. Typical applications include separation of mixtures of water and alcohol (such as ethanol, isopropanol and butanol), water-acetic acid mixtures and petrochemical aromatic-aliphatic mixtures. This paper is focused on separation of water from organic solvents using membranes that preferentially permeate water. Such membranes are available or under development. The process is illustrated with two representative mixtures: ethanol (light component)/water (heavy component), and acetic acid (heavy component)/water (light component) mixtures. In both cases, the combination process reduces the energy consumption of the same separation by almost 50% compared to stand-alone distillation. A laboratory demonstration of the new process has confirmed the low energy usage. The first field demonstration of the process started in June 2010.

ICOM580

Synthesis and Gas Transport Properties of Copolyimide based on Room Temperature Ionic Liquid Diamines.

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In this study, a 6FDA-MDA polyimide was copolymerized with room temperature ionic liquids to create a mechanically strong and CO_2 selectively permeate membrane. Room temperature ionic liquids (RTIL) can be designed to possess a great solubility to CO_2 which can be achieved by controlling the anion structure because the anion is the major effect of CO_2 solubility. In this research, two diamino functionalized RTILs coupled with a CO_2 affinity anion, bis [(trifluoromethyl) sulfonyl] imide ([Tf_2N]), have been successfully synthesized through Boc-protected method. The two novel RTILs, 1,3-di(3-aminopropyl)-imidazolium bis [(trifluoromethyl) sulfonyl] imide([$C_{3\text{-}NH2}C_{3\text{-}NH2}Im$][$Tf_2N$]) and 1,12-di[3-(3-aminopropyl) imidazolium]dodecane bis[(trifluoromethyl) sulfonyl] imide ([$C_{12}C_{3\text{-}NH2}C_{3\text{-}NH2}Im_2$][$Tf_2N$]$_2$) have been copolymerized with 6FDA dianhydride and MDA diamine and formed block and random copolymers (PI-RTIL). The copolymers were casted into dense films for gas separation experiment. The molecular weight (M_w/M_n), FTIR spectroscopy, density, thermal stability (T_d), glass transition temperature (T_g) and pure gases (H_2, N_2, O_2, CH_4 and CO_2) permeability coefficients of PI-RTIL copolyimides at 35 ºC over a range of pressures with different mole compositions of RTILs were experimentally determined. It showed that with the RTILs composition increase, the M_n/M_w, T_d and T_g decreased; the density increased; the gas permeability decreased; the permeation selectivity of H_2/CO_2, O_2/N_2 did not change while those of the CO_2/CH_4 increased. The detailed information will be introduced in the presentation.

ICOM545

Supported ionic liquid ceramic membranes for gas separation

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An ionic liquid (IL) is a salt with a melting point below 100°C, mostly consisting of a bulky organic cation and an inorganic respectively organic anion. These substances exhibit special properties like an extremely low vapor pressure and a high thermal stability compared to common organic solvents. The broad spectrum of anion-cation combinations can be utilized to "design" a customized ionic liquid with special desired features. Ilconich et al. [1] show that ionic liquids can be used to separate gas mixtures by using a membrane as a support. Consequently this system is called supported ionic liquid membrane (SILM).
Our purpose is to develop a CO2 and CH4-selective SILM for gas separation at temperatures up to 250°C, which can be used for flue gas treatment and natural gas purification. Therefore we focused on thermally stable and chemical inert ceramic membranes as support materials.
As a first step pressure drop measurements were carried out to quantify the single gas absorption for CO2, N2, CH4 and CO of various ionic liquids at different temperatures (RT - 250°C) and moderate pressure (up to 6 bar). It was possible to correlate the reciprocal molar mass with the absorption ability (Figure 1). The second step was to prepare SILMs from ceramic membranes with particular ILs and to measure single gas as well as mixed gas permeation. The SILMs tested so far show a high stability for a pressure range up to 6 bar at temperatures up to 200°C. Selectivities for CO2/N2 separation of S= 20 can be observed (Figure 2). Thereby CO2 permeabilities of P= 600- 800 barrers were measured.

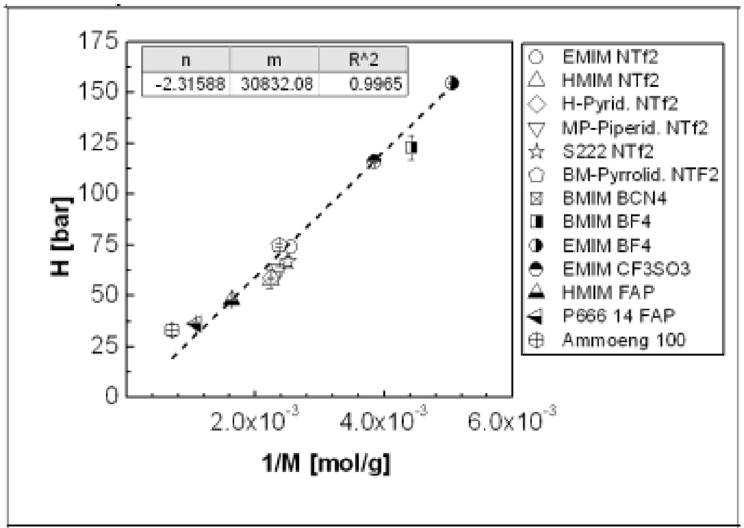

Figure 1: Henry's law constant for CO_2 with different ionic liquids at 60°C plotted against 1/molar mass

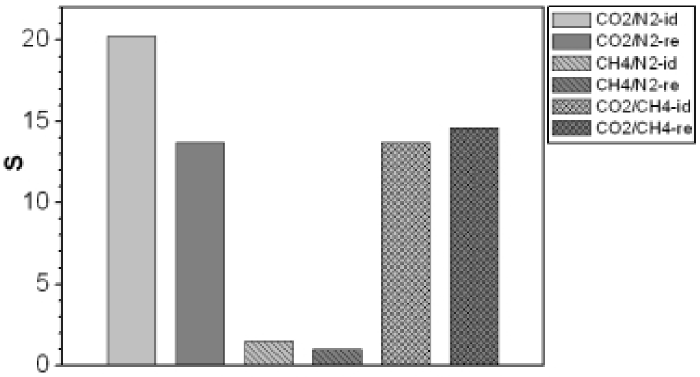

Figure 2: Ideal and real selectivities of an EMIM BF4 - SILM, at 60°C, for CO_2/ N_2, CH_4/N_2 and CO_2/CH_4

CO2 capture 3

ICOM1854

Thermally Rearranged Polymer Membranes with Tuned Microcavities for CO_2 Capture

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Microporous materials have various benificial properties (e.g. large surface area, high pore volume and appropriate pore width in the materials) for enhanced sorption, diffusion, and the improved permeation properties beyond conventional nonporous materials. Compared to inorganic microporous materials such as silica, alumina, zeolite and metal-organic frameworks (MOFs), organic microporous materials are advantageous in their synthesis, mass production, and processability for numurous applications. Since T. Matsuda reported a novel poly[1-(trimethylsilyl)-1-propyne] with high fractional free volumein 1983, in the last few decades, polymeric materials retaining microporous characteristics have been developed: poly(substituted acetylene)s, amorphous fluoropolymers, polymers with intrinsic microporosity (PIMs) and thermally rearranged (TR) polymers.

Thermal rearrangement of ortho-funtional polyimides is a robust and irreversible process to render thermally and chemically stable rigid-rod polymers. The thermal conversion in stiff, rigid heteroaromatic rings cause increase of free volume elements as well as change of polymer structure confirmed by various analytic method such as FT-IR, NMR, TGA, DSC, WAXD, density, PALS, SAXS and gas permeation measurements. TR-polymers have bimodal cavity sizes of 0.3-0.4 nm and 0.7-0.9 nm, and narrow cavity size distributions as a shape reminiscent of aquaporins which has bottlenecks connecting adjacent chambers so that those can yield both high permeability and high selectivity based on high diffusivity of small gas penetrants.

Most of all, the greatest benefit of these TR-polymers is the ability to control their separation performances for specific gas applications including CO_2 capture from flue gas by using various polymer structures and templating molecules with heating time and temperature. Copolymerizations with pristine polyimide or polypyrrolone in the main chain as well as the control of conversion ratio of precursors provide simple and convenient method to govern diffusivities and diffusion selectivities. Changes of ortho-functional groups also contribute to the physical properties because the side groups can affect the intermolecular distances and topologies of precursor and the resulting TR polymer membranes as well as act as templating molecules during thermal rearrangement. Moreover, other precursor polymers such as poly(hydroxyl amide) and schiff-base polymers can be thermally treated in solid states and bring in microcavities and high separation performances for specific gas pairs such as H_2/CO_2 and H_2/N_2.

Understanding of these diverse routes correlated with the cavity size and distribution of the materials can provide the evidence to the high gas separation performances and also the method of tuning the microcavities in TR-polymers for targeted applications. Here, gas transport properties of various precursors and TR-polymer membranes will be summarized overall and analyzed with microcavities for CO_2 capture.

ICOM1459

Bench- scale test of Pd membrane reactor for CO_2 capture

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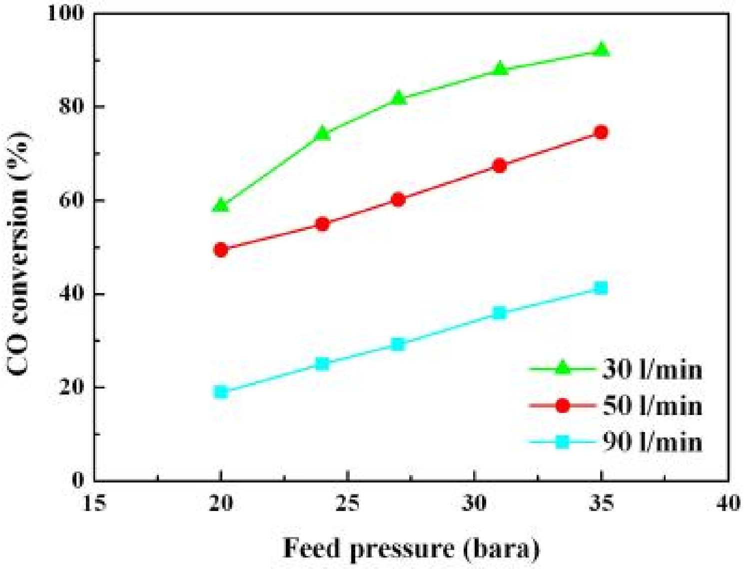
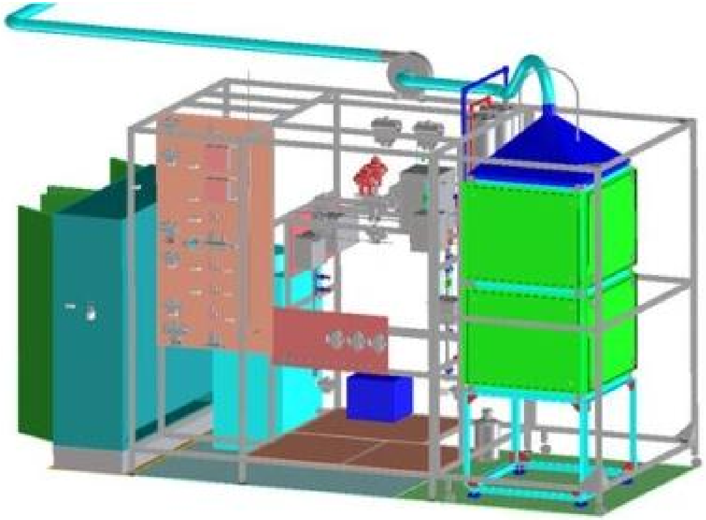
Due to the high H_2 permeability and selectivity, Pd membranes show a great potential for application in power plants equipped with CO_2 capture. Here natural gas is converted into a hydrogen stream and a CO_2 rich stream available for underground storage. This is done by water gas shift membrane reactor that combines shift conversion of syngas (generated from the natural gas) with high-temperature membrane separation, thus shifting the reaction equilibrium towards high conversions. A process development unit (PDU) for testing membrane reactors has been constructed at ECN



. It has a potential capacity of 0.6 m^2 surface area by using 8 tubular membranes of 0.5 m in length and 50.8 mm in diameter, and can be operated up to 40 bar(a) and 873 K, thereby reaching a bench-scale. This paper will summarize the performance of Pd membranes in WGS-mixture separation and WGS membrane reactor under high temperature/pressure conditions for CO_2 capture application. The syngas-mixture separation, i.e. without a catalyst, was carried out at 673 K and up to 35 bar(a) with Al_2O_3 supported ultra-thin Pd membranes from two different membrane suppliers, which both showed a high H_2 permeance and selectivity. Long term stability testing up to 50 days under the above conditions revealed stable operation of the membrane. In addition, the inhibition effects of WGS-components [1], the influence of mass transfer in the gas phase and support pores, and the effect of different sweep gases on the H_2 permeation were investigated, which aided the understanding on the H_2 permeation through the composite membranes. High H_2 permeance and sufficient selectivity were obtained. In the water gas shift reaction test, i.e. with catalyst, near complete CO conversion



and H_2 recovery were achieved under conditions mimicking CO_2 capture in power plants. A steady performance was achieved for both the membranes and the membrane reactor performance [2]. Thus it is concluded that hydrogen selective membranes can be considered a promising option for CO_2 capture.

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Acknowledgements

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ICOM934

Optimization of pilot scale PVAm/PVA blend membranes with high pressure resistance for natural gas sweetening

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In order to increase heating value (Wobbe index) and reduce corrosion of pipelines, acid gas in natural gas must be removed (sweetening) to meet the specifications. Today the most widely used technology for natural gas sweetening is amine absorption. Nevertheless, optimized membrane technology draws more and more attention as an energy-saving, environment-friendly and low-cost alternative for this process. The main problems that limit the use of membranes are their poor performance at high pressures and in the presence of highly sorbing components. A polyvinylamine/polyvinylalcohol (PVAm/PVA) blend CO_2 selective membrane with fixed amino groups as CO_2 transport carriers has been developed and patented in our group to overcome these limitations. In this membrane, the reversible reactions of CO_2 with amino carriers in PVAm facilitate the CO_2 transport, resulting in both high CO_2 permeance and CO_2/CH_4 selectivity, while the entanglement of PVAm with PVA, a mechanically robust polymer, enhances polymeric network with good membrane forming properties.

This study is to further optimize the PVAm/PVA blend and/or mixed matrix FSC membranes for natural gas sweetening with a focus on the high pressure resistance of the membranes, and the challenges related to the upscaling of the PVAm/PVA blend flat sheet membrane. Three approaches have been studied: (1) the use of commercially available PVAm with higher molecular weight in the PVAm/PVA blend membrane. The mechanical properties and separation performances of PVAm/PVA blend membranes with PVAm of higher molecular weight (e.g, PVAm MW 340,000 from BASF) have been tested; (2) optimization of dip-coating procedure. The precise control of the coating layer thickness is important in the optimization. The effects of the viscosity, concentration of casting solutions and the coating layers on thickness have been investigated. Membranes with upscaled size (300×300mm) were prepared. (3) CNTs were introduced to the PVAm/PVA blend membrane as nano-fillers or nano-spacers, which reinforced the membrane mechanical properties and improved the membrane swelling capacity (and hence CO_2 separation efficiency) at high pressures.

PVAm/PVA blend membranes with various selective layer thicknesses have been measured at pressures 5bar, 20bar, 40bar, 60bar and 80bar, respectively. A pilot scale high pressure permeation rig designed and built-up in our group is used in this test. The optimization of the pilot scale module and operation parameters are also part of this study.. So far, a selectivity of CO_2/CH_4 up to 50 and CO_2 permeance up to 0.45 $m^3(STP)/m^2.h.bar$ have been documented.

ICOM1758

Is selectivity the main parameter in membrane fabrication and design for post-combustion carbon capture?

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Post-combustion carbon capture (PCC) from flue gas using solvent extraction technology is well understood and is currently used in different industrial applications. However, this technology has a serious drawback in the form of an energy penalty introduced, which can be in the range of 10-40% of total electricity produced. Membranes have good potential to compete with solvent technology though currently being challenged by high opex.

This study is concerned with techno-economics of gas membranes for post combustion carbon capture (PCC). A systematic methodology is developed for analysis of membrane systems considering multicomponent flue gas with CO_2 as target component, which avoids simplifying assumptions namely multicomponent flue gas represented by CO2/N2 binary mixture or considering the co/counter current flow pattern of hollow-fibre membrane system as mixed flow.

Optimal regions of flue gas pressures and membrane area were determined within which a techno-economical process system design could be feasible. Fibre length was found to be an important parameter in membrane system design having negative impact on product recovery. High selectivity showed to not necessarily have notable impact on PCC membrane performance, rather, a medium selectivity combined with medium or high permeance could be more advantageous (Figure 1). Vacuum process was found to require a notably higher area (i.e. higher capex) than a pressurized process, however the vacuum process was found to be less energy intensive resulting in lower opex.

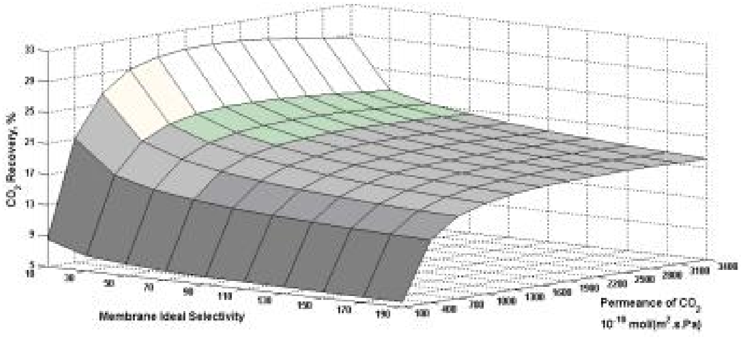

Figure 1. Impact of membrane permeance and selectivity on CO_{-2} recovery at T=50 °C, P_{f0}= 2.0 bar, P_{p0}= 0.2 bar, membrane area of 80 m^2/(mol/s), concentrations, mol%: CO_2= 13.0, N_2= 80.4, O_2= 3.6 and H_2O = 3.0 and, cocurrent flow pattern.

ICOM233

The Effects of Water Vapor in CO_2 Separation using Polyimide Membranes

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Gas separation membranes have potential in both pre and post-combustion CO_2 capture from flue gases. For the successful implementation of such membrane gas separation technology, it is necessary to synthesize efficient and durable membranes that perform well over many years of service. While in the laboratory most workers use dense polymeric films, asymmetric flat sheet membranes are often used in industrial spiral-wound modules to maximize the plant productivity. These asymmetric membranes contain a very thin active layer that is more susceptible to plasticization compared to dense films. This plasticization will limit the ultimate lifespan of the membrane and reduce the permeability and selectivity of the membrane separation unit.

Water vapor, a known plasticizer in membrane systems, can hardly be avoided in real industrial gas streams. It often exhibits very different plasticization behavior compared to other common plastizers such as CO_2 because of its high hydrogen bonding affinity. The presence of water vapor hence is not always desirable in membrane gas separation systems as it often lowers the overall performance of the membrane due to plasticization and/or competitive sorption of water clusters.

In this work, the water vapor-induced plasticization behavior in two polyimide films (Matrimid® 5218 and 6FDA-TMPDA) is under study. The wet gases under study include pure methane, nitrogen and carbon dioxide, as well as their mixtures. The effects on membrane permeation performance under conditions of different water activity are reported. The impact of having one (water vapor)
and two (water vapor and carbon dioxide) plasticizers present on the system behavior is also discussed.

Membranes for biorefinery applications 2

ICOM1775

Separation of bioactive peptides by Membrane technologies : an overview

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In recent years, functional foods and nutraceuticals has attracted much attention, particularly for their impact on human health and prevention of certain diseases. Consequently, the production and properties of bioactive peptides has received an increasing scientific interest over the past few years. Considering that most functional peptides are present in complex matrices containing a large number of hydrolyzed protein fractions, their separation and purification are required. Conventional pressure-driven processes can be used for amino acids and peptides separation but are limited by their fouling problems and their low selectivity when separating similar sized biomolecules. To improve the separation efficiency, an external electric field was applied during pressure-driven filtration. However, the pressure gradient brings about the accumulation of peptides at the nearby membrane surface and affects the membrane transport selectivity. Processes combining an electrical field as a driving force to porous membranes have been developed for the separation of biopeptides to obtain better purified products. Compounds of higher molecular weights than the membrane cut-off can be separated. The first trials were carried-out to perform the separation of amino acids and peptides with a filtration module specially designed and using one ultrafiltration membrane. More recently, electrodialysis with ultrafiltration membranes has been developed to fractionate simultaneously acid and basic peptides, using a conventional electrodialysis cell, in which some ion exchange membranes are replaced by ultrafiltration ones. The perspectives in this field will be the understanding of the interactions of peptides and membrane as well as the development of new membrane materials limiting or increasing these interactions to improve the selectivity and the yield of production of specific peptides.

ICOM1572

Development of High Temperature Bipolar and Conventional Electrodialysis

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EURODIA INDUSTRIE S.A., Rungis cedex, FR

A new challenge for EURODIA has been to develop a high temperature ED technology to improve the overall performance and open up new applications. This presentation will illustrate how this challenge has been successfully addressed.

Until now, the maximum operating temperature for ED has been 50°C.
With operating temperature at 65°C, microbiological infection will be minimized, especially when ED is processing fermentation broths or sugar solutions, which is a limitation for these applications. In addition, the transport kinetics through membranes will be more efficient with a lower electrical resistance, thus leading to a lower specific power consumption compared to operation at 40 to 50°C.

The limited number of EDBM plants in operation is the result of many factors, mainly industry concerns over reliability and cost. The relatively high investment of EDBM systems limits its use so far to higher value products, such as organic acids (Lactic, Gluconic, Succinic…). The possibility for EURODIA to develop a new technology at high temperature will enhance the potential for EDBM applications thanks to a lower energy consumption. The total energy consumption should be reduced by up to 20% for EDBM units. To reach this goal, specific Neosepta® membranes and Eurodia proprietary spacers have been developed. One of such development programs received a "EUREKA" label in 2010.

The comparison between EDBM at 40°C and 60°C for the splitting of Sodium Gluconate is presented in table1. At the same current density, the voltage is approx. 25% lower at high temperature, independently of the concentration of the produced NaOH.

	NaOH = 1N	NaOH = 1N	NaOH = 1.5N	NaOH = 1.5N
	BP/Cation	BP.HT/Cation	BP/Cation	BP.HT/Cation
Current density (mA/cm2)	89	100	90	100
Voltage (V/cell)	2.4	1.8	2.5	1.8
Demineralization rate (%)	84.8	85.2	84.5	85.3
Current efficiency (%)	88	87	80	83
Temperature	36	61	35	61
Base production (eq/h.m2)	29.5	32.4	26.8	31.1
Energy consumption (W/eq)	98.6	81.7	104.7	78.75
Energy benefit (%)		17		25

Table 1 : Sodium Gluconate conversion to pH=2.4(final conductivity = 4-4.5) by Bipolar ED at different temperatures

For conventional electrodialysis at high temperature (EDC-HT), a first plant has been started in the US in December 2010 for the production of a specialty chemical (confidential). The application objective is to remove HCl from the feed product. This feed product has too high a viscosity to be treated at 40°C. Standard EDC stacks can be subjected to a maximum pressure drop of 3 bars, allowing the treatment of solutions at a maximum viscosity of ~10 cp.
The development of new EDC-HT stacks, with advanced polymeric materials that can be exposed to 65°C and special monopolar Neosepta membranes, now allows the treatment of such chemical solutions. At this temperature, the pressure drop in the EDC-HT stacks is reduced to 2 bars. Two EUR40 stacks are operating in parallel, in batch mode.
This first plant will be considered as a reference in the chemical industry.
The next challenge for EURODIA is to test its new EDC-HT stacks in the sugar and starch industry to demineralize sugar or

glucose syrups as an alternative to, or in combination with, ion exchange resins in order to minimize the discharge of salt effluents.

ICOM1021

A novel membrane-integrated fermentation reactor (MFR) system: application to pyruvic acid production

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It is known that continuous cultivation with cell recycle systems using membrane has excellent productivity in fermentation. However, industrial application of the system has not been realized, because membranes previously used showed serious problems such as fouling, low permeability and no heat-tolerance in autoclaving. This paper demonstrates the performance of a novel bio-reactor system, which is named Membrane-integrated Fermentation System (MFR), for effective continuous fermentation, equipped with autoclabable polyvinylidene difluoride (PVDF) membrane modules. The PVDF membrane was designed for Membrane Bio-reactor (MBR) used for wastewater treatment and has small average pore size, about 80 nano-meter, and narrow pore size distribution in order to avoid clogging of pores with microorganisms. A schematic diagram of the MFR system is shown in figure 1.

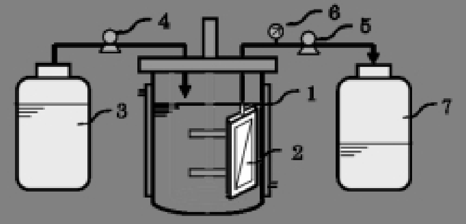

Figure 1. Schematic diagram of the Membrane-integrated Fermentation Reactor
1, fermentor; 2, microfilter module; 3, media reservoir; 4, feed pump; 5, filtrate pump; 6, transmenbrane pressure meter; 7, filtrate reservoir.

The membrane module is submerged in the fermentation broth and permeate flow from the membrane module is controlled by a peristaltic pump. Continuous pyruvic acid production by a yeast *Torulopsis glabrata* using MFR system remarkably improved its productivity compared to the conventional batch fermentation system. The results of continuous production of pyruvic acid by using MFR system clearly demonstrated the system could be run for long term (>300 h) with excellent productivity without membrane fouling, when the operation was carried out under the conditions of filtration rate below the critical flux value (around 0.4 m/day).

The time profiles of batch pyruvic acid production and continuous one with the MFR system are compared in figure 2. In the batch production, 41 g/l pyruvic acid was achieved at 49 h and the yield from glucose (p/g ratio) was 0.43 g /g-glucose (figure 2a). On the other hand, in the continuous operation, pyruvic acid accumulation resulted in 36 g/l, glucose concentration remained less than 2 g/l after 56 h and ethanol which is the main by-product, was less than 8 g/l (figure 2b). The pyruvic acid production reached to the range of 3.5 - 4.2 (3.7 on average) g/l/h, and the p/g ratio was in range of 0.35 - 0.43 (0.39 on average) g/g-glucose, (figure. 2c). The volumetric productivity of pyruvic acid in MFR system was about 4-fold higher than that in batch fermentation. Although a cell density of fermentation broth reached 600 as OD_{660}, the TMP was maintained below 5 kPa throughout the operation (figure 2d), and the sign of the membrane fouling was not observed at all.

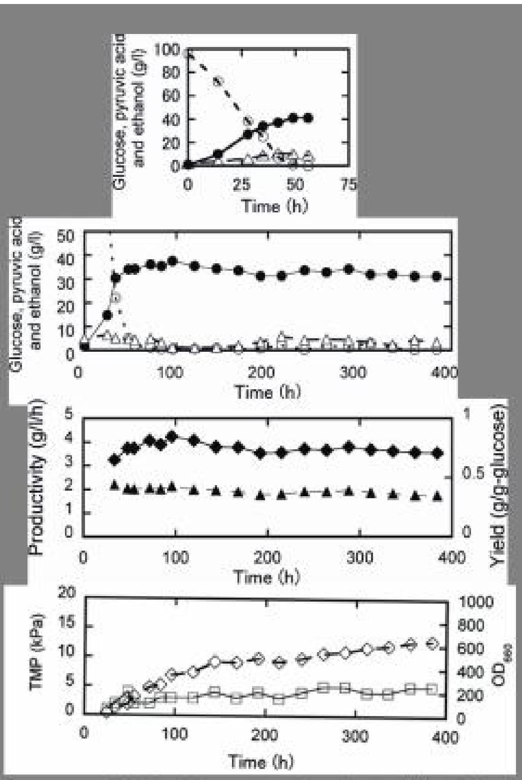

Figure 2. Time-courses of the batch pyruvic acid production (a) and the continuous one (b, c, d) with the MFR system.
Concentration: glucose (open circle), pyruvic acid (closed circle), ethanol (open triangle)
Yield of pyruvic acid (closed triangles), productivity of pyruvic acid (closed diamonds), TMP (open squares) and cell concentration (open diamonds).

In conclusion, the MFR system developed in this study is simple and highly efficient, and requires no special equipment. It would be applicable to many other fermentative production processes.

This work was partially supported by a grant from the New Energy and Industrial Technology Development Organization (NEDO), Japan.

ICOM290

Dynamic microfiltration in microalgae concentration

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Microalgae are a promising and second generation raw materials to produce biodiesel and other valuable products (biorefining concept) because several factors: they do not compete with food industry, they have large lipid contents and they have a high reproduction capability, they have a reduced cost, etc. [1]. The process to produce biodiesel from microalgae consists, roughly, in three steps. First, a culture and a harvesting process have to be performed; this step includes the concentration of the microalgae after its growth. Second, the lipids have to be extracted from the microalgae and third, a transesterification reaction and separation process should be performed to obtain the final product [2].

Membrane filtration can be a reliable process to be used in the concentration step [3], if it is optimized and properly combined with common ones as sedimentation, flocculation and others. Because of the size of the solutes that are relatively large, microfiltration or ultrafiltration membranes are generally enough to achieve high rejections. Additionally, trans-membrane pressures (TMP) below 2 bar are sufficient, consequently, being a low-demanding energy process. Nevertheless, the main drawbacks of membrane processes to concentrate microalgae are membrane fouling and concentration polarization [4], which reduce dramatically the flow rate, decreasing the performance of the operation and increasing the cost. To reduce the effect of these phenomena and among others dynamic filtration can be used instead of static processes to decrease the abovementioned phenomena. Dynamic membrane modules contain some moving elements near the membrane which increases the flow turbulence [5]. The most important consequence of this is that shear stress over the membrane is also increased, reducing the cake that can be formed over the membrane or preventing solute accumulation over it.

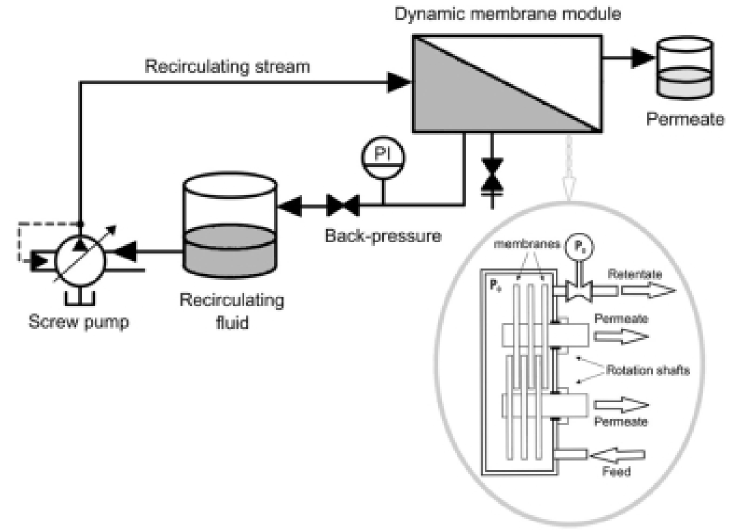

Figure 1. Experimental setup.

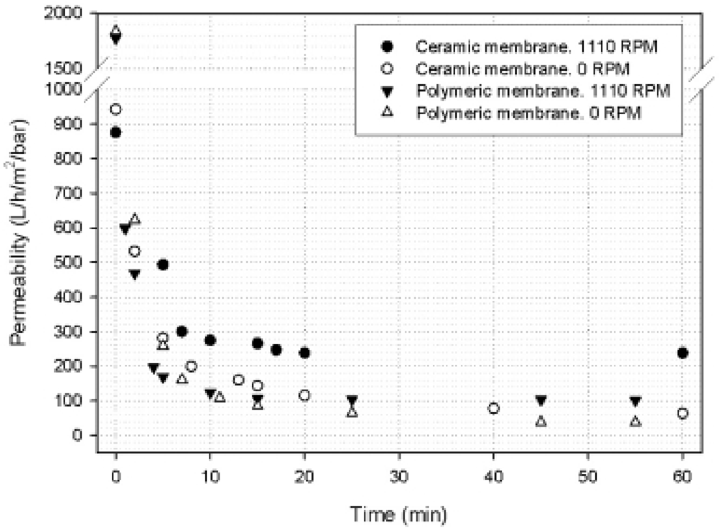

Figure 2. Variation of the permeability with time for polymeric and ceramic membranes with a mean pore size of 0.5 µm at different rotational speeds for Phaeodactylum Tricornutum.

In this work, three microalgae strains (Nanochloropsis Gaditana, Phaeodactylum Tricornutum and Chaetoceros Calcitrans) have been concentrated using a rotating cross-flow filtration set-up (KMPT, Dynamic Crossflow Filter DCF 152/0.14), considering as variables the rotating speed, TMP and membrane material and pore size. Commercial ceramic membranes offer higher performance than Teflon commercial membranes in terms of flow, reproducibility and use, independently of the pore size (between 0.5 and 2 micrometers). TMPs near 1 bar offer higher performance than values near 2 bar. Volume flow reduction decreases with rotating speed. Considering average values, they range from 95.2 % ± 1.9 % at 0 rpm to 75.3 % ± 9.7 % at 1110 rpm.

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ICOM1292

Hybrid Membrane Separation Processes for Organic Acid Recovery in Anaerobic Fermentation Broth

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Biobutanol, one of clean fuels, can be produced by using fermentation and chemical catalyst processes. In the anaerobic fermentation process, organic acids such as butyric acid are produced by microbial activity, and they can be converted into alcohols (e.g., butanol) in a catalytic process. Since butyric acid itself, however, has a negative effect on the microbial metabolism, the concentration of butyric acid in fermentation broth need to be kept constant via selective removal of butyric acid using continuous separation processes. Although there are many separation processes of interest such as extraction, stripping, adsorption and distillation, most of them often needs high energy consumption or toxic chemical effluents to the environment. In this study, the hybrid membrane separation processes for energy-efficient organic acid removal and recovery is proposed. To separate organic acids from fermentation broth, organic acids and water permeate selectively through membrane while other organic components and salts in fermentation broth should not pass across the membrane. In the first step, we applied nanofiltration membranes to recover selectively aqueous organic acid solutions from the fermentation broth. By changing the membrane surface charge depending on pH in feed, the effective organic acid separations were achieved because organic acid rejection increased with higher pH while the rejection of other organic compounds and inorganic salts stayed constant. Various kinds of nanofiltration membranes, including high-flux reverse osmosis membranes were evaluated for selective organic acid recovery under optimized operation conditions to see the effects on the separation performance such as membrane flux, rejection and fouling behavior. In the second step – the concentration of organic acid in aqueous organic acid solutions, we selected forward osmosis (FO) membrane process for low energy consumption. Organic acids can be continuously concentrated by using FO process with high osmotic pressure of draw solutions such as common inorganic salts. The effects of operation parameters and types of membranes in such FO process were studied for economic organic acid concentration.

Membranes for energy generation 1

ICOM1777

Developments in hollow fiber production for Osmotic Power generation

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The search for new energy sources has led to a number of new developments. One of the most sustainable "new" energy sources is salinity power. Salinity power has two different approaches to exploit the chemical difference between salt water and fresh water is:

1. Reverse Electro Dialysis (RED) here, ions are transported through an alternating series of ion exchange membranes from the salt water to the fresh water compartment. Electricity is generated from oxidation and reduction reactions at the anode and cathode respectively.

2. Pressure Retarded Osmosis (PRO) here, water bodies move through a semi-permeable membrane. The electricity is generated by the hydrostatic pressure build up at the "salty side" of the membrane.

In this presentation we focus on the PRO process. Considering that the salinity of seawater yields osmotic pressures of 27 bars and the osmotic pressure of river water is negligible, a large portion of the osmotic pressure can be used for power generation by controlled mixing of salt and sweet water via a semi permeable membrane. PRO is most efficient when operated at a pressure in the range of 11-15 bars, equivalent to a water head of 110-150 meters generating a hydropower of 1MW/m^3 freshwater. Energy created by osmotic power has very little impact on the environment and is renewable; the process does not consume salt or water.

In PRO, like in Reverse Osmosis (RO), the membrane's selective layer is facing the salty stream. The PRO process distinguishes from the RO process by the direction of the water transport. Contrary to RO, in PRO the water and salt flux are going in opposite directions. This results in the build up of an internal concentration polarization layer that substantially affects the mass transfer of water across the membrane. Contrary to pressure driven processes, this concentration polarization cannot be minimized by applying a cross flow. For this reason, the PRO-technology requests specific tailor made membranes.

The research at EMI in cooperation with Statkraft focuses on the development of an efficient PRO hollow fiber membrane. An ideal PRO-membrane combines a high water flux with a low salt flux while the support structure has a low contribution to fouling and concentration polarization. The morphology of the support layer dictates to a big extent the membrane performance and is related to the membrane thickness, tortuosity and porosity. The contribution of the support layer to the overall separation is represented by the structure parameter S. The value of S, and thereby the inner structure of the membrane, is decisive for its efficiency in the PRO-process.

For independent structure optimization of the selective skin and support layer, EMI explored two routes:
1. dip-coating
2. dual layer dry-wet phase inversion spinning process

Both routes allow an independent optimization and characterization of the fiber substructure as well as the skin layer. In the first case, substructure characterization is performed before coating the selective layer. In the second case, the skin layer is removed by oxygen plasma to reveal the substructure for characterization.

In the presentation, we will focus on the PRO-concept to produce sustainable energy. Next to this we will focus on the design and development of tailor made PRO-membranes.

ICOM1155

Integration of membrane and spacer functionality in Reverse Electrodialysis

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Introduction

The salinity difference between salt water and fresh water can be used to generate energy. This energy is captured in Reverse Electrodialysis (RED) using ion exchange membranes, which are selective for either anions (anion exchange membrane, AEM) or cations (cation exchange membrane, CEM). When salt and fresh water are on either side of such a membrane, the salinity gradient generates an electric potential over the membrane. This voltage accumulates when a series of alternating AEMs and CEMs are stacked with salt and fresh water in between (Figure 1). RED can be used as a renewable energy source where salt and fresh water mix naturally; a potential of 2.6TW is available from the global runoff of river water to the sea [1].

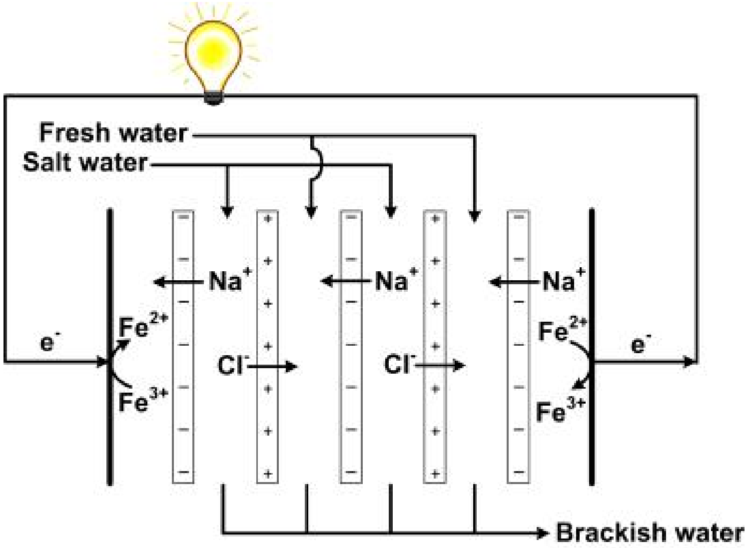

Figure 1: Principle of Reverse Electrodialysis.

Spacers, usually non-conductive fabrics, separate the different membranes. However, the insulating spacer material limits the available area for ion exchange (spacer shadow effect), and hence increases the internal resistance significantly [2]. This leads directly to lower power outputs. A membrane with a profile of ion conductive ridges (referred as profiled membranes) allows the integration of the membrane and spacer functionality. Such a profiled membrane can be prepared by hot pressing a thermoplastic membrane into a profiled mould. Profiled membranes make the use of non-conductive spacer obsolete as the profile of the membranes allows the separation thereof. A stack with profiled membranes eliminates the spacer shadow effect, and hence a lower internal resistance is expected.

Experimental

Measurements were performed in a stack (5 membrane pairs, 10x10cm) with profiled membranes, which were prepared by hot pressing heterogeneous ion exchange membranes into an aluminum mould with straight grooves. The results were compared to the same stack using flat membranes and traditional, non-conductive spacers. Artificial sea water (0.513M) and river water (0.017M) was used as feed water. The internal resistance was split into an ohmic part (R_{ohmic}, i.e. the resistance under alternating current conditions) and a non-ohmic part ($R_{non-ohmic}$, associated with concentration polarization).

Results

Figure 2 shows the results, plotted against the power that was required to pump the feed water, which was calculated from the pressure drop over the feed water. The ohmic resistance is significantly lower when profiled membranes are used instead of non-conductive spacers (Figure 2a). However, the non-ohmic resistance was in general higher (Figure 2b), which indicates less mixing in the boundary layers adjacent to the membranes. Although the sum of ohmic and non-ohmic resistance is about the same in this first profiled prototype, profiled membranes do have good prospects for RED. The ohmic resistance can be further reduced since the lower pumping power allows thinner feed water compartments. The mixing rate can be improved by optimizing the profile geometry, leading to lower non-ohmic resistances. In that way, such profiled membranes combine a relatively low internal resistance with low pumping costs, making RED an attractive alternative for sustainable power generation.

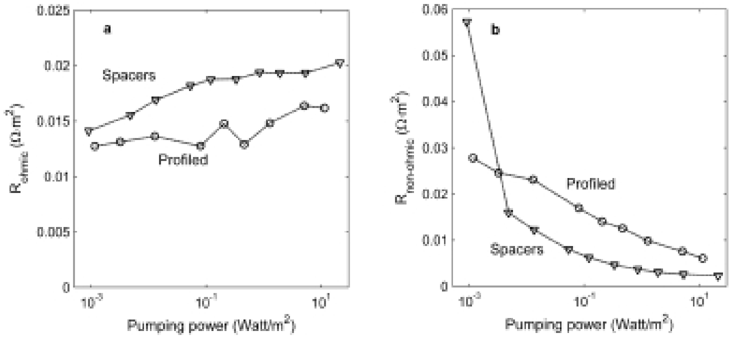

Figure 2: Ohmic (a) and non-ohmic resistance (b), for a stack with traditional spacers and one with profiled membranes.

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ICOM1748

Temperature and concentration effects on the power production efficiency in a PRO power plant

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Salinity power is a renewable energy resource with a significant potential world-wide which has lead to increasing attention in recent years. The principle is to utilize the mixing entropy when mixing freshwater with sea water. Pressure retarded osmosis (PRO) is one of the technical feasible processes which can be used to extract this energy. In PRO freshwater and sea water are separated by a semi permeable membrane which ideally allows only water to be transported through the membrane. The transport of water through the membrane is caused by the difference in osmotic pressure across the membrane skin, and the net volume increase on the sea water side due to mass transport against a pressure gradient can be utilized to run a turbine.

SINTEF has in cooperation with Statkraft, which is one of Europe's largest power production companies on renewable energy, worked for a number of years to develop a technical feasible process. Several critical aspects must be addressed in order to optimize future commercial PRO plants, i.e. developing a membrane with sufficient high water permeability (A), low salt permeability (B) and a short effective diffusion length (S) in the support structure; an overall understanding how the different variables influence the PRO performance; a membrane module with high packing density and low pressure drop in both flow channels; a high efficiency energy recovery unit; and, a understanding of pre-treatment and cleaning protocols required to control fouling.

The presentation will address the interaction between temperature, concentration and membranes with different characteristics (A, B, S) and their impact on the PRO performance. Laboratory experiments are performed, and the results are modeled with a mass transport model that includes concentration polarization on both sides of the membrane, as well as in the support structure of the membrane itself. An understanding how these variables affect the PRO performance is crucial both for developing a feasible PRO membrane, and for optimizing the operation of a PRO plant which will experience natural seasonal variation in both temperature and salt concentration in the water sources. Further, the results will be compared and discussed in relation to observations done during operation of Statkrafts PRO prototype at Tofte.

ICOM720

Influence of Monomer Concentration on the Performance of Polyamide-based Thin Film Composite Membranes in Osmotically Driven Membrane Processes

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Osmotically driven membrane processes, e.g. forward osmosis (FO) and pressure-retarded osmosis (PRO), are emerging membrane separation technologies in which water diffuses through a semi-permeable membrane under an osmotic pressure difference across the membrane. Unlike in the pressure-driven membrane processes, membrane performance in the osmotically driven processes is non-linearly determined by the membrane separation properties and driving force. Therefore, it is worthwhile to understand how the membrane properties contribute to membrane performance under different conditions. For thin film composite (TFC) membrane of which the rejection layer is prepared via interfacial polymerization, the concentration of reactive monomer significantly determines the membrane permeability and selectivity. In the present work, the influence of monomer concentration and the resultant membrane separation properties on FO performance are systematically studied. Flat-sheet TFC membranes are prepared by interfacial polymerization with varied concentrations of monomers, i.e. m-Phenylenediamine (MPD) and trimesoyl chloride (TMC), on top of identical polysulfone substrates. Water flux and salt flux of the resulting membranes under different testing conditions were measured.

Two series of membranes were prepared. In the first series, MPD concentration varied from 0.5 wt% to 2.0wt % and TMC concentration was fixed at 0.5 wt/v%. As MPD concentration increased, the membrane permeability decreased while the salt rejection increased due to the denser rejection layer formed. Under FO conditions, both water and salt flux declined with increasing MPD concentration when 0.5 M NaCl draw solution was used. With 2.0 M NaCl as draw solution, however, there was only marginal change in water flux of different membranes. In the second series, TMC concentration was increased from 0.05 wt/v% to 1.0 wt/v% and MPD concentration was constant at 1.0 wt%. Membranes with higher TMC concentration exhibited improved water permeability but lower salt rejection due to lower cross-link density of rejection layer. Increase in both water and salt flux was observed when 0.5 M NaCl draw solution was used. When 2.0 M NaCl draw solution was used, however, water flux tended to reduce with increasing TMC concentration. One major reason for the above non-linear behavior is the internal concentration polarization (ICP). At low water flux level, the FO performance is mainly controlled by membrane permeability. Under high osmotic pressure, concentration of feed solution or dilution of draw solution within the porous substrate becomes severer. Thus ICP plays a dominant role over membrane permeability at high draw solution concentration. Moreover, ICP can be further enhanced by salt diffusion from draw solution to feed solution. Therefore, water flux deceased with increasing TMC concentration because of the low-salt-rejection membranes formed.

ICOM1182

Development of forward osmosis and pressure retarded osmosis technology in Singapore

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Forward osmosis (FO) has attracted increasing attention for water and energy applications in recent years. The Singapore Membrane Technology Centre (SMTC) has been involved in several FO-related projects. This presentation will highlight our latest progress in various aspects of FO research including a) membrane and process performance modeling [1-3]; b) novel FO membrane development [4,5]; c) FO fouling evaluation [3,6,7]; and d) novel FO process development. The modeling of FO membrane performance (water flux and solute flux) will be briefly discussed. This leads to a set of membrane design criteria for optimal FO performance. Novel FO membranes with superior FO performance will be discussed. FO fouling and FO process development will also be briefly discussed.

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NF/RO 3

ICOM1839

Organic Solvent Nanofiltration – An Overview

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Abstract: This presentation will provide a brief overview of the field of nanofiltration of organic solvent-based systems. In the late sixties and seventies, often research in the area of reverse osmosis (RO) membrane fabrication yielded membranes showing very low salt rejections with aqueous solutions. Such membranes were also commercially available for a number of applications. These were failed RO membranes but de facto nanofiltration membranes till FilmTec Corporation coined the word nanofiltration (NF) and introduced NF series membranes for two types of aqueous solution applications in the mid eighties. The earliest solvent-stable NF membranes were introduced by Membrane Products Kiryat Weizmann in late eighties and early nineties. Research interest has expanded significantly ever since focused on rejections of solutes having molecular weights in the range of 150-1000 while the organic solvent passes through.

Organic solvent nanofiltration (OSN) membranes are generally prepared from solvent-stable polymers as asymmetric or integrally skinned membrane; polyimide membranes are typical examples even though they are not useful for a range of polar aprotic solvents. Alternately the membranes are crosslinked to develop solvent stability on appropriate supports. A crosslinked silicone coating is used in a number of membranes. Interfacial polymerization is an additional technique employed to develop a solvent-resistant skin on a solvent-stable support. A brief overview of the developments in this area as well as the nature of the membrane modules will be provided. Carbon nanotubes (CNTs) are being used to develop OSN membranes as well. Such membranes may employ the inner core of the CNTs for solvent transport and solute rejection; alternately reduced interaction of the outside surface of surface-functionalized CNTs in CNT-polymer composite membranes may provide nanocorridors in interfacially-polymerized membranes for improved solvent flux in OSN.

Membranes for OSN are being utilized in a number of applications the largest being lube-oil dewaxing. Potentially there are many applications in the pharmaceutical, chemical and petrochemical industries due to its athermal processing capabilities. Coupling OSN membrane modules with reactors can allow a number of ways to enhance reaction conversion and selectivity. Such potentials of OSN remain to be realized.

ICOM510

Chlorine Resistant Hollow Fiber Nanofiltration Based On Modified Polysulfones

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Abstract

Nanofiltration plays already an important role in water treatment processes, typically used for removal of hardness, colour and micropollutants. The existing nanofiltration membranes are based on the well-known spiral wound concept, and suffer from two major disadvantages: need for sophisticated pre-treatment and lack of chlorine resistance. In this paper the development of a novel type of capillary nanofiltration membrane will be discussed, demonstrating that the mentioned disadvantages for existing nanofiltration concepts are becoming obsolete.

Introduction

Most capillary membranes used for ultrafiltration are produced using polysulfone or polyvinylenedifluoride as the basic polymers. Hydrophilicity is often introduced by blending these with hydrophilic polymers as polyvinylpyrrolidone[1]. The existing reverse osmosis and nanofiltration membranes are based upon either polyamides or cellulose acetate. Major drawback of these membranes is their low chlorine stability. This severely reduces the possibilities for disinfection, and subsequently their applications for potable water purification. Furthermore, the hydraulic cleaning possibilities of spiral wound elements is limited. Backwashing by reversing the filtration flow damages the membrane while forward flushing is less (energy) efficient due to the spacer. Next to this, spiral wound modules require excessive pre-treatment. Big advantages of the capillary membrane concept are hydraulic cleaning possibilities and the fact that the pre-treatment can be reduced to a very simple sieving process.

Membrane Development

The capillary nanofiltration membranes are based upon modified polysulfone polymers. Herewith we introduce certain charged hydrophilic groups in the polymer matrix. Applying a special phase inversion process combined with proprietarily spinneret chemistry, very thin selective layers can be obtained, introducing nanofiltration properties. Given the fact that this new generation of nanofiltration membranes is based upon well-known polysulfone materials, comparable chlorine resistance is obtained. The mechanism of degradation of the membranes is based on random chain scission, comparable to PES ultrafiltration membranes[2] (see figure1). Performance is based on the retention of a low molecular weight dye (Sunset Yellow, 452 g/mol).

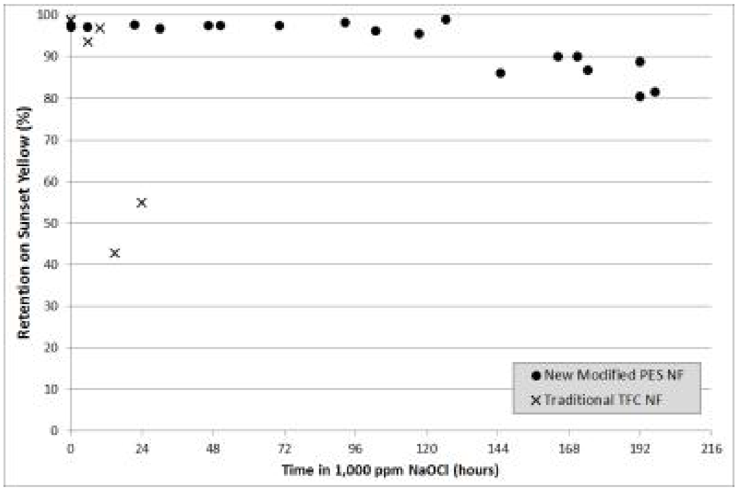

Figure1: Comparison of degradation for traditional TFC and novel modified PES capillary NF-membranes with NaOCl (1.000ppm, pH=8, T=25°C).

By changing the charge of the polymer, separation performance of the membrane can be tuned. Moderate charge levels results in an open nanofiltration membrane with limited rejection on bivalent ions. These membranes are ideal for the production of potable water, when mainly organic contaminants need to be rejected. Increasing the charge of the polymer results in a more dense nanofiltration membrane with comparable permeabilities, of which the salt retention is increased and typically based on

Donnan exclusion[3] (see figure2).

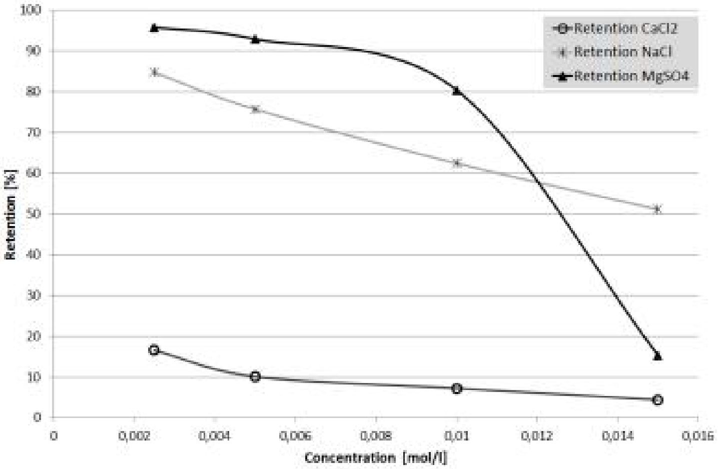

Figure2: Retention of the capillary NF membrane with high charges (permeability=10 l/m^{2}bh).

Outlook

In this presentation will be presented a new membrane filtration concept based upon capillary nanofiltration. This concept requires no dedicated pre-treatment, and uses chlorine stable membranes. The separation properties of the membrane are dependent on the tailor-made polymer characteristics. Next steps will be changing and increasing the charge in the separation layer to further enhance the properties.

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ICOM694

Correlation between volumetric properties and mass transfer of sugars through NF membrane: influence of the ionic composition

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Recent studies have shown that unexpected performances can be obtained with NF membranes, when applied to the treatment of solutions containing significant amount of salt. The influence of the salts on the transfer of neutral organic solutes, like carbohydrates and organic acids, was thus pointed out (1,2). More precisely, it was observed that, in different situations, the transfer of organic solutes can be increased by the addition of salt. It was also reported that this increase depends on the salt concentration and on the salt nature. The improvement of the transfer of the neutral specie can be ascribed to a decrease of the solute hydrodynamic radius, to an increase of the pore radius, or more probably to a combination of both. Different assumptions have been advanced to explain these variations. For instance, it was suggested that, the addition of salt can lead to a decrease of the solute radius. Indeed, it was established that carbohydrates are less hydrated in presence of salts (3).
The objective of this work was to go further through the understanding of the mechanisms governing the mass transfer of organic species through NF membranes with a focus on the role of ions. The methodology was based on the investigation of the relationship between relevant physicochemical parameters which characterize the hydration state of neutral solute and those characterising their mass transfer through membranes in solutions of different ion composition.
The mass transfer of the organic solutes through a NF membrane (Filmtec NF) was studied in a diffusion regime. Sugars of increasing molecular weights (xylose, glucose and sucrose) were used as organic species. Different electrolytes (NaCl, Na_2SO_4, $CaCl_2$, $MgCl_2$) were chosen with respect to their valence, since it is linked to the hydration level. A specific procedure has been developed to dissociate the influence of the presence of salt on the neutral solute on one hand and on the membrane material on the other hand. The results showed that the mass transfer modification is mainly due to the influence of salt on the solute. Then, the mass transfer parameters were put in parallel with the apparent molar volume of sugars measured in solutions of different ionic compositions. Indeed, these volumetric properties characterize the hydration state of neutral solute with respect to the ionic composition (3). A good quantitative correlation has been established between the mass transfer through NF membrane and the apparent molar volume.
Consequently, the mass transfer of neutral solutes through NF membranes in solutions of different ion composition was tightly linked to their hydration state.

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ICOM503

Thin Film Nanocomposite Membranes with Seawater RO Performance

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Previous work demonstrated that incorporating zeolite molecular-sieve nanocrystals into polyamide thin films significantly enhanced water flux without significantly reducing observed solute rejection. In that work, zeolite nanocrystal size was selected to be the same size as polyamide film thickness, thereby, creating a percolation threshold through the thin film with each nanocrystal. It was hypothesized that zeolite molecular-sieves improved membrane permeability while maintaining selectivity by acting as preferential flow paths for water; however, a series of zeolite-polyamide coating films prepared with impermeable pore-filled zeolite molecular seives produced fluxes intermediate between the pure polyamide films and nancomposite films prepared with pore open molecular sieves – at the same zeolite loading. This result offered indirect evidence that an alternate mechanism, besides molecular-sieving, could be responsible for the enhanced membrane performance. Subsequently, two additional mechanisms for the observed flux enhancement were proposed: (a) defect formation due to zeolite nanocrystal aggregation in the organic solution and (b) heat release from the zeolites by hydration during the interfacial polymerization reaction, which produced changes in the structure of the polyamide films.

Here, we report on pure polyamide thin film composite (TFC) and zeolite-polyamide thin film nanocomposite (TFN) reverse osmosis (RO) membranes prepared with four different post-treatment regimes applied after interfacial polymerization. Both TFC and TFN hand-cast membranes were more permeable, hydrophilic and rough than a commercial seawater RO membrane; however, salt selectivity was more variable. All hand-cast TFC membranes exhibited higher salt rejection than the commercial membrane. Two TFN membranes exhibited lower salt rejection – suggesting the presence of defects – while two exhibited higher salt rejection than the commercial RO membrane. Polyamide films formed in the presence of zeolite nanocrystals were universally less crosslinked than similarly cast pure polyamide films, but more crosslinked than the commercial membrane. At the very low nanoparticle loadings evaluated, hand-cast TFC/TFN membrane separation performance did not correlate with structural changes in the polyamide thin film. This suggests that defects (in low rejection TFN membranes) and preferential flow paths for water offered by the molecular-sieves (in high rejection TFN membranes) largely governed differences between pure polyamide and zeolite-polyamide membrane flux and rejection.

ICOM1373

Responsive Membranes for Water Treatment

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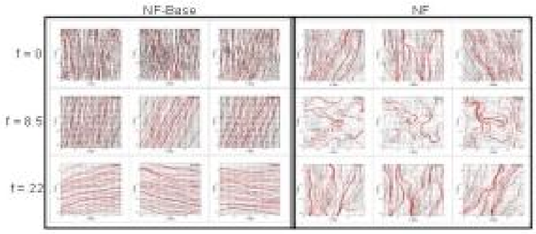
Membrane processes such as reverse osmosis, nanofiltration, ultrafiltration, microfiltration and membrane distillation find applications in water treatment. Membrane processes often require far less energy than alternative unit operations making them particularly attractive for water treatment applications. Unfortunately membrane fouling often limits the use of membrane separations for water treatment. Development of advanced antifouling membranes will be essential if the potential for low energy membrane separations is to be realized for water treatment. Our research focuses on the development of new multi-functional mem-branes, i.e., membranes that carry out two or more functions cooperatively to achieve desired per-formance. Here results will be presented
for surface modification of commercially available nanofiltration membranes in order to make them responsive to an oscillating magnetic field.

Commercially available nanofiltration membranes (NF 270) have been modified using atom transfer radical polymerization to grow poly(2-hydroxyethyl methacrylate) chains from the surface of the membrane. Next a Gabriel synthesis reaction was used to convert the alkyl halide end group of the polymer chains to primary amines. Carboxylic acid coated iron oxide nanoparticles were then attached to the chain ends through an amide linkage. Successful surface modification of the membranes has been monitored using X-ray photoelectron spectroscopy.

Movement of the magnetically responsive brushes has been visualized using particle image velocimetry. The figure



gives a typical result. Three time lapse velocity field measurements (base membrane left, modified membrane right) with overlaid two-dimen-sional streamlines illustrate the spatial flow topology for magnetic oscillation frequencies of *f* = 0, 8.5 and 22 Hz. There is a clear frequency dependence of flow topology for magneti-cally functionalized membranes with peak complexity at *f* = 8.5 Hz. The streamlines for the base membrane correspond to 'background' flow currents from thermal effects of the PIV laser picked up due to high magnification (0.4 microns/pixel). As can be seen in an oscillating magnetic field, the magnetic nanoparticles attached to the polymer chain ends move like the cilia of microorganisms which induces mixing at the membrane-fluid interface at low Reynolds number. Our data indicate that this motion is sufficient to cause mixing up to a distance of 0.5 mm from the membrane surface.

Dead end filtration experiments have been conducted using feed streams consisting of aqueous solutions of $MgSO_4$ and $CaCl_2$. The Table

Salt rejection (%)				
	500 ppm $CaCl_2$		2000 ppm $MgSO_4$	
	Control	Modified	Control	Modified
With Field	34.4	40.4	66.5	74.4
Without Field	32.5	34.2	66.0	67.7
Filtrate Flux (L m^{-2} h^{-1})				
With Field	13.4	9.6	5.4	6.0
Without Field	12.8	7.8	5.6	4.0

summarizes some of our results. All fluxes for the modified membranes are less due to grafting of a nanolayer. The presence of an oscillating magnetic field has little effect on the flux for unmodified membranes though the rejection increases slightly. Since the ionic species in solution can also respond to the oscillating magnet field this could lead to a decrease in concentration polarization and hence higher rejection. Importantly our results indicate improved fluxes and rejection for modified membranes in the presence of an oscillating magnetic field. These results demonstrate successful modification of nanofiltration membranes in order to make them responsive to an oscillating magnetic field. Further, the movement of the polymer chains induces mixing at low Reynolds number and is also expected to suppress fouling.

Membranes for fuel cells 3

ICOM1794

Current developments in aromatic polymer electrolyte membranes

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Hydrocarbon-based (HC) polymer electrolyte membrane (PEM) materials are under intensive investigation as replacements for commercial perfluorinated-type materials such as Nafion® for reasons of cost reduction, potentially higher operating temperatures, and reduction in fuel crossover. However, HC-PEMs face several challenges to overcome before they can be effectively used in fuel cell devices. They contain sulfonic acids that have intrinsically lower acidity than fluorosulfonic acids, requiring higher ion exchange capacity to achieve effective conductivities. This may lead to excessive swelling in a humidified environment, leading to a loss of mechanical integrity. Control of dimensional swelling is particularly important to minimize dimensional mismatch at the membrane electrode assembly interface, leading to mechanical failure and electrode delamination. Chemical stability of PEMs is also an important consideration for durability, and is another leading cause of failure. In addition, for automotive applications where higher operating temperatures are encountered, HC-PEMs tend to show a marked decrease in conductivity in a reduced-humidity environment.

To help address some of the challenges discussed above, attempts are being made to design PEMs which have chemically stable structures and the ability to retain adequate proton conductivity in a reduced humidity environment. Some background of these efforts by other researchers will be presented. Our current work focuses on PEMs which contain polymeric structures having uniformly-spaced sulfonic acid groups in the conducting block, allowing self-organization of polymers into hydrophilic proton-conducting domains and hydrophobic domains. New types of blocky PEM architecture are reported. Segmented copolymers have been prepared having sulfophenylated units along the hydrophilic segment, unlike block or segmented copolymers reported previously. Fully aromatic comb copolymer systems with hydrophilic grafts have also been prepared, which have unique architecture. Some of the PEMs exhibit unusually low dimensional swelling in the planar direction and good proton conductivity under partially hydrated conditions relative to other HC-PEMs.

ICOM310

Effect of water state on properties of anion exchange membranes for solid state alkaline fuel cells

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Recently, solid-state alkaline fuel cells (SAFCs) using anion exchange polymers as an electrolyte have been attracting worldwide attention owing to the usage of non-precious metals as a catalyst and the adoption of liquid fuels with high energy density. An anion exchange membrane (AEM) is one of the vital components of SAFCs. The followings are required to AEMs: high hydroxide ion conductivity to lower the potential loss, low fuel permeability to employ liquid fuels and thermal stability in alkali condition.

To achieve all those goals of AEMs, the importance of water state in membranes are taken note. In general, caused by the affection of hydrophilic groups, water absorbed in ion exchange membranes is broadly classified into one of two groups, bound or free water, where the mobility is different for each. The transport behavior of molecules in these different configurations will be different.

In this research, to control the water state in the membranes, novel aromatic anion exchange pore-filling membranes (PF-AEMs) are developed by filling anion exchange polymers into the pores of the porous substrate. Because the mechanical strength of the substrate suppresses the swelling of the inside polymer, PF-AEMs contain only bound water even under fully hydrated condition. Comparing PF-AEMs to cast membranes which are films of the polymer, the effect of water state on the membrane properties: hydroxide ion conductivity, methanol permeability, water self-diffusivity and the hydrothermal stability are studied.

As anion exchange polymers, amminated polysulfones with different ratio of quaternary ammonium group were used. Surprisingly, the permeability in the PF-AEMs was suppressed about 7 to 84 times than that of cast membranes. However, the conductivity of the PF-AEMs was only about 3 to 14 times smaller than that of cast membranes. That is, PF-AEMs have higher selectivity than cast membranes.

To investigate the reason of the higher selectivity of PF-AEMs, self-diffusion coefficient of water (D_{H2O}) in the PF-AEM and the cast membrane was measured by PFG-NMR. Self-diffusion coefficient of OH^- (D_{OH-}) of the same membranes was also calculated by Nernst-Einstein equation. The results are shown in table 1. The D_{H2O} of the PF-AEM was 14 times smaller than that of the cast membrane. This low mobility of water in PF-AEM leads to restrict the permeation of methanol molecules. Moreover, in the PF-AEM, the D_{OH-} was 1.5 times higher than the D_{H2O}. This is the first report to show higher self-diffusion of ion than water in AEMs. This result presents the evidence that the OH^- is conducted not only with hydrated water but also through water using hydrogen bonding and disbonding.

Table 1. Self-diffusion coefficients of hydroxide ion (D_{OH-}) and water (D_{H2O}) in each membrane at 25℃. (10^{-6} x cm^2/s)

Self diffusion coefficient	Cast membrane	Pore-filling membrane
D_{OH}-	3.1	0.97
D_{H2O}	9.2	0.65

Then, hydrothermal stability of the membranes was evaluated by immersing the membranes in 100℃ water. Interestingly, the change of ion exchange capacity over time in the PF-AEMs was smaller than that of the cast membranes.

In conclusion, PF-AEMs have achieved hydroxide ion conduction through bound water, the restriction of fuel permeation and the improvement of the stability.

ICOM1254

Stretched PFSA Membranes for Hydrogen/Air and Direct Methanol Fuel Cells

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Nano-crystallites, acting as physical crosslinks in a perfluorosulfonic acid (PFSA) membranes, play a crucial role in improving mechanical properties and in slowing species permeation. When a semi-crystalline polymer or particle/polymer composite membranes is used in a direct methanol fuel cell (DMFC), the crystalline domains or inorganic particles slow methanol crossover, but they may also decrease proton conductivity and/or introduce undesirable impurities into the electrochemical device.

To develop a durable and high performance proton exchange membrane (PEM) for fuel cell applications, we have been systemically studying stretching effects on PFSA polymers for both hydrogen and methanol feeds. PFSAs represent a family of commercially available polymers with a perfluorinated backbone and side chains that terminate in hydrophilic sulfonic acid groups. Three major types of PFSA commonly used in fuel cells were studied: DuPont's Nafion® (with a long side chain of −O–CF_2CFCF_3–O–$(CF_2)_2$–SO_3H), 3M Corp. PFSA (a short-side-chain version of Nafion with –O–$(CF_2)_4$–SO_3H pendant groups), and Aquivion from Solvay Solexis (with a very short side chain of –O–$(CF_2)_2$–SO_3H). The effect of uniaxial stretching on the morphology and properties of these polymers was probed, where solution-cast membranes were stretched at a temperature above the polymer's α-transition temperature.

With a large number of CF_2-CF_2 repeat units between side chains in the main PTFE backbone, three PFSA polymers (i.e. Nafion 1100EW, 3M 1000EW and 825EW, Aquivion 830EW) show an increase in crystallinity upon uniaxial stretching, with a decrease in methanol permeability and no change in proton conductivity. As shown in Figure 1, a DMFC employing a stretched 3M 825 EW PFSA membrane with a draw ratio (DR) of 4 exhibits a 31% improvement in power density at 0.4V, as compared to a Nafion 117 membrane.

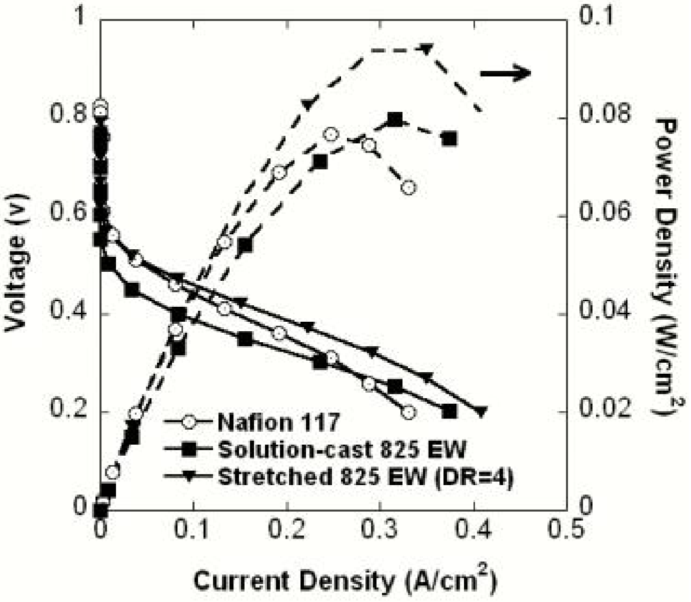

Figure 1. Direct methanol fuel cell performance of Nafion® 117, an unstretched 825 EW PFSA, and a stretched 825 EW PFSA (DR=4) membranes. Fuel cell operating conditions: 60°C, 1.0 M methanol at 1.5 mL/min, ambient pressure air at 500 sccm, 4.0

mg/cm^2 catalyst loading for the anode and cathode.

Interestingly, the 3M 733 EW PFSA polymer has no crystallinity before/after stretching. However, the nanostructure of ionic domains varied with DR. In WXRD, the ionomer peaks of a stretched membrane were found to shift to higher values of 2θ, and a new ionomer peak appears when the DR is greater than 4. For a stretched 733 EW membrane (DR=4), there is a 120% increase in storage modulus with a proton conductivity equal to that of an unstretched film. This combination of properties makes stretched 3M 733 EW PFSA a promising PEM for a hydrogen/air fuel cell. From an open circuit voltage humidity cycling test at 80°C, it was found that the lifetime of a stretched 3M 733 EW PFSA membrane (DR=4) was 350% greater than that of an unstretched membrane (Figure 2).

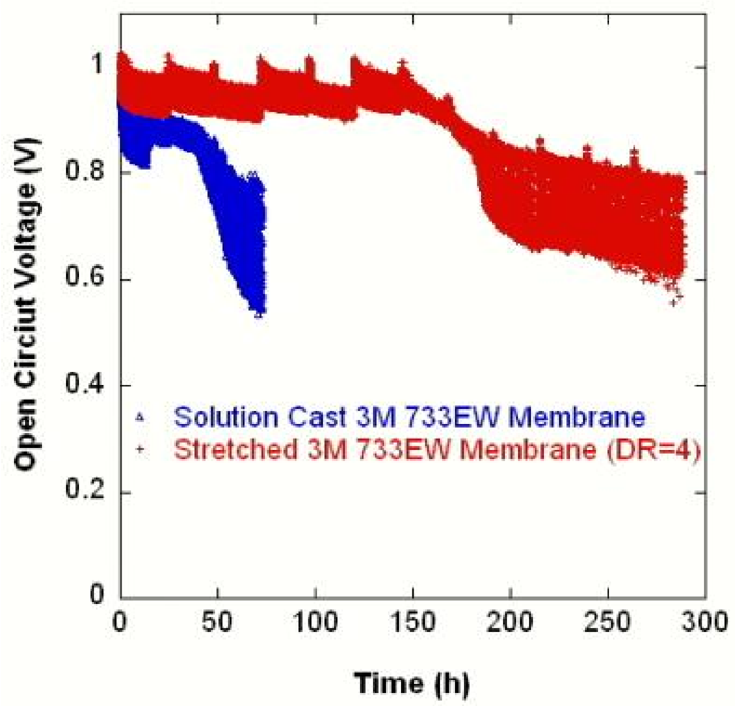

Figure 2. Hydrogen/air fuel cell humidity cycling tests for MEAs (25cm^2) prepared from 3M 733 EW PFSA, solution cast (unstretched) and stretched (DR=4).

ICOM863

Gas permeation in fuel cell membranes: challenges and mitigation strategies

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An advanced hydrogen-based fuel cell power train system for the automotive industry must meet a number of demanding requirements to become commercially attractive. These include requirements of fuel cell vehicles (FCV), such as improvements in fuel economy, power efficiency, and durability to provide suitable vehicle range and costs.

Key challenges that are directly associated with MEA components include relatively high MEA costs, relatively low mass activity of the cathode catalyst under current catalyst loadings, relatively low MEA durability, poor ionic conductivity of solid polyelectrolyte (SPE) membranes at low relative humidity and high temperature, and excessive gas permeability of the perfluorosulfonic acid (PFSA) SPE membranes (Lee et al. 2009). For example, nitrogen gas permeability of humidified membranes in automotive fuel cell stacks is required to be less than 4 Barrer permeability units (Kundu et al. 2009).

Increased gas permeation rate in fuel cell membranes not only results in inefficient fuel utilisation, but also leads to mixed electrochemical potentials and other fuel-cell specific operational problems (Bessarabov and Kozak 2007). Hydrogen and oxygen gases that permeate through the membrane are consumed producing heat and water leading to fuel inefficiency. The cell voltage obtained at low current densities is strongly affected (reduced) by gas cross-over.

Extensive diffusion of oxygen from the cathode to the anode may lead to the formation of hydrogen peroxide, which can significantly shorten the lifespan of the membrane under certain conditions in fuel cell stacks. On the other hand, an increase in nitrogen concentration in a fuel tank due to the permeation process might cause a significant change in overall fuel cell performance if hydrogen fuel is recycled during a fuel cell stack operation and the diffusion rate of nitrogen gas in membranes is high.

Abovementioned and some other effects such as Pt band formation in the membranes and mitigation strategy associated with gas-cross in membranes will be discussed in this paper.

References:
Kundu, S., M. Cimenti, S. Lee, D. Bessarabov. 2009. Fingerprint of the automotive fuel cell cathode catalyst degradation: Pt band in the proton-exchange membranes. *Membrane Technology* 10: 7-10

Bessarabov, D. and P. Kozak. 2007 (a). Measurement of gas permeability in SPE membranes for use in fuel cells. *Membrane Technology* December: 6-9

Lee, S., D. Bessarabov, R. Vohra, 2009. Degradation of a cathode catalyst layer in PEM MEAs subjected to automotive-specific test conditions. *International Journal of Green Energy* 6: 594–606

ICOM1209

New monomers, polymers and membranes for fuel cells and electrolysis

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Due to the high cost and partially unfavorable properties of perfluorosulfonic acid (PFSA) fuel cell membranes, there is a world-wide intense search for alternative proton-conducting membranes. Next to the PFSA membranes, arylene main-chain ionomers show the highest stabilities in fuel cells and related electro-membrane processes such as electrolysis. Therefore our R&D work focuses onto the development of novel arylene monomers (partially fluorinated and perfluorinated), homopolymers prepared from these and commercial monomers by polycondensation of the fluorinated aromatics. Examples for the new monomers are 2,2-bis(4-fluoro-3-sulfonatophenyl)-hexafluoropropane, 2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene sulfonic acid, and trisulfonated bis(4-fluorophenyl)phenyl phosphine oxide. These novel monomers were polycondensated with several types of bisphenols and bisthiophenols, ending up in novel arylene main-chain polymers having advantageous properties in terms of proton-conductivity, and thermal and chemical stability. Moreover, also multiblock copolymers have been prepared consisting of a hydrophilic and proton-conductive nanophase and a hydrophobic nanophase which essentially contributes to the mechanical stability via suppression of water and methanol uptake/swelling. The homopolymers and block-copolymers have been blended with several types of basic polymers, among them different polybenzimidazoles (PBI) and self-prepared polymeric bases containing pyridine groups, which led to reduced water uptake/swelling of the membranes, compared to the pure polymers, by formation of ionical cross-links between the acidic and the basic blend component. Acid-excess blend membranes were prepared for the use in air-breathing direct methanol fuel cells (DMFC). Base-excess blend membranes which were subsequently doped with phosphoric acid were produced for the use in mid-temperature H_2 fuel cells.

Acid-excess sulfonated homopolymer-PBI blend membranes and acid-excess sulfonated multiblock-copolymer-PBI blend membranes performed much better in DMFC than PFSA-type membranes which is mainly due to their lower methanol (meOH) uptake and permeability. This strongly increased performance, compared to the PFSA membranes, could especially be monitored when using high meOH concentrations of 30% in DMFC. Interestingly, in 30% meOH the pure multiblock ionomer membranes

were instable because of extreme swelling, while the block-co-ionomer/PBI blends remained stable, which clearly showed the morphology-stabilizing effect of the ionical cross-linking network. Base-excess PBI/sulfonated polymer blend membranes were initially tested in terms of thermal and chemical stabilities by immersion in Fenton´s Reagent for up to 120 h. It could be clearly seen that the blend membranes were more stable than pure PBI membranes against hydroxyl radical attack which can be traced back to the stabilizing ionical network within these membranes. Exploration of the molecular weight degradation of the blend membranes by Fenton´s Test revealed that only slight molecular weight degradation took place during the test. The most stable of these membranes have been tested in a mid-T hydrogen fuel cell at temperatures from 125 to 200°C, yielding a good performance.

Parallel Sessions

Thursday, July 28th 2011

Afternoon Session 1, 13.40 – 15.10

Gas and vapor separation 6

ICOM1845

How gases dissolve in liquids

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In my talk I will introduce a few intuitive ideas related to the mechanism gas dissolution in liquids. I will next try to convince you that these ideas provide an experimental route to obtain information on the strength of solute-solvent interactions, based on a very simple analysis of experimental solubility data. Applied to gas and vapor solubility in polymers, information is obtained on the strength of the intermolecular polymer-penetrant interaction, furthermore providing a new angle on correlations between solubility and penetrant critical properties. Based on an analysis of hydrocarbon versus fluorocarbon vapor sorption in PDMS, I will advocate the use of the *binding enthalpy* as a new measure for polymer-penetrant interactions.

Literature:
T.A. Ozal, N.F.A. van der Vegt, *J. Phys. Chem. B* **2006**, *110*, 12104-12112.

N.F.A. van der Vegt, V.A. Kusuma, B.D. Freeman, *Macromolecules* **2010**, *43*, 1473-1479.

ICOM616

Solubility controlled separation of hydrocarbons C_1-C_4 using novel high free volume polymeric membranes

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So far it was assumed that solubility controlled permeation that allows removal of heavier hydrocarbons from methane is characteristic, among glassy polymers, only for polyacetylenes. Now we can report that the same behavior has been observed for the first time for membrane materials of another class: derivatives of additive norbornene polymers bearing $Si(CH_3)_3$ groups. The polymers were prepared by Prof. E.Finkelshtein and his colleagues in TIPS. The formulas of these glassy high free volume polymers and permeabilities of individual n-butane are given in Fig.1.

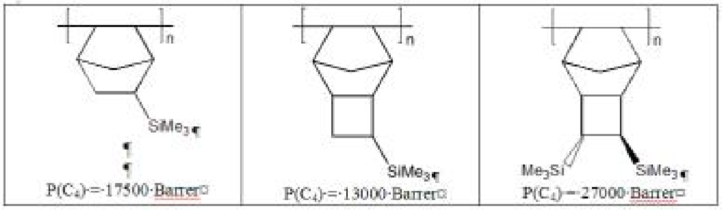

Fig. 1. Polymers studied

The transport parameters (permeability coefficients, separation factors) were determined in separation of mixtures of n-butane and methane. The content of butane in the feed was in the range 3.7-9.4% and simulated the composition of associated petroleum gas. The experiments were carried out at room temperature and feed pressure of 2-6 atm. All three novel membrane materials were studied in the form of dense films. The polymers studied reveal a distinct solubility controlled permeation not only in the experiments with individual gases but also with gas mixtures: the permeate streams were strongly enriched (by a factor of 5-8 depending on boundary conditions) with heavier component (C_4H_{10}), permeability of methane was reduced by a factor 3-4 in the presence of butane vapor (as compared to permeability of pure methane), and high permeability of butane was observed. It can be assumed that these polymers have partly opened pore structure of their free volume and the mechanism proposed for poly(trimethylsilyl propyne) implying suppression of diffusion of light component of the mixture (methane in this case) is also applicable for
new Si-containing poly(cycloolefins).

The investigated additive norbornene type Si-containing polymers can be considered as interesting membrane materials for separation of hydrocarbon gases.

The work leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. NMP3-SL-2009-228631, project DoubleNanoMem.

ICOM748

Prediction of mixed gas solubility and solubility-selectivity in glassy polymers

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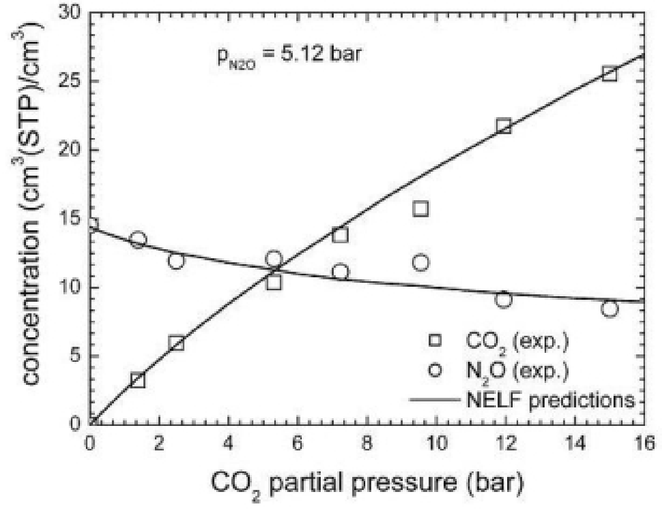
The evaluation of the mixed gas solubility in glassy polymers is of fundamental importance for the development gas separation membranes. For rubbery polymers the usual equation of state (EoS) models, in their multicomponent version, can be conveniently applied to calculate multiple gas solubility in the equilibrium phases; for the case of glassy polymers, on the contrary, the same thermodynamic tool cannot be used. The general approach called Non Equilibrium Thermodynamics of Glassy Polymers (NET-GP) [1], coupled to the Lattice Fluid (LF) model for the representation of substances [2,3], was showed to be able to predict the solubility of gases and vapors in glassy polymers at various pressures based on pure component parameters.

The above approach is here applied to the modeling of multicomponent gas solubility in a pure glassy polymeric matrix, to predict the solubility of binary gas mixtures in pure glassy polymers as CH_4/CO_2 in Poly(2,6-dimethylphenyleneoxide) (PPO), C_2H_4/CO_2 and N_2O/CO_2 in poly(methylmetacrylate) (PMMA), at room temperature and at various pressures, for which experimental data are available [4-5]. The presence of polar and swelling penetrants, gives rise to significant interactions, which make the solubility of mixed gases differ significantly from the corresponding pure component values. In the above calculations, the gas-polymer binary energetic parameters kij are adjusted on the solubility data of the single gas in the polymer, and the gas-gas binary interaction parameter is considered zero in view of the generally high dilution of gaseous components in the polymer. In the sorption of pure swelling penetrants, one can assume reasonably that the polymer density decreases linearly with the penetrant pressure, according to a swelling coefficient, k_{sw}, that can be measured directly or evaluated by fitting the pure gas solubility data on the NELF model predictions. The swelling induced by the gaseous mixture in the polymer is then assumed to follow a simple additive rule based on the penetrant partial pressure in the external gaseous phase.

Figure 1 shows that the N_2O content in the PMMA, at given partial pressure of N_2O, is lowered by the increase of CO_2 partial pressure; the same effect is observed for the CO_2/CH_4 pair in PPO, that is not shown here for the sake of brevity. The NELF model is able to predict the experimental behavior observed for mixed gases solubility in both systems; the agreement is indeed remarkable in both cases in the whole pressure range investigated. The parameters used for the case shown are: $k_{CO2/PMMA} = -0.015$, $k_{N2O/PMMA} = 0.007$; $k_{sw,CO2} = 15.4 \times 10^{-4}$ bar^{-1}; $k_{sw,N2O} = 18.6 \times 10^{-4}$ bar^{-1}. The present approach allows also to estimate predictively the mixed gas solubility-selectivity of N2/CO_2, CO_2/CH_4 and H_2/CO_2 mixtures in several glassy polymers including polyimides such as Matrimid, 6FDA-6FpDA and Ultem in a wide range of pressures, allowing to detect significant deviations from the ideal selectivity behavior.



ICOM128

Permeability upper bound predictions from transition state theory using the nonequilibrium lattice fluid model

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An upper bound on the permeability and permeability selectivity combination possessed by known polymeric materials confounds the development of industrial membrane gas separation processes. First reported in the literature by Robeson (Journal of Membrane Science, 62, 165-185, 1991, Journal of Membrane Science, 320 390-400, 2008), changes in primary and secondary chain architecture that increase permeability also tend to decrease permselectivity and vice versa.

Freeman proposed a theoretical explanation for this upper bound (Macromolecules, 32, 375-380, 1999). The theory provides good estimates of the location of the upper bound but predicts all materials fall on this line, contrary to experiment, and fails to capture the dependence of transport on the identity of the specific chemical species present.

Recently, we demonstrated how the non-equilibrium lattice fluid theory predicts the existence of an upper bound for solubility selectivity. The theory clearly captures how solubility and solubility selectivity depend on gas and polymer material properties. Moreover, it demonstrates how the upper bound arises from limitations on the maximum bulk modulus possessed by available polymeric materials.

This theoretical analysis is used to predict diffusivity and diffusivity selectivity using transition state theory. Following the analysis of Gray-Weale et al. (Macromolecules, 30, 7296-7306, 1997), the energy change associated with forming the diffusion transition state is calculated using non-equilibrium lattice fluid theory to provide the required material parameters. The results indicate an upper bound exists on diffusivity and diffusivity selectivity which when combined with the solubility upper bound provides an a priori prediction of the permeability upper bound.

Membrane formation 4

ICOM1812

NOVEL MEMBRANE CONCEPTS PAVING THE ROAD FOR IMPROVED AND NEW EXTRA-CORPOREAL THERAPIES

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Gambro Dialysatoren GmbH, Research & Development, DE

In 2010, approximately 205 million dialyzers (with an average surface area of 1.7 m^2) were manufactured for the treatment of nearly 2 million dialysis patients worldwide. The majority (~80%) of these dialyzers are equipped with synthetic polymeric membranes: no other application in membrane technology has reached this advanced level of development. Production of dialyzers is a continuous process, whereby membrane production is integrated into the manufacture of the dialyzer. This large membrane-surface area requires highly automated manufacturing plants to produce high-quality and safe products. The continuous request for increased removal rates of uremic toxins and improved biocompatibility results in new membrane generations. For optimized application, the inner diameter of the hollow-fiber membranes range from 180 to 220 µm. Synthetic polymeric membranes have a wall thickness of between 30 and 50 µm. The design of the membrane and the dialyzer are crucial. Optimal mass transfer between blood and dialysate has to be guaranteed, and this is also influenced by the dimensions of the membrane surface.

In the second part new possibilities to tailor membrane separation characteristics will be presented. In addition to the standard dialysis membranes more advanced High Cut-Off membranes have been developed that allow effective removal of substances in the molecular weight range between 25 and 50 kDa (middle molecular weight substances).This unique membrane development (High-Cut-Off membrane) gives access to a whole group of new extra-corporeal therapies. One example are patients with multiple myeloma suffering from elevated serum concentrations of monoclonal free light chains (FLCs), which can result in irreversible renal failure secondary to cast nephropathy. In-vitro and in-vivo results using a High-Cut-Off membrane will be presented. Kappa and lambda FLC sieving coefficient and clearance were studied in-vitro in hemodialysis and hemodiafiltration mode. The ability of the membrane to reduce serum free light chain levels in-vivo was investigated in a clinical pilot study with patients who presented with dialysis dependent renal failure and multiple myeloma. Clearance rates of both FLCs were many times higher using the high cut-off membrane compared with a conventional High Flux dialysis membrane.

In the third part of this presentation membrane use in regenerative therapies applying tubulus and stem cells will be discussed. Regenerative therapies using stem cells represent a promising and innovative alternative to conventional symptomatic therapies for the causal treatment of chronic and acute diseases. Besides using kidney-derived cells in extracorporeal systems to replace cellular kidney function, there are several approaches to the use of stem cells. Membranes have also been utilized in cell-based extracorporeal systems to treat patients with kidney disease. In addition, specialized, highly efficient membranes have been developed for stem-cell growth in hollow-fiber bioreactors as a technological prerequisite for cellular therapies and other applications.

ICOM1696

Polyvinylalcohol Composite Nanofiltration Membranes Resistant to Oxidizing Agents

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Thin-layer composite polyamide (PA) membrane is accepted as a reference for nanofiltration (NF) process due to its excellent saline rejection and hydraulic permeability. However, one of the major factors reducing the overall performance of the NF processes is fouling, which may cause irreversible reduction in productivity. In particular, biofouling is the one of the most serious fouling problems and polyamide membranes are particularly susceptible to it.

Biofilm growth can be controlled by addition of biocides, especially those with oxidizing characteristic. However PA membranes are quickly degraded when exposed to oxidizing agents, such as aqueous chlorine, commonly used in water disinfection. It is known that after exposition to 500 ppm.h to chorine the salt rejection decreases and the water flux increases. In order to protect the
membrane, the chlorine should be completely removed in the pre-treatment stage, increasing costs and allowing the growth of microorganisms throughout the system and, especially, the biofilm formation on the membrane surface.

New polymer material with enhanced resistance to fouling and oxidation is subject of many research works. By far, the simplest technique to prepare a composite membrane is the dip-coating using a diluted polymer solution, which allows the use of several polymers to prepare the top layer. Polyvinylalcohol (PVA) is an attractive material because it is an hydrophilic polymer with low fouling potential, has chemical stability, low cost and it can be easily deposit on top of many existing porous supports.

The aim of this work is to investigate the preparation of nanofiltration composite membranes by using PVA as top layer, prepared by dip coating technique. The proprieties of the PVA dense layer were investigated by varying the hydrolysis degree of PVA, 80 and 99%, and by using different crosslinking agents and temperatures. The characterization of crosslinked PVA was performed by DSC, TGA and FTIR analysis, as well as by determination of the water swelling degree.

Ultrafiltration and microfiltration hollow fibers were used as porous support for the PVA selective layer. The supports and the composite hollow fibers were characterized by SEM.
The permeation performance was determined in a lab experimental set-up with a sodium sulfate solution, after and before chlorite exposure. The composite hollow fibers showed sodium sulfate rejection around 98% and much higher resistance to chlorine than commercial PA membranes.

ICOM1752

Preparation of PVDF membranes with inter-connected pores by a combination of Nips and Tips

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PVDF flat sheet membranes with highly inter-connected pores were fabricated via a combination of Tips (Thermally induced phase separation) and Nips (Non-solvent induced phase separation). The casting solution at a thermodynamics meta-stability was prepared by using the triethyl phosphate (TEP) as the solvent. The asymmetric ultra- and symmetric micro-filtration membranes were prepared by adjusting the polymer concentration and quench bath composition, respectively. Finger-like pores were totally eliminated and highly inter-connected pores were formed in both membranes. The morphology, crystallization, and mechanical strength of PVDF membranes were characterized by Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and tensile strength testing respectively. The mean pore size and pore size distribution of PVDF membranes were investigated by a bubble-point porometer. Pure water flux and fouling resistance to protein of the membranes were investigated. All results showed that all PVDF membrane possessed highly inter-connected pores and narrow pore size distributions. The ultra- and micro- filtration PVDF membrane exhibited a pure water flux of 120 and 1860 L/m^2 h with the corresponding mean pore size of 0.11μm and 0.26μm respectively.

ICOM379

Chemistry in a spinneret

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"Chemistry in a spinneret" is a novel concept of simultaneous membrane formation and chemical modification in a one-step spinning process for fabricating assymetric composite hollow fiber membranes. This method is based on a controlled crosslinking reaction between the membrane forming polyimide P84 and the crosslinking agent poly(ethylene imine) (PEI) dissolved in the bore liquid (Figure 1). Based on the interplay between phase inversion and crosslinking, the membrane morphology, chemistry, charge and hydrophilicity can be tuned.

In fact, two different types of membranes can be fabricated depending on the composition of the chemically active bore liquid, namely the ratio solvent/nonsolvent, here N-methylpyrrolidone (NMP)/water.

The first type is a membrane with a dense, crosslinked, gas selective inner layer (thickness in the range 1.4-6.1 µm, Figure 2A) having a mixed gas CO_2/N_2 selectivity ~12 in presence of water vapour. This membrane is formed when the ratio NMP/water is high (e.g. 8:1). Higher amount of NMP in the bore liquid delays phase inversion giving time for crosslinking with PEI. This results in the formation of dense crosslinked skin which hinders the flow of PEI further through the wall of the fiber. We obtain a hollow fiber having a crosslinked inner layer insoluble in NMP, whereas the rest of the membrane is basically P84 dissolving in NMP. The second type of membrane is obtained when the ratio NMP/water in the bore liquid is low (e.g. 1:8). Phase inversion happens rapidly and a porous structure is formed before the crosslinking can occur (Figure 2B). In this case, PEI transport across the wall takes place and the entire fiber is crosslinked becoming solvent resistant. The pure water flux of such a membrane is about 45 l/(m^2 bar h) and this membrane is selective for the separation of similar size proteins, bovine serum albumin (BSA) and hemoglobin (Hb), due to the positive charge of the membrane caused by the free amine groups of PEI which were not used for the crosslinking. The isoelectric point of the new membrane is basic (pH 9.3), much higher than that of the P84 membrane (pH 3.75).

A systematic study of various batches of hollow fiber membranes produced with different compositions of dope solution, bore liquid and shell liquid shows that the thickness of dense crosslinked layer can be controlled by concentration of PEI in the bore liquid and the ratio solvent/nonsolvent in the bore liquid, shell liquid and dope solution.

The new method of fabricating composite hollow fiber membranes is simpler and less time consuming in comparison to other multi-step techniques. It may open perspectives towards fabrication of novel gas separation, nano- and ultrafiltration membranes. The concept of chemistry in a spinneret might be especially attractive in the field of solvent resistant membranes being a technique that is less expensive and more environmental benign as it does not require large amounts of solvents, normally involved in the post-treatment crosslinking.

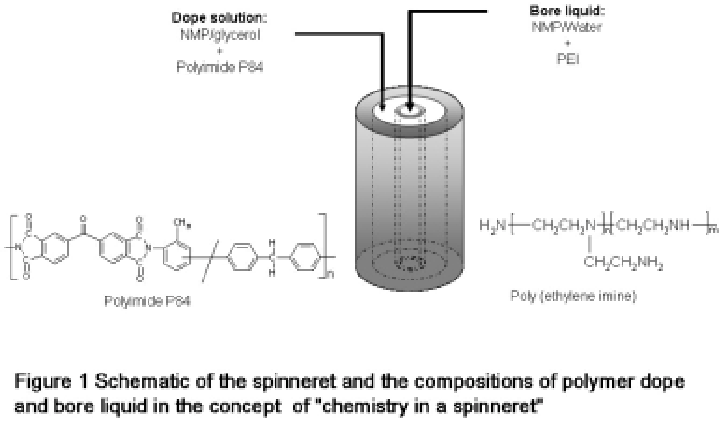

Figure 1 Schematic of the spinneret and the compositions of polymer dope and bore liquid in the concept of "chemistry in a spinneret"

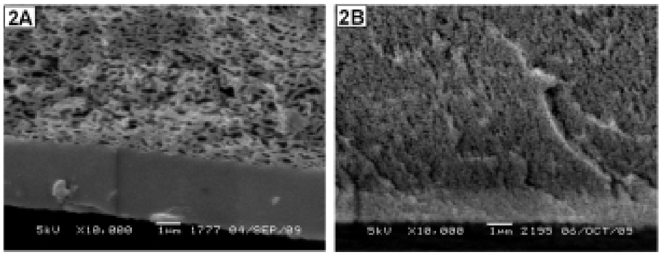

Figure 1 SEM images of the bore side of the hollow fiber membranes produced with bore liquid composed of: (A) 20 % PEI, 70 % NMP, 10 % H_2O, (B) 10 % PEI, 10 % NMP, 80 % H_20

Metal membranes

ICOM1824

Porous stainless steel hollow fibers with shrinkage controlled small radial dimensions

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Metals have distinct properties that can be beneficial for use in membrane science. Thin dense metal films, in particular palladium, in theory can display infinite selectivity for hydrogen over other gasses. Porous metals do not display such high selectivity in molecular separations, but have unparalleled mechanical, chemical, and conductive properties that make them suitable for use as membrane support in applications were other materials fail. In this work we present a method for cost effective fabrication of porous stainless hollow fiber membranes with an outer diameter that can be regulated down to ~250 µm. Such small radial dimensions are comparable to those of typical polymeric hemodialysis and gas separation hollow fiber membranes, and allow a very high surface-area- to-volume ratio.

Polymeric hollow fiber membranes are made in large quantities via the dry-wet spinning process, in which a polymer solution is pressed through a spinneret and coagulated in a bath of non-solvent. To illustrate how well established this process is, millions of membrane modules are produced annually for hemodialysis, each containing approximately one kilometer of hollow fiber. Despite the low price of such modules, typically $10-20, deficiencies in their production process can result in the death of a dialysis patient.

Successful attempts have been reported for fabrication of porous ceramic hollow fibers, made via dry-wet spinning of a polymer solution containing inorganic particles followed by heat treatment. During thermal treatment the polymer is removed and the ceramic particles are sintered together. The resulting fibers generally have moderate mechanical strength. In this work, we show that replacing the ceramic particles with stainless steel results in fibers that have superior mechanical properties and allow for welding and brazing.

After dry-wet spinning, the polymer fibers containing the stainless steel particles display a morphology that combines sponge like structures and macro voids. This morphology is related to the dynamics of the phase inversion process and can be tuned by changing the spinning conditions and the composition of the spinning mixture. The final fiber properties, such as the structure on the micrometer scale and the related pore size distribution, are strongly affected by the sintering temperature. For relatively high particle loadings, similar to those reported for ceramic particles in other studies, the morphology of the stainless steel fibers is preserved during thermal treatment, apart from some shrinkage due to densification. For relatively low particle loadings, thermal treatment results in extensive shrinkage of the fiber. The shrinkage can result in extraordinarily small radial dimensions, and occurs predominantly at temperatures just exceeding the glass transition temperature. Here, under the right conditions, dynamics of surface energy driven viscous polymer flow allow for disappearance of macro void volume.

ICOM1143

PdCu membranes by electroless plating for hydrogen purification

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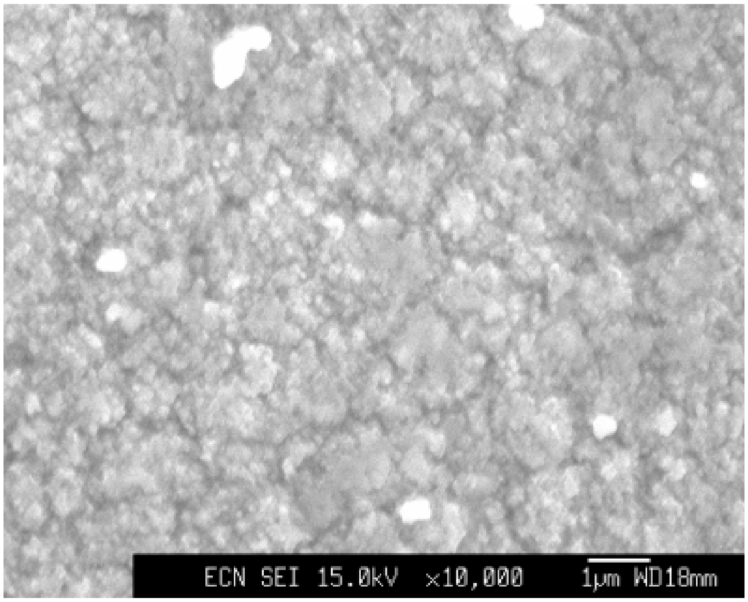
PdCu membranes by electroless plating for hydrogen purification

Hydrogen production is increasing as it is a valuable commodity in refining and petrochemical processes and as it is also a promising energy carrier, via fuel cells, in the automobile sector to reduce air pollution. In this scenario, hydrogen selective membranes are viable and promising candidates for hydrogen purification processes due to their high permeability, specially the Pd-based membranes. Pd alloy membranes have been studied as embrittlement phenomena, encountered for pure Pd membranes, is minimized. The PdCu alloy is being widely studied due to its better resistance to hydrogen sulphide and sulphurous component. Their permeance values are in the range of the Pd ones, or even higher.

PdCu membranes were prepared through sequential electroless plating over Pd membranes with ceramic tubular supports. Different PdCu membranes, with Pd content between 45 and 77 wt% and a total metal layer between 0.5 and 1.9 µm of thickness, were prepared varying the plating time. The mixture of the Pd and Cu was necessary to obtain a permeable membrane, as the Pd is the one with the ability of dissociating hydrogen. This alloying step was performed in two ways, with and without monitoring the hydrogen flux during alloying to compare and establish the required alloying time to obtain high permeance membranes. Finally, permeance tests were performed at different pressures; including temperature cycles in hydrogen and nitrogen to observe membrane stability. The hydrogen permeance values of the membranes were high, between $1.5\cdot10^{-3}$ and $4.5\cdot10^{-3}$ mol/(s·Pa$^{0.5}$·m^{2}) and stable, even after the temperature cycles in hydrogen.

	wt% Pd	PdCu or Pd ayer (micron)	T (K)	Permeability mol/smPa^{n}	Selectivity	n	Ref.
M1-PdCu	63.0	1.025	673	1.8E-9	>300	0.653	c
M2-PdCu	64.5	1.450	673	2.1E-9	>400	0.645	c
M3-PdCu	44.4	0.942	673	9.9E-11	>100	0.748	c
M4-PdCu	59.8	1.000	673	9.2E-10	>450	0.65	c
M5-PdCu	76.9	0.934	673	1.4E-9	>1000	0.65	c
PdCu/PSS	90	5	673	2.1E-9	<4	0.6	[Gao]
PdCu/PSS	59	10	673	7.7E-13	∞	1	[Gao]
PdCu/Al2O3	92	5.0	753	1.4E-11	>1000	1	[Zhang]
PdCu/Al2O3	95	7.0	753	1.6E-11	900	1	[Zhang]
Pd		0.35	673	1.1E-12	1140	1	[Li]
Pd		10	740	2.8E-9	970	0.65	[Li]
Pd		1	683	1.3E-11	400	1	[Keuler]

Surface morphology and metal layer of the prepared membranes were characterized with Emission Scanning Electron Microscope (SEM) images. The alloying of the metal was analysed measuring its composition with an electron Dispersive X-Ray equipment (EDX). SEM images were taken after the copper plating, after the alloying and after the hydrogen permeance tests to analyse the effect of each step on the surface morphology. Alloying of the copper increases the surface roughness and big metal particles occur on the surface.



The electroless plating method was adequate for thin PdCu metal layer membrane preparation as the resulting membranes showed high hydrogen permeability and were stable even when temperature cycles were performed in hydrogen atmosphere. The plating step was easy and quick and the characterization of the membranes using the SEM images provided valuable information about the influence of the metal alloying and hydrogen permeance on the surface morphology.

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ICOM1875

Pre-combustion fuel decarbonization with pure palladium and palladium alloy membranes

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Integration of Pd or Pd alloy membranes with reforming or WGS reactors, for pre-combustion fuel de-carbonization, is attractive for the reduction in CO2 emissions. Recovery of CO_2 at high pressure and high purity (>90 mol%) as well as carbon conversions in excess of equilibrium limits may be achieved using various process schemes [1, 2]

CRI/Criterion is in the process of commercializing Pd and Pd alloy membranes on sintered porous metal supports. Successful evaluations of CRI/Criterion H_2 separation membranes in membrane steam reformers and as high temperature membrane separators have been performed by CRI/Criterion [3 - 6], and by third parties [7].

Figure 1 shows an extended trial of a CRI/Criterion Pd membrane (15cm L x 2.5cm OD) separating H_2 from gas blends (430-450°C, DP 18 – 45 bar). The feed gas composition simulated the partially cooled unshifted product from conventional methane steam reforming: 51.6% H_2, 29.4% H_2O, 12.5 - 14.9% CO_2, 0 - 2.4 % CO and 4.1% CH_4. The pressure was varied to simulate pressure fluctuations in a plant environment. The changes in pressure were carried out in a few seconds.

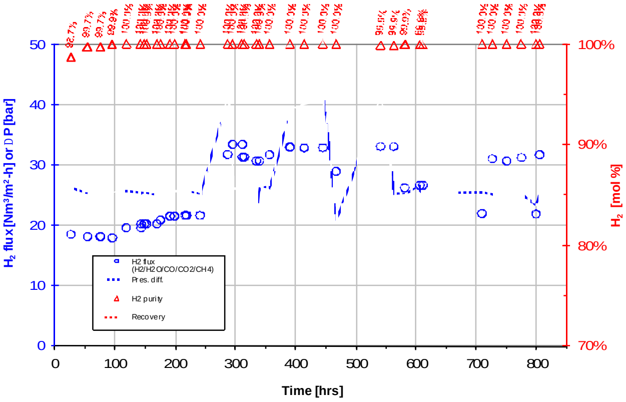

Figure 1: 800 hrs Pd membrane trial under realistic simulated process conditions

The same membrane was then subjected to changes in temperature to demonstrate the robustness to temperature fluctuations as shown in Figure 2

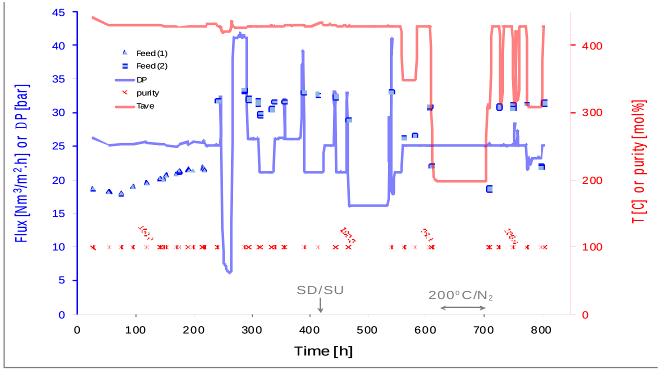

Figure 2: Temperature cycling to demonstrate temperature stability of Pd membranes

Figure 3 shows the hydrogen flux for a Pd membrane for which CO was introduced into the feed gas in a two step process. The compositions in the feed were identical to those tested in the past for CO inhibition. Each time the CO feed was increased; the CO2 in the feed was reduced to keep the total molar feed constant. The results indicate that there was no significant CO inhibition for Pd membranes under the conditions studied (430°C and up 1.3 bara CO partial pressure).

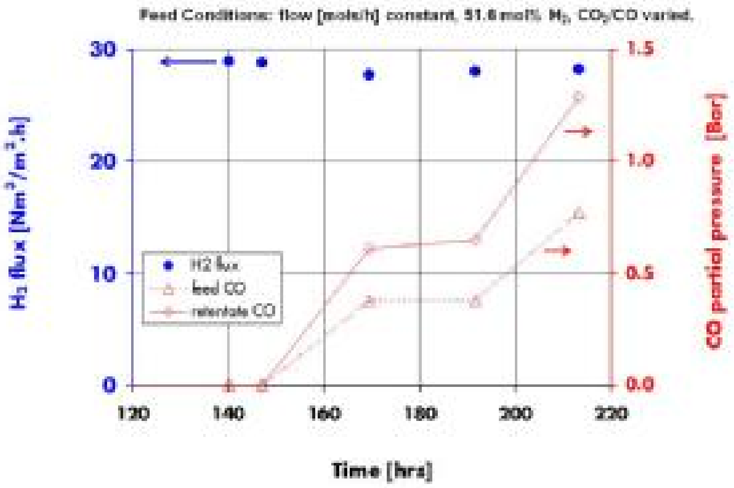

Figure 3: CRI/Criterion Pd membrane does not suffer from CO inhibition (430°C and up 1.3 bara CO partial pressure). Recent on-going tests at 430°C, 29 bar ΔP with a CRI membrane in a 40% H_2, 19% N_2, 41% H_2O mixture (total feed flow of 1500 SLPH) show a remarkable performance over 5000 hours at present delivering 99.99 % pure Hydrogen in figure 4.

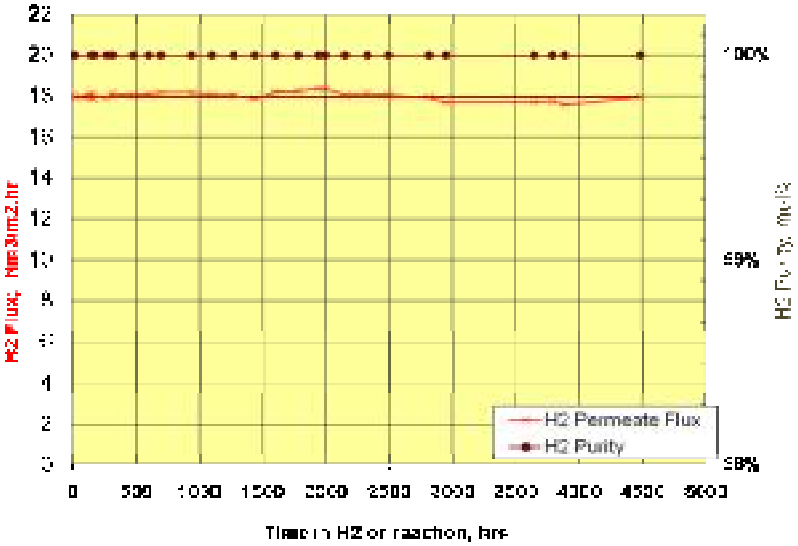

Figure 4 Long term stability testing of a CRI Pd membrane in steam, nitrogen, hydrogen mixture.
CRI Membranes tested in the last two years have shown continued robust performance over long periods of time as indicated in Table 1.

Membrane No.	Test Period (hrs.)	% H_2 Purity at end	Permeate Flux ($Nm^3/m^2/hr$)	Effluent Flux ($Nm^3/m^2/hr$)	Temperature, ˚C	Pressure, barg	Conditions/ temp gas composition
1	7000	98.16	15.07-17.96	9.10-11.39	430-450	30	(H_2, N_2, steam),(CO,CO_2,CH_4,H_2, steam)
2	4000	99.3	17.93-18.41	8.74-9.22	430-450	29-40	H2, N2, steam
3	2300	99.75	9.11-9.35	2.32-2.45	500-505	28.6-29.4	Steam methane reforming
4	5000	100 in progress	17.89-18.16	9.23- 9.42	430-450	28.85-29.15	H2, N2, steam
5	900	99.94 in progress	15.94-22.99	7.1-11.07	430-450	29	CO,CO2,CH4,H2, steam
6	800	100	21.84-33.09	6.15-23.6	430-450	29-45	CO,CO2,CH4,H2, steam

Table 1: Overview of long term testing of CRI Pd membranes

CRI/Criterion has produced membranes of this type as large as 2"OD by 48"L, by welding two separate 24"L sections. These membranes can be produced with a hydrogen permeance in the range of 40-70 [$Nm^3/m^2.h.bar^{0.5}$]. Both the hydrogen flux and the separation selectivity is stable at temperatures of 300-500°C and differential pressures of 26-42 Bar.

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ICOM955

Characterization of monometallic and bimetallic iron-based nanoparticle films

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There has been a growing interest in using iron-based nanoparticles in water treatment due to their catalytic properties. Monometallic and bimetallic iron nanoparticles are reactive in an aqueous system and can be designed for targeted removal of specific organic and inorganic water contaminants. Iron metal nanoparticles undergo surface oxidation through reactions with both water and oxygen and produce reactive species that are then utilized to oxidize or reduce a specific contaminant. Through the oxidation process, iron metal is oxidized to ferrous iron, which in turn can participate in the Fenton reactions and produce reactive oxygen species and hydroxyl radicals. Iron metal oxidation also produces hydrogen gas (through reaction with water), which can react with organic compounds through reduction reactions. The catalytic properties of iron nanoparticles can be enhanced through particle stabilization by organic chelating compounds and through secondary metal coatings. Both organic stabilizers and secondary metals (*e.g.*, palladium, copper) affect the oxidation of the nanoparticles and ultimately, nanoparticle reactivity.

For reactive nanoparticles to be used in water treatment, the particles must be contained or immobilized within the treatment system. One potential method to contain the nanoparticles is to incorporate the particles into polymeric membranes; ideally, these mixed matrix membranes would be designed such that the membrane continues to function as a physical barrier to filtrants, while the reactive nanoparticles degrade or adsorb dissolved contaminants that typically pass through conventional membranes. However, the first step towards the use of reactive nanoparticles for water treatment is to understand how to control nanoparticle formation, aggregation, and oxidation in an aqueous system.

This research investigates iron nanoparticle synthesis and oxidation for monometallic iron nanoparticles and bimetallic iron-palladium nanoparticles. Several organic stabilizers are compared in their ability to control particle aggregation and size during nanoparticle synthesis, as well as control particle oxidation over time. Electrosteric interactions are thought to be the primary mechanism for particle stabilization when the particles are coated with organic compounds containing carboxyl-or phosphate-functional groups. Techniques such as thermogravimetric analysis and electron microscopy are used to evaluate particle (QCM) morphology and stabilizer surface coverage on the nanoparticles. Quartz crystal microbalance techniques are used to evaluate the mass change of the nanoparticles during surface oxidation in an aqueous environment. QCM crystals are coated with nanoparticle-stabilizer films, and the changes in crystal resonant frequency and frequency dissipation allow quantification of nanoparticle oxidation rate and film viscoelasticity, respectively. Finally, x-ray diffraction and electron paramagnetic resonance (EPR) are used to evaluate changes in particle crystallinity, magnetism and radical production as the particles are oxidized.

Electromembrane processes 2

ICOM1842

Research activities on electro-membranes and the related processes in China

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The development of synthetic ion exchange membrane (electro-membrane) reported by Juda and McRae[1] in 1950 stimulated both commercial and academic interest in such membranes and the related processes. Nowadays, synthetic ion exchange membranes have been improved by various methods and have many practical uses. The processes based on electro-membranes such as diffusion dialysis, conventional electrodialysis, Bipolar membrane dialysis, etc., can realize some new synthesis processes to achieve the maximal utilization of resources and pollution prevention. They can also be flexibly coupled with many other technologies and obtain a better function by means of technological symbiosis and can realize closing loops when inputting waste materials as the feedstock and carrying out production, resource regeneration and effluent treatment at the same time. In this report, the recent development on electro-membranes and the related processes in China will be reported and some researches on acid/salt separation membranes (anion exchange membrane), base/salt separation membrane (cation exchange membrane) and reaction/separation membrane (bipolar membrane) will be given as examples.

Acknowledgements
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ICOM191

Ion exchange membrane electrodialysis of saline water and numerical analysis

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1. Introduction

An ion exchange membrane electrodialysis process is classified to a continuous, a batch and a feed-and-bleed process. The electrodialysis program of these processes was developed in the previous investigations[1–3)]. In this investigation, a practical-scale electrodialyzer was operated for concentrating seawater. The performance of the electrodialyzer was computed with the electrodialysis program inputting the same conditions applied to the electrodialysis operation. The reasonability of the program is discussed by comparing the operating performance of the electrodialyzer with calculated one.

2. Experiment

45 or 90 pairs of ion exchange membranes; Aciplex K172/A172 or K182/A182 (Asahi Chemical Co.) were integrated in an electrodialyzer (Membrane area (S) 48.5 dm^2 = 50 cm width (b) ×97 cm length (l), distance between the membranes (a) 0.05 cm). Establishing a continuous process, seawater (Temperature T □) was supplied to desalting cells and applied current density I/S (I; electric current). After steady state was realized, cell voltage V_{cell} was measured. Salt concentration in the desalting cells C' and that in the concentrating cells C'' was analyzed. The electrodialysis operation was repeated changing T and I/S incrementally.

3. Electrodialysis program

The electrodialysis program of the continuous process consists of the following five steps;

Step 1 Mass transport (Fig. 1)

Step 2 Current density distribution (Fig. 1)

Step 3 Cell voltage (Fig. 1)

Step 4 NaCl concentration in a concentrated solution and energy consumption

Step 5 Limiting current density

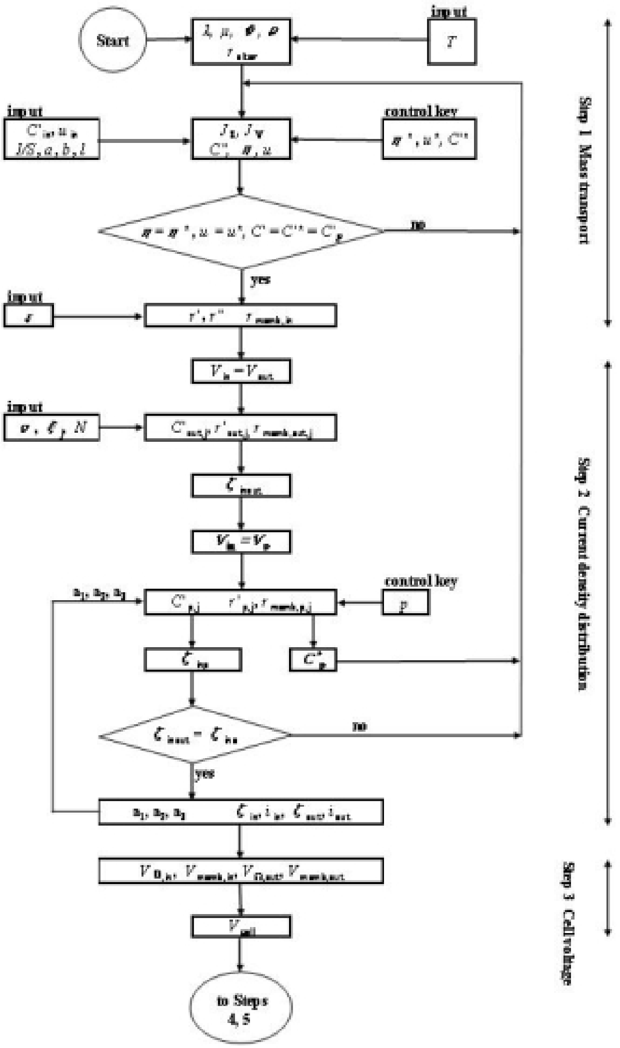

Fig. 1 Simulation of performance of a continuous electrodialysis process (Steps 1 - 3).

4. Resuts and discussion

The observed performances of the electrodialyzer X_{obs} obtained by the experiment are plotted against calculated ones X_{cal} obtained by the simulation taking seawater temperature T and current density I/S as parameters. X includes; ion flux across a membrane pair J_S (Fig. 2); solution flux across a membrane pair J_V; cell voltage V_{cell}; energy consumption E; etc. The observed values are generally the same to the computed ones. Current density distribution, electric resistance of a cell pair, limiting current density etc. are discussed.

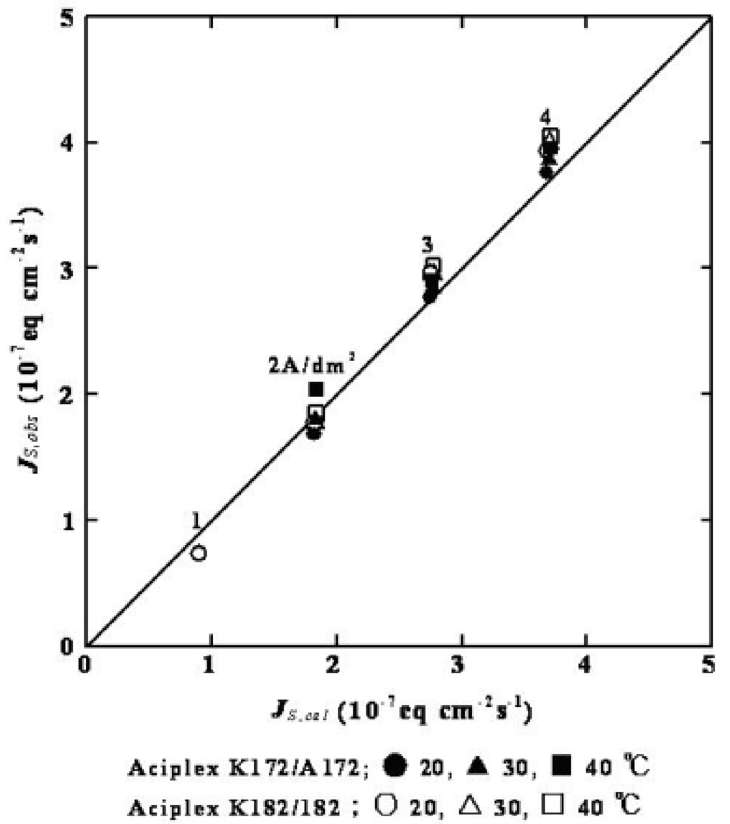

Fig. 2 Ion flux across a membrane pair.

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ICOM1152

Impact of the interactions between ion exchange membranes and sugar/electrolyte solutions on the mass transfer of sugars

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The need of efficient processes, like membrane operations, and specially nanofiltration and electrodialysis, to treat liquids containing together mineral species and organics is more in more important. However, it was recently pointed out that the presence of salts can change significantly the process performances because of the resulting modification of the organic solutes transfer through the membrane [1,2]. These effects can be due to different mechanisms, not yet completely understood. For instance, with polymeric ion exchange materials, like those used in electrodialysis, the electrolyte composition can change the membrane characteristics because of membrane/solute interactions [3]. On the other hand, the characteristics of organic solutes, like sugars, are modified as well when changing the electrolyte composition [4]. Obviously, the process performances are fixed by the coupling of these effects, depending on the fluids composition, the membrane characteristics and the operating parameters. Further investigation is required to push the implementation of membrane processes for new applications as well as for improving existing ones with respect to such criteria like environmental impact or product quality.

In this work, we studied the impact of the membrane/electrolyte interactions on the transfer of sugars through ion exchange membranes. The experimental study has been carried out in a diffusion regime with CMX or AMX membranes. Different sugars (xylose, glucose, sucrose) were used and different electrolytes (NaCl, NH_4Cl, Na_2SO_4, $CaCl_2$ and $MgCl_2$) have been selected with respect to their valence, since it is linked to their hydration. A dedicated experimental procedure was used to distinguish between the effects due to membrane/electrolyte interactions and those expected to be due to solute/electrolyte interactions in solution. The membranes are first soaked until equilibrium in the corresponding solution of electrolyte in order to dissociate both effects. In the conditions investigated here, it was observed that the modification of the transfer of sugar through the ion exchange membranes is mainly due to the resulting change of the membrane material characteristics, coming from membrane/electrolyte interactions. It was shown that the sugar transfer can vary up to a factor 5, depending on the electrolyte composition, the sugar and the membrane
considered. A qualitative correlation has been also established between the hydration scale of the membrane counter-ion and the mass transfer of sugars.

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ICOM937

Pre-desalination with electrodialysis for SWRO

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Although seawater reverse osmosis (SWRO) is currently the only non-thermal desalination process in practical use, its characteristics make it difficult to approach the ideal reversible process. SWRO has a low water recovery (determined by the osmotic pressure) and relatively high energy consumption. A breakthrough in development of SWRO membranes can not be expected; at maximum a recovery of 40-60% could be obtained with membranes that can stand ultra-high pressures. In our project, an alternative development of desalination is introduced in which the osmotic pressure difference is reduced prior to SWRO with use of electro-membranes, like in electrodialysis (ED). ED has overlooked distinctive and complementary assets compared to SWRO enabling an operation close to the reversible limit, at least to the first extent of the desalination process. ED is an ideal pre-desalination step as: (i) the water recovery is not limited by a driving force (e.g., pressure), (ii) the specific energy consumption is directly proportional to the salt removal, (iii) the process economy allows low ionic fluxes and thus low irreversible losses, (iv) the system can be operated with infinitesimal changes in salinity (a pre-requisite for reversibility), and (v) the pre-treatment efforts can be kept limited. In our presentation, we evaluate this hybrid ED-SWRO scheme by using a validated model.

Membrane characterization 4

ICOM1832

Membrane characterization: it just keeps on getting better

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Working in membrane science and technology requires knowledge across multiple scales and physical principles. Thus, characterization is a broad rubric which encompases several goals including: properties of the starting structure, performance properties during use, and material properties after use. The most common measurements made in characterization are transport properties (for example, hydraulic permeance, colloidal particle sieving, solute permeability, and solute solubility); structural characteristics (such as, pore size distribution, pore shape, porisity gradient through thickness, and porosity); surface properties (that is, charge, composition, energy, roughness); as well as, a variety of application-specific items, such as, solute-membrane affinity, electrical properties, and catalytic activities. To these ends, membranes are probed with photons, phonons, electrons, positrons, and all manner of waves. And the advances in characterization result from improvements in instruments, computational hardware and software; innovations on the part of individuals and large groups of investigators; and lower economic hurdles for access to specialty equipment. This presentation will provide an overview of the general activities and resources being applied towards characterization in membrane science and engineering. I will identify some interesting activities and challenges within several core areas of interest including porosimetry, surface analysis and fouling, visualization, and material properties.

ICOM1326

Nanoprobe imaging molecular scale pores in nanofiltration polymeric membranes

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Nanofiltration is used in many membrane separation processes such as desalination, diafiltration, extraction, or organic solvent nanofiltration (OSN). Over the past decade OSN has been attracting a growing number of researchers and industrial enterprises due to its unique ability to achieve molecular separation in harsh solvent media. Integrally skinned asymmetric (ISA) P84 co-polyimide membranes formed by phase inversion have shown good separation properties and stability in various organic solvents[1-2].

At present the physically examination of nanofiltration membranes by imaging, in terms of pore size and nanostructure, has proved elusive. In particular, no technique has been developed to “see” nanopores with dimensions in the 0.5 − 2 nm range. These pores are crucial in the functional performance of nanofiltration membranes, and understanding the nanoporous architecture of these materials might lead to improve tailored design of membranes for specific separation processes.

Imaging of nanoporous polymers at sub-nanometer resolution is generally believed to be very difficult. A possible characterization technique could be transmission electron microscopy (TEM), which can operate within the required resolution. However, the major problem in imaging at this scale is insufficient electron contrast of polymers, which has made distinguishing their structural phases at the nanoscale practically infeasible.

Our proposed solution to overcome this problem is *in-situ* lodging of high electron contrast nanoprobes into the membrane pores, and so by mapping of these marker particles using TEM, polymer nanostructures could be imaged at magnifications down to almost the macromolecular level. For this purpose we fabricated osmium dioxide (OsO_2) nanoparticles having the mean size of 1.06 ± 0.23 nm, dispersed them in organic solvent to achieve homogenous medium and filter through a range of OSN P84 co-polyimide membranes. Given that these probes specifically target the nanofiltration transport-active pores, they can be mapped under the TEM, and thus pore size distribution and even polymer chain structure can be evaluated and correlated with membrane functional characteristics such as flux and rejection.

OSN P84 co-polyimide membranes with a range of molecular weight cutoffs (MWCO) have been used in this work. The pore size is found to correlate well with membrane separation performance (Fig.1); membranes with measured MWCO of 400, 1100, and 1400 g mol^{-1} were analyzed using this method to have pore sizes of 0.69 ± 0.16 nm, 1.22 ± 0.25 nm, and 1.30 ± 0.23 nm, respectively. Furthermore, we show by analyzing nanoparticle sizes in feed and permeate solutions, that the separation mechanism in nanofiltration is based on sieving of the permeating solutes by their size.

In addition to the pore size, the technique can characterize a type of transport, measure the skin layer thickness, detect dead-end pores or nano-sized defects (Fig. 2), and have a potential to analyze morphologies of various nanoporous permeable membranes.

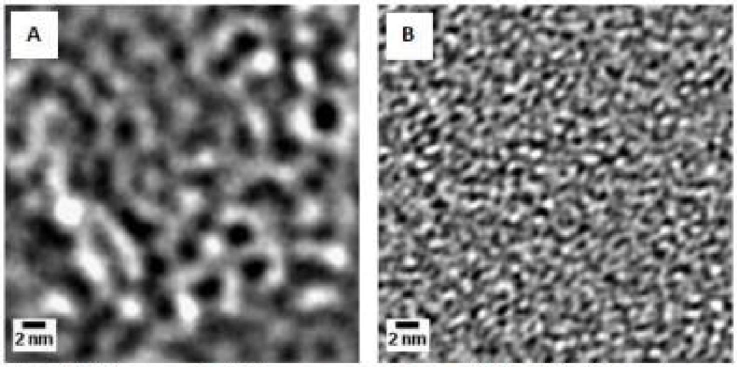

Fig.1. TEM images of skin layer cross sections of P84 polyimide membranes revealing differences in nanoporous structures with regards to membrane MWCOs. (A) membrane with MWCO of 1100 g mol^{-1}. (b) membrane with MWCO of 400 g mol^{-1}.

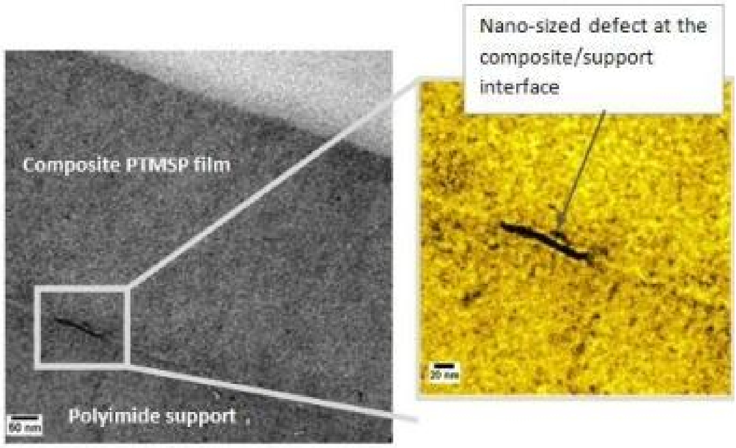

Fig. 2. TEM cross sectional images of composite Poly[(1-trimethylsilyl)-1-propine] (PTMSP) supported by P84 polyimide membrane; an example of capability of the nanoprobing technique in detection of nanoscale defects at the composite-support interface.

1 See-Toh, Y. H., Silva, M. & Livingston, A. G., *Journal of Membrane Science* **324**, 220-232 (2008).

2 See Toh, Y. H., Lim, F. W. & Livingston, A. G., *Journal of Membrane Science* **301**, 3-10 (2007).

ICOM630

Towards Real-time, Non-invasive and Sensitive Characterization of Forward Osmosis Process

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In contrast to numerous modern approaches to study the membrane structure, most of which are considered invasive and lack of sensitivity, this paper presents a feasible non-invasive and sensitive analytical technique for the Forward Osmosis (FO) process: real-time characterization can be realized by measuring membrane electrical properties using electrical impedance spectroscopy (EIS). The EIS instrument measures conductance and capacitance across the membrane sample over a wide range of frequencies, deriving the system impedance based on the Maxwell-Wagner model. Each layer of the membrane can be represented by a parallel combination of a capacitance and a conductance pathway in series (Coster, Kim et al. 1992; Kavanagh, Hussain et al. 2009). The effects of draw solution concentration and membrane orientation on concentration polarization (CP) and fouling were systematically examined using INPHAZE™ EIS, with varying frequencies ranging from 10^{-2} to 10^{5} Hz. Each EIS experiment comprised three spectra and each run was repeated to ensure consistency and reproducibility.

Our results show that the EIS was able to detect internal concentration polarization (ICP), a unique phenomenon in FO that diminishes the osmotic driving force. Results also indicated that a higher draw solution concentration led to a more discrete and smaller impedance pattern due to higher water flux generated and more severe internal CP at increased draw solution concentration. Under the same draw solution concentration, when the orientation was the active-layer-facing-the-feed-solution (AL-FS), the impedance of overall system was smaller. This observation is consistent with the more severe internal CP in this membrane orientation. FO membrane also experienced less fouling under the AL-FS orientation, which was indicated by impedance spectra showing a smaller value compared to the active-layer-facing-the-draw-solution (AL-DS) orientation. These results demonstrated the feasibility and potential of using EIS as a novel approach to evaluate FO process and characterize FO membrane.

Reference:

Coster, H. G. L., K. J. Kim, et al. (1992). "Characterisation of ultrafiltration membranes by impedance spectroscopy. I. Determination of the separate electrical parameters and porosity of the skin and sublayers." Journal of Membrane Science 66(1): 19-26.

Kavanagh, J. M., S. Hussain, et al. (2009). "Fouling of reverse osmosis membranes using electrical impedance spectroscopy: Measurements and simulations." Desalination 236(1-3): 187-193.

ICOM1132

Comparison between characteristics of depth profiles for conventional and spin-coating interfacially polymerized membranes probed with variable monoenergy slow positron beam

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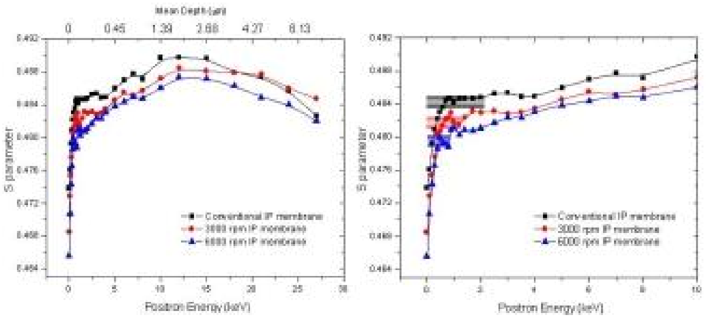
The following will be discussed in this study: both the fundamental physical and chemical structures of thin-film composite (TFC) membranes fabricated using the conventional and spin-coating interfacial polymerization (IP) techniques in which a selective layer of polyamide was formed onto a microporous surface-modified polyacrylonitrile (*m*PAN) support. The TFC membranes were characterized with respect to their thickness (using variable monoenergy slow positron beam (VMSPB)), chemical composition (using attenuated total reflectance-Fourier transform infrared (ATR-FTIR)), and morphology (using contact angle device, scanning electron microscopy (SEM) and atomic force microscopy (AFM)). Free-volume parameters and obtained layer thicknesses were correlated with the flux and the water concentration in the permeate which were determined from the pervaporation (PV) separation of 90 wt% aqueous ethanol solution. It was found that the water concentration in the permeate was mainly controlled by the free-volume properties of the polyamide skin layer. The active layer of polyamide TFC membranes formed through spin coating was thin and dense than conventional IP, and this was supported by the data obtained with the use of VMSPB.



S parameter as a function of positron incident energy keV (mean depth) at different interfacial polymerization method.

Membrane and surface modification 4

ICOM1830

Reduction of organic and biofouling in water treatment membranes

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Membrane technology is widely applied for water treatment and receiving more attention. Especially reverse osmosis (RO) membranes have been getting more application in the field of drinking water treatment associated with their advantages including superior water quality, easier control of operation, lower cost and maintenance. Nevertheless, one of the serious problems arising during membrane filtration is membrane fouling by natural organic matter or bacteria. Membrane fouling can cause an increase in hydraulic resistance and a flux decline, increase operation and maintenance costs, and shorten the membrane life.

Fouling phenomena can be classified into two types, organic fouling and biofouling. The research about the biofouling reduction will be introduced in this presentation. In order to avoid the biofouling of membranes, chlorine is commonly used as a disinfectant. However, such chloro-treatment cannot be applied to the polyamide RO membrane because amide group is easily destoroyed by this treatment. Therefore, the present work aimed at the antifouling of the RO membrane by immobilizing lysozyme as an antimicrobial emzyme. Lysozyme was immobilized onto the RO membrane surface by using condensation reaction, and antibiofouling property of the obtained membrane was investigated.

A polyamide layer was prepared by an interfacial polymerization on a polysulfone support membrane using *m*-phenylenediamine, sodium dodecyl sulfate and 1,3,5-benzenetricarbonyl trichloride. 6-aminocaproric acid was then immobilized on the membrane surface. Next, lysozyme as the antimicrobial enzyme was immobilized on the membrane surface by a condensation reaction using water soluble carbodiimide and N-hydroxysuccinimide. The prepared membranes were evaluated by measuring immobilized lysozyme activity, water flux, NaCl rejection, and SEM observation of the surface morphologies.

The result of the antimicrobial activities showed that no growth of *B. subtilis* occurred after the culture in the medium with the lysozyme-immobilized membrane, while bacteria was observed in the case of the commercial RO membrane. These observations indicate that lysozyme had bacteriolytic activity. The biofouling test showed that antifouling property was clearly improved in the lysozyme-immobilized membrane. This suggests that lysozyme on the membrane surface killed the bacteria and prevented from the biofilm formation. In this work, lysozyme was successfully immobilized onto the RO membrane surface by using condensation reaction without loss of its antimicrobial activity.

The research about the reduction of organic fouling will be also mentioned. To reduce the organic fouling, the membrane coating by layer-by-layer method was carried out. Poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS) were used as polycation and polyanion, respectively. This kind of coating on the RO membrane was very effective to reduce the fouling by BSA, sodium alginate and humic acid.

ICOM1360

Surface Engineering of Polymer Membranes: Affinity Membranes Based on Surface Glycosylation

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Introduction

High specific affinity membranes based on the interactions between ligands and receptors have aroused extensive attentions due to the benefits of high specificity, short processing time, low pressure drop, and easy scale-up[1]. However, the selection of ligands and their density on the membrane surface can greatly affect the separation performance. Carbohydrates are extensively found on various cell surfaces and mediate many important biological processes via "glycoside cluster effect"[2]. In addition, carbohydrate as a polyol can reversibly bind boron acids which are of widely spreading in natural water and wastewater. Therefore, membranes with high-density carbohydrates are expected to construct as a novel affinity membrane for the specific recognition/separation of carbohydrate-binding proteins and meanwhile for the high-efficiency removal of boron impurities from natural water and industrial wastewater. To achieve these aims, various saccharides such as glucose, galactose, mannose, lactose and maltose, were immobilized on the surface of microporous polypropylene membrane (MPPM) by chemical coupling reactions. Their affinity properties to lectins and boron acid were extensively evaluated.

Results

Affinity membranes with an extensive range of glycosyl density from 0 to 11 μmol/cm^2 were facilely prepared by surface glycosylation. Click chemistry possesses an enormous advantage of high efficiency with an average reaction degree of glucose over 80%, which increases the surface glycosyl density. The hydrophilicity of glycosylated membranes was greatly improved by covalent immobilization of saccharides, which effectively inhibited the non-specific adsorption of proteins. Specific recognition capability of these glycosylated affinity membranes was evaluated with lectins (Con A and PNA). The membrane surfaces with glucose, mannose and maltose moieties recognize Con A and the others (galactose and lactose) specially recognize PNA as a result of the "glycoside cluster effect". The membranes performed a specific adsorption to Con A and an excellent detachment capability over 90%. Meanwhile, the glycosylated affinity membranes from poly(AEMA)-modified MPPMs were also used for the reversible removal of boron acid. These affinity membranes show an ecological-friendly removal of boron acid with efficiency about 40%. In addition, boron acid bound on the affinity membranes was facilely removed by changing the pH to 2. Membrane regeneration was achieved with de-ionic water and the recovery is almost 100% after two recycles.

Conclusion

Saccharides were covalently immobilized onto MPPM surface with a high density by UV-induced grafting and subsequent coupling reactions. The glycosylated affinity membranes possess excellent capability for carbohydrate-protein recognition by the "glycoside cluster effect". They can also be used for the removal of boron impurities in natural water and industrial wastewater.

Acknowledgement

The author thanks financial support from the NNSFC (Grant no. 50933006).

References

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ICOM1243

IMPROVEMENT OF BIOFOULING RESISTANCE BY MEMBRANE MODIFICATION WITH POLY VINYL ALCOHOL AND PROPOLIS

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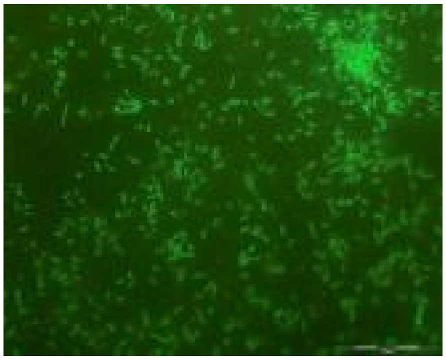
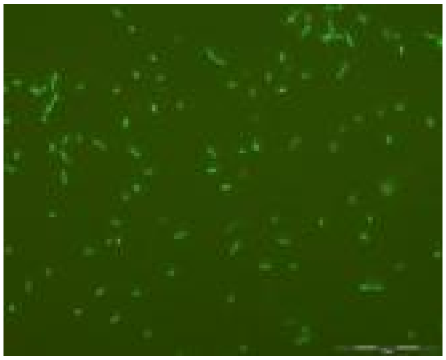
Federal University of Rio de Janeiro, Chemical Engineering Program, Rio de Janeiro, RJ, BR

Biofouling is one of the most serious fouling problems in reverse osmosis membranes, reducing the process efficiency and increasing operational cost. The main challenge of this process is to develop membranes with enhanced resistance to biofouling. This work investigates an alternative to reduce biofouling modifying the surface of a commercial reverse osmosis membrane. The modification was promoted by insertion of a thin layer of polyvinylalcohol (PVA), wich is a hydrophilic and low fouling polymer. Besides, propolis was introduced in PVA solution to give a biocide characteristic to it. The water permeate flux and NaCl rejection of the modified membranes was evaluated and the anti-microbial properties were analyzed using *Listeria monocytogenes* as standard microorganism.

Reduction in the hydraulic permeability indicated an additional resistance for water permeation related with the coated layer. However, the saline rejection remained around 98%, a characteristic value of reverse osmosis membranes. The anti-microbial property of the membrane coated with PVA and propolis was demonstrated by a drastic decrease on cell viability of *Listeria monocytogenes*, as shown in Figure 1. It seems that Propolis acted as an inhibitory agent for the adhesion of the microorganisms to the membrane surfaces and subsequent biofilm development.



Epifluorescence microscopy of *Listeria monocytogenes* biofilms stained for viability. Unmodified membrane



Epifluorescence microscopy of *Listeria monocytogenes* biofilms stained for viability. Propolis/PVA coated membrane (mass ratio 10:1).

ICOM998

Gaseous sulfonation of mesoporous polymer membranes for improved fouling resistance

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Membranes have proven to be economic and efficient materials for separation technology, and their utility benefits a broad range of applications and industries. However, membrane separations are often hindered by fouling. This phenomenon is a common bane of membrane technology, and it has inspired a great amount of research into mitigating its detrimental effects, which include reduced separation efficiency and shortened lifetime of membrane materials.

Sulfonation of membranes or membrane polymers has been found to be an effective method in reducing the effects of fouling. It is used commercially and continues to be of academic interest. The method involves the chemical modification of membrane polymers with a sulfonation agent, which produces sulfonic acid groups along the polymer chain. By introducing sulfonic acid groups, the charge density, charge polarity and hydrophilicity of membrane materials can be modified. And by modifying these properties, membrane materials can be designed to exhibit improved fouling resistance.

Gaseous sulfonation of polymer membranes offers two advantages over conventional sulfonation methods: 1) it allows separate membrane preparation and sulfonation; 2) and gaseous sulfonation agents can penetrate into mesopores more efficiently than liquid sulfonation agents, permitting sulfonation of both the membrane surface and the surface of the pores. However, gaseous sulfonation may cause severe loss of material integrity.

In this study gaseous sulfonation was conducted, and pre-prepared polymer membranes were sulfonated by exposing them to a gas mixture of sulfur trioxide and nitrogen at different conditions. Characterization of membrane composition, charge, and hydrophilicity indicate that gaseous sulfonation can be used to modify pre-prepared polymer membranes without significant loss of material integrity. Further study will be conducted to evaluate filtration performance and fouling resistance of the sulfonated membranes.

Parallel Sessions

Thursday, July 28th 2011

Afternoon Session 2, 15.40 – 17.10

Waste water treatment 3

ICOM1804

Future of Membrane Technologies for Wastewater Reclamation

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The issues of water shortage and depletion of fresh water supply related to climate change place a great demand for alternative water resources, particularly wastewater reuse. The increased need to secure a high quality water supply from reclaimed water has resulted in the emergence of advanced membrane technologies, including membrane bioreactors (MBR) utilizing MF/UF membranes. The MBR process has shown to provide high quality effluent, with high BOD removal and complete TSS reduction. However, this conventional MBR process is not able to meet the effluent quality for reuse, and requires tighter membrane technologies, such as reverse osmosis (RO). The overall footprint of an MBR+RO system is much smaller than typical wastewater reuse facilities based on conventional activated sludge and tertiary treatment processes. In the future, however, wastewater management systems will be more decentralized for the optimum use of energy and resources, and thus, MBR systems should be further simplified and compact.

Research on the MBR process has increased exponentially over the last decade, and is expected to keep increasing in the future. Despite rigorous research activities, membrane fouling still remains as a major obstacle for the practical applications of MBR technology. Various factors affecting fouling of the MBR process have been investigated and documented in numerous publications. However, many full-scale MBR plants have still suffered from deterioration of membrane productivity, mainly due to fouling. Thus, more scientifically designed fouling control methods are expected to develop in the future. A novel method utilizing a biological mechanism, known as Quorum Sensing, is one example.

Environmental concerns regarding the protection of natural water resources put more pressure on the development of MBR processes that are more effective for the control of biological nutrients, such as nitrogen and phosphorus. A variety of MBR processes have been configured with biological nutrients removal (BNR) systems, with their performance demonstrated for different applications, but have only shown limited success. Therefore, it is common to see additional chemical methods incorporated into the MBR process to satisfy regulatory requirements. The development of the MBR process coupled with more efficient BNR systems will be the primary research topic for the future.

MBR systems using low pressure membranes cannot retain organic species and ions. To overcome these limitations, high retention membrane bioreactors (HR-MBRs) have recently been investigated. HR-MBRs use high rejection membranes, such as nanofiltration (NF), forward osmosis (FO) and membrane distillation (MD), in place of MF/UF. This allows a combination of the conventional MBR and high rejection membranes in a single step. However, this technology is still in its early stage of development, and many challenges, such as low recovery and accumulation of ions in the bioreactors, still have to be resolved.

Due to the high costs of electricity and an increasing concern over greenhouse gas emissions, energy reduction in wastewater treatment and reuse is becoming increasingly important. The MBR process will be evolved further to achieve high efficiency with low energy consumption. Especially, anaerobic biological treatment using membranes (AnMBR) will be investigated and developed in the future.

ICOM1303

Separation of cadmium from phosphorous rich real drainage water by MEUF. Study of the permeate flux in semi pilot scale.

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The objective of this study was to evaluate the feasibility of Micellar-enhanced ultrafiltration (MEUF) to separate cadmium from phosphorous. The research was conducted in collaboration with a fertilizer company, whose phosphorous-rich drainage waters were contaminated with low concentrations of cadmium, which needed to be removed from the waters prior to their utilization on-site. The removal of cadmium by MEUF was performed in semi-pilot scale. In MEUF, the anionic surfactant forms large amphiphilic aggregate micelles when it is added to aqueous streams at a concentration higher than its critical micelle concentration (CMC). The heavy metal cations can be mostly trapped by the micelles due to electrostatic interaction and thus retained by the ultrafiltration membrane. Anionic phosphates will not be trapped by the micelles and they will pass through the membrane to the permeate obtaining the separation from the heavy metals. In addition, the metal cations not trapped by the micelles and the surfactant monomers will also pass through the ultrafiltration membrane to the permeate.

In this study, the anionic surfactant used was sodium dodecyl sulphate (SDS). The effect of transmembrane pressure (2, 3 and 4 bars), feed flow velocity (0.13, 0.24 and 0.35 m/s) and SDS feed concentration (40, 60 and 80 mM) on the permeate flux were also evaluated. The MODDE 8.0-programme (Umetrics) was used as a tool in statistical experimental design for evaluating the effect of these factors on the steady
permeate flux. In addition, rejection coefficients of cadmium and phosphorous were also calculated in order to evaluate the feasibility of MEUF for the separation of phosphorous from cadmium.

The validity of the fitted models was evaluated with ANOVA, and the results show that the regression models are statistically significant with a 95% confidence level.

This paper reports that, using MEUF, separation of phosphorous and cadmium is possible by using MEUF. Phosphorous was not retained by the membrane and successful cadmium rejection coefficients were achieved. Rejection coefficients of cadmium increased from 70 % to 81 % when increasing the SDS feed concentration from 40 to 60 mM. Then, a plateau in cadmium rejection coefficient was observed after 60 mM of SDS. This research shows that all three factors studied (transmembrnae pressure, feed flow velocity and SDS feed concentration) had a statistically significant effect on the steady permeate flux. Further, the interaction between the feed velocity and pressure showed also a statistically significant effect. This study will continue by complementing the screening design to response surface methodology in order to estimate the effect of quadratic terms and to find the optimal conditions for maximum steady permeate flux.

ICOM933

Optimization and Techno-Economic Analysis of Electrodialysis for RO Brine Minimization

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[1]K.U.Leuven, Department of Chemical Engineering, Leuven, BE, [2]Katholieke Hogeschool Brugge-Oostende, Department of Industrial Sciences and Technology, Oostende, BE, [3]KaHo St.-Lieven, Department of Industrial Engineering, Gent, BE, [4]K.U.Leuven, Department of Microbial and Molecular Systems, Leuven, BE

This work focuses on a systematic study on the process optimization and a techno-economical analysis of a pilot ED system for treatment of RO concentrate from a WWTP secondary effluent. The content of this work is:

(1) A lab scale ED was used to simulate the pilot system and get the preliminary operational parameters for batch experiments of the pilot ED;

(2) Batch experiments on the pilot ED were conducted before the long-term feed-and-bleed operation to reduce the start-up salt concentration;

(3) Continuous experiments on the pilot ED were performed to optimize the operational parameters from economical aspect (investment cost of the system not included), i.e., energy consumption of the system;

(4) The environmental impact evaluation on the whole system in view of the brine discharge, H_2 generation and CO_2 emission will be addressed and discussed in this work.

In the pilot investigation, different feed flow rates (200 Lh^{-1}, 300 Lh^{-1}, 400 Lh^{-1} and 500 Lh^{-1}) under the same current (5A) and different currents (1 A, 3 A, 5 A, 7 A and 9 A) under the same flow rate (300Lh^{-1}) were applied to investigate the relationship between the flow rate, current and salt removal. Furthermore, in order to operate the system without scaling, decarbonation using acidifying/aeration was necessary. Thus, acidifying the feed (RO concentrate) or the ED concentrate was investigated respectively to exam the feasibility to prevent scaling.

Figure 1 illustrates the correlations between salt removal (%) with applied current (A) and flow rate (L h^{-1}). In this figure, block point is salt removal under 300 L h^{-1} with different current, and circle point means salt removal under 5 A with a different flow rate (dash-dot line: an estimated salt removal trend). By applying this curve, a desired salt removal (i.e., 75% in this case) can be obtained by adjusting the flow rate and current. As an example, with the flow rate of 200 L h^{-1}, a current of 8 A has to be applied to achieve 75% of salt removal. This method is a theoretical estimation and is valid below the limiting current density.

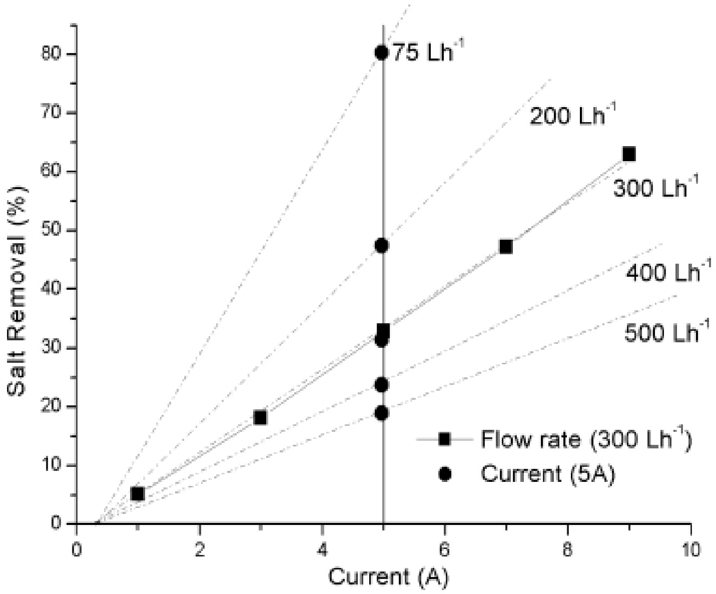

Table 1 shows the cost analysis of the ED system under 6 different currents with a constant flow rate of 300 L h^{-1}. It is clear that the energy consumption by ED increases with increasing current. It also leads to the increase of intrinsic removal capacity. However, the energy cost and the total cost have a lowest value at current 3 A.

Flow Rate	(Lh^{-1})	300	300	300	300	300	300
Pressure	(Bar)	0.25	0.25	0.25	0.25	0.25	0.25
Current	(A)	1	3	5	7	9	11
Voltage	(V)	3.0	7.8	11.3	14.7	19.0	27.9
ED	(kW)	0.003	0.023	0.056	0.103	0.171	0.307
Pump (X3)	(kW)	0.011	0.011	0.011	0.011	0.011	0.011
Intrinsic Removal Capacity	(%m^3h^{-1})	1.59	5.49	8.70	11.88	15.99	20.01
Energy Cost	(Eurocent m^{-3})	6.0	4.2	5.2	6.5	7.7	10.7
Total Cost	(Eurocent m^{-3})	49.0	47.2	48.2	49.5	50.7	53.7

It reveals that the ED system is most cost-effective at a current of around 3-5 A at 300 L h^{-1} of flow rate for desalinating the feed (conductivity range 3.90-4.14 mS cm^{-1}). Results show that to desalinate $1m^3$ of the RO concentrate, the cost is around 47.2 Eurocent m^{-3}. However, if decarbonates the ED concentrate, the cost can be lowered to only 18.2 Eurocent m^{-3}. Based on the techno-economical analysis, ED was proved to be a good option for the RO concentrate treatment and reclamation in the WWTP.

ICOM1487

Recovery of biophenols from olive mill wastewaters by integrated membrane processes

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Olive mill wastewaters (OMWs) represent a serious environmental problem of Mediterranean countries where the olive processing in an important and traditional industry since ancient times.

The detrimental environmental impact of OMW is related to its highly polluting organic load arising from polyphenolic compounds with low biodegradability.

The powerful pollutants prohibit OMWs to be directly discharged. Several treatment procedures including physical, chemical, biological or combined technologies have been propose to reduce undesirable properties of OMWs prior to disposal [1]. Recently, in relation to the major interest for the natural compounds with biological activities, researches have been also oriented to the recovery of polyphenols as high value compounds, transforming OMWs from effluents to raw material with high potential economic value. Indeed, several studies have shown excellent biological properties such as antioxidant, free radical scavenging, antimicrobial and anticarcinogenic activities of the biophenols of OMWs [2]. These compounds are usually synthesized by chemical methods that are responsible of their high price. Consequently, methods to concentrate and purify polyphenols from OMWs have become a subject of dramatically increased interest in the last several decades.

Application of membrane technologies to recovery of antioxidants from OMWs is of interest due to their several advantages (mainly low energy consumption, no additive requirements and no phase change) in comparison with other technologies such as solvent extraction, supercritical fluid extraction and chromatographic separation [3].

This research was undertaken in order to evaluate the influence of nominal molecular weight cut-off, membrane material and operating conditions on the selectivity of ultrafiltration (UF) and nanofiltration (NF) membranes towards biophenols contained in OMWs produced according to a 3-phase centrifugation process. The performance of the investigated membranes was also evaluated in terms of permeate flux and membrane fouling. Finally, combinations of different membrane processes were analysed for the fractionation of OMWs into by-products in order to develop a natural product suitable to be used as health food supplement and natural food antioxidant.

The results obtained in the present study supply useful indications for the development of a proper system design aimed at: 1) the optimization of the selective separation of valuable compounds; 2) the reduction of the polluting load of OMWs; 3) the recovery of significant amount of water with good characteristics both for recycling and agricultural irrigation.

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Mixed matrix membranes 2

ICOM1829

Advances in mixed matrix membranes for gas and vapor separations

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Over the past two decades, the need to improve the performance of polymeric gas separation membranes above Robeson's upper bound has driven the development of mixed matrix membranes. These materials comprise of rigid permeable or impermeable particles dispersed in a continuous polymer matrix. A variety of fillers such as zeolites, carbon molecular sieves, silica, molecular organic frameworks and even carbon nanotubes have been used for this purpose. The idea behind mixed matrix membranes is to create nano-composite membranes whose effective transport properties are a synergistic combination of the inherent properties of the pure components. In a typical example the molecular sieving properties of a zeolite would be combined with the high permeability of the polymer to maximize selectivity and flux. Also, such a combination simultaneously takes advantage of the desirable mechanical and processing properties of the polymer during membrane fabrication. However, the selection and matching of materials as well as the methods of preparation have a profound impact on the overall performance of the mixed matrix membrane. Interfacial defects, particle size, shape and distribution in the matrix as well as changes in polymer chain packing in the presence of fillers and the resulting microstructure of the membrane, all affect the permeability and selectivity of the composite membrane. Hence, simple combinatorial mathematical models that predict the effective transport properties of the mixed matrix membrane based on the intrinsic properties of the pure components have to be used with caution. Successful mixed matrix materials comprising of molecular sieve entities embedded in a polymer matrix, for example, need to have an optimized interface that minimizes the resistance to transport between the two phases. Mixed matrix membranes containing impermeable fillers that perturb polymer chain packing and introduce additional free volume elements into the polymer matrix (thus enhancing transport) must have the filler present as a fine dispersion and promote strong interactions between the rigid particles and the polymer matrix, (since weak interactions may lead to the formation of non-selective voids, resulting in Knudsen flow and compromised selectivity). Thus, probably the most challenging problem facing the development of viable mixed matrix membranes today deals first with our physical understanding of the interfacial region and second with the actual control of the interface between the two components.

ICOM1202

Effect of annealing temperature and residual solvent on single and binary CO_2/CH_4 transport properties of SAPO-34/Ultem® mixed-matrix membranes

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Polymer-zeolite mixed-matrix membranes (MMMs) are promising alternatives to polymeric membranes and zeolite membranes in terms of increased selectivity and processibility, respectively. Zeolites embedded into a polymeric matrix combine the molecular sieving ability of the former and the ease of formation into larger defect-free modules of the latter. However, certain existing issues must be considered for the selection of materials in designing a zeolite/polymer MMM. Ideally, zeolite pore size must hold a value close to the kinetic diameter of one of the gases to be separated, and the possible formation of voids in the zeolite/polymer interphase must be completely prevented. Additionally, a suitable annealing process must be applied to the membranes, in order to control the effect of residual solvent on the overall properties of MMMs. The residual solvent effect in MMMs has not been studied in detail.

In this study, polyetherimide, Ultem® (T_g, 215°C), was chosen as the polymer, whereas a silicaaluminophospate, nano-sized (300-400 nm) SAPO-34, was chosen as the molecular sieve. In addition, NMP (n-methyl pyrrolidone) (b.p. 205°C) was used as solvent. Prior to incorporation into the polymeric phase, zeolite particles were primed, in order to enhance adhesion of the two components in the final MMM. Ultem® has a relatively high CO_2/CH_4 selectivity, and SAPO-34 has a pore size of 3.8 Å, which is same as the kinetic diameter of CH_4 (3.8 Å), and larger than kinetic diameter of CO_2 (3.3 Å). The MMMs prepared with 20% zeolite content were annealed at 150°C (below T_g and b.p. of NMP), 200°C (below T_g, close to b.p. of NMP), and 220°C (above T_g and b.p. of NMP) for 48 hours, respectively. SEM analysis showed good adhesion, TGA analysis showed decreased amounts of solvent, and DSC measurements showed increased T_g values, all increasing with higher annealing temperature. As shown in Figure 1, CO_2 permeability (measured at 35°C and 4 bar upstream pressure) decreased for membranes annealed below T_g, whereas a slight increase was observed for membranes annealed above T_g. CO_2/CH_4 selectivity increased with increasing annealing temperature reaching to an ideal selectivity of 120 for the membrane annealed at 220°C. Both were attributed to the plasticization effect of residual solvent favoring the smaller penetrant, as well as the preferential sorption of CO_2 in NMP compared to CH_4, decreasing with the decreasing amount of residual solvent. It is also speculated that the residual solvent trapped in the zeolite/polymer interphase is relatively more difficult to remove than that in the bulk of the polymer and therefore smaller size zeolite particles may enhance the influence of residual solvent on the MMM transport properties. Despite the competitive sorption phenomena occurring in permeation of gas mixtures, mixed gas measurements (at 35°C and 4 bar) of MMM annealed above T_g showed a CO_2/CH_4 selectivity of 52 at 50/50 molar composition which is higher than that of pure polymer (39 at 50/50) but lower than ideal selectivity for the same membrane.

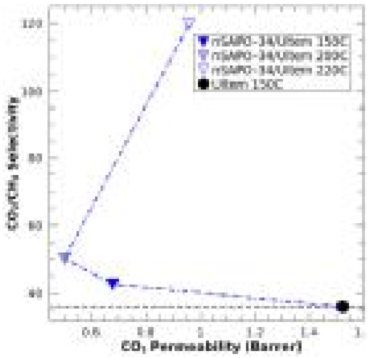

Figure 1. Single gas permeability and selectivity behavior of SAPO-34/Ultem MMMs (20% zeolite content) annealed at different temperatures.

ICOM1591

Metal-Organic Framework Based Mixed Matrix Membranes for Gas Separations

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Mixed-matrix membranes (MMMs) combine the features of polymers and zeolitic materials. Such composites are composed of nanoporous inorganic additives dispersed in a polymeric matrix. This type of material combines the favorable attributes of both components such as the processibility of the polymeric matrix and the inherent superior gas separation properties of the inorganic additive. The ideal MMM consists of well-dispersed particles with as high a loading as possible. It has been a challenge to prepare zeolite/polymer membranes with loadings much higher than 30-40% (w/w). In contrast we have found that related metal organic frameworks (MOF) and zeolitic imidazolate frameworks (ZIFs) can be dispersed in polymers with loadings greater than 80%. The organic nature of the framework may facilitate interactions with the polymer that allow good dispersion of the MOFs and ZIFs. Thus it may be possible to achieve membrane performance that is much closer to the pure molecular sieve membrane. Recent results for the preparation of MMMs based on ZIF-8, ZIF-7, ZIF-90 and MIL-53 in polyimides including Matrimid, VTEC and 6FDA-durene as well as polybenzimidazole will be presented. The MMMs permeability properties were tested for H_2, CO_2, O_2, N_2, CH_4, C_3H_8, and various gas mixtures. The permeability and selectivity properties for these MMMs were close or above the upper bound region of various Robeson plots including H_2/CO_2 and CO_2/CH_4. Further improvements in the polyimide mixed matrix membrane performance were achieved by preparing a thin skin of crosslinked polymer on top of the membrane.

ICOM602

Mixed matrix gas separation membranes based on PIM-1 and nanoparticles of zeolite - MOF - ZIF-8

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Big interest is attracted now to mixed matrix membranes (MMM) for gas separation containing various nano-particles. Such membranes allow noticeable increase in permeability and, sometimes, simultaneously permselectivity. In most works the choice of such additives included particles of fumed silica and other oxides. Other nano-particles can be of great interest too.

In this presentation we shall report the results of first such study whereas polymer of intrinsic microporosity PIM-1 being used as the matrix and Zeolitic Imidazolate Framework (ZIF-8) being used as nano-additive. This MOF compound has sodalite structure and Zn serves as the metal component..

It was shown that the introduction of such additives significantly increases permeability of MMM as compared to pure polymer. As can be seen from Table 1 permeability coefficients increase by a factor 1,5-4 due to adding large quantity of ZIF-8 particles.

Table 1. Permeability coefficients P (Barrer) and permselectivity of MMM with different content of ZIF-8.

ZIF-8, mass %	H_2	O_2	CO_2	α(O_2/N_2)	α (H_2/CH_4)
0	1630	580	4390	3.2	5.2
10	2560	820	4815	3.3	8.0
32	2980	870	4270	4.5	13.0
60	6680	1680	6300	4.7	15.6

It is quite unusual that for the MMM studied increase in permeability is accompanied by a growth of permselectivity, as is obvious from Table 1. It was demonstrated that the MMM studied reveal outstanding combinations of gas permeability and selectivity, since on several Robeson diagrams [1] for a number of gases (O_2/N_2, H_2/CH_4, H_2/N_2, CO_2/CH_4, CO_2/N_2) the data points that belong to MMM with ZIF-8 content of 10-60% are located above upper bounds. Some examples are shown in Fig.1. The data points are taken from Database TIPS, upper bounds are drawn according to Robeson (2008). Treatment with EtOH results in increase in permeability accompanied with some reduction of permselectivity. The growth of permeability is mainly caused by increases in the diffusion coefficients. A discussion of the transport mechanism will be given in the presentation.

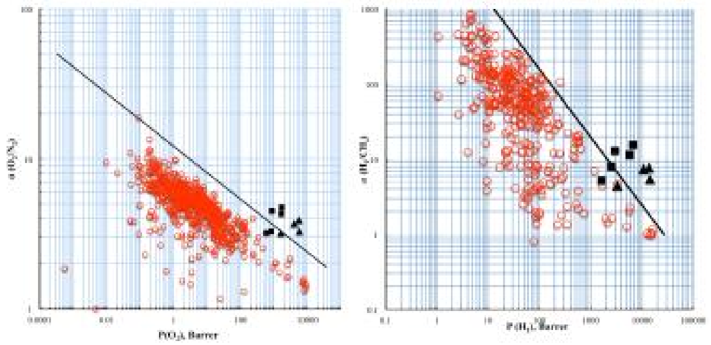

Fig.1. Robeson diagrams for O2/N2 and H2/CH4 pairs: squares "as cast", triangles after EtOH treatment.

The work leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. NMP3-SL-2009-228631, project DoubleNanoMem.

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Carbon membranes 1

ICOM1807

Carbon Molecular Sieve Membranes for Large Scale Gas Separations

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Carbon molecular sieve (CMS) membranes can provide separation performance well beyond the so-called “upper bound” trade-off curve of polymeric membranes for many challenging gas separations. Asymmetric hollow fiber membranes are preferred for large scale, high pressure applications, due to the ability to form high surface area-to-volume ratio fiber modules. Especially for CMS membranes, fibers have an additional advantage over flat sheet or spiral module forms, since they offer better mechanical strength and ease of formation into practical devices. CMS fibers can be prepared by pyrolyzing polymer fibers, well above their glass transition temperatures. State-of-the- art gas separation properties will be compared with theoretical values predicted using single gas permeation and sorption experimental results. Also realistic consideration will be offered regarding key hurdles that still must be overcome in this technology to make it practical.

ICOM1314

Structural and performance evolution of carbon membrane from grafted polypyrrole

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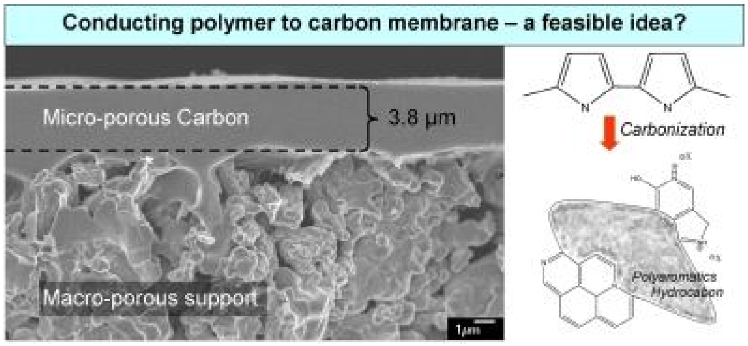
Little is known about the suitability of conducting polymer as a precursor to carbon membrane. Its conjugated nature and strong polymer chain association creates huge defects in the carbon structure during pyrolysis, making it unfavorable for membrane synthesis. As such, this study aims to alleviate this by grafting aliphatic side chains to the conjugated backbone. Polypyrrole (PPy) is selected as the conducting polymer and is reacted with dodecylbenzene sulfonic acid (DBSA) to form a branched structure, whereby DBSA is sandwiched in between the PPy segments. This allows the formation of a continuous matrix of PPy-DBSA membrane on a porous ceramic substrate. The adhesiveness of carbon membrane to the ceramic substrate is promoted by introducing chemical bonding between the polymer precursor and ceramic surface during the coating process, ensuring the integrity of the pyrolyzed carbon membrane. Defect-free microporous asymmetrical carbon membrane shown in Figure 1 is obtained.



The performance of the membrane is tuned by incorporating carbon nano-tubes into carbon matrix. Thermal and spectral analysis methods are carried out to understand the structural transformation of PPy-DBSA during pyrolysis. This study opens up the possibility of using conducting polymer as a carbon membrane.

ICOM985

Defect-Free Ultrathin Carbon Membranes for Gas Separation

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Porous carbons are widely used for many useful technological applications such as adsorption, catalysis and gas separation. In the field of gas separation, the carbon membranes from inert pyrolysis of organic materials, including carbon molecular sieve and nanoporous carbon membranes, have been extensively studied over the last two decades. These carbon membranes have different pore sizes and shapes, depending on types of organic precursors such as various resins and pitches, thermal treatment history and other factors such as partial oxidation and the amount of heteroatoms in the organic precursors. In general, carbon molecular sieve membranes show ultrahigh gas selectivity as a result of size-sieving mechanism and also high gas permeability as compared to typical polymeric membranes. However, carbon membranes obtained from organic polymers have critical disadvantages over polymeric membranes in the practical viewpoint of membrane fabrication. Once, high temperature necessary for carbonization demands high energy-consumption, and the heat treatment will need a long time in fabrication process. The most critical one is to be too difficult to make defect-free membrane without any pinholes and cracks and also hard to achieve thin-film layer for high flux membranes. For thin-film carbon membranes, porous ceramics or steel supports should be necessity but at elevated temperature crack formation is also unavoidable because of different thermal expansion coefficients between carbons and support layers. In this paper we will provide a new insight into the preparation of defect-free ultrathin carbon membranes for advanced gas separation. Using new technology, we are able to place ultrathin carbon layers on the surface of any porous substrates including polymers, ceramic, and steel. Furthermore, heat treatment process at an elevated temperature will be unnecessary for making carbon composite membranes. All these membranes show high gas permeation properties as well as high gas selectivity. We will discuss these new carbon materials in terms of structure-property relations with gas transport behavior.

ICOM1426

Upscaling fabrication of aligned carbon nanotubes membranes : opportunities and challenges

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ATomic and Renewable Energy Commission, Laboratory Francis Perrin, Gif sur Yvette, FR

Promising membranes made of a variety of carbon nanotubes have emerged in the recent years (1). Several designs for carbon nanotubes membranes exist according to the nanotube arrangement. Certainly the most promising membrane concept is the one based on aligned carbon nanotubes where gas or liquid can flow through their central core (2, 3). In this case, it is expected that water molecules can flow through them with no friction (4) enabling high flux and high selective membranes.

Although the large potential handling of nanotube membrane (dispersed or aligned nanotubes) the main question that hamper their industrial interest amongst the community is two fold : Which process could be developed to upscale the fabrication of carbon nanotubes membranes and how much their properties will be degraded by up-scaling the process.

According to the community concerns, our presentation will stress on the following:
1. Upscaling nanotubes growth through aerosol assisted CVD process to reach A4 format carpets (aligned growth versus growth and alignment)
2. Filling the space between nanotubes with different polymers
3. Using different nature of nanotubes by functionalization (6) while keeping the alignment unchanged (7)
4. Opening of the nanotubes by chemical or plasma treatment

We review the readiness of each step, point the challenges to overcome, the risk of performances losses in terms of nanotube shapes, porosity and nanofluidic behaviour, the consequences and the potential cost in comparison with commercially available membranes.

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Membrane contactors and reactors 2

ICOM1782

Nanostructured Multifunctional Membranes as Contactor and Reactor

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Membrane-based separations and reactions have wide applications ranging from clean water production to selective separations, chemical synthesis and biotechnology. The creation of nanostructured membranes functionalized with ionizable macromolecules provides promising applications in a variety of areas, such as high capacity toxic metal capture, in-situ nanoparticle synthesis, and catalysis. The most remarkable features of low-pressure membrane approach are: operations as a membrane contactor and reactor, and separation selectivity and tunability (by changing operating pH, ionic strength or pressure). Examples will be given for the creation and applications (including contactors) of nanostructured membranes: 1) use of pore functionalized polypeptides for responsive behavior and high capacity metal capture, 2) stacked-nanocomposite membranes with layer-by-layer (LbL) assembly for incorporation of enzymes (catalase, glucose oxidase), for tunable product yields, and for chloro-organic destruction from water by free radical reactions and 3) in-situ, green synthesis of 20 – 50 nm Fe and Fe/Pd nanoparticles for degradation of pollutants by a reductive pathway. Functionalization of microfiltration-type membranes with polymers and biomolecules to create nanostructured domains in pores offers high trans-membrane flux and exceptional versatility. For many sequential reactions (such as, A à B à C) one can obtain high selectivity and product yield (with minimal separation needs) using stacked membranes immobilized with different enzyme. The free radical-based oxidative destruction of organic pollutants involved the use of two-stack membranes (one containing glucose oxidase enzyme, and the other contained immobilized Fe(II)) using glucose to generate hydrogen peroxide. The formation of bioreactor with nano-domain interactions and mixed matrix nano-composite membranes display remarkable versatility compared to conventional membranes. For the nanoparticle synthesis aspects in membrane, we conducted the synthesis of supported Fe and Fe/Pd nanoparticles (NP) in membrane pores using “green” reducing agents and demonstrated the reactivity of these NPs toward dechlorination of toxic organics from water at room temperature.

ICOM1402

Highly breathable, d*ense* barrier membranes based on polymerized room-temperature ionic liquid composites that block mustard agent simulant vapor

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Protection of individuals from exposure to highly toxic chemical warfare agents (CWAs) in vapor form is a major operational concern in the military. This concern has also recently become extremely important in civilian defense and first responder safety since the use of these compounds in terrorist attacks in the last decade. Traditional protective barrier materials against CWAs have typically been *impermeable, dense* polymer materials (e.g., heavily cross-linked butyl rubber and coated fabrics). They provide protection for the wearer by completely blocking the passage of all gases and liquids; but in doing so, they can also cause heat stress and fatigue with prolonged use because of the lack of water evaporation for personal cooling. Consequently, water vapor "breathability" in individual protective garments is an extremely important practical requirement. In general, the desired range for water vapor transport rate in chemical protective suits is commonly accepted to be >1500 g m^{-2} day^{-1}. A number of porous protective garment materials have been developed that provide various levels of water vapor permeability but still provide good rejection of CWAs. The majority of these membrane materials are macroporous or fiber matte fabrics containing sorbents (i.e., activated carbon) physically trapping CWAs or highly specialized reagents or catalysts for chemically neutralizing CWAs. We have developed a new class of *dense*, reactive, polymer-based barrier materials that exhibits extremely high water vapor transport at room temperature and is able to completely block the passage of a sulfur mustard simulant vapor (2-chloroethyl ethyl sulfide, CEES or half-mustard). These new polymers are based on a very hydrophilic, polymerized room-temperature ionic liquid (poly(RTIL)) matrix that is (1) physically blended or copolymerized with organic amines or (2) physically blended with a basic zeolite Na-Y as the reactive additive for CEES vapor blocking. In this composite system, the ionic, hydrophilic poly(RTIL) affords the desired high water vapor permeability, while the reactive component acts to chemically bind and detoxify the CEES vapor. Initial vapor transport studies performed at a U.S. Army testing facility showed that these dense films afford water vapor transport rates of >1800 g m-^{2} day^{-1}, while showing 0% CEES vapor penetration after 22 h of exposure. To our knowledge, a *dense*, highly breathable CWA vapor barrier material with these properties is unprecedented. Surprisingly, the use of amines as reactive agents for mustard agent (simulant) blocking in the design of CWA protective materials has also not been reported in the literature.

ICOM1123

A continuous hybrid photocatalysis - ultrafiltration process for polysaccharide degradation

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Heterogeneous photocatalysis is a well known advanced oxidation process, which has not been exploited to a significant extent yet, mainly due to technical problems. One of them is the difficulties associated with the separation of the catalyst nano-particles, from the effluent product, in systems where these particles are dispersed in the treated liquid to achieve increased conversion rates. Moreover, in almost all reported studies so far batch systems are employed for the photo-degradation, where the problem of catalyst separation is acute. A novel system will be described, which involves coupling the photocatalysis process with ultrafiltration, thus, permitting continuous steady operation, with a fixed quantity of dispersed TiO_2 catalytic nano-particles. Results will be presented demonstrating the very good performance of such a continuous hybrid process for the degradation of a polysaccharide (sodium alginate), dissolved in the feed-water at relatively small concentration (of order 10 mg/L). Using a hollow-fiber UF module, submerged in an aerated tank, and periodic backwashing, membrane fouling was suppressed and steady operation was achieved. Moreover, the TiO_2 particles were totally rejected by the membranes and retained in the system. Experiments carried out with catalyst concentration in the range 0.25 to 1.50 g/L and constant UV-A radiation of 17.9 J/s (in a 9 L capacity system), show quite high alginate mineralization rates with a maximum TOC removal (~75%) at TiO_2 concentration 0.75 g/L (Figure 1). Three backwash frequencies employed (i.e. one minute backwashing after either 5 min, 9 min or 15 min filtration period) resulted in approximately the same percentage TOC removal; however, the smaller frequencies are desirable for practical applications as they lead to greater permeate productivity. Based on the present very encouraging results, research needs are indicated for employing this novel hybrid system to other water treatment tasks.

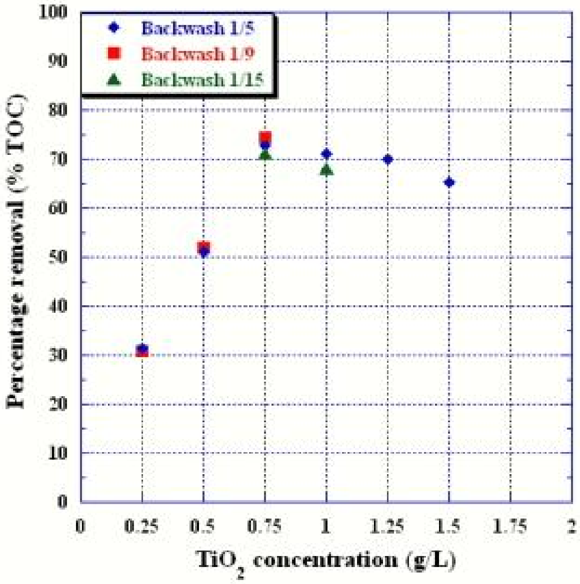

Figure 1. Effect of catalyst loading on the photocatalytic degradation of sodium alginate under steady state conditions

ICOM359

Filtration membranes loaded with Metal Nanoparticles for catalytic reduction of organic compounds

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Metal Nanoparticles (MNPs) are powerful objects for catalytic reactions [1]. Their high specific surface gives them unique physico-chemical properties that differ from bulk material.
However, in order to take profit of these properties, it is important to avoid aggregation by maintaining the stability of the NP in the material. This challenge is hard to perform in liquid phase but it has been demonstrated that is possible to stabilize MNPs in polymeric matrices without a significant loss of reactivity, maintaining high level of catalytic efficiency [2,3].

In our current research line, we develop catalytic membrane reactors (CMRs) containing MNPs by means of which reaction and separation steps can be performed simultaneously in the same unit.

We intend to demonstrate that membrane processes including catalysis can be an alternative to the synthesis of chemical compounds by conventional batch processes taking profit of the separation of the reactants and products. The advantageous catalytic properties of nanomaterials can increase CMRs performance whereas the integrity of nanomaterials can be guaranteed inside the membrane polymeric matrices.

It is important to notice that, in many instances, for achieving the above objective it is necessary that the polymeric support has functional groups capable to retain nanoparticle precursors (i.e. sulfonic groups which bond metal ions)[3]. Once the precursor is immobilized, MNPs can grow inside the polymeric matrix by chemical reduction of metal ions. In this sense, to provide the necessary functionalization to membranes, two different strategies have been used in this work. Firstly, polysulfone ultrafiltration membranes were modified by UV-photografting using sodium *p*-styrene sulfonate as a vinyl monomer. This procedure yields covalent bonding between the charged polymer and the membrane substrate[4].

Another way to obtain functional material is to add charged polymer chains to the initial polymeric material used to made membrane. To achieve this goal, we have blend poly(methylmethacrylate-co-acrylic acid) with PVDF, taking profit of their blending compatibility.

The catalytic performance of developed membrane has been evaluated by using the reduction of *p*-nitrophenol to *p*-aminophenol by sodium borohydride as a model reaction. Membrane with Pd- and/or Au-MNPs have been tested in dead-end filtration-reaction experiments giving as a result that complete *p*-nitrophenol degradation is possible depending on operation parameters such as applied pressure and permeate flux.
Membranes have been characterized in terms of their morphology by Scanning Electron Microscopy and Transmission Electron Microscopy.(cf figure 1)

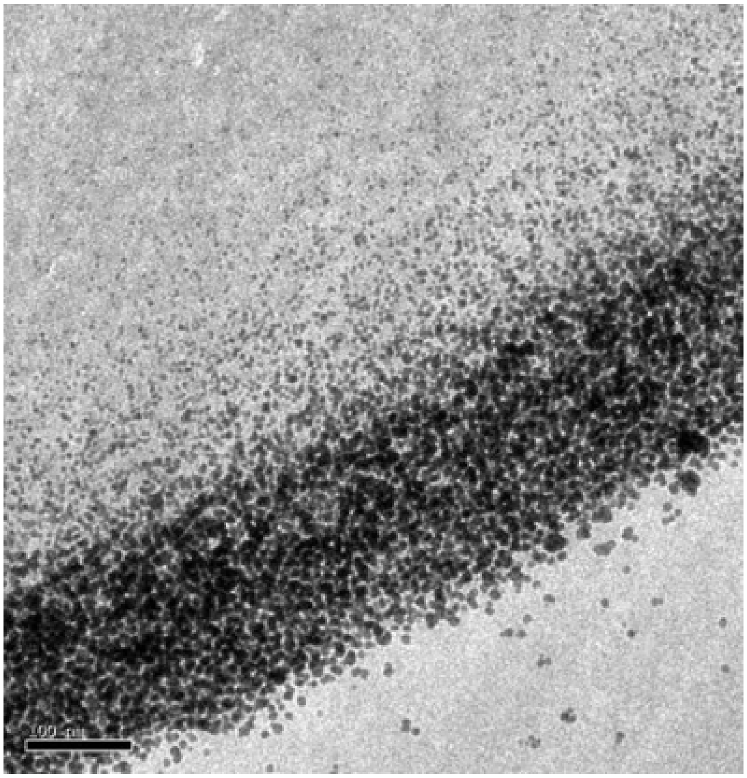

figure1. Hollow fiber membrane loaded with Palladium nanoparticles

The next step will be to use such membrane reactors for catalytic hydrogenation of organic compounds.

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Inorganic membranes 3

ICOM1851

Inorganic Membranes for High Temperature Gas Separation and Reaction

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Inorganic membranes mainly consist of porous and dense membranes and are well suited for high temperature applications. Although porous inorganic membranes give high permeation fluxes, their separation selectivity are generally too low for many important gas phase separation applications. On the other hand, dense inorganic membranes are non-porous and theoretically, only one gas component can permeate through the membrane, thus giving “infinite” separation factors. This presentation will provide an overview of the recent development of inorganic membranes for high temperature gas separation and membrane reactor applications. The discussion will concentrate mainly on inorganic membranes for energy applications at high temperatures, including, among others, ion transport membranes (ITM) for air separation, silica membranes for hydrogen separations and with a special emphasis on composite Pd and Pd/alloy membranes for hydrogen separation and reaction applications. The presentation will conclude with perspectives on the future of inorganic membranes, in general and dense membranes, in particular.

ICOM706

Influence of water vapor on hydrogen permeation flux through 2.5 µm Pd-Ag membranes

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Hydrogen permeation experiments were performed to evaluate the influence of water vapor on hydrogen permeability in Pd-Ag membranes of 2.5 µm thickness. In particular, hydrogen flux in pure hydrogen tests as well as in binary mixtures containing also nitrogen or water vapor have been measured on Pd-Ag (80-20% by weight) hydrogen selective membranes, at temperatures ranging from 573 to 723K and at a transmembrane pressure differences up to about 3 bar. The membranes, supplied by NGK Insulator Ltd., Japan, showed a very high hydrogen permeance and lifetime, as well as virtually infinite selectivity (exceeding 10000 for H_2-N_2 mixtures). The experiments in hydrogen-nitrogen mixtures were carried out at different temperatures, hydrogen concentrations and feed flow rates and confirmed the existence of a non negligible concentration polarization phenomenon in the experimental module. The gas phase mass transport coefficients, and the dimensionless numbers characterizing mass transport, were evaluated at the different operative conditions revealing a linear correlation between Sherwood and Péclet numbers. Interestingly, as shown in Figure 1, the hydrogen permeate fluxes measured with feeds containing H_2-H_2O mixtures resulted generally lower than those obtained for the nitrogen-hydrogen mixtures performed at the same hydrogen mole fraction and operative conditions: in particular, the hydrogen flux depletion increased with decreasing temperature and/or increasing the concentration of water vapor. All the experimental evidences suggest a clear interaction between water vapor and the metallic layer, leading to a lower hydrogen adsorption capacity of the membrane surface. That phenomenon is reversible, since the original permeance of the
membrane was restored once the water vapour was removed from the feed, and is apparently due to a competitive H_2-H_2O adsorption on the Pd-Ag surface. The hydrogen flux depletion was then modelled by considering the simultaneous effects of gas phase resistance and competitive adsorption on the surface, through a modification of Ward and Dao mathematical approach for the analysis of permeation in pure palladium membranes. The model was developed following the same line of thought considered for the description of CO poisoning and, as shown in figure 2, allowed to obtain a rather good agreement between experimental data and calculated results.

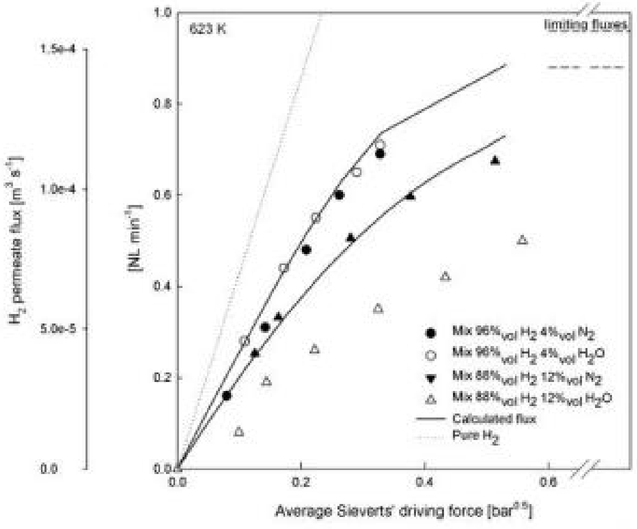

Figure 1. Experimental hydrogen permeate flux versus the average Sieverts' driving in H_2-N_2 and H_2-H_2O mixture containing 96% and 88% vol of H_2 at 623 K.

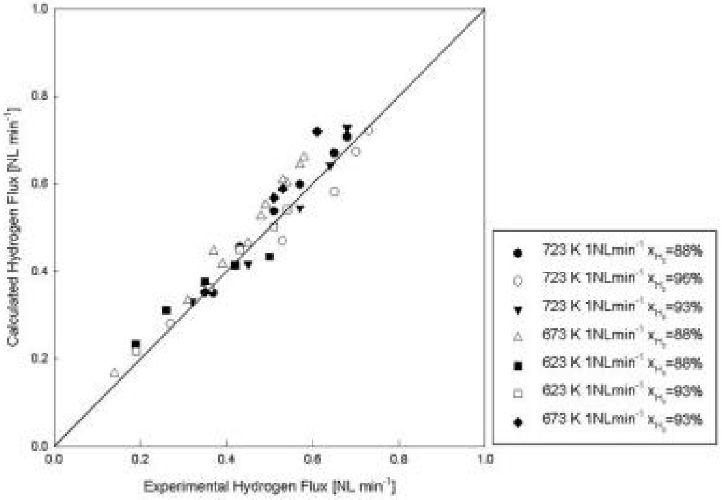

Figure 2. Parity plot between experimental and calculated data for H2-H2O mixtures considering the concentration polarization phenomenon and a competitive adsorption on the metal interface.

ICOM979

Mordenite-type zeolite membrane for the dehydration of acetic acid

Masahiko Matsukata[1,2], Masatoshi Narashima[1], Ken-ichi Sawamura[1,2], Shintaro Daikohara[1], Yasushi Sekine[1,2], Eiichi Kikuchi[1,2]
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Acetic acid (AcOH) is a base chemical, which is largely used for the production of terephthalic acid, acetate ester in petrochemical industry. Low relative volatility of water and AcOH caused a large energy demand in the distillation separation of water/AcOH
mixtures. Our preliminary study suggested that installing a membrane separation unit after a distillation tower can drastically reduce energy demands for the dehydration of
AcOH. In this study, we successfully developed a mordenite-type zeolite membrane with a high water/AcOH permselectivity by controlling its microstructure. We will report the membrane synthesis, separation performance, and plausible separation mechanism.

Mordenite, a kind of zeolite having both high stability against acid and hydrophilic nature, has two kinds of channels, a large straight channel of 0.67x0.70 nm along *c*-axis and a narrow zig zag channel of 0.26x0.56 nm along *b*-axis. Mordenite-type membranes were prepared on the outer surface of tubular porous alumina support (o.d. = 10 mm, the effective membrane area = 6.28 cm^2) by a secondary-growth method including dip-coating of zeolite seeds on the support surface and successive hydrothermal growth of seeds. Vapor permeation tests were performed at atmospheric pressure by feeding a stream containing 10 kPa of steam and 10 kPa of AcOH. Fig. 1 shows that the XRD patterns and top views of two types of mordenite membranes. Orientation of mordenite crystals was controlled by the composition of hydrogel used for the secondary growth of seeds. We found that denser hydrogel gave c-oriented membrane while leaner hydrogel tended to result in randomly-oriented membrane.

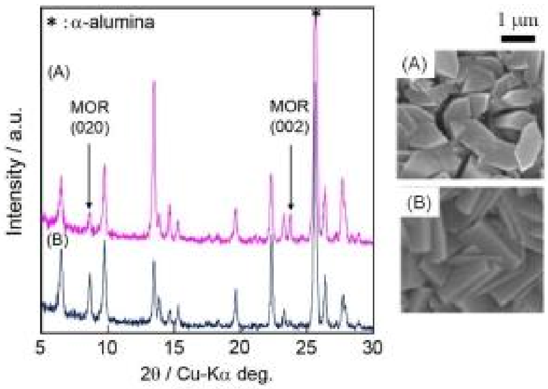

Fig. 1 XRD patterns and typical FE-SEM images of the surface of mordenite membranes : (A) c-oriented, (B) randomly -oriented

In the vapor permeation tests, after water was fed to membrane at 10 kPa and its permeance reached a steady state, 10 kPa of AcOH was additionally fed. Fig. 2 compares the time courses of water permeance at 398 K for these mordenite membranes with different crystal orientation. The water permeances were greater than 10^{-7} mol^{-2} s^{-1} Pa^{-1} for both mordenite membranes before the introduction of AcOH (plots on the ordinate axis). The water permeation through the c-oriented mordenite membrane was significantly hindered and decreased to about 3×10^{-8} mol^{-2} s^{-1} Pa^{-1} with the introduction of AcOH. The permeances of AcOH through both mordenite membranes were very small and thus high water/AcOH separation selectivity (>1000) was obtained. Since the kinetic diameter of AcOH is smaller than the diameter of large straight channel along *c*-axis and larger than the size of pores along *b*-axis, AcOH would adsorb in the micropores along *c*-axis but be difficult to enter the micropores along *b*-direction. Namely, we suppose that molecular-sieving property of the narrower channels worked in the randomly-oriented membrane, and that co-adsorption of AcOH in the larger pores resulted in the strong hindrance of water permeation through the c-oriented membrane.

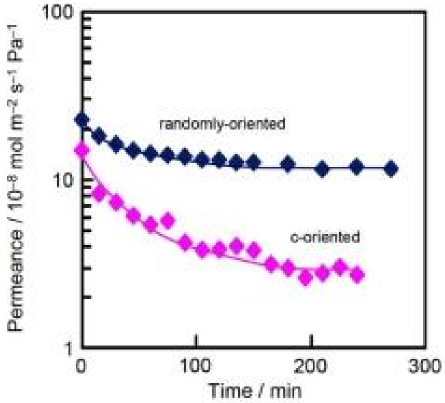

Fig. 2 Effect of AcOH on the time course of water permeation at 398 K.

In conclusion, mordenite-type zeolite membrane shows large water selectivity in separation of AcOH/water mixture. The orientation of mordenite crystals would govern adsorption of AcOH in the micropores of mordenite, resulting in control of the effect of co-adsorption of AcOH on water permeance.

ICOM797

Adsorption, structural changes and membrane performance of ZIF-8 and SAPO materials in the presence of seawater ions

Mikel Duke[1], Bo Zhu[1], Cara Doherty[2], Matthew Hill[2], Moises Carreon[3]
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Zeolitic imidazolate frameworks (ZIFs), a subfamily of MOFs based on transition metals and imidazolates as linkers, with exceptional thermal and chemical stability, are very promising for the fabrication of MOFs membranes. The ZIF-8 structure has a small pore aperture of 0.34 nm. SAPO-34 is a class of zeolite having pore size of 0.38 nm, and is also a promising candidate for membrane fabrication. Numerous efforts have been made to demonstrate the gas separation and liquids pervaporation on these materials, but little explores the application in water treatment. Desalination is a major application for membranes and inorganic based materials may evolve as the next generation of desalination membranes useful for treating aggressive waters (e.g. with scouring particles or harsh/acidic chemicals) found in industries such as mining. Although these materials possess pore sizes suitable for ion selective transport, their structures are influenced by ion adsorption and exchange which would in turn influence their performance in water treatment applications. In this work we show results of the uptake of common ions found in saline waters including Na^+, K^+, Ca^{2+}, Mg^{2+} and Cl^-. As shown in Table 1, ZIF-8 was found to release a large quantity of Na^+ when simply immersed in water, with some Al^{3+}, Ca^{2+} and K^+ also released from the structure. When exposed to seawater, the material instead adsorbed around 4-7 wt% of these ions and also Mg^{2+}. SAPO-34 also adsorbed these ions to about the same degree (Table 1 - in mg/L), but released a large quantity of Al^{3+} into the seawater.

Sample	**Al**	**Ca**	**K**	**Mg**	**Na**
DI water	UD	UD	UD	UD	UD
ZIF-8 exposed to DI water	9.0	8.9	13.2	UD	920
SAPO-34 exposed to DI water	14	4.0	10	UD	UD
Seawater	UD	287	284	884	8269
ZIF-8 exposed to seawater	UD	261	261	840	7950
SAPO-34 exposed to DI water	583	272	152	866	8066

N_2 adsorption results for the materials (Table 2) show a small loss in accessible surface area, possibly due to filling of the structure with ions. Positron annihilation lifetime spectroscopy (PALS) and powder XRD was also used to assess changes to porosity and crystalline structure. Membrane permeation of pure and saline water was carried out to compare characterisation to diffusion performance.

Sample	**S_{BET} (m^2/g)**	**Micropore fraction (%)**
Original ZIF-8	1113	91
DI water exposed ZIF-8	907	91
Seawater exposed ZIF-8	806	89
Original SAPO-34	517	89
DI water exposed SAPO-34	406	89
Seawater exposed SAPO-34	401	91

Membrane bioreactors 3

ICOM1791

Biochemical membrane reactors: key technology to implement knowledge-based sustainable growth

Lidietta Giorno
University of Calabria, Institute on Membrane Technology, ITM-CNR, IT

The fast growing demands for food, energy, water, high quality and high-tech goods are among the most serious challenges the world is facing nowadays. New advanced technologies are needed to bridge the gap between economic growth and environmental sustainability. Membrane assisted biotransformation and simultaneous separation, the key feature of biochemical membrane reactors, will play a crucial role in this contest.

A clear example is represented by the fast growth observed in recent years of membrane bioreactors in wastewater treatment. They represent the main technology able to meet the standard of water quality required by regulations on environmental protection.

In addition to water treatment, many application fields benefit of biochemical membrane reactors, including food, pharmaceutical and bio-refinery. They are unique in contributing to develop intensified production lines able to avoid by-products while favouring products and co-products, i.e. achieving high mass intensity with small foot-print equipment.

Membrane bioreactors, where membrane serves as a separation unit but does not contribute to the reaction itself, are at an advanced stage of development compared to biocatalytic membrane reactors, which combine bioconversion and separation at the membrane level. Biocatalyst stability, especially towards cleaning cycles, is the most challenging aspect of the latter configuration.

The lecture will illustrate the advances of various biochemical membrane reactors configurations as well as their traditional and new application fields, with special emphasis to examples running on a productive scale. Future perspectives, research and innovation needs will be outlined.

ICOM756

Continuous small scale reactor system for screening and characterisation of biocatalysts

Evgenij Lyagin[1], Anja Drews[2], Subhamoy Bhattacharya[1], Matthias Kraume[1]
[1]Technische Universität Berlin, FG Verfahrenstechnik, Berlin, DE, [2]Hochschule für Technik und Wirtschaft Berlin, FB II, LSE, Berlin, DE

Introduction

Continuously operated membrane reactors offer versatile advantages for enzymatic and co-factor regenerating reactions over batch operation. However, commercially available biocatalyst screening and characterisation systems mostly work in batch or fed-batch mode only. So, the primary goal of this project is the development of a membrane-based screening and characterisation system that meets versatile requirements: it should be suitable for parallel continuous operation and for homogeneous catalysis. Monitoring and control of temperature, pH, residence time (HRT), catalyst activity and power input shall also be possible. Particularly HRT, i.e. flux control, at that small scale presents a bigger problem than at industrial scale, especially considering that the overall system should be affordable.

Materials

Cellulose hydrolysis by enzymes from *Trichoderma reesei* (Sigma) which is inhibited by its products was chosen as a model reaction which additionally has high fouling potential for the proof of concept. A PES membrane (10kDa MWCO) was used to retain the enzyme.

Results

A prototype with 2 parallel reactors (100 mL scale) was designed and constructed. For the precise HRT control, a flow rate PID-controller with the feed pressure as the actuator was integrated in the system. Figure 1 exemplarily shows the development of the feed pressure over time. The specified flow rate of 10 mL/h could be maintained over the whole duration of the experiment and thus a control of HRT with an accuracy of ±1 % was possible. However, Figure 1 shows also that by successive pore closures and compacting of deposits, a long-term experiment can be hazardous. An increase of the feed pressure up to the maximum allowable reactor pressure can lead to a premature abortion of the experiment.

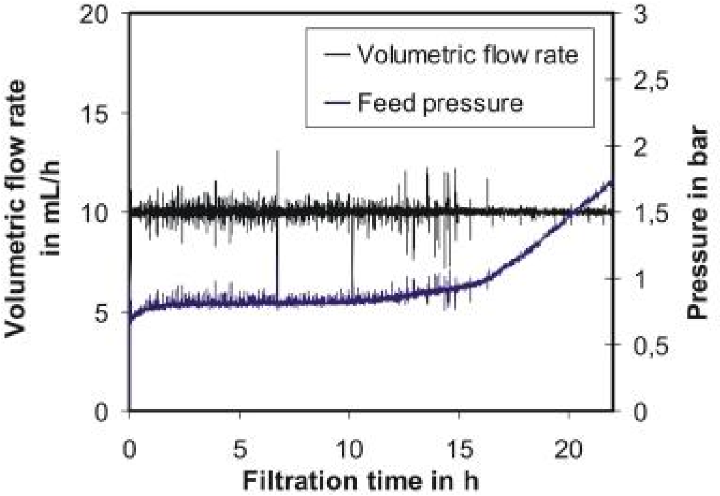

Figure 1. Volumetric flow rate and feed pressure development over time, $c_{S,0}$= 25 g/L

So, without the possibility of backflush, a concept for fouling suppression relying purely on relaxation, was worked out. Figure 2 shows results from using this concept. Regular pressure releases (depending on HRT every 6-24 hours) led to more effective deposit layer removal from the membrane by means of the mixing device. The gradual TMP decrease after each relaxation could be an indication of a slow decompaction of deposits.

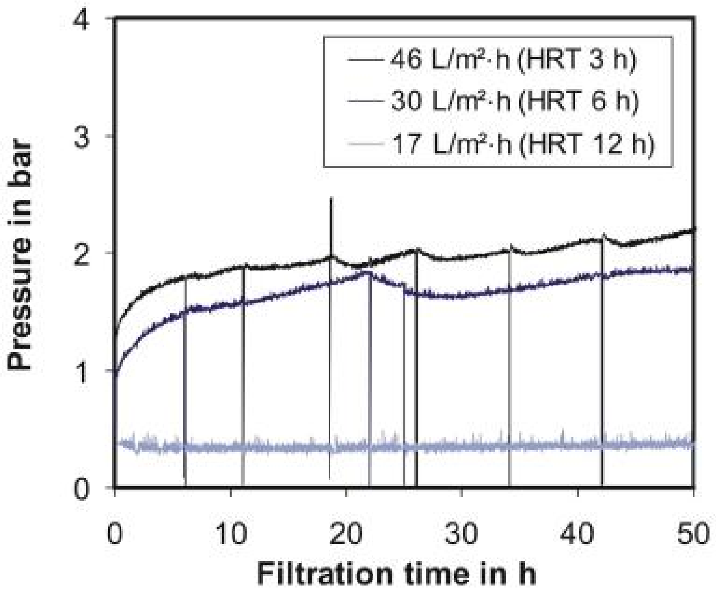

Figure 2. Fouling suppression during cellulose conversion with flow rates from 7.5-30 mL/h, $c_{S,0}$ = 25 g/L

So, in this manner, a precise flow control from 5-90 mL/h and HRT from 1-18 h with an accuracy of ±2 %, respectively, was realised over 100 hours. For the pH or catalyst activity control, i.e. dosing of additional buffer or enzymes, a concept for precise dosing was elaborated and realised. It allows dosing of liquid volumes from 0.3-1 mL with ±0.1 mL precision (data not shown) without disturbing normal continuous operation.

This work is part of the DFG-Cluster of Excellence (EXC 314) “UniCat”.

Publications:

Lyagin et al., *Biotechnol. J.* ***2010**, 5, 813-821.*

ICOM1026

Study and development of an enzymatic membrane working in supercritical conditions for the synthesis of natural label esters

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Institut Européen des membranes, Génie des procédés membranaires, Montpellier, FR

During the last years, environmental problems and cost issues of chemical synthesis processes generally working at high temperature (100-200°C) and pressure (10-50 bar) and using organic solvents have become of fundamental importance. [1]

In this work, a new method for ester synthesis is developed based on three key points: firstly the reaction is catalysed by enzymes thus improving process cost (lower temperature, reduced number of stages) and process performance (enhanced selectivity). Secondly, the enzyme is immobilized on a membrane support and the reaction is carried out in a continuous enzymatic membrane reactor in order to intensify the process. Finally, to replace organic solvents, supercritical carbon dioxide is chosen for its attractive properties like being environmental friendly, allowing efficient mass transfer and having relatively low critical conditions (31°C, 74 bar).

This study is based on three main steps:

- The development and the optimization of a large scale enzymatic membrane

- The optimization of the supercritical process (experimental study and modelling)

- The evaluation of the process performance (cost, comparison with existing processes)

The development of enzymatic membrane has been achieved by developing an immobilization protocol inspired from a previous work in which the enzyme from *Candida Antarctica* lipase B is covalently attached to a polymer layer previously adsorbed on a porous ceramic membrane with glutatraldehyde as cross linker. [2]

The first part of the study consisted to a scale-up of the immobilization protocol from a 15 cm length, 1 channel membrane to a 120 cm length, 39 channels one. The validation of the scale-up has been done by reaction essays in liquid phase in the continuous enzymatic membrane reactor. Two reactions were tested: hydrolysis of butyl acetate and synthesis of anisyl acetate. Performances were similar for the different membrane scales thus validating the scale-up.

Then, the enzymatic membrane was used for the synthesis of anisyl acetate in supercritical carbon dioxide in an enzymatic membrane reactor. Different configurations (continuous and discontinuous) were investigated. In parallel, the modeling of the enzymatic membrane reactor is carried out.

[1] Oliveira, M.V., et al., *Kinetic modelling of decyl acetate synthesis by immobilized lipase-catalysed transesterification of vinyl acetate with decanol in supercritical carbon dioxide.* The Journal of Supercritical Fluids, 2009, 50(2), 138-145.

[2] Magnan, E., et al, *Immobilization of lipase on a ceramic membrane: activity and stability*. Journal of Membrane Science, 2004, 241, 161-166.

Acknoledgements
The authors acknowledge the French ANR (Agence Nationale pour la Recherche) for the financial support (Project ANR-08-CP2D-08).

ICOM757

Development and validation of a high-throughput membrane bioreactor (HT-MBR) as a tool for fouling study and membrane development

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[1]*Katholieke Universiteit Leuven, Centre for Surface Chemistry and Catalysis, Faculty of Bioscience Engineering,, Leuven, BE,*
[2]*Katholieke Universiteit Leuven, Laboratory of Aquatic Ecology and Evolutionary Biology, Leuven, BE*

High-throughput (HT) technology has proven to be a powerful tool to rapidly and efficiently screen materials and processes. The objective of this study was to investigate the applicability of HT technology for membrane bioreactors (MBRs). For this purpose, a first prototype HT-MBR consisting of six parallel filtration membrane modules was developed. The performance of the system was validated by studying its reproducibility, scalability and reliability in terms of the critical flux (CF) and filtration index (FI). The tests were performed using both lab-made Polysulfone membranes (PSF_L) and commercial Polyvinylidene Fluoride ($PVDF_T$) membranes from Toray. The system could be used to measure the CF simultaneously in parallel operation for six different membranes while percentage standard deviations (%σ) on the FIs were respectively 2-7, 3-23 and 7-16% for repeated filtrations, filtrations in different module positions (interchanged positions) and filtrations with different module areas. Improved reproducibility was obtained for tests using the commercial $PVDF_T$ membrane with a %σ of 5-7 and 4-7% for repeated filtrations on single position and interchanged positions, respectively, as ascribed to more homogeneous membrane properties over different samples. The overall results prove that the developed HT-MBR can be used as an efficient tool for fouling studies, for testing and developing membranes for MBR application and for studying the overall MBR process. Also, using six replicate membrane modules allows for a level of statistical analysis that normally can not be performed on conventional MBR testing systems due to time, energy, cost and technical limitations.

ICOM 2011

Friday, July 29th 2011

Plenary Lecture 3

Friday, July 29th 2011

ICOM1859

Carbon Dioxide Capture in Metal-Organic Frameworks

Zoey R. Herm, Jeffrey R. Long, Eric D. Bloch, Thomas McDonald, Kenji Sumida, Jarad Mason, Hye Jin Choi, Aude Demessence, Deanna M. D'Alessandro, Leslie J. Murray
Lawrence Berkeley National Laboratory, University of California, Berkeley Materials Sciences Division, Department of Chemistry, US

Efforts to utilize metal-organic frameworks, a new class of materials exhibiting high surface areas, tunable pore dimensions, and tailorable surface functionality, for CO_2 capture will be presented.[1] Open metal coordination sites on the framework surface can deliver a high CO_2 loading capacity at low pressures.[2] However, additional criteria, such as water stability and the selective binding of CO_2 over N_2, must also be considered. Towards that end, we have targeted air- and water-stable frameworks bearing surfaces coated with alkylamine groups. Use of 1,3,5-benzenetristriazolate as a bridging ligand has led to sodalite-type frameworks of the type $M_3[(M_4Cl)_3(BTTri)_8]_2$, possessing open M^{2+} coordination sites and exhibiting good chemical and thermal stability. Attachment of ethylenediamine to the M^{2+} sites within this structure can generate a material that selectively binds CO_2 over N_2.[3] In addition, the application of frameworks with redox-active transition metal sites for the capture of O_2 from air will be discussed.[4]

(1) D'Alessandro, D. M.; Smit, B.; Long, J. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 6058.

(2) Sumida, K.; Horike, S.; Kaye, S. S.; Herm, Z. R.; Queen, W. L.; Brown, C. M.; Grandjean, F.; Long, G. J.; Dailly, A.; Long, J. R. *Chem. Sci.* **2010**, *1*, 184.

(3) Demessence, A.; D'Alessandro, D. M.; Foo, M. L.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 8784.

(4) Murray, L. J.; Dincă, M.; Yano, J.; Chavan, S.; Bordiga, S.; Brown, C. M.; Long, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 7856.

Parallel Sessions

Friday, July 29th 2011

Morning Session, 10.30 – 12.20

Gas and vapor separation 7

ICOM1788

Recent Advances and Future Directions in Gas Separation Membranes

Benny D. Freeman
University of Texas at Austin, Department of Chemical Engineering, Texas Materials Institute, and Center for Energy and Environmental Resources, US

This presentation will discuss structural features important in the use of polymers as rate-controlling membranes for gas separations. In particular, materials having desirable combinations of high permeability and high selectivity based upon solubility selectivity (e.g., butane removal from natural gas, CO_2 separation from H_2 or N_2) or diffusivity selectivity (e.g., CO_2 removal from natural gas) will be presented. For example, cross-linked poly(ethylene oxide) (XLPEO) polymers, which are flexible, rubbery polymers identified as promising materials to remove polar and acid gases, such as CO_2, from mixtures with light gases, such as H_2. One member of this family of materials was reported to have a CO_2 permeability coefficient of approximately 500 Barrer and a CO_2/H_2 mixed gas selectivity of 30 at -20C.[1] Such materials achieve high selectivity based upon their high solubility selectivity favoring CO_2 transport. Prepared by cross-linking low molecular weight poly(ethylene glycol) diacrylate with other poly(ethylene oxide) acrylates, XLPEO polymers exhibit good separation properties thanks to ethylene oxide group interaction with CO_2 and suppression of crystallinity normally found in high molecular weight, linear poly(ethylene oxide).

Polymers can also be tailored to achieve high selectivity based upon high diffusivity selectivity. In this case, highly rigid, glassy polymers with proper free volume element size and size distribution are desirable. Polyimides with ortho-position functional groups may be solution-processed to form conventional films and membranes. Such materials can undergo thermal rearrangement to form highly rigid benzoxazole or benzithiazole structures having very high permeability coefficients and high selectivity. For example, one member of this family was prepared having a CO_2 permeability coefficient of 1610 Barrer and a CO_2/CH_4 selectivity, under mixed gas conditions, of 42-46, depending on the partial pressure of CO_2 in the mixture.[2] These thermally rearranged (TR) polymers are insoluble in common solvents, giving them good chemical stability, and highly thermally stable, which are important attributes for membranes that would be used in chemically or thermally aggressive environments.

The overarching message from this presentation is that polymers can be exquisitely tuned to have favourable permeation properties. Materials may be designed to achieve high selectivity by being more soluble to one molecule than another or by having a strong ability to sieve gas molecules based on minute differences in gas molecule size. In both cases, the structure of the polymer may be optimized to permit rapid permeation.

[1] Lin, H., E. van Wagner, B.D. Freeman, L.G. Toy, and R.P. Gupta, "Plasticization-Enhanced H_2 Purification Using Polymeric Membranes," *Science,* **311(5761)**, 639-642 (2006).

[2] Park, H.B., C.H. Jung, Y.M. Lee, A.J. Hill, S.J. Pas, S.T. Mudie, E. van Wagner, B.D. Freeman, and D.J. Cookson, "Polymers with Cavities Tuned for Fast, Selective Transport of Small Molecules and Ions," *Science*, **318**, 254-258 (2007).

ICOM292

Cyclic membrane gas separation processes: Why? When? How?

Eric FAVRE, Lei WANG, Jean Pierre CORRIOU, Christophe CASTEL
LRGP CNRS, ENSIC, Nancy, FR

The analysis of membrane gas separation processes under transient conditions for practical applications is a rather unexplored domain. One of the main advantage of membrane processes compared to other separations is indeed their ability to work under steady conditions, without any separate regeneration step. Nevertheless, unique separation performances can be obtained in some cases when a transient regime is applied, especially when the differences between the diffusion coefficients of the permeating species largely exceed the differences in permeability. Paul explored this issue a pioneering study, based on a cyclic process with synchronous valve operation [1]. We recently extended the analysis thanks to numerical simulation methods and optimization techniques which offer the possibility to explore asynchronous operation modes [2]. The possibility to achieve very high selectivity for some gas pairs can be considered as the main interest of cyclic membrane processes.

This communication intends to provide an analysis of the gaseous mixtures for which high separation performances, unattainable through steady operation, can be achieved through transient conditions. An extensive computation has been performed on numerous gas pairs in order to identify the most interesting mixtures for cyclic membrane gas separation processes.

In a second step, the simulation and optimization techniques have been applied to different systems, based on reported permeability data through a given polymer. The main outcome of this study is a chart where steady state and cyclic separation performances are compared. An example is given on figure 1.

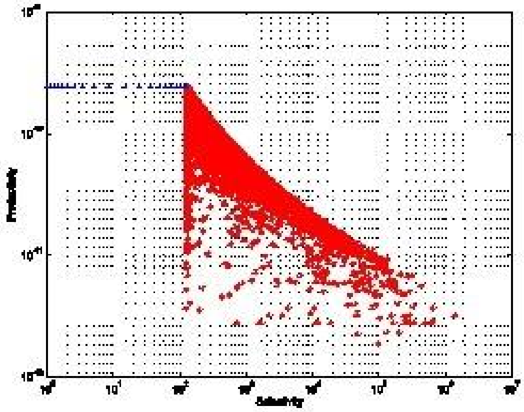

Figure 1: Example of a master chart which compares the selectivity / productivity trade-off between steady state operation (cross) and unsteady state cyclic operation (dots) for a given system.

Numerous charts of this type have been prepared and will be discussed, especially for gaseous mixtures of industrial interest. The different processes which have been already proposed for cyclic membrane gas separations will finally be critically discussed.

Paul, D.R. "Membrane separation of gases using steady cyclic operation." *Ind. Eng. Chem. Process Des. Dev*, 1971: 375-379.

Corriou, J.P., C. Fonteix, et E. Favre. «Optimization of a pulsed operation of gas separation by membrane.» *AIChE Journal* 54, n° 5 (2008): 1224-1234.

ICOM1604

Effect of Hydrogen Pressure on Permeability of Ni-based Amorphous Membranes

Sang-Mun Kim[1], Michael Dolan[2], Narendra Pal[1], Wen-Ming Chien[1], Joshua Lamb[1], Anjali Talekar[1], Dhanesh Chandra[1], Stephen Paglieri[3], Ted Flanagan[4]
[1]University of Nevada, Reno, Reno, Nevada, US, [2]CSIRO, Division of Energy Technology, Kenmore, QLD, AU, [3]TDA Research, Inc., Wheat Ridge, Colorado, US, [4]The University of Vermont, Burlington, Vermont, US

Amorphous Ni-Nb-Zr alloys are a promising alternative to Pd alloy membranes having similar permeabilities with a significantly reduced materials cost. For both Pd and amorphous Ni-Nb-Zr membranes there is found to be a linear dependence of flux upon ($p^{1/2}_f$ - $p^{1/2}_p$) indicating that the slow step is bulk diffusion. The permeability through such membranes is a product of the solubility and diffusion coefficient. In this paper, the hydrogen permeability of a $(Ni_{0.6}Nb_{0.4})_{70}Zr_{30}$ membrane was determined to be 6.97×10^{-9} mol $m^{-1}s^{-1}p^{-0.5}$ (Δp_{H2} = 0.2 MPa, 350 °C) and the dependence of the permeability on the differential pressure across the membrane, Δp_{H2}, was examined. For a Pd membrane (48 μm) an increase in Δp_{H2} reduces the H permeability whereas for the Ni-Nb-Zr membranes, an increase of Δp_{H2} increases the permeability. The diffusion coefficients of H through the amorphous alloys were determined from the H flux and isotherms which had been measured using a Sievert's apparatus. The temperature dependences of the H permeability, the H solubility and the H diffusion coefficient in the amorphous membranes will also be given. The crystallization temperature and activation energy for crystallization of these membranes will also be reported.

ICOM421

Fabrication of the thin planar and tubular BSCF oxygen membranes using thermoplastic process route

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Ceramic membranes with mixed ionic and electronic conductivity (MIECs) have received extensive interest for application in oxygen separation, solid oxide fuel cells and the partial oxidation of methane to syngas. From point of view of requirements, such as high oxygen flux and mechanical stability during operating conditions, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is demonstrated to be one of the most promising materials that show high oxygen permeation flux and favorable phase stability at high temperatures. The investigations have shown that the performance of MIECs membranes, related to permeation flux, has been improved by reducing the membrane thickness.

This work concerns to use thermoplastic forming which helps to produce thin-walled structure with a thickness below 1 mm, in order to reach higher performance.
Tubular and planar membranes have been prepared by thermoplastic forming method using commercial BSCF powder as raw material as well as polystyrene (PS) and stearic acid (SA) as binder components. In this study, a powder content of 48, 52, 54 and 56 percentages by volume was evaluated to achieve non deformed membrane structures after heat treatment.

The influence of powder content on the microstructure of tubular membrane was examined and the relative density of sintered tubes independent of powder content was higher than 95% after sintering at 1150 ºC/2 h. The tubular membranes showed an unexpected deformation during the binder removal. To investigate the deformation behavior during thermal treatment, pellets were pressed by using warm pressing method and feedstocks with different powder content.

Special debinding experiments indicated that a high powder content (> 56 vol. %) is remarkably effective to minimize the deformation of free standing planar membrane during thermal debinding. These results confirm with our results on debinding tubular thin structures with BSCF material (same powder content). Nevertheless these results are in contrast to previous work, for fabricating tubular ZrO2 and LSCF, were 50 to 52 vol.% powder content was sufficient to produce thin wall ceramic tubes.

With changing the binder system, we have achieved a feedstock with high powder content and low viscosity. Plasticity is sufficient to extrude thin tubular membrane with low longitudinal curvature and small deviation in wall thickness.

For oxygen flux investigation, measurements were carried out on the planar thin structure with a wall thickness of 0.6 mm and sintered at 1000 and 1100℃. The microstructure was studied by SEM and EBSD method. An average grain size of 5 and 30um were obtained for 1000℃ and 1100℃, respectively. Oxygen permeation flux indicated that oxygen permeation flux is independent on grain size of the membranes in the studied parameter.

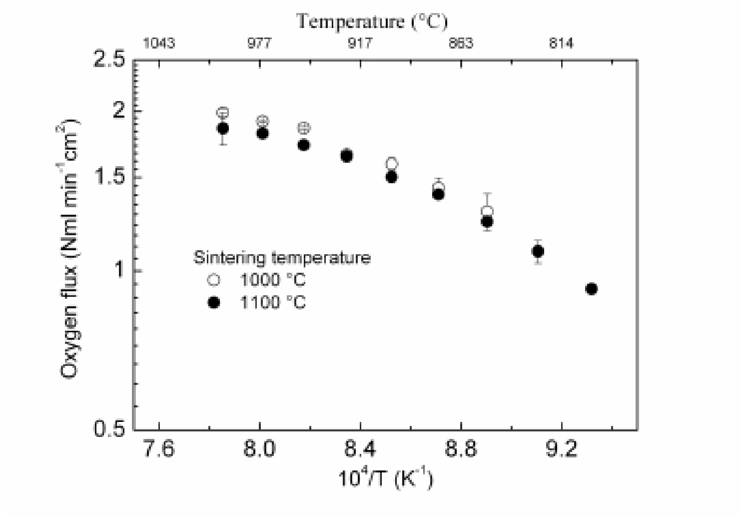

Fig. 1. Inverse Pole Figure Maps on FWD picture for membrane sintered at 1100 °C.

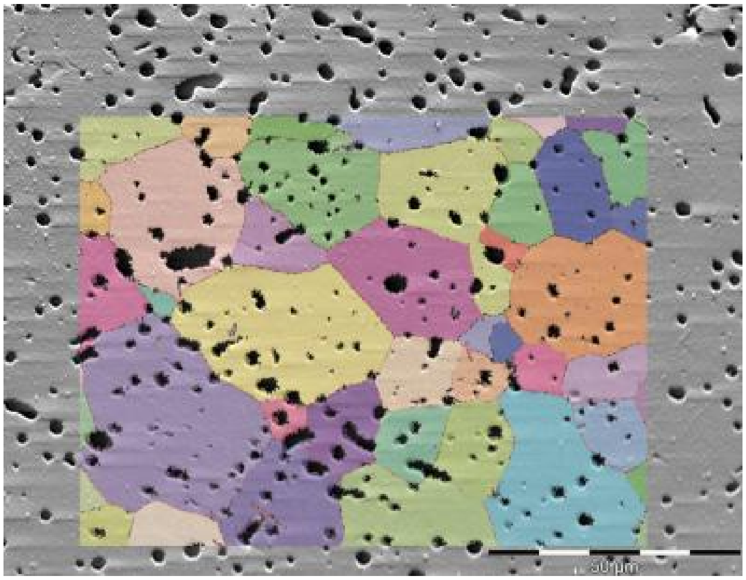

Fig. 2. Temperature dependence of oxygen permeation flux through the different BSCF membranes sintered at 1000 °C and 1100 °C for 2 h, air flow rate = 350 Nml/min and sweep flow rate 100 Nml/min.

ICOM906

Humidity harvesting with water vapor selective membranes

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Air contains significant amounts of water vapor, making it an interesting source for point of use or off grid (using renewable energy) water production. Water vapor can be recovered from air by cooling, thereby condensating water vapor, which is already done by several companies. Dutch rainmaker [1] uses the mechanical energy from the windmill to drive a heat pump directly. Therefore, no turbine is necessary, which is one of the most expensive components of the windmill, thereby lowering the cost of water production. Another advantage of the windmill is that it can be used in locations where no electricity or fuel is available. Air is cooled until it reaches the dew point where water starts to condense. A post treatment is necessary in order to remove contaminants from water. This process requires significant amounts of energy and the water needs to be purified further in order to remove contaminants from the water which are present in air. Water vapor selective membranes offer the advantage that they only direct water vapor towards the condenser, allowing for a more energy efficient operation and producing water with a superior quality (ultra pure water). This process is schematically depicted in Figure 1.

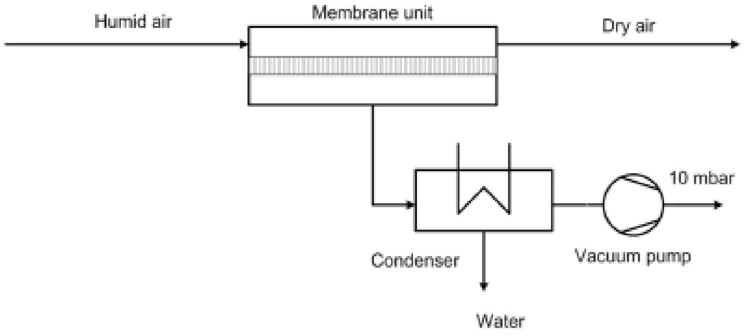

Figure 1: Water production with water vapor selective membranes.

One of the challenges for this membrane application is to increase the mass transfer rate of water vapor through the membrane by reducing concentration polarization via an optimized aerodynamic and stack design. Also the air properties (temperature, humidity) affect the performance of the membrane system. The selectivity of the membrane is an important parameter determining the performance of the composite membrane. Also the pressure ratio (ratio of the feed pressure, p0, to permeate pressure, pl, across the membrane) is an important parameter. The performance of several composite membranes will be evaluated for their applicability for making water from air.

[1] www.dutchrainmaker.nl

NF/RO 4

ICOM1797

Renewable Energy Powered Membrane Systems: Photovoltaic and Wind Powered Nanofiltration

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This keynote lecture reviews a decade of work on direct coupling of renewable energy sources (namely photovoltaics and wind) with nanofiltration (NF). Direct coupling of DC electricity avoids the use of inverters and batteries and results in fluctuations in the energy supply to process pumps and other equipment. These energy fluctuations result in variations in transmembrane pressure and flowrate. Such fluctuations will affect system performance (both positively and negatively) and the essence of this research has been to determine, in a systematic manner, the safe operating window of such a system.

The constraints imposed via the safe operating window are of short, medium and longer term. Concentration polarisation, for example, will have immediate effects on system performance, fouling in a medium term result of operation, while possible increased wear on the system will evidence itself in the longer term due frequent system shut down as a result of intermittent energy provision during cloudy and/or calm periods. System performance can be summarised in terms of: Water productivity: flux and cumulative permeate volume vary with membrane type, pressure and operating conditions.

Contaminant retention (salt and inorganic contaminants - fluoride, nitrate, nitrite, uranium, arsenic and boron) rely on membrane characteristics and water chemistry. Potential for sustained high retention of such contaminants is a key advantage of nanofiltration over competing processes.

Specific energy consumption: the amount of energy required to produce a volume of water is an important factor as water problems often result in energy problems. Reducing the specific energy consumption is important to achieve a low system life cycle cost and, thus, cost of water. The safe operating window specifies the amount of solar irradiance or wind speed required to operate the system at acceptable performance. Results of short term tests will be presented that outline the impact of systematic energy fluctuation on performance. Findings illustrate system resilience in the short term towards significant energy fluctuations. Such fluctuations were provided from both controlled variation of frequency, period, amplitude and off time as well as real wind and solar data. Novel insights can be drawn from a drastically different research approach that examines a membrane system outside its defined operating specification. Methodology provides the opportunity to explain performance at random real time variation of energy that opens new opportunities for membrane technology integration and systems development. The goal of this systems development work is to realise decentralised membrane technologies able to operate independent of infrastructure such as electricity grid of civil works. This opens currently underexploited markets of humanitarian aid and international development. Current limitations are operating and maintenance regimes that ascertain long term technical sustainability of systems in harsh environments. The next decade of research will require a concerted effort of innovation to develop new operating protocols and long-term testing.

Related Journal Publications

Schäfer, A.I. ; Broeckmann, A. ; Richards, B.S. (2007) Renewable energy powered membrane technology. 1.Development and characterisation of a photovoltaic hybrid membrane system, Environmental Science & Technology, 41, 998-1003

Richards, B.S. ; Capão, D.P.S. ; Schäfer, A.I. (2008) Renewable energy powered membrane technology 2. The effect of energy fluctuations on performance of a photovoltaic hybrid membrane system, Environmental Science & Technology, 42(12); 4563-4569

Rossiter, H. ; Graham, M. J. ; Schäfer, A.I. (2010) Impact of speciation on behaviour of uranium in a solar powered membrane system for treatment of brackish groundwater, Journal of Separation and Purification Technology, 71, 89–96

Richards, L. ; Richards, B.S. ; Schäfer, A.I. (2011) Renewable energy powered membrane technology: Effect of contaminant speciation on retention and membrane deposition, Journal of Membrane Science, 369, 188-195

Park, G.L. ; Schäfer, A.I. ; Richards, B.S. (2011) Renewable energy powered membrane technology: The effect of wind speed fluctuations on the performance of a wind-powered membrane system for brackish water desalination, Journal of Membrane Science, 370, 34–44

ICOM643

Are electrostatic interactions always involved in transport mechanisms of charged species during nanofiltration in concentrate acid phosphoric media?

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Raw phosphoric acid that is industrially produced by the so-called “wet route” contains a lot of impurities, out of them are metallic ones (few ppm). Before commercialisation, it purification is needed that is commonly obtained from a cascade of physico-chemical treatments. For many years now, we try to propose the integration of nanofiltration in this purification process [1, 2].

Even if we are still far from performances' prediction, NF is widely used in diluted aqueous media where transport mechanisms are well identified, out of them: steric hindrance, electrostatic interactions between membrane and charged solutes, as well as dielectric effects able to modulate electrostatic interactions and solvation occurring outside and inside the pores, of course in different extents.

Very few studies deal with NF in extreme conditions as in concentrate inorganic acid (for instance 5.5 – 5.9 M H_3PO_4) , probably mainly due to the lack of sufficiently stable and membrane materials allowing high retention. MPF-34 membrane from Koch matches with the two types of requirement

Moreover, in concentrate acid media, interactions between metal species (for instance) and acid are predominant toward that involving simple solvation phenomenon due to water. Consequently, the system physico-chemistry is widely modified compared with that occurring in water.

The aim of this paper is to understand transport phenomenon of
(i) phosphoric acid itself (5.9 M - 0.12 M) versus more or less dissociation state. Acid forms are H_3PO_4, $H_2PO_4^-$, HPO_4^{--},

(ii) metallic impurity containing iron, namely free and complexed forms. In 20 mM Fe solutions, iron forms can be $Fe(H_2PO_4)_4^-$, $Fe(H_2PO_4)^{++}$, $Fe(HPO_4)^+$ and Fe^{3+}

NF of raw industrial phosphoric acid (5.9 M) containing impurities involving more than 19 identified elements in various chemical forms show negative rejection of monovalent chloride.

Three model solutions of 20 mM iron chloride in H_3PO_4 (5.9 M, 1.2 M and 0.12 M) are nanofiltered. Retention of all forms of phosphoric acid and of iron are determined at VRR= 1.2 corresponding to significantly different fluxes, decreasing from 13 to 0.1 $10^{-6\ m.s^{-1}}$ when the phosphoric acid concentration increases from 0.12 to 5.9 M.

Retentions always range in the same order, suggesting a negatively charged active membrane : $Fe\ (H_2PO_4)_4^- > (Fe(H_2PO_4)^{++} > FeHPO_4^+) > H_3PO_4 > H_2PO_4^- > H^+ > Cl^-$.

These analyses allow concluding that Donnan mechanism is still dominant during NF in 5.5 M phosphoric acid where acid is mainly uncharged and thus poorly retained but iron mainly present as a negatively charged iron complexe is highly retained thanks to electrostatic repulsions and consequently monovalent chloride, the more mobile membrane co-ion, is negatively rejected.

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ICOM530

A novel type of composite membrane containing zwitterions for nanofiltration with high water flux and improved antifouling performances

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This article provides a novel method for introducing zwitterionic polymers into nanofiltration membranes, with the aim of achieving high water flux and good antifouling performances. In detail, terpolymers P(DMC-HEA-DMAPS) composed of the 2-methacryloyloxy ethyl trimethylammonium chloride (DMC), 2-hydroxyethyl acrylate (HEA) and 3-dimethyl(methacryloylo xyethyl) ammonium propane sulfonate (DMAPS) was synthesized via the free-radical copolymerization. Chemical structures and compositions of these polymers were characterized by fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA), respectively; and were found to be tunable by varying feed ratios and reaction conditions. Subsequently, composite nanofiltration membranes (CNFMs) were prepared by dip-coating the polymer solution (1.5 wt%) onto polysulfone ultrafiltration (PSF-UF) supporting membrane, followed by crosslinking with glutaraldehyde (GA) (0.3 wt%) at 50 °C for 3 h. Performances of CNFMs were characterized with field emission electron microscopy (FESEM), atomic force microscopy (AFM), dynamic water contact angle and nanofiltration test. It is interesting to find that nanofiltration performances of CNFMs were significantly improved with introducing the zwitterionic groups into membranes. As shown in Fig. 1, the highest nanofiltration performance was obtained for CNFM3 with 3.18 mol% DMAPS, e.g. R_{MgCl2} = 96.5%, J_{MgCl2} = 47.8 L.m^{-2}.h^{-1}, respectively (testing with 1 g.L^{-1} $MgCl_2$ aqueous solution at 0.6MPa and 25 °C). Meanwhile, the shielding effect of salt ions in feed solution on nanofiltration performances of CNFMs was strongly depressed by zwitterions DMAPS. Moreover, antifouling performances of CNFMs were investigated with filtration of 1 g.L^{-1} $MgCl_2$ or 1 g.L^{-1} $MgCl_2$ +0.1 g.L^{-1} BSA solutions at pH = 4.2±0.1, pH = 4.7±0.1 and pH = 5.5±0.1, respectively. Experiment results demonstrated that the extent of fouling for CNFM3 was significantly reduced and most of the fouling was reversible, suggesting good antifouling property of composite nanofiltration membranes CNFMs with zwitterions (as shown in Fig. 2).

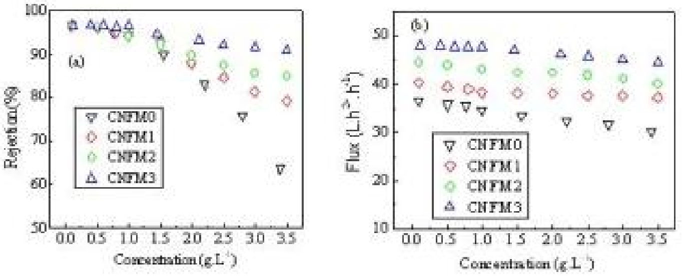

Fig. 1. Effect of salt concentration in feed solution on nanofiltration performances of CNFM0 (pristine membrane), CNFM1 (1.48 mol% DMAPS), CNFM2 (2.92 mol% DMAPS) and CNFM3 (3.18 mol% DMAPS) testing with $MgCl_2$ aqueous solution at 0.6 MPa and 25 °C

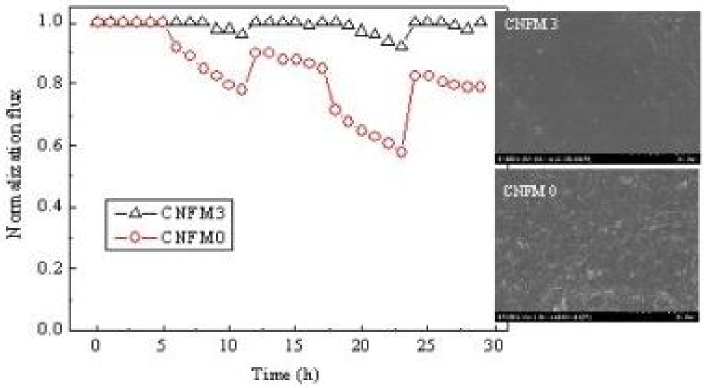

Fig. 2. Time dependent normalization flux of CNFM3 and CNFM0 testing with 1g.L^{-1} MgCl$_2$ and 1 g.L^{-1} MgCl$_2$ +0.1 g.L^{-1} BSA aqueous solutions (pH = 4.7±0.1) at 0.6 MPa and 25 ^{o}C

ICOM960

Progress of RO Membrane Technology Based on Morphology Analyses

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Membrane technologies are regarded as the most powerful tools to solve water shortage we face, since they make it possible to supply high-grade water with low cost and low energy consumption. RO membrane technologies have made great progress in last 50 years. However, still more improvement of membrane performance is demanded to achieve lower energy consumption and higher water quality in seawater and brackish water desalination field.

Fundamental researches for RO membranes on investigating physical and chemical properties to obtain further excellent performance have been being executed. In our past work, positron annihilation lifetime spectroscopy (PALS) study showed that there is the correlation between the pore size and the solute removal performance in RO membranes. Analyses by solid state nuclear magnetic resolution (NMR) provided much information on chemical structure and precise water content of polyamide layer of RO membranes, and molecular dynamics (MD) simulation based on the information resulted in good agreement with pore size measured by PALS. The study gave us a parameter of pore size to control solute removal ratio of RO membrane for achieve higher water quality.

In order to realize improvement of energy saving, it is indispensable to obtain the parameters influencing on water permeability of membrane. In this presentation, we will discuss the results of morphology analyses conducted to find them. A precise image of cross section of protuberance structure of RO membrane surface is given by transmission electron microscopy (TEM) analysis through a special treatment of membrane for preserving the structure as shown in figure 1, and it enabled a quantification of surface morphology.

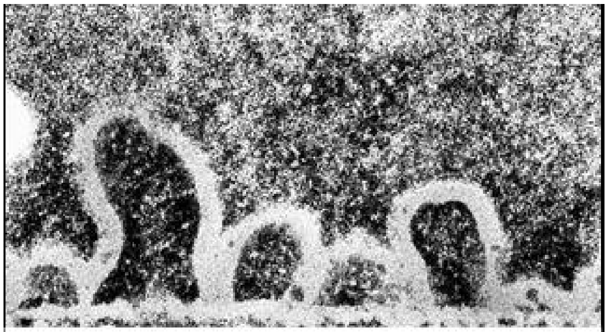

Figure1. Cross section of RO membrane (TEM image)

According to the precise image and elemental analysis of cross section of the protuberances, since the inside of protuberance was proved as a cave-like structure, the contribution of this structure to water permeability was agreeable. With the comparison between membranes having different water permeability, larger membrane surface area or thinner membrane thickness showed higher water permeability. Consequently, the correlation between the morphology of protuberance and water permeability of membrane was revealed, and new parameters for the estimation of the RO membrane structure, surface area and thickness were obtained. Thus, the total structural study relating to the RO membrane performance of solute removal and water permeability has been greatly progressed by the pore size and the morphology analyses. New energy-saving and high rejection membranes utilizing these studies and its utility study will be also introduced.

ICOM651

Polyvinyl alcohol/activated carbon composite thin layer to improve chlorine resistance of RO polyamide membranes

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The Membrane Separation Processes (MSP) has been widely used for water desalination as an alternative to produce potable water. Reverse Osmosis (RO) and Nanofiltration (NF) are the most used processes for water desalination and much research attention has been focused on better process performance. However, the membrane fouling is still the most serious drawback. In order to avoid or minimize fouling in RO membranes, it is necessary several steps of water pre-treatment. Oxidizing biocides as chlorine and its derivatives leads to degradation of the active skin layer of the polyamide (PA) thin-film-composite (TFC) membranes.

This work investigates the use of composites films formed by crosslinked polyvinyl alcohol (PVA) and powdered activated carbon (PAC) upon RO polyamide membranes as a protective layer against oxidizing agents. PVA was chosen as a polymeric matrix due its suitable properties like high hydrophilicity and feasibility to form dense films.

PVA membranes were prepared by casting 1%wt. aqueous solution of hydrolyzed PVA 99%. Chemical and physical stability of PVA membranes were provided by crosslinking

reaction with glutaraldehyde (GA), mainly because this compound reacts at mild temperatures. Activated carbon was used as load in the polymeric composite due to its known characteristics of adsorbent material.

The chlorine adsorption was investigated at room temperature (25°C) and basic pH (10.5), by adding 50 mg of PAC samples to 200 mL of NaClO 500 mg.L^{-1} solution under constant stirring. Samples were taken at regular intervals and the adsorbate concentration (NaClO) was determined by volumetric titration with sodium thiosulphate solution ($Na_2S_2O_3$). The equilibrium was achieved after 4 hours. Composite PVA/PAC membranes were prepared using the same methodology described for PVA membranes. PAC was previously dried at 60°C for 2 hours and added to polymeric solution around 16% wt. in relation to PVA. Adsorption isotherms were obtained for the adsorbent (PAC), PVA membranes and PVA/PAC composite membranes. The results showed that the adsorbent material (PAC) remains with high adsorption capacity for NaClO (1250 mg/g) even imbibed in PVA matrix.

The chlorine resistance of all TFC RO membranes tested was evaluated in aqueous sodium hypochlorite solution (300 ppm) including sodium chloride (NaCl; 2000 ppm) at pH 9,5 (25ºC) for 96h. Figure 1 shows the effect of exposure time on the NaCl rejection and Figure 2 on the hydraulic permeability.

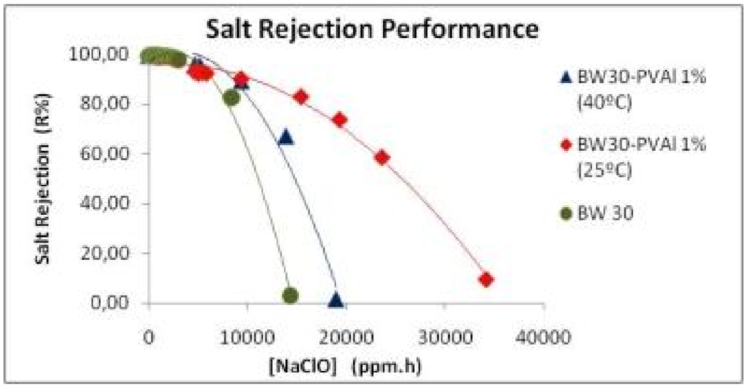

Figure 1 - Effect of exposure time (ppm.h) on salt rejection of the membranes tested

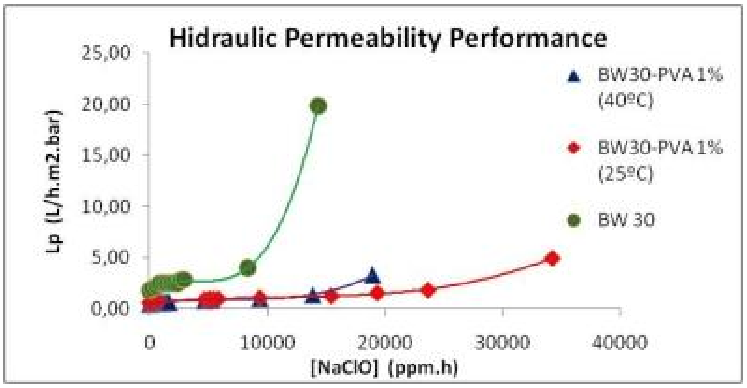

Figure 2 - Effect of exposure time (ppm.h) on hydraulic permeability of the membranes tested

It is clear from Figure 1 and Figure 2 that the covered TFC commercial membrane (BW30/PVA) showed best performance when compared to virgin membrane. The results indicate the effective use of this extra coating layer to protect RO membranes in presence of chlorine, avoiding their degradation.

Biomedical membrane applications 2

ICOM1840

Membrane technology for tissue engineering

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Membranes play an important role in medical applications and in a number of life-saving treatments. The total membrane area produced for medical applications almost matches all other industrial membrane applications together and the value of medical membrane products is larger than all other applications combined [1].

In this lecture we discuss the application of membranes for tissue engineering; a discipline which aims to produce tissues or organs from natural and / or synthetic components [2]. Usually, cells are seeded within a scaffold, a structural device that defines the geometry of the replacement tissue and provides environmental cues that promote tissue regeneration. To obtain complex viable tissue the scaffolds should have:

(i) High porosity and pore connectivity to ensure sufficient transport of oxygen and nutrients towards the cells and allow removal of metabolic products. It is a challenge to obtain a complex network of blood vessels and capillaries to supply nutrients to cells in *in vitro* built tissues [3].

(ii) Nano- and / or micro-topographical features that aid in the control of cell behavior resulting in better functioning tissues [4, 5]. Recent studies reveal that topographical cues alone, without any inductive factors present in the culture medium, may drive stem cell differentiation [6].

Development of vascularized 3D-scaffolds that have cellular recognition features, a crucial requirement for obtaining complex tissues, remains a great challenge despite excellent progress of the past years.

We will show how membrane technology can assist in the above mentioned important issues [3-5]. Specific attention will be paid to optimized design of cell culture bioreactors for effective delivery of nutrients and oxygen to cells. Besides, we will present interesting new results of how membrane surface topography affects tissue formation and on high-throughput screening of cell-material interactions.

In this lecture we will emphasize the important role membrane scientists can have in the field of tissue regeneration, even though they cannot solve the issues alone. Better interaction between membrane scientists, biologists, bioengineers, medical doctors and others is needed and we hope that this lecture will stimulate such contacts and interactions.

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ICOM1241

High performance macroporous membrane adsorbers with tailored protein selectivity

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Separations with membrane adsorbers are a rapidly growing field of application for functional macroporous membranes [1]. The most important driving force is the increasing importance of biopharmaceutical therapeutics such as recombinant proteins or monoclonal antibodies where the capturing, purification and polishing steps in downstream processing are still the main cost factors [2]. The key advantages in comparison with conventional porous adsorbers result from the pore structure of the membrane which allows directional convective flow through the majority of the pores. The separation of substances is based on their reversible binding on the functionalized pore walls; most frequently used interactions are ion-exchange and various types of affinity binding. However, there is still a large interest in improvement of performance for established materials and in development of novel materials. Specific aims are membrane adsorbers with higher dynamic binding capacity and membrane adsorbers with higher affinity and selectivity for certain target substances, based on robust chemical ligand architectures.

The overall aim of this project is to improve membrane adsorbers by novel surface functionalizations of suited macroporous base membranes and to explore their application in bioseparation. One particular focus is the purification of recombinant monoclonal antibodies produced in cell cultures. The basis is previous work using surface-selective photo-initiated grafting or surface-initiated atom transfer radical polymerization (SI-ATRP) for membrane pore functionalization (for a recent review see [3]). Here we will report on novel results regarding preparation and evaluation of the following materials:

- protein-specific membrane adsorbers with complex grafted glycopolymer layers via one- or two-step SI-ATRP routes for lectin capturing [4];

- membrane adsorbers with grafted zwitter-ionic polymer layers for novel protein purification (polishing) protocols;

- photo-grafted libraries of protein-selective polymers based on the combination of functional monomers comprising specific binders for amino acids or epitops on protein surfaces (cf. [5]) for antibody capturing;

- protein-imprinted polymer membrane adsorbers via a novel two-step surface functionalization strategy (scaffold grafting via SI-ATRP and subsequent surface-selective photo-initiated cross-linking polymerization in the presence of a scaffold-bound template protein).

The interplay between surface functionalization route, grafted functional polymer structure, protein binding mechanism and separation performance will be discussed. The focus of ongoing work is on materials with tailored selectivity and high dynamic capacity which are suited for mass separation in the biotechnology industry.

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ICOM1035

FLAT AND HOLLOW FIBER MEMBRANE SYSTEMS FOR THE RECONSTRUCTION OF HIPPOCAMPAL NEURONAL NETWORK

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The function and repair of nervous system depends on the cellular intrinsic genetic program and the extracellular environment. Many attempts have been focused on seeking on biomaterials, cell sources and novel designs of tissue-engineered neuronal bridging devices in order to generate safer and more efficacious nervous tissue repairs.Various devices using synthetic and biological substrates are being developed as biomaterial bridges as peripheral nerve grafts. In particular micro- and nano-structured membranes with high selective permeable properties may guide the axon regeneration with the surface geometry by governing the mass transfer of molecules between the cell microenvironment and the external milieu. Thus, the membrane allow the generation of a precisely controlled microenvironment that mimic specific features of the in vivo local environment.

In this paper the authors will show the strategies performed to generating neuronal tissue engineered structures by using semipermeable membranes and neurons isolated from hippocampus, which is an important telencephalic region, owing to its vital role in the consolidation of several forms of learning and memory. Controlled design and preparation of polymeric membranes in flat and hollow fiber configurations with appropriate physical, chemical and biological cues, which are relevant to induce the neuronal regeneration will be presented. In particular the influence of membrane configuration (e.g., flat, tubular), surface properties (e.g., roughness, pore size, porosity, spatial features) and physico-chemical properties (e.g., wettability) on neuronal outgrowth and differentiation will be discussed.

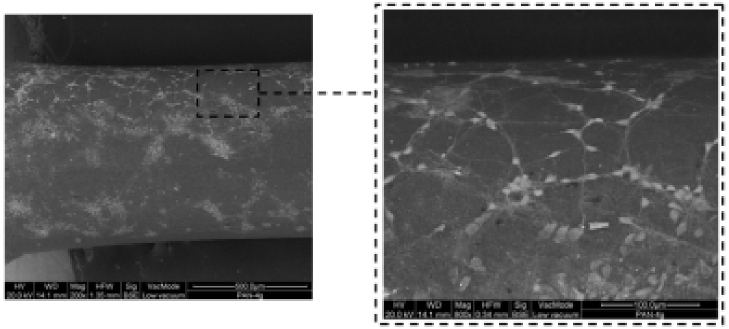

Figure 1. Hippocampal neurons on polyacrylonitrile hollow fiber membranes.

We demonstrated that the investigated membranes supported the adhesion and growth of hippocampal neurons enhancing neuronal differentiation and neurite alignment. In particular, primary hippocampal cells cultured on polyacrylonitrile hollow fiber membranes were able to recreate in vitro a 3D neural tissue-like structure that, mimicking the hippocampal tissue, could be used as a tool for the study of natural and pathological neurobiological events

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ICOM1764

Differentiation Ability of Adipose-derived Stem Cells Separated from Adipose Tissue by A Membrane Filtration Method

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Adipose-derived stem cells (ADSCs) are a promising cell source in regenerative medicine, of particular utility for cell therapies and tissue engineering, because adipose tissue can easily be harvested in large quantities compared to bone marrow, and ADSCs have high proliferation rates in culture. Recent studies of stem cells have suggested that ADSCs can be differentiated into mesoderm (mesenchymal) lineage cells, including osteoblasts, adipocytes, and chondrocytes. ADSCs are isolated from adipose tissue by liposuction and centrifugation followed by cultivation on cell culture dishes for at least one passage. The cultivation of cells derived from adipose tissue is necessary to purify ADSCs (i.e., "the culture method" for the purification of ADSCs) because the adipose tissue contains not only ADSCs but also adipose and other types of cells. The culture process for the purification of ADSCs requires several days, at minimum. If ADSCs can be purified from adipose tissue in a short period of time (i.e., less than 2 hrs) by using a cell purification device such as the membrane filtration method, cell therapy and tissue engineering applications using autologous ADSCs might become more efficient.

Adipose-derived stem cells (ADSCs) were purified from mice adipose-tissue cell solutions by the conventional culture method and the membrane filtration (i.e., batch-type filtration and perfusion-type filtration) method in this study. The ADSCs expressing the mesenchymal stem cell marker CD73 were concentrated in a recovery solution through one sheet of polyurethane (PU) foaming membranes with a pore size of 11 µm, and in a permeate solution through five sheets of Nylon mesh filters with a pore size of 11 µm, by the perfusion-type filtration method. This provided a concentration of cells expressing the marker that was 1.7 times higher than that of cells in the primary adipose-tissue cell solution. The ADSCs in the recovery solution that went through the PU foaming membranes but not through the Nylon mesh filters showed greater adipogenic and osteogenic differentiation ability than the cells contained in the primary adipose-tissue cell solution. The perfusion-type filtration effectively recovered ADSCs with a greater ability to differentiate into adipocytes and osteoblasts than the cells recovered by batch-type filtration. These results suggested that the ADSCs with adipogenic and osteogenic differentiation ability tended to adhere to PU membranes but not to Nylon mesh filters when using perfusion-type filtration. The relationship between the ratio of cells expressing the mesenchymal stem cell surface marker (i.e., CD73) and the adipogenic and osteogenic differentiation ability of the cells was also investigated.

ICOM789

Dual-fibrous composite membranes consisting of electrospun chitosan nanofibers and poly(DL-lactide) microfibers: *in vitro* and *in vivo* cell activity for skin tissue regeneration

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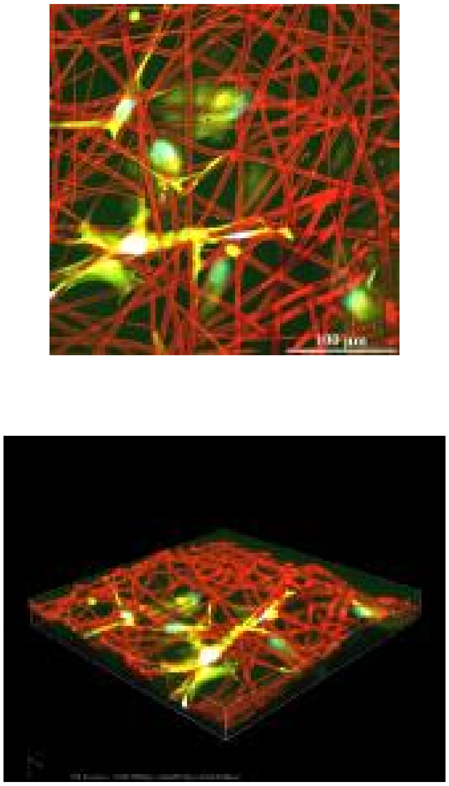
Preparation of three-dimensional (3D) scaffolds is of great importance for various aspects of tissue regeneration engineering. Electrospun fibrous membranes have various biological advantages with respect to extracellular matrix (ECM)-mimic structure and cellular activity, their usage has been limited due to the low shape-ability of the multi-scale 3D-continuous structures. In this work, we present enhanced cell growth and proliferation through dual-fibrous composite membranes as 3D cell scaffolds fabricated using integrated electrospinning process. Composite scaffolds of poly(DL-lactide) (PDLLA) with controlled internal fibrous structures of 3 µm in diameter and covered a electrospun chitosan (CS) nanofibers with well-aligned fibrous structures of 200-1000 nm in diameters. The 2D structure of CS/PDLLA scaffolds and the 3D morphology of cell proliferation were characterized using scanning electron microscopy (SEM) and laser scanning confocal microscope (LSCM) (as figure 1) observation, respectively. *In vitro* cell studies have been performed using human fibroblasts and keratinocytes in dual-fibrous composite membranes of CS/PDLLA cultured scaffolds for 1, 3, and 5 days to assess cell attachment, viability, ingrowth depth, and proliferation. Results from *in vivo* subcutaneous implantation onto mice' skin for two-weeks indicated CS/PDLLA fibrous membranes significantly enhance the ability of skin tissue regeneration. These Dual-fibrous composite membranes are promising 3D cell scaffolds for skin tissue regeneration.



Three-dimensional cell growth and proliferation on the Dual-fibrous composite membranes of CS/PDLLA fibrous scaffolds (a) 2D confocal image and (b) 3D confocal image.

Membrane contactors and reactors 3

ICOM1783

MEMBRANE CONTACTORS

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New Membrane operations are today of interest for mass and energy transfer between different phases. In these categories which complete the unit operations necessary for a redesign of process engineering, Membrane Distillation, Membrane Crystallisers, Membrane Emulsifier, Membrane Strippers and Scrubber, Membrane Condensors are attracting attention.

The possibility of integrating these Membrane units for solving existing problems or limits in various industrial production is interesting.

Increasing recover factor and minimising brine disposal problems in seawater and brackish water desalination is a typical case. The development of fuel cells systems combined with H2 production, the optimization of dehumidification systems are other example under investigation.

Important progress in the process intensification strategy can be reached by the further development of these units. Exergetic analysis and the use of new metrics can facilitate the evaluation of appropriate energy consumptions and overall costs.

ICOM155

Process intensification by novel enthalpy Aixchangers

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Introduction

Air-conditioning processes are accompanied by an exceptional high loss of energy. A first step into process intensification is the use of ordinary heat exchangers. However, next to sensible heat (temperature of the air), also latent heat (amount of water vapor in air) has a considerable contribution to the energy losses. Application of counter current enthalpy exchangers reduce the energy demand in general and lead to desired energy savings as well as CO2 emission reductions [1,2]. Unfortunately state of the art enthalpy exchangers have not gained general acceptance in domestic building ventilation. Rotary enthalpy wheels suffer from a lack in hygiene. Membrane based solutions show up to now insufficient moisture transfer rates considering their high investment costs. If the investment and operating costs could be reduced, while the transfer rates are improved, a commercial viable technology may be within reach.

Module design

This work presents a membrane based enthaply exchanger with an innovative module design. The modules are based on a special layer-by-layer technique as shown in Fig. 1. Alternating glue line patterns are applied on dense, thin flat sheet membranes to interconnect a defined number of layers. The membrane stack is unfolded subsequently, for instance by a mechanical force or via an inflation process.

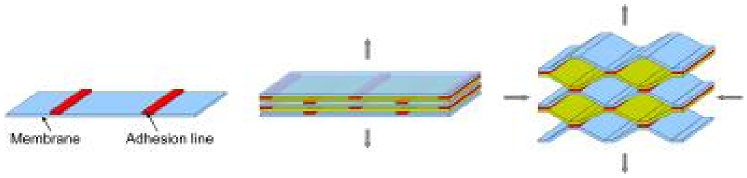

Fig.1: Principle of module assembly

Due to a special arrangement of the glue line pattern this manufacturing process leads to an inherently stabilized honeycomb structure in the inner part of the module. By applying the adhesion lines via a computer controlled automated process, the stack geometry can easily be fit to different types of existing air conditioning systems. Compared to state of the art enthalpy exchangers the honeycomb structure makes additional support, spacer or sealing technology superfluous. Mechanical strength, compatibility with different kinds of glue and excellent water vapour permeabilities are indispensable for constructing a modul with appropriate attributes.

Results

First modules have been assembled in labscale and shown the general feasibility of the novel concept. Crucial steps of the production process are presented as well as the results of initial stage experiments. Experimental data on exchange rates and pressure loss are discussed in order to characterize the module performance and quantify the potential of the concept. Module parameters such as width of glue lines, interspace between glue lines and shape of the honeycombs influence the inner module structure and therefore the module properties significantly.

Acknowledgements

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ICOM945

Perfluorinated membrane dehydrator to enhance reliability of wind turbine gearbox and other hydraulic fluid systems

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Ingression of ambient moisture over time into lubrication and hydraulic fluid systems causes major operational and maintenance problems. Water affects the physical and chemical properties such as viscosity, load carrying characteristics and thermo-oxidative stability of the fluid, promotes surface corrosion, and reduces service life and performance of bearings. Ester-based fluids such as poly-ol ester lubricants or phosphate ester hydraulic fluids can undergo hydrolysis in the presence of water and heat resulting in acids and alcohols. Acids once formed catalyze the hydrolysis reaction to produce even more acids.

We have developed a thermally and chemically stable perfluorinated membrane-based system to dewater lubricating and hydraulic fluids. The system is designed for easy installation into an existing lubrication circuit using a kidney loop configuration. With gear oil circulated on one side of the membrane module and a vacuum in combination with sweep air on the other side, the device can remove free, emulsified and dissolved water effectively. The membrane works by molecular sieving mechanism. The larger hydrocarbons or esters that are present will not permeate through the membrane and the only material that will be lost of any significance will be the small molecules such as water vapor. The driving force for water permeation is provided by the vacuum and sweep air. The chemical inertness of the membrane is able to withstand the relatively harsh thermal and chemical environment associated with lubricating or hydraulic fluids. The paper will discuss the novel membrane-based oil dewatering technology. Results from the laboratory and field evaluation studies obtained at wind turbine and nuclear power plant sites for the continuous removal of water from the gearbox lubricant and hydraulic fluids to well below saturation levels will be presented.

ICOM1226

The use of membrane contactors for the separation of paraffin/olefin mixtures by absorption into RTILs reactive media

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Traditionally industrial olefin/paraffin separation is being performed by distillation, which represents one of the most important but also the most costly process in the petrochemical industry. For this reason in recent years the development of an alternative process is becoming increasingly important. Among a number of different separation technologies, reactive absorption of olefins can provide an encouraging alternative to intensify the conventional separation process. Additionally, membrane contactors present some advantages over traditional contactors since they provide large specific area, hence allow high propylene fluxes in a modular, small, robust, safe and a cheaper way.

For many years it is known the capacity of olefins to react with some transition-metal cations via π-bound complex formation mechanism. This reaction can be easily reverted by temperature or pressure swings. Room temperature ionic liquids (RTIL) are proposed as potential substitutes for conventional solvents as reaction media because in addition to their well-known and remarkable properties, they present a strong affinity for the olefinic compounds compared to saturated hydrocarbons and provide stability to the solubilised metal cation.

After having determined the absorption equilibrium and kinetics of the separation of propylene-propane mixtures in the reactive medium Ag^+-BMImBF$_4$ [1-3] the performance of different gas-liquid contactors was evaluated [4,5] concluding that the use of membrane contactors could be hindered by the higher mass transfer resistance exerted in the liquid side. Thus, in this work we present a new automated system with a more suitable design of the membrane module that is provided with crossflow configuration in order to improve the hydrodynamics in the shell side and therefore increasing the mass transfer rate. High propylene absorption fluxes and purified propylene stream in the desorption step are obtained, thus intensifying the process and reducing the separation effective costs in a sustainable way.

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ICOM141

Removal of CO_2 and H_2S from Natural Gas through Membrane Contactors

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The use of natural gas has grown as an alternative energy and chemical raw material due to its excellent combination of properties, price and warranty reserves in the world. Still, some harmful components and impurities must be removed to minimize serious damage to health, such as hydrogen sulfide (H_2S), and to increase the heating power of natural gas, such as carbon dioxide (CO_2). Moreover, in the presence of moisture, both generate acids that corrode pipes and equipments. The conventional technology uses liquid absorbents that preferentially remove these contaminants, typically in large size packed columns and the main problems encountered are flooding and foaming, since the gas mixture also dispersed in contact with the liquid. For these devices, the main challenge is to minimize the size of the bubbles of the dispersed phase and maximizing the amount of bubbles to increase the contact area. As an alternative, hollow fiber membranes have been used to promote gas-liquid contact in a non-dispersive way. In this case, the two phases drain on opposite sides (the lumen of the membranes and shell of the module) with contact only at the membrane interface. Thus, the gas and liquid flow can be operated independently, avoiding the problems of flooding and foaming. Another advantage is the increase in surface area, providing a more efficient mass transfer and higher packing density. The modular characteristic of membrane processes makes possible to change the production capacity in a wide range of operation simply by adding more modules. Due to the compact nature of the membrane devices less physical space is required, being an interesting feature for applications in offshore platforms. Table 1 compares the surface area of membranes with other devices.

Table 1: Specific area of some contactors (Yan et al., 2007)

Apparatus	Specific surface area (m^2/m^3)
Bubble column	1 ~ 10
Packed column	100 ~ 800
Mechanically agitaded column	50 ~ 150
Plate column	10 ~ 100
Membrane contactor	1500 ~ 3000

On the other hand, an important drawback of membrane contactors has been the eventual partial or complete wetting of the membrane by the liquid phase, reducing the mass transfer efficiency. This study evaluated the use of composite membranes as an alternative to avoid the wetting of membranes, comparing the process performance with usual microporous membranes contactors. Commercial porous and composite hollow fiber modules were tested for CO_2 and H_2S removal from a gas stream in an experimental set-up designed to study the effect of the main operating variables such as, liquid and gas flow rates and temperature, for different absorbents. The results indicated higher efficiency using composite membranes, with was related to reduction of membrane wetting. For all absorbents, it was observed lower CO_2 absorption when the temperature increased, which can be attributed to reduction in the gas solubility in the liquid phase. Tests with composite membranes assembled in a contactor with area of 176 cm^2 and length of 17.5 cm showed removals up to 73% of CO_2 and 66% of H_2S from a typical feed with methane using a sodium hydroxide solution as absorbent. The use of diethanolamine solution also showed satisfactory results, since it can be recycled, and demonstrates therefore the flexibility and the potential of the process.

Membrane fouling 5

ICOM1825

Some recent advances in membrane fouling control

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Fouling is inherent to membrane filtration processes, and significantly increases their running costs (downtime operation, chemicals, environmental footprint, membrane ageing). Therefore, a lot of efforts have been oriented, from the very early years of the development of membrane filtration, towards the control of material build-up in and on the filters. The corresponding strategies are as diverse as the fouling mechanisms themselves, which can be roughly classified into particle deposition, gel formation and scaling, adsorption and biofouling, although they often occur simultaneously and in synergy. Their relative importance in the operating costs depends on the type of application.

It is now well established that particle deposition or gel formation at the membrane surface can be limited by controlled flux operations with reference to the concept of critical flux, which is not clearly defined for macromolecules. However, in field conditions, the critical flux values are often low and plants must be operated beyond these values for being profitable. Mechanical cleaning is then often preferred to chemical cleaning to periodically restore the membrane properties. We shall comment various means of using mechanical energy to control membrane fouling, such as unsteady flows in smooth or corrugated channels, slug flows, vibrating or rotating systems. Back flushing or back pulsing is also an option which has been investigated since the 90's and is currently very much used in industrial plants.

These techniques are however not efficient at removing adsorbed species. To avoid or reduce the use of chemicals for cleaning, then tailoring membrane surface minimizing adsorption is the option and has been the aim of numerous works over the last decades, not all successful. We shall briefly survey the various options investigated (grafting hydrophilic polymers (PEG, PVP, …) by various means (plasma, UV activation,…)) and comment some of the very best results obtained recently by some groups, who prepared amphiphilic polymers on purpose by phase inversion. Spectacular reversibility of fouling by proteins, humic acids or polysaccharides is obtained. Such materials are promising as they can be potentially used in combination with mechanical devices with a much higher efficiency than standard materials.

It is more and more clear today that chemical cleaning and sanitation is not the right strategy to eliminate biofouling as some organic material always remains on and in the membranes, which creates nests for the attachment of colonies. We shall then discuss some of the very interesting works published recently on attempts to control the intercellular communication, in order to limit biofouling

Finally, the optimization of the frequency of cleaning steps, which are in general, operated on a discontinuous mode has to be discussed. The smaller their frequency is the best, but on the other hand, waiting too long between two cleaning steps may lead to consolidated fouling layers, and therefore less efficiency. The development of on-line fouling sensors or detection systems such as ultrasonic reflectometry will be commented, with regards to the needs of process control and optimisation.

ICOM710

Hydrogels as anti-biofouling coating materials on RO and NF membranes: The role of chemical and physical effects

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Hydrogels show reduced adhesion to microorganisms and thus have potential to be used as anti-biofouling coating materials in membrane filtration (1). Towards development of optimal coating for RO and NF membranes for use in desalination and water treatment we examine the effects of both chemical structure and physical swelling on bacterial adhesion to hydrogels. For this purpose bulk hydrogels were first prepared from monomers fully or partly meeting well-known chemical criteria for low affinity to proteins, which included poly(ethylene glycol) methacrylate (PEGMA), 2-(methacryloyloxy)ethyl dimethyl-(3-sulfopropyl) ammonium hydroxide (SPE), and acrylamide (AAm) with addition of a cross-linker N,N′-methylenebisacrylamide (MBA). The swelling factors (swollen to dry volume ratio) of hydrogels in water was varied between 5 to 35 through the fraction of MBA and showed relatively weak variations with pH. The mesh size of the hydrogel networks was estimated to be in the range 10 to 35 nm; thereby hydrogels were impenetrable to bacteria, but could be slowly penetrated by proteins, as was indeed observed.

The adhesion of bacteria was evaluated using deposition of *Pseudomonas fluorescens* (in log growth phase) on a clean gel layer covalently anchored to glass slides. The experiments were carried out in a parallel plate flow chamber at wall shear rate 6 s^{-1}. Deposition of bacteria showed a linear kinetics, from which a deposition (mass transfer) coefficient could be calculated and compared for different gels. The results are summarized in Fig. 1 and indicated that the effects of chemistry and swelling on bacterial deposition are commensurate. For instance similarly cross-linked AAm gels were superior to SPE gels due to higher swelling, even though one could expect the opposite based on chemical criteria only. PEGMA gels were superior to the other gels due to inherent antifouling characteristics of PEG moieties, despite their lower swelling. The results suggest that both swelling and chemistry of hydrogels needs to be considered for design of optimal anti-biofouling coatings.

Tests of water permeation under pressure showed that hydrogels were highly compressible, i.e., permeability changed with pressure gradient, yet measured permeability indicated that even a compressed 100 nm thick hydrogel coating would negligibly interfere with water flow in RO/NF processes. Preparation and performance evaluation of RO membranes with hydrogel coatings is presently underway. Bacterial deposition of modified membranes is assessed in a way similar to free hydrogels. To compare bacterial deposition with swelling, as in Fig. 1, swelling of thin surface hydrogel layer coated onto RO membrane is measured using AFM and attenuated total reflection FTIR spectroscopy.

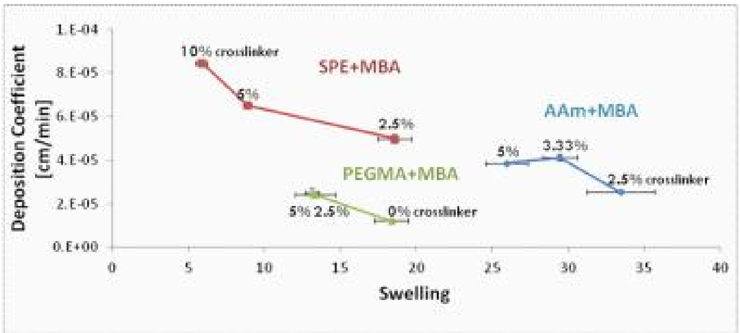

Figure 1. Bacterial deposition coefficient versus swelling ratio for different gels. Percentage of MBA is indicated near each point.

Acknowledgements. Financial support by the German-Israeli Foundation for Scientific Research and Development (GIF, #953-25. 10/2007) is gratefully acknowledged.

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ICOM197

Fabrication and Characterization of Low-fouling Piezoelectric Vibrating Membranes

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Membrane fouling, which results in a decline in the permeate rate during filtration, has been recognized as the main problem in using membranes, especially in water treatment applications. Several mechanisms are involved simultaneously in membrane fouling and several techniques have been employed to control the process. These approaches can be grouped into different categories: (1) pretreatment of feed, (2) modification of membrane bulk or surface. (3) modification of operating parameters and (4) cleaning procedures, fluid instability, and using field enhancement, such as the application of magnetic and ultrasonic fields. Researchers have suggested that fluid instability, produced with different techniques such as using turbulence promoters, can be more useful in overcoming concentration polarization and membrane fouling. The idea of this research was exploring the possibility of using membrane itself as the source of turbulence: a vibrating membrane.

Piezoelectric membranes were produced and the effect of membrane vibration on controlling membrane fouling was studied. PVDF membranes were chosen, both because of their potential piezoelectric properties and their application in membrane fabrication. PVDF is a semicrystalline polymer and has at least four known crystalline structures (α, β, γ and δ) but the all-trans(β) phase is mainly responsible for piezoelectric properties. Common melt or solution processing techniques do not yield the β-phase due to thermodynamic limitations. Poling in an intense electric field is one of the techniques can be used to change the crystalline structure of PVDF from a non piezoelectric form to the β-phase.

Here, electrical poling was used as it is suitable for pre-manufactured industrial PVDF membranes. Out of plane surface displacements measured using Laser Doppler confirmed the reverse piezoelectric activity of the membranes. Vibration measurements performed in air and water showed that the water did not damp the piezoelectric vibration, and the vibration increased strongly with increasing AC signal amplitude or DC offset voltage of the electric signal. A cross flow membrane module was used, and AC signals at different frequencies were applied to the membranes during the filtration process, in order to investigate the effect of piezoelectric vibration on filtration performance. These experiments showed that exciting the fabricated piezoelectric membranes increased the average flux and delayed membrane fouling. The experiments also showed that increasing the cross flow rate boosted the antifouling effect of piezoelectric vibration.

ICOM566

Critical flux and dynamic monitoring of fouling distribution in submerged hollow fiber membrane via UTDR

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The concept of critical flux has been widely used in the operating process of submerged hollow fiber membranes. Although the operation at the critical flux or sub-critical flux can effectively alleviate membrane fouling and prolong the service life of membrane, the optimism operation condition is actually relative to the length of hollow fiber membrane and aeration rate during the operation process of submerged hollow fiber membranes. Consequently, the development of non-destructive technique in situ to investigate the fouling distribution along hollow fiber membrane as well as its performance under the operation of the sub-critical flux so as to provide the quantitative information about optimism operation condition is great of importance. In our previous study, ultrasonic time-domain reflectometry (UTDR) and wavelet transform was successfully utilized to detect and quantify fouling distribution on the surfaces of hollow fiber membrane (Journal of membrane science, 2010). This study describes the extension of UTDR for dynamical monitoring of the fouling profile of the submerged hollow fiber membrane under the operation of sub-critical flux.

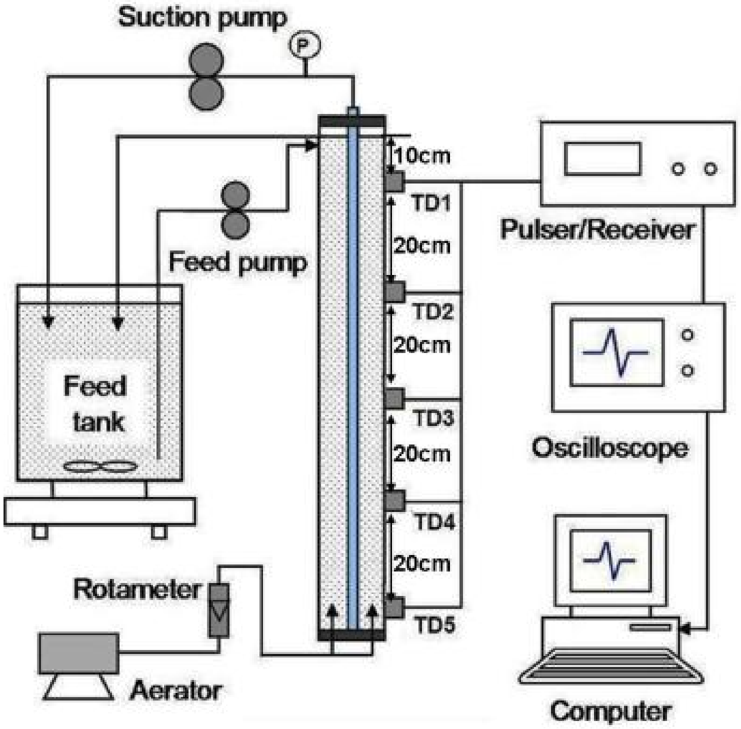
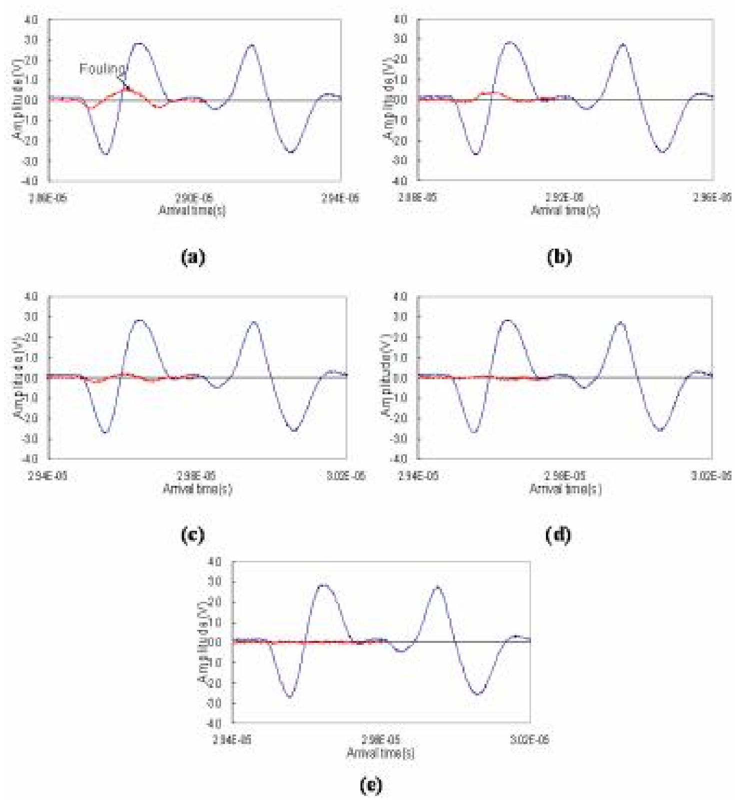


Figure 1. Schematic of experimental setup: the submerged microfiltration system and the ultrasonic measurement system

In order to perform this analysis, five 10 MHz ultrasonic sensors employed were mounted along the tubular test module with a single hollow fiber membrane evenly (Fig. 1). A polyethersulfone hollow fiber membrane with ID/OD 1.0/1.6 mm, the mean pore size of 0.1μm and a length of 100cm was employed to treat 5g/L yeast solution (4.5μm mean diameter). The constant flux filtration experiment was carried out by top suction, and air was injected from the bottom of the module. The critical flux obtained by flux-stepping method was 14L/(m^2.h).



(a) (b) (c) (d) (e)

Figure 2. The acoustic response signals of hollow fiber membrane (blue line) and fouling (red line) obtained by TD 1(a), TD 2(b), TD 3(c), TD 4(d) and TD 5(e) after 180min fouling experiment with constant flux of 9L/(m^2.h) (Note: the corresponding critical flux was 14L/(m^2.h))

The experimental results showed that the deposition of fouling at the upper part of the hollow fiber membrane under the operation of the sub-critical flux and aeration rate of 15 ml/min was still visualized by ultrasonic reflectometry as shown in Fig. 2. It suggests that the fouling could not be entirely prevented even if under the operation of the sub-critical flux. Further, the gradual accumulation of the foulants near the open end of hollow fiber membrane with the operating time could be observed even though the aeration rate increased from 15 ml/min to 45 ml/min. It implies that the augment of aeration is incapable of avoiding the membrane fouling. It could only weaken fouling and reduce deposition rate. Moreover, the deposition of fouling on the membrane surface did not reduce obviously with shortening the effective length from 100cm to 80cm at the constant flux of 9L/(m^2.h). Overall, the critical flux as a parameter of membrane fouling control is correlative with the length of hollow fiber membrane and aeration rate during the operation process of submerged hollow fiber membranes at least.

ICOM1321

Effect of transient shear on membrane filtration

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Concentration polarization and fouling reduce performance as well as increasing costs. In order to mitigate these effects, understanding the cause and effects of these phenomena is crucial. It has been hypothesized, and to a certain extent shown, that amelioration of fouling can be achieved through the use of time varying shear for example use of air-sparging or sharp changes in crossflow velocity. Indeed the VSEP devise is based upon the exploitation of high frequency vibration [1]. The concept of critical flux [2] established in 1995 has been used widely to avoid severe fouling. Critical flux was originally defined by the flux below which a decline in flux over time does not occur. Today, it is widely used as the flux above which severe fouling or a TMP jump is observed although a separate term such as threshold flux is preferable. Critical flux changes with hydrodynamic and operating conditions [2], and it is of interest to explore the reasons for this further and to exploit the potential benefits of transient shear. With the use of Anton Paar rheometer, effect of shear on critical flux and the effect of transient shear are being closely studied for a wide range of frequencies and amplitudes.

Preliminary work involved the use of DOTM [3] (Direct Observation Through Membrane) equipment at Nanyang Technological University, Singapore. The feed was freshwater algae, Chlorella Sorokiniana. In Oxford, a new special membrane filtration cell design to fit an Anton Paar rheometer, is being used to investigate transient shear. The original constant shear filtration cells of Vasan [4] and Hughes [5] had so much inertia that rapid changes in the shear were impossible. The rheometer has been programmed to give a very wide variety of shear regimes, including intermittent sharp changes of direction. As with the Hughes Cell, transmembrane pressure is limited to less than 1 bar.

In the preliminary work (figure 1), shear was shown to have positive as well as negative effects on fouling of microfiltration membrane. The analysis of permeate has clearly shown that a maximization of shear rate was not ideal. The new equipment has precise control of shear, and model feed are used instead of a biological feed in order to eliminate uncertainties due to changes in feed characteristics. Intensity, frequency, and intermittency together with effect of radial positions are explored. The new cell is operational and the results for alginate and latex particles will be presented at the conference.

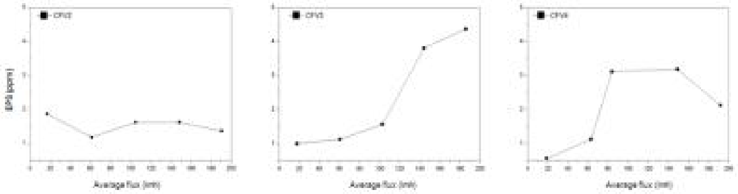

Figure 1: Extracellular polysaccharide (EPS) content in the permeate at different crossflow velocity.

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Membrane and surface modification 5

ICOM1849

Membrane and surface modifications

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Often, in membrane based separation processes the properties of the membrane surface that contact the feed stream can have a significant effect on membrane performance. For example, membrane surface properties have been show to affect the rate of fouling during processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Modifying just the membrane surface has the potential to retain the properties of the bulk membrane material but modify the interactions between components of the feed and the membrane surface.

As an example, given the critical role membrane hydrophobicity plays during membrane fouling, numerous studies have focused on producing more hydrophilic polyamide membranes for reverse osmosis and nanofiltration applications. Strategies have been developed to make the polyamide barrier film more hydrophilic (for thin film composite polyamide membranes). In this approach, a hydrophilic nanolayer is localized at the filtration surface, where it can directly reduce fouling while not compromising the chemical, thermal and mechanical properties of the membrane. Many different procedures have been described for surface modification of polyamide nanofiltration and reverse osmosis membranes. Adsorption of hydrofluoric acid by membrane immersion leads to a more hydrophilic surface and reduced fouling. Several studies have investigated the use of in situ redox initiated graft polymerization to grow a number of different hydrophilic polymers from the surface of polyamide membranes in order to reduce membrane fouling. Other methods that have been used include atom transfer radical polymerization and UV initiated free radical polymerization. In all of these surface modification methods it is essential that the properties of the base membrane are not compromised.

Surface modification may also be used to produce responsive membranes. Responsive membranes contain monomer units that can change their conformation in response to an external stimulus such as pH, ionic strength, temperature, light, electric field, magnetic field etc. The change in conformation of the monomer units may be used to change the separation properties of the membrane in response to changed environmental conditions. Porous membranes are generally made responsive by grafting responsive polymer layers from the membrane external surface and, often, the pore walls. Surface modification must again ensure that the properties of the base membrane are preserved while grafting responsive groups to the membrane surface.

Two different approaches are employed for membrane functionalization. The “grafting to” approach introduces preformed, end-functionalized small molecules or large macromolecules to the membrane surface. The “grafting from” method is a heterogeneous, surface-initiated polymerization process whereby polymer chains grow from initiator sites on the membrane surface by monomer addition from solution.

In this presentation an overview of various commonly used membrane surface modification methods will be discussed. The differences between grafting to and grafting from the membrane will be highlighted. Applications of membrane surface modification such as the development of anti fouling membranes will be discussed. In addition, preparation of advanced responsive membranes by surface modification will be addressed. Here the focus is generally on developing multifunctional responsive membranes. Potential future applications of responsive membranes will also be discussed.

ICOM1559

Enhancement of membrane UV-grafting processes using Electron Paramagnetic Resonance

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This work aims at developing functional membranes capable to respond reversibly to non-mass stimuli by changing their chemical and structural characteristics, using a UV-grafting methodology. A new approach is proposed using Electron Paramagnetic Resonance (EPR) in order to acquire a better understanding of the mechanisms of free radical formation inherent to the UV-grafting process and their impact on the membrane characteristics. Ultimately, the EPR technique allow at implementing more adequate methodologies for development of efficient stimuli responsive membranes.

The present work proposes the enhancement of the development of photo-responsive membranes through the use of EPR technique. Photo-responsive membranes are obtained by UV-grafting of photochromic molecules containing azobenzene side chains and vinyl groups (directly involved in the grafting process) at the surface of UF polyethersulfone (PES) membranes. These compounds undergo reversible chemical and conformational changes when exposed to UV-visible light, allowing a controlled switch of the chemistry of membrane surface and/or membrane structure.

UV-grafting consists in the irradiation of the membrane surface with UV-light leading to the formation of radical sites that act as polimerization initiators and where monomers with the selected functionality will graft[1,2]. The selection of suitable experimental parameters, such as the monomer concentration, irradiation time, UV-light intensity and wavelength is crucial in a membrane functionalization process, in order to obtain the ideal grafting degree and the minimum membrane degradation. In this context, EPR spectroscopy[3] is an attractive technique since it provides qualitative and quantitative information about the kinetics of radical formation and fading.

EPR analysis were carried out to evaluate the influence of the irradiation time, the presence of O_2 and monomers containing vinyl groups, in the formation and fading of radicals at the surface of the PES membrane[4] (Figure 1). The efficiency of UV-grafting methodology was assessed through determination of the grafting degree and the physic and chemical characterization of the membrane surface, using different complementary techniques, such as FTIR-ATR, X-ray photoelectron spectroscopy (XPS) and impedance spectroscopy.

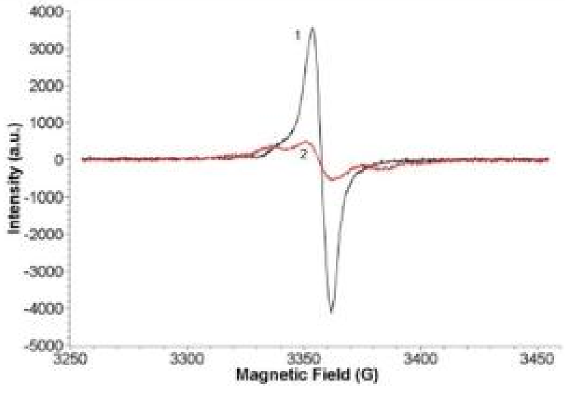

Figure 1 - EPR spectra obtained for a polyethersulfone (PES) membrane upon irradiation in the absence (1) and presence (2) of the monomer N-vinyl pyrrolidone (NVP).

Together, the information provided by EPR technique and the chemical characterization of the membrane surface allows for a suitable selection of the UV-grafting parameters, leading to the development of effective stimuli responsive membranes, which are expected to contribute to the mitigation of membrane fouling problems.

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ICOM965

Performance of TiO_2 coated PES UF membranes by a low temperature hydrothermal (LTH) process

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Abstract

Titania nanoparticles (synthesized by Sol-Gel technology and functionalized) were dip coated onto the polymeric membranes by a low temperature hydrothermal (LTH) process. Both in-house and commercial polyether sulphone (UF) membranes were used as substrate. To characterize and investigate the quality of the coating different techniques such as SEM, EDAX, AFM, TGA, FTIR, XPS, XRD, and surface and contact angle goniometry were used. In our previous work [1-2] we have shown that by LTH process a uniform coating layer with good stability and durability was obtained. Furthermore the modified membranes had lower protein absorption than control membranes. Long term superhydrophilicity without continuous UV light irradiation was achieved after 3 cycles of coating. However, initial modifications using membranes with tight pores had poor flux performance (permeability) due to pore collapse during heat treatment involved in LTH process. Here, we report that by optimising the LTH conditions and substrate structure, membrane with good antifouling performance was obtained. The effects of heat treatment and different additives (for functionalisation of nanoparticles) on the quality of coating were also investigated. Moreover by manipulating the preparation conditions of LTH process it may be possible to achieve superhydrophobic surfaces with applications in other areas such as membrane distillation.

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ICOM441

Surface-modified polyamide-imide membranes for pervaporation separation of butanol isomers

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Isomer separation is always a challenging topic in the chemical industry. Among various separation technologies, pervaporation provides an applicable way to achieve a higher selectivity since the separation is based on the differences in solubility and diffusivity of the penetrants. In this study, a novel cyclodextrin (CD) derivative, m-xylenediamine-β-cyclodextrin (m-XDA-β-CD), has been synthesized and employed to graft β-CD on membrane surface via chemical bonding for the pervaporation separation of n-/tert- butanol isomers. The reaction mechanisms for the m-XDA-β-CD synthesis and the membrane surface grafting are confirmed by Fourier transform infrared spectroscopy (FTIR) and Thermogravimetric analysis (TGA) characterizations.

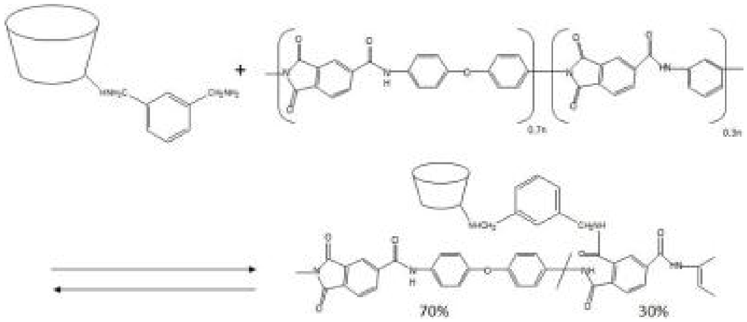

Fig. 1. The reaction mechanism of the surface grafting of the flat-sheet membrane with m-XDA-b-CD.

The as-fabricated novel CD-grafted polyamide-imide (PAI) membranes show homogeneous morphology and significant improved separation performance as compared to the unmodified PAI membranes and PAI/CD mixed matrix membranes made of physical blends.

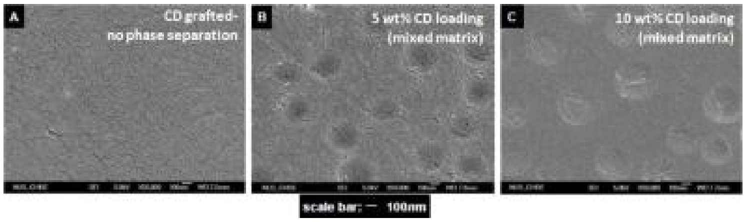

Fig. 2. SEM morphologies of the CD grafted PAI dense membrane and PAI/CD mixed matrix membranes.

The effects of chemical modification time and dope concentration on the asymmetric membrane have been studied. The results show that both flux and separation factor display an up-and-down trend with an increase in modification time. The maximum flux of 12.5 g/m^{2}hr occurs at 0.5 hour, while the maximum separation factor of 2.63 at 5 hours. An increase in dope concentration results in an increase in separation factor but a decrease in flux. The optimal separation performance can be found with the CD-grafted PAI membrane cast from a 22 wt. % dope concentration, which exhibits a total butanol flux of 15 g/m^{2}hr and a separation factor of 2.03. This newly developed membrane with surface-immobilized CD may open new perspective for the development of next-generation high-performance multilayer membranes or hollow fiber pervaporation membranes for liquid separations.

ICOM1404

Small molecule deposition to improve membrane fouling resistance

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Membrane fouling in water purification processes causes dramatic decreases in membrane performance. Membrane surface modifications are effective at remediating fouling of many common contaminants. Dopamine was recently found to non-selectively deposit from buffered alkaline solution onto virtually any surface, rendering the surface very hydrophilic after only a few minutes of contact with dopamine solution. Membranes of various types and compositions showed reduced fouling while filtering a synthetic oil-water emulsion. Deposition conditions, including pH, dopamine concentration, and deposition time, were evaluated for their effects on the performance of dopamine-modified reverse osmosis membranes. Dopamine coatings showed good resistance to many cleaning chemicals but deteriorated in the presence of hypochlorite. Because dopamine forms a non-selective coating on any surface tested to date, its deposition provides a route to universal membrane modification, eliminating the need to choose membrane-specific chemistries for further surface modification. Dopamine coatings have previously been used as a platform for molecular conjugation in membrane biomaterials applications. Poly(ethylene glycol) ad-layer formation on the dopamine-modified surface further improved membrane performance in oil-water emulsion filtration. Due to the non-specific nature of dopamine deposition, entire membrane modules may be easily modified by flowing dopamine solution through the module, allowing coating of the membrane, spacers, and pressure vessel. Dopamine-modified modules may be further modified with poly(ethylene glycol) by a similar technique.

Despite recent interest in dopamine coatings in membrane, biomaterial, and other applications, the chemical nature of the dopamine coating has not been conclusively determined. Using a variety of spectroscopic techniques, it was demonstrated that the dopamine coating is formed primarily through non-covalent bonding, likely *via* a combination of strong hydrogen bonding, charge transfer among the monomers, and π-stacking. The proposed molecular structure may have important implications for understanding other similar catecholamine-derived networks including eumelanins and for developing variations of this unique surface modification agent. Molecules with functionalities similar to dopamine, such as hydroquinone and catechol, showed similar deposition behavior from alkaline solution and imparted fouling resistance on modified membranes. Deposition of a variety of small molecules from alkaline solution, therefore, provides a facile means of modifying water purification membranes for improved fouling resistance.