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# CAREER: A New Class of Modified Mesoporous Silica Membranes with Controlled Pore Size and Surface Functionalization Through Unique Synthetic Approaches

William J. DeSisto

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**Final Report for Period:** 05/2011 - 04/2012**Submitted on:** 06/15/2012**Principal Investigator:** DeSisto, William J.**Award ID:** 0547103**Organization:** University of Maine**Submitted By:****Title:**

CAREER: A new class of modified mesoporous silica membranes with controlled pore size and surface functionalization through unique synthetic approaches

**Project Participants****Senior Personnel****Name:** DeSisto, William**Worked for more than 160 Hours:** Yes**Contribution to Project:****Post-doc****Graduate Student****Name:** Higgins, Scott**Worked for more than 160 Hours:** No**Contribution to Project:**

Scott has graduated with Ph.D. and is currently a post-doc at the University of Hawaii in the area of fuel cells.

**Name:** Cassidy, David**Worked for more than 160 Hours:** Yes**Contribution to Project:**

David Cassidy was the main graduate student on this project. He successfully defended his thesis and will work as an industrial post doc at a local company developing inorganic membranes for biofuel processing applications.

**Name:** Kennard, Raymond**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Ray has been involved in initiating a collaboration with Professor Mike Mason to apply single molecule imaging techniques to mesoporous silica membranes. Ray has now defended his Ph.D. thesis and has taken a position with a local company, Orono Spectral Solutions, Inc.

**Name:** Ghampson, Isaac**Worked for more than 160 Hours:** No**Contribution to Project:**

Tyrone has collaborated with our group by preparing a series of catalysts supported on various mesoporous silicas and evaluating their catalytic activity for hydrodeoxygenation of bio-oils. This type of work can open up opportunities in identifying separation opportunities for biofuel processes and catalytic membrane reactors. Tyrone was funded to travel to Chile and completed his work there in May 2011. He has defended his Ph.D. thesis and now works as an engineer at Unidad de Desarrollo Tecnologico in Concepcion Chile.

**Undergraduate Student****Name:** Young, Eric**Worked for more than 160 Hours:** No**Contribution to Project:**

Eric graduated and is now a graduate student at the University of Texas in Chemical Engineering

**Name:** Siegfriedt, Abigail

**Worked for more than 160 Hours:** No

**Contribution to Project:**

Abbie has just finished her undergraduate career at the University of Maine, graduating in May 2011. In conjunction with this project, Abbie completed her engineering capstone and honors thesis work, graduating with Highest Honors. Her project/thesis focused on exploring ceramic membranes for dilute acetic acid recovery within a biorefinery. She examined energy savings and process economics by employing hybrid membrane/distillation systems to replace both traditional distillation and liquid-liquid extraction systems.

**Name:** Ecker, James

**Worked for more than 160 Hours:** No

**Contribution to Project:**

Jamie has been involved in the synthesis and characterization of mesoporous thin films for membrane supports.

**Name:** Alvial, Edgardo

**Worked for more than 160 Hours:** No

**Contribution to Project:**

Student from an university in Chile spent two months in my laboratory working on constructing a pervaporation unit and testing it.

**Name:** Royce, Alex

**Worked for more than 160 Hours:** No

**Contribution to Project:**

Student spent some time during two semesters characterizing membranes.

**Name:** Ogoke, Ogechi

**Worked for more than 160 Hours:** No

**Contribution to Project:**

Student spent some time during two semesters characterizing membranes.

## Technician, Programmer

## Other Participant

## Research Experience for Undergraduates

### Organizational Partners

### Other Collaborators or Contacts

We collaborate with Professor Carl Tripp at the University of Maine for surface chemistry characterization of our membranes. We also collaborate with Professor Mike Mason on single molecule imaging spectroscopy of membranes and Professor Doug Ruthven on membrane analysis. We are also using our membranes as supports for combinatorial evaluation of catalysts in thermal biomass conversion. In addition we have been collaborating with Cerahelix, a local startup company interested in developing ceramic membranes for dilute aqueous product recovery in biofuels production. We also collaborate with Professor Nestor Escalona of the University of Concepcion, Chile in evaluating catalytic activity of catalysts supported on mesoporous silica.

## Activities and Findings

### **Research and Education Activities: (See PDF version submitted by PI at the end of the report)**

#### Research activities

The diffusive transport of permanent gases was modeled through alkyl-modified silica membranes and the Knudsen model was confirmed.

Significant progress was made in depositing alumina via ALD into mesoporous silica membranes and correlating deposition cycles with changes in pore size distribution.

Procedures were developed for preparing mesoporous silica membranes on porous supports under different environmental conditions.

Techniques were developed for measuring the diffusive transport of single molecules through mesoporous membranes.

Organic/Inorganic membranes were prepared using molecular layer deposition on mesoporous silica membranes for the first time.

Eric Young graduated with High Honors completing his Honors Thesis and is enrolled at University of Texas graduate school.

Scott Higgins graduated with a Ph.D. Scott is now at the University of Hawaii on a postdoctoral appointment

Ray Kennard successfully defended his Ph.D. thesis and is now employed at Orono Spectral Solutions, Inc.

Abigail Siegfriedt graduated with Highest Honors and has accepted a position with Verso, Corp.

Tyrone Ghampson successfully defended his Ph.D. thesis and is now employed at Unidad de Desarrollo Tecnológico, Concepcion Chile.

David Cassidy successfully defended his Ph.D. thesis and is now employed as an industrial post doc with Cerahelix, Inc., Orono, Maine.

### **Findings: (See PDF version submitted by PI at the end of the report)**

The attachment of alkyl groups (C18) via monochlorosilane reaction did modify the mesoporous silica membrane, yet no appreciable separation was achieved for light gas molecules.

Techniques were developed for single molecule imaging of a dye molecule within the pore of a mesoporous membrane. Results gave intrinsic adsorption behavior of a dye molecule within the silica membrane.

Atomic layer deposition into mesoporous silica membranes and reaction conditions are correlated with membrane modification

Research has been initiated into quantifying transport heterogeneities in membranes using single molecule imaging spectroscopy

Hybrid separation systems involving membranes for dilute acetic acid recovery in biorefineries were modeled and indicated that with appropriate configuration with a still,

membranes with modest separation factors (>20) would significantly reduce the energy burden on the still for separation.

The reduction of pore sizes in mesoporous membranes via ALD is highly sensitive to reactant exposure conditions suggesting this is a valid method for selectively reducing larger pores while leaving smaller pores intact.

Molecular layer deposition using trimethylaluminum and both oxalic and o-phthalic acids as precursors was demonstrated as a new membrane synthesis technique for preparing inorganic/organic membranes using a controlled deposition technique.

#### **Training and Development:**

Research skills include inorganic membrane synthesis and characterization, modification of membrane surfaces through chemical attachment of precursors, design and fabrication of an atomic layer deposition reactor, and utilization of an atomic layer deposition reactor to modify mesoporous membranes in a controlled manner to reduce pore size and change surface functionality. Process simulation skills were developed to incorporate membranes into hybrid separation systems were developed. Other skills include technical writing and technical presentation.

#### **Outreach Activities:**

Outreach activities included high school student mentoring. Several presentations were given to middle school classes in science. The focus was alternative energy. As part of the presentation, the cost of separations was discussed and its impact on energy costs and the chemical processing industry. I have attached a brief list of comments from one class to provide a sense of the feedback and interest in the topic.

Hello,

Thank you again for taking the time to discuss energy topics with the students. I got a lot of great feedback and wanted to share some of it with you.

\* I thought that the presentation was very interesting!

\* It was a cool presentation and I think I learned a lot about energy types in Maine. I liked going a little deeper into what we had been learning, and I thought that it was a worth while presentation.

\* I also really liked how he had examples and stuff for us to look at.

\* I liked how he asked the class questions and included us.

\* He had some really cool ideas and facts!!!

\* I thought it was interesting when he explained how the materials used for making paper were extracted from the trees.

\* I think it would be worthwhile to try and find a simple way to make ethanol from the different parts of a tree, and since there is so many trees in Maine, we could use ethanol for fuel.

\* It was also cool to see how much money is spent on heating every month.

\* I learned a lot about biomass and what he's doing with it.

\* i learned about lots of new ways people are helping the environment and I enjoyed seeing this new information in a presentation.

\* One thing I learned was that gasoline and oil are the two most expensive forms of energy to heat a home with.

\* I am glad that he came in to share that with us.

\* Overall I thought the presentation was clear and showed a lot about how we can make the earth a more environmentally place for everyone.

\* I liked it because my parents don't usually tell me what they pay for the house or anything concerning our bills. It gave a sense to why they were always so strict about keeping the door closed even if it was only open for less than 30 seconds.

\* I thought it was really interesting how the wood could be separated into different products, and how the waste products could be used again.

As you can see, the students really enjoyed your presentation and they learned a lot. Thank you so much. Lissa

### **Journal Publications**

Kennard, R; DeSisto, WJ; Giririjan, TP; Mason, MD, "Intrinsic property measurement of surfactant-templated mesoporous silica films using time-resolved single-molecule imaging", JOURNAL OF CHEMICAL PHYSICS, p. , vol. 128, (2008). Published, 10.1063/1.286875

Higgins, S; McCool, BA; Tripp, CP; Ruthven, DM; DeSisto, WJ, "Covalent Attachment of Monochlorosilanes to Mesoporous Silica Membranes using Supercritical Fluid Deposition", SEPARATION SCIENCE AND TECHNOLOGY, p. 4113, vol. 43, (2008). Published, 10.1080/0149639080241469

Ruthven, DM; DeSisto, WJ; Higgins, S, "Diffusion in a mesoporous silica membrane: Validity of the Knudsen diffusion model", CHEMICAL ENGINEERING SCIENCE, p. 3201, vol. 64, (2009). Published, 10.1016/j.ces.2009.03.04

Higgins, S; DeSisto, W; Ruthven, D, "Diffusive transport through mesoporous silica membranes", MICROPOROUS AND MESOPOROUS MATERIALS, p. 268, vol. 117, (2009). Published, 10.1016/j.micromeso.2008.06.03

Higgins, S; McCool, BA; Tripp, CP; Ruthven, DM; DeSisto, WJ, "Covalent Attachment of Monochlorosilanes to Mesoporous Silica Membranes using Supercritical Fluid Deposition (vol 43, pg 4113, 2008)", SEPARATION SCIENCE AND TECHNOLOGY, p. 263, vol. 44, (2009). Published, 10.1080/0149639080270887

Cassidy, DE; DeSisto, WJ, "Atomic Layer Deposition-Modified Ordered Mesoporous Silica Membranes", CHEMICAL VAPOR DEPOSITION, p. 22, vol. 18, (2012). Published, 10.1002/cvde.20110693

Kennard, R; DeSisto, WJ; Mason, MD, "Molecular diffusivity measurement through an alumina membrane using time-resolved fluorescence imaging", APPLIED PHYSICS LETTERS, p. , vol. 97, (2010). Published, 10.1063/1.351848

I. Tyrone Ghampson, Catherine Sep??veda, Rafael Garcia, J.L. Garc??a Fierro,, "Comparison of alumina- and SBA-15-supported", Applied Catalysis A: General, p. , vol. , (2012). Accepted,

### **Books or Other One-time Publications**

#### **Web/Internet Site**

#### **Other Specific Products**

#### **Contributions**

**Contributions within Discipline:**

Analysis of alkyl-modified mesoporous silica membranes.  
 Atomic Layer Deposition techniques for modifying mesoporous materials.  
 Development of single molecule imaging techniques for characterization of porous materials.  
 Process simulation of hybrid membrane systems for dilute acetic acid recovery.  
 Molecular Layer Deposition methods demonstrated for creating inorganic/organic layers within porous membrane supports.

**Contributions to Other Disciplines:**

Established techniques for single molecule imaging within mesoporous silica membranes.  
 Using membranes as supports in the combinatorial evaluation of catalysts for thermal upgrading of biomass.

**Contributions to Human Resource Development:**

Human resource development included mentoring of three high school students, training of six undergraduate research assistant and training or partial training of four graduate research assistants.

Scott Higgins graduated with a Ph.D. in Chemical Engineering and is currently on the research faculty of the Hawaii Natural Energy Institute, University of Hawaii at Manoa.

David Cassidy graduated with a Ph.D. from the University of Maine and is currently employed as an industrial post-doc at Cerahelix, Inc.

Raymond Kennard graduated with a Ph.D. from the University of Maine and is currently employed at Orono Spectral Solutions, Inc.

Tyrone Ghampson graduated with a Ph.D. from the University of Maine and is currently employed as a Research Engineer, Unidad de Desarrollo Tecnológico, Concepcion, Chile

Eric Young graduated with High Honors (Honors thesis topic was inorganic membranes) and is currently enrolled at the University of Texas in the Department of Chemical Engineering as a Ph.D. candidate.

Abigail Siegfriedt has graduated with Highest Honors in Chemical and Biological Engineering, B.S. and is currently employed at Verso, Paper.

**Other Undergraduate Students**

James Ecker, B.S. Chemical Engineering, Engineer, Verso Paper, Bucksport, Maine

Edgardo Alvial, Undergraduate Engineering Student, INACAP, Concepcion, Chile

Alex Royce, Undergraduate Chemical Engineering Student, University of Maine

Ogechi Ogoke, Undergraduate Chemical Engineering Student, University of Maine

**High School Students**

Rachel Joyce, Home schooled, Veazie, ME, graduated with B.S. in Civil Engineering, University of Maine 2012

Elizabeth Nelson, Orono HS, Orono, ME, second year student at Houghton College

**Contributions to Resources for Research and Education:**

Physical resources include all equipment developed in the laboratory as part of this project. These include an atomic/molecular deposition system designed for membrane modification, membrane characterization equipment such as permeance and perm-porosimetry measurements, fluorescence-based optical measurement facilities for membrane characterization, and techniques for inorganic membrane synthesis. A pervaporation unit was also designed and constructed that is capable of use for an undergraduate laboratory experience.

**Contributions Beyond Science and Engineering:**

Cerahelix, a small, local technology company is making efforts at commercializing inorganic membranes for pervaporation for biofuel

production applications. They are exploring techniques for membrane fabrication based on results in our laboratory. I have been heavily involved in their efforts acting as consultant, making laboratory equipment available, and helping with direction of their company. Cerahelix has successfully obtained a Phase II SBIR grant and has hired David Cassidy, a Ph.D. student on this project. They have also been successful in obtaining private funding.

### **Conference Proceedings**

Cassidy, D;Higgins, S;McCool, BA;DeSisto, WJ, Atomic Layer Deposition as a Tool to Modify Mesoporous Silica Membranes, "OCT 13-15, 2008", ATOMIC LAYER DEPOSITION APPLICATIONS 4, 16 (4): 151-157 2008

### **Categories for which nothing is reported:**

Organizational Partners

Any Book

Any Web/Internet Site

Any Product



**Final Report**  
**NSF CAREER Award 0547103: A new class of modified mesoporous silica membranes with controlled pore size and surface functionalization through unique synthetic approaches**

**William J. DeSisto**

**Final Summary**

The objective of this work was to investigate novel methods to prepare membranes that would result in a higher degree of control over the membrane properties. The novel methods were focused on atomic and molecular layer deposition techniques used to deposit very thin layers within the porous structures of inorganic membranes. The challenges to this work is defining the reaction chemistry, understanding limitations of reactions with small pores (nanometer-sized), and characterizing the final membrane to determine the effect of synthesis conditions and overall usefulness.

More specifically, the focus of membrane synthesis included controlling both final pore size through controlled reduction of the support membrane and incorporating organic functionality into the membranes to enhance separations by selective adsorption. This led to work on mesoporous silica membrane synthesis and characterization, the demonstration of using supercritical fluids to facilitate chemical reactions within porous membranes for alkyl-functionalization, understanding the limitations of atomic layer deposition on inorganic membrane pore size reduction and demonstrating a novel technique for inorganic/organic membrane synthesis based on molecular layer deposition.

Additional focus included efforts to merge membrane transport characterization techniques with fluorescent-based spectroscopies to provide further insight into membrane properties. This led to the demonstration of single-molecule spectroscopic methods for characterizing membranes including physical properties and transport properties.

Additionally, a student was funded on a short visit to Concepcion, Chile to initiate work on utilizing porous silica materials as supports for hydrodeoxygenation catalysts, critical for upgrading bio-oils based on thermal conversion of biomass.

The PI (DeSisto) received tenure in 2006. He has taught classes in the undergraduate curriculum for chemical engineers including introduction to chemical engineering calculations, advanced materials, unit ops laboratory and process design (capstone). He has incorporated several examples of his research into class curriculum. He has also been active in the thermal conversion of biomass to fuels and chemicals and is expecting to merge the membrane work he has done here with new applications in that field.

Future prospects for continuing this work on many levels exists. The emergence of new separation needs in the biofuels production sector will stimulate membrane research. Cerahelix, Inc., a local company in Orono, ME, is focused on developing inorganic membranes for biofuels separation processing applications and is utilizing some of the methods developed in this work. Fundamental work in continuing to explore novel membranes and membrane synthesis can certainly build upon this work including an exciting new area of MOF membranes. The MLD work initiated here may impact that as a demonstration of controlled growth of MOF-like structures within existing porous structures.

Over the course of this work, four Ph.D. students were funded or partially-funded and have all graduated and working. Six undergraduates have been trained, two with Honors Theses. Three high school students were mentored. Nine papers were published and two more are in preparation stage. Eight presentations at meetings were given (two invited). A listing of activity is provided below followed by annual reports for all years of the project. Finally, a summative article published in an Innovations Magazine is attached.

## Activity Summary

### *Publications*

1. Cassidy, D. and DeSisto, W.J., Atomic Layer Deposition Modified Mesoporous Silica Membranes, *Chemical Vapor Deposition*, **18**, 22-26 (2012).
2. Kennard, R.; DeSisto, W.J.; Mason, M.D., Molecular diffusivity measurement through an alumina membrane using time-resolved fluorescence microscopy, *Applied Physics Letters*, **97**, 213701 (2010).
3. Ruthven, D. M.; DeSisto, W. J.; Higgins, S., Diffusion in a mesoporous silica membrane: Validity of the Knudsen diffusion model. *Chemical Engineering Science* **64** (13), 3201-3203 (2009).
4. Higgins, S.; DeSisto, W.; Ruthven, D., Diffusive transport through mesoporous silica membranes. *Microporous and Mesoporous Materials* **117** (1-2), 268-277 (2009).
5. Higgins, S.; McCool, B. A.; Tripp, C. P.; Ruthven, D. M.; DeSisto, W. J., Covalent Attachment of Monochlorosilanes to Mesoporous Silica Membranes using Supercritical Fluid Deposition (vol 43, pg 4113, 2008). *Separation Science and Technology* **44** (1), 263-263 (2009).
6. S. Higgins, B.A. McCool, C.P. Tripp, D.M. Ruthven and W.J. DeSisto, Covalent attachment of monochlorosilanes to mesoporous silica membranes using supercritical fluid deposition, *Separation and Purification Technology*, **43**, 4113 (2008).

7. R. Kennard, W.J. DeSisto, T.P. Giririjan, M. Mason, Intrinsic property measurement of mesoporous silica membranes using time-resolved single molecule imaging, *Journal of Chemical Physics*, **128**, 134710 (2008).
8. Cassidy, D.; Higgins, S.; McCool, B. A.; DeSisto, W. J., Atomic Layer Deposition as a Tool to Modify Mesoporous Silica Membranes. In *Atomic Layer Deposition Applications 4*, Londergan, A.; Bent, S. F.; DeGendt, S.; Elam, J. W.; Kang, S. B.; VanderStraten, O., Eds. 2008; Vol. 16, pp 151-157.
9. S. Higgins, R. Kennard, J. DiCarlo and W.J. DeSisto, "Preparation and Characterization of Non-Ionic Block Co-Polymer Templated Mesoporous Silica Membranes," *Journal of Membrane Science*, **279**, 669-674 (2006).

### *Presentations*

1. W.J. DeSisto and D. Cassidy, Atomic Layer Deposition: a nano tool for modification of porous structures, XXV International Congress of Chemical Engineering and XVIII Chilean Congress of Chemical Engineering, 2011, Santiago, Chile.
2. (invited) W.J. DeSisto, Atomic Layer Deposition for Membrane Modification, Electrochemical Society, 2008, Honolulu, HI.
3. D. Cassidy and W.J. DeSisto, Defect reduction in mesoporous silica membranes via base-catalyzed atomic layer deposition, Gordon Research Conference on Nanoporous Materials, 2008, Waterville, ME.
4. (invited) W.J. DeSisto, Atomic Layer Deposition for Membrane Modification, American Chemical Society, 2007, Boston, MA.
5. R. Kennard, W.J. DeSisto, T.P. Garirijan, and M. Mason, Intrinsic property measurement in mesoporous silica membranes with time-resolved single molecule imaging, North American Membrane Society Annual Meeting, 2007, Orlando, FL.
6. S. Higgins, B.A. McCool, C.P. Tripp and W.J. DeSisto, Covalent attachment of monochlorosilanes to mesoporous silica membranes with supercritical fluid deposition, North American Membrane Society Annual Meeting, 2007, Orlando, FL.
7. S. Higgins and W.J. DeSisto, "Preparation and Characterization of Mesoporous Silica Membranes using a Non-Ionic Block Co-Polymer Template," North American Membrane Society Meeting, May 2006, Chicago, IL.
8. R. Kennard and W.J. DeSisto, "Single Molecule Spectroscopic Characterization of Silica Membranes Prepared by Micellar Templating," North American Membrane Society Meeting, May 2006, Chicago, IL.

### *Theses as Major Advisor*

1. "Synthesis and Characterization of Mesoporous Silica Membranes Synthesized by Atomic and Molecular Layer Deposition," David E. Cassidy, University of Maine, 2012.
2. "Characterization of Inorganic Membranes using Fluorescence Spectroscopic Methods," Raymond Kennard, University of Maine, 2012.
3. "Synthesis and Characterization of Metal Nitride-based Catalysts for Hydrodeoxygenation," Isaac Tyrone Ghampson, University of Maine, 2011.
4. "Evaluation of Membrane Performance on Separating Acetic Acid from Water Compared to Competing Technologies," Honors Thesis (Highest Honors) and Capstone, Abigail Siegfriedt, University of Maine, 2010.
5. "Novel Characterization of Mesoporous Silica Membranes," Eric M. Young, Honors Thesis (High Honors), University of Maine, 2008.
6. "Synthesis and Characterization of Hybrid Mesoporous Silica Membranes," Scott R. Higgins, Ph.D. Thesis, University of Maine, 2008.

### *Student Participation*

#### *Ph.D. Students*

Scott Higgins, Research Faculty, Hawaii Natural Energy Institute, University of Hawaii at Manoa

Raymond Kennard, Staff Research Engineer, Orono Spectral Solutions, Orono, Maine

David Cassidy, Industrial Post-Doctoral Fellow, Cerahelix, Orono, Maine

Tyrone Ghampson, Research Engineer, Unidad de Desarrollo Tecnológico, Concepción, Chile

#### *Undergraduate Students*

Eric Young, B.S. Chemical Engineering, University of Maine, Ph.D. Candidate, University of Texas

Abigail Siegfriedt, B.S. Chemical Engineering, Engineer, Verso Paper, Jay, Maine

James Ecker, B.S. Chemical Engineering, Engineer, Verso Paper, Bucksport, Maine

Edgardo Alvial, Undergraduate Engineering Student, INACAP, Concepción, Chile

Alex Royce, Undergraduate Chemical Engineering Student, University of Maine

Ogechi Ogoke, Undergraduate Chemical Engineering Student, University of Maine

*High School Students*

Jennifer Brown, Orono HS, Orono, ME, graduated with B.S. in Biological Engineering, University of Maine 2011

Rachel Joyce, Home schooled, Veazie, ME, graduated with B.S. in Civil Engineering, University of Maine 2012

Elizabeth Nelson, Orono HS, Orono, ME, second year student at Houghton College

## Annual Report 2006

We have prepared and characterized organically-modified mesoporous silica membranes using supercritical fluid CO<sub>2</sub> fluid deposition. Supercritical CO<sub>2</sub> fluid deposition has been shown to increase both diffusion and concentration of the reactants at the reaction site, a particular advantage when the reaction site is inside a small pore, where access can be limited. The pre-modified mesoporous silica membranes were prepared by surfactant-templated synthesis on alpha-alumina disk-shaped supports. These mesoporous silica supports had a mean pore size distribution of 5 nm. The alkyl modification of the silica membranes was achieved by the covalent attachment of trimethylchlorosilane (TCMS) and octadecyldimethylchlorosilane (ODMCS) using triethylamine (TEA) as a catalyst in supercritical-CO<sub>2</sub>. Successful attachment was confirmed through infrared spectroscopic identification of methyl and methylene groups and also a decrease in single gas permeance of light gases through the modified membrane. The synthesis process did not degrade the support membrane, was relatively efficient, and was free of organic solvents required for synthesis. The dominant transport modes in the membranes were Knudsen and surface flow. Separation factors for methane and propane over nitrogen were not increased relative to the support, indicating that neither surface flow was enhanced nor size selectivity improved for the membrane system studied. Supercritical CO<sub>2</sub> fluid deposition was demonstrated an effective technique for reaction of functionalized silanes on the surface of silica membranes.

We have conducted experiments on the synthesis and characterization of mesoporous silica membranes used as supports for subsequent pore size and surface chemistry modification. Surface chemistry modification experiments have been conducted using trimethylchlorosilane and octadecyldimethylchlorosilane. These experiments were carried out by reaction in supercritical CO<sub>2</sub> to explore this new method for membrane modification. Experimental characterization includes infrared spectroscopy of the membrane surface, single gas permeation measurements, and adsorption branch porosimetry measurements. Additional work was done on designing and fabricating an atomic layer deposition system for pore size reduction experiments. This work has included refurbishing used equipment, procuring new equipment, computer programming for automated control and general experimental planning.

Educational activities include incorporating current data collected from research and using this data as a teaching vehicle for my introduction to chemical engineering calculations class. Advising two graduate students in research, one undergraduate in research, and one high school student in developing a teaching module has also taken place.

## **Annual Report 2007**

### **ALD of porous silica membranes**

An ALD reactor has been constructed for depositing silica layers into mesoporous silica membranes. The reactor will deliver three reactants through a GC valve into a custom reactor chamber configured to hold porous disc supports. An additional reactor is being constructed for alumina deposition from trimethylaluminum and water. Experiments are expected to commence shortly in this area.

### **Functionalized silica membranes**

We have continued our research in functionalized silica membranes. Two papers have been submitted. The first paper entitled, Covalent attachment of monochlorosilanes to mesoporous silica membranes using supercritical fluid deposition, was submitted to a special edition of Separation and Purification Technology focused on functionalized membranes. The abstract for this paper follows below. We have prepared and characterized organically-modified mesoporous silica membranes using supercritical CO<sub>2</sub> fluid deposition. Supercritical CO<sub>2</sub> fluid deposition has the potential to increase both diffusion and concentration of the reactants at the reaction site, a particular advantage when the reaction site is inside a small pore, where access can be limited. The unmodified mesoporous silica membranes were prepared by surfactant-templated synthesis on  $\alpha$ -alumina disk-shaped supports. These mesoporous silica supports had a mean pore diameter of 5 nm. The alkyl modification of the silica membranes was achieved by the covalent attachment of octadecyldimethylchlorosilane (ODMCS) using triethylamine (TEA) as a catalyst in supercritical-CO<sub>2</sub>. Successful attachment was confirmed through infrared spectroscopic identification of the removal of the band due to isolated silanols accompanied by the appearance of bands due to methyl and methylene groups. We also directly measured a ~90% reduction in permeance of light gases through the modified membrane. The synthesis process did not degrade the support membrane, was relatively efficient, and was free of organic solvents required for traditional synthesis. The dominant transport modes in the membranes were Knudsen and surface flow. Ideal separation factors for methane and propane over nitrogen were not increased relative to the bare support, indicating that neither surface flow was enhanced nor size selectivity improved for the membrane system studied. Supercritical CO<sub>2</sub> fluid deposition was demonstrated as an effective technique for reaction of functionalized silanes on the surface of silica membrane.

A second paper entitled, Diffusive transport through mesoporous silica membranes, was submitted to the Journal of Microporous and Mesoporous Materials. This paper provided a more thorough analysis of the permeance and separation data. The abstract is given below. The results of a detailed study of the permeation of several light gases through unmodified and modified mesoporous silica membranes are reported. The base membranes which were synthesized by dip-coating multiple layers of a templated silica onto a macroporous alumina support showed relatively high permeances with evidence of both support resistance and a contribution from viscous flow, in addition to Knudsen diffusion, through the active layer. The behavior of the modified membranes, which were prepared by silanation of the original membranes with

octadecyldimethylchlorosilane, was more interesting. Permeances were lower and there was no evidence of support resistance or viscous flow. Permeation through the active layer appeared to occur by a Knudsen-like process. Permeance and permeance ratios measured in both single component and binary systems showed the characteristic inverse dependence on the square root of the molecular weight (or the molecular weight ratio) but the temperature dependence was much stronger than expected for classical Knudsen flow. The behavior of CO<sub>2</sub> was somewhat anomalous yielding permeances that were about 25% larger than that for propane which has the same molecular weight.

## **Measurement of Intrinsic Pore Properties in Mesoporous Silica Membranes**

This work is the result of collaboration between Mike Mason and me. We are looking to measure intrinsic properties of mesoporous silica membranes using single molecule imaging spectroscopy. One paper has been accepted to the Journal of Chemical Physics. The abstract is given below. Mesoporous silica membranes fabricated by the surfactant templated sol-gel process have received attention because of the potential to prepare membranes with a narrow pore size distribution and ordering of the interconnected pores. Potential applications include ultrafiltration, biological separations and drug delivery, and separators in lithium-ion batteries. Despite advancements in synthesis and characterization of these membranes, a quantitative description of the membrane microstructure remains a challenge. Currently the membrane microstructure is characterized by the combination of results from several techniques, i.e. gas permeance testing, XRD, SEM, TEM, permporometry. The results from these ensemble methods are then compiled and the data fitted to a particular flow model. Although these methods are very effective in determining membrane performance, general pore size distribution, and defect concentration, they are unable to monitor molecular paths through the membrane and quantitatively measure molecular interactions between the molecular specie and pore network. Single molecule imaging techniques enable optical measurements that probe materials on nanometer length scales through observation of individual molecules without the influence of averaging. Using single molecule imaging spectroscopy, we can quantitatively characterize the interaction between the probe molecule and the interior of the pore within mesoporous silica membranes. This approach is radically different from typical membrane characterization methods in that it has the potential to spatially sample the underlying pore structure distribution, the surface energy, and the transport properties. Our hope is that this new fundamental knowledge can be quantitatively linked to both the preparation and the performance of membranes leading to the advancement of membrane science and technology. Fluorescent molecules, 1,1-dioctadecyl-3,3,3,3-tetramethylindo-carbocyanine perchlorate (DiIC-18), used to interrogate the available free volume in their vicinity, were loaded into the mesoporous silica membranes at subnanomolar concentrations. The mesoporous silica films were prepared using a non-ionic ethylene oxide-propylene oxide-ethylene oxide tri-block copolymer surfactant, Pluronic P123, on single crystal silicon substrates using dip-coating of a silica sol. Membranes were prepared resulting in an average pore diameter of approximately 5 nm as measured by helium, nitrogen permeance and porosimetry. Fluorescent images and time transient experiments were recorded using a custom built single molecule scanning confocal microscope at differing temperatures (10°C, 20°C, 30°C, 40°C, and 50°C). Time dependent polarization anisotropy was used to obtain the enthalpy of adsorption and Henry's law constant of the probe molecule.



## Educational Activities

Two graduate students and one undergraduate student were mentored and received experience in membrane synthesis and characterization. Data collected was used in an Introduction to Chemical Engineering Calculations course given to second semester first-year students. The material was well-received. Students enjoyed “real” examples as a basis for learning concepts. Of the three high school students mentored so far, two have entered engineering (both females). One is in our department, Chemical and Biological Engineering, and the other is in Civil Engineering. The third student is expected to graduate from High School this spring.

## **Annual report 2008**

### **ALD of porous silica and alumina membranes**

Two ALD reactors are build and functional. A diffusion pump is being added to the systems to reduce pressure and increase pump down times. Initial experiments on the ALD of silica in mesoporous silica supports indicate that a significant defect reduction was accomplished. This was quantified using permeance measurements as a function of pressure drop. Initially, >90% of defects (defined as pores contributing to viscous flow) were eliminated after ALD modification. This work is being carried out by one Ph.D. candidate (David Cassidy) and two undergraduate students (Abby Siegfriedt and James Ecker). This work was presented at the Gordon Research Conference on Nanoporous Materials in June 2008. An international collaboration is being planned between the University of Edinburgh (Stefano Brandani) and University of Maine (DeSisto). Brandani has an interest in modeling adsorptive and diffusive properties of membranes and is a natural fit with DeSisto's background in synthesis.

Additional work has been initiated on ALD modification of mesoporous silica powders. The reasons for this include preparation and characterization of new materials for adsorbents and catalyst supports as well as gaining a more detailed understanding of ALD of the mesoporous materials. Advantages include controlling pore size and perhaps imparting hydrothermal stability of the silica materials through surface passivation.

Additional work is being conducted on preparing and characterizing mesoporous silica thin films on supports suitable for single-molecule imaging.

### **Functionalized silica membranes**

The graduate student being supported on this portion of the grant has graduated with a Ph.D. in May 2008 and is planning to post doc in the area of fuel cells. The two papers that were submitted (as of the last writing) were accepted for publication and now in print. An additional paper is being submitted, entitled "Diffusion in Mesoporous Silica Membranes". This paper provides experimental evidence confirming Knudsen flow in mesoporous silica membranes and contradicts some recent papers published proclaiming deviations from Knudsen flow based on molecular modeling studies that were not backed up with experimental evidence.

### **Measurement of Intrinsic Properties in Mesoporous Silica Membranes**

One of the challenges in characterizing micro/nanostructures in membranes and porous materials is unpacking the heterogeneity inherent to these materials. Single molecule spectroscopy is one method for addressing this issue. Last year, in collaboration with Professor Mike Mason, we began looking at single molecule imaging methods to characterize properties of mesoporous silica membranes. Recently, we have focused our efforts on using fluorescence photoactivation localization microscopy (FPALM) to

characterize the heterogeneity in mesoporous silica films. A caged dye molecule was loaded into the pores of a silica membrane. In the FPALM technique many dye molecules can be loaded and turned on/off at particular times, and located with very high precision (spatial resolution on the order of tens of nanometers). We have initial data on mesoporous films. We are currently in the process of collecting reference data (on non porous films and substrates). Our hope is that we can locate and quantify regions that have a high concentration of molecules that may indicate the presence of defects. Combined with our ALD process for selective pore size reduction, we hope to observe defect healing in porous films. This has both fundamental and practical significance in the membrane field.

## **Educational Activities**

Two graduate students and two undergraduate students were mentored and received experience in membrane synthesis and characterization. One graduate student received his Ph.D. and has accepted a post-doctoral position in the area of fuel cells.

## Annual Progress 2009

### Characterization of mesoporous silica membranes

We are continuing to use a broad range of fluorescence-based techniques to obtain preliminary intrinsic kinetic and thermodynamic quantities in inorganic membranes. These include bulk measurements of diffusion on ideal membranes using time-resolved fluorescence, localized measurements of guest/host interactions within ordered mesoporous silica films using single molecule imaging (already published), and imaging heterogeneous structures within mesoporous silica films using Fluorescence Photoactivation and Localization Microscopy (FPALM). The preliminary data described below demonstrates our ability to make sensitive and meaningful fluorescence measurements in a mesoporous material system, a necessary first step toward achieving our vision of 2D mapping of heterogeneity in membranes and porous materials. As a result of these preliminary experiments, *Professor Mike Mason and I have submitted two proposals to NSF for continued funding.*

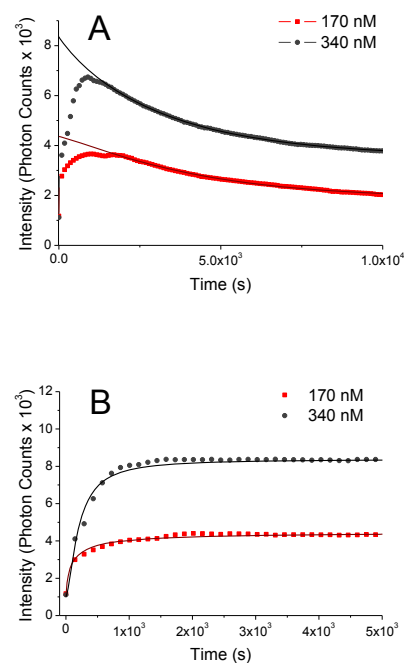
#### **Bulk Measurements of Diffusion**

We have carried out preliminary time-dependent fluorescence measurements of the diffusion of an organic dye through a model membrane (Anodisc™). By integrating over the entire sample area, the maximum possible signal-to-noise, and hence, time resolution was achieved. The measurement of the entire parent distribution ensures the accuracy of the mean diffusivity. This data is necessary for calibrating collective single molecule data.

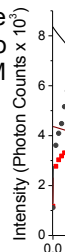
Time-dependent fluorescence data was collected in an inverted fluorescence microscope. A 200  $\mu\text{L}$  aliquot of nanomolar concentration fluorescein was added to one side of the 20nm pore diameter Anodisc™ membrane. Fluorescence data was collected on the opposite side of the membrane versus time and is plotted in Figure 2A (points) along with model generated data (solid lines) representing the expected dye photobleaching rate (the dye simultaneously diffuses and bleaches). In Figure 2B, the data shown has been corrected, removing the effects of photobleaching, and fit to a simple sigmoidal growth model showing the time-dependent dye concentration due to diffusion through the membrane for two initial dye concentrations.

#### **Fluorescence Photo-Activation Localization Microscopy (FPALM)**

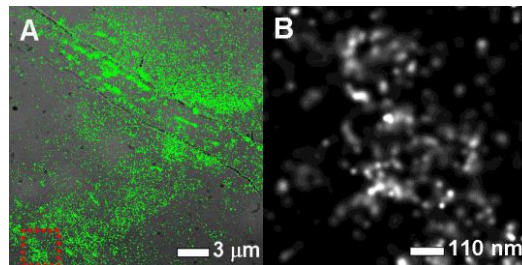
Our work with single molecule imaging provided valuable local information,



**Figure 1. Bulk molecular diffusion.** A) Comparison of raw fluorescence intensity data (points) versus time and expected effect due to photobleaching (solid) for two starting dye concentrations. B) Corrected data and fit to sigmoidal growth model for 170 nM and 340 nM initial dye concentrations.



identification of probe molecules required separation between molecules, resulting in limited ability to map heterogeneity. In effect, we were required to undersample the pore network. As part of an ongoing high resolution imaging initiative, a new technique, Fluorescence Photo-Activation Localization Microscopy (FPALM) was developed. Recently, we have obtained preliminary FPALM data for ~ 500 nm thick mesoporous silica membranes deposited on glass and loaded with photoactivatable fluorescein. FPALM images are shown in Figure



**Figure 2.** Mesoporous silica film FPALM data. A) Brightfield image localized single molecule positions superimposed (green). B) Expanded view of boxed region (red in A), where feature sizes are determined by localization precision.

2. A typical 30 x 30 μm region of the membrane including a visible defect feature is shown in Fig 2A where the positions of approximately 100,000 single molecules, determined via FPALM, are superimposed in green. Qualitatively, in regions on either side of the crack feature, the probe molecules appear to be relatively homogeneously distributed. In stark contrast, molecules appear to aggregate along the crack feature, likely due to the high surface energy associated with these regions. A zoomed-in region of Fig 2A is shown in Fig. 2B, illustrating the dramatic improvement in image resolution and fluorescence labeling density possible with FPALM. The position of each molecule is plotted as a Gaussian spot with a width of ~5 nm (approximately the localization precision in this sample).

In summary, FPALM measurements on membranes resulted in increased aerial coverage of probe molecules, thereby increasing our ability to map the heterogeneity of membrane properties. Because the dynamics of transport, obtained from the bulk measurements described above, are much slower than the time required for a typical FPALM measurement, it is now possible to observe molecular transport while simultaneously locating those molecules with extremely high spatial resolution and large aerial density. Hence, we now have the potential to two-dimensionally map transport properties. Intrinsic to this map will be the underlying heterogeneity and spatial distribution of membrane properties.

## Atomic Layer Deposition Modification of Silica Membranes

Last year's research was focused on two areas of Atomic Layer Deposition of Mesoporous Silica membranes. One part was on producing consistent mesoporous silica membranes and utilizing more characterization techniques of the produced membranes. The other area was on Atomic Layer Deposition of one of the mesoporous membranes produced.

We are currently producing two different silica sol-gel membranes. One uses CTAB as the surfactant and the other with Pluronic-123. The membranes were produced using evaporated induced self-assembly in a humidity and temperature

controlled environment. In order to confirm that we were producing highly porous membranes in the desired pore size range, nitrogen porosimetry was performed. We were able to repeatedly produce membranes, with the average pore size of 28Å for the CTAB membrane and 75Å for the P-123 membrane. Figure 1 shows the pore size distribution of the CTAB membrane collected.

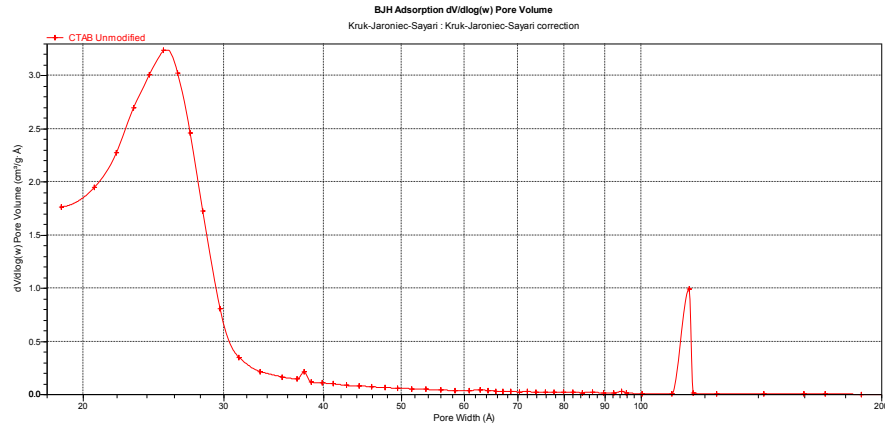


Figure 1 – Nitrogen Porosimetry of CTAB membrane

The membranes were examined for ordered pore structure and consistency for each sample produced. The order was examined using XRD of membranes on dip coated glass slides. For the CTAB membranes it was confirmed to have a highly ordered cubic structure. The XRD for CTAB is shown in Figure 2. The P-123 membrane produced a hexagonal order. We worked to change our procedure to produce a cubic structure for P-123 but were not successful.

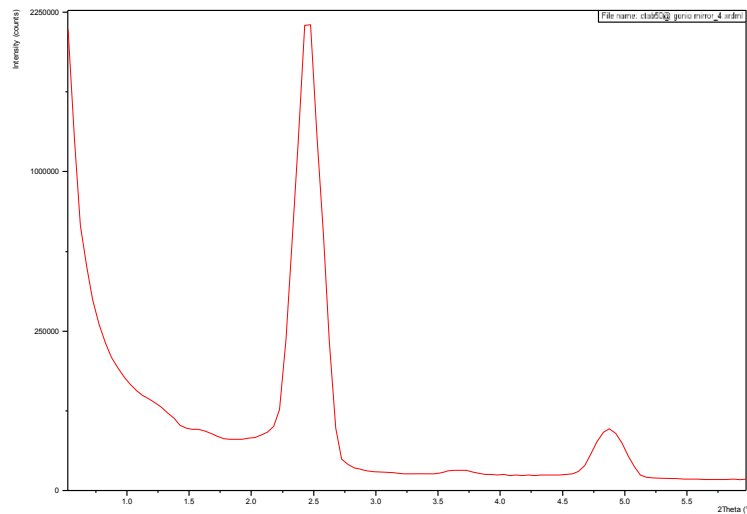


Figure 2 – XRD of CTAB membrane

The membranes characterization of the sol-gel was compared with the dip-coating the membranes on a ceramic support. The CTAB membranes produced a more consistent product and were analyzed using a hexane permoporometry setup. The hexane permoporometry measured a similar pore size distribution as the nitrogen porosimetry, around 25Å.

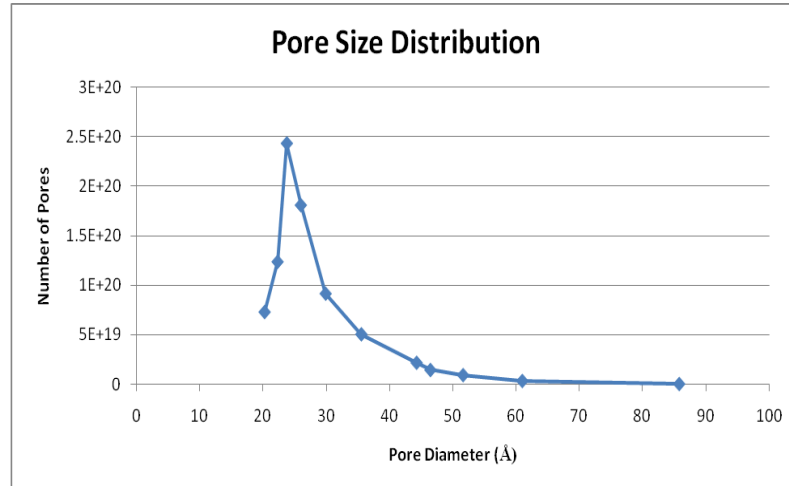


Figure 3 – Pore Size Distribution of CTAB Membrane

The membranes were finally modified using Atomic Layer Deposition using trimethyl alumina and water as precursors. The membranes were measure using the hexane permoporometry after each cycle of atomic layer deposition. Figure 4 shows the changes after each cycle. There was no observed shift in the pore size but we were able to fill the smallest pores and gradually reduce the larger pores after each cycle.

These results are significant. Under the given reaction conditions, the precursors were limited to diffusion and reaction in the larger pores. Qualitatively, this was successful in reducing the size of larger pores while leaving the smaller pores unchanged. These reaction conditions would prove useful in reducing defects in the membranes while leaving the pore size determined by the template unchanged.

Future work includes quantifying the pore size reduction in relation to individual layer thicknesses. We have also begun developing a model for relating the deposition conditions, precursor vapor pressure and exposure time, to the diffusion into pores with sizes on the order of 2-8 nm. Our initial calculations indicate that exposure times as well as evacuation times for unreacted precursors must be increased several orders of magnitude above those determined for flat surfaces. In addition, we will modify similar membranes under different reaction conditions in attempts to modify the smaller pores in the membranes.

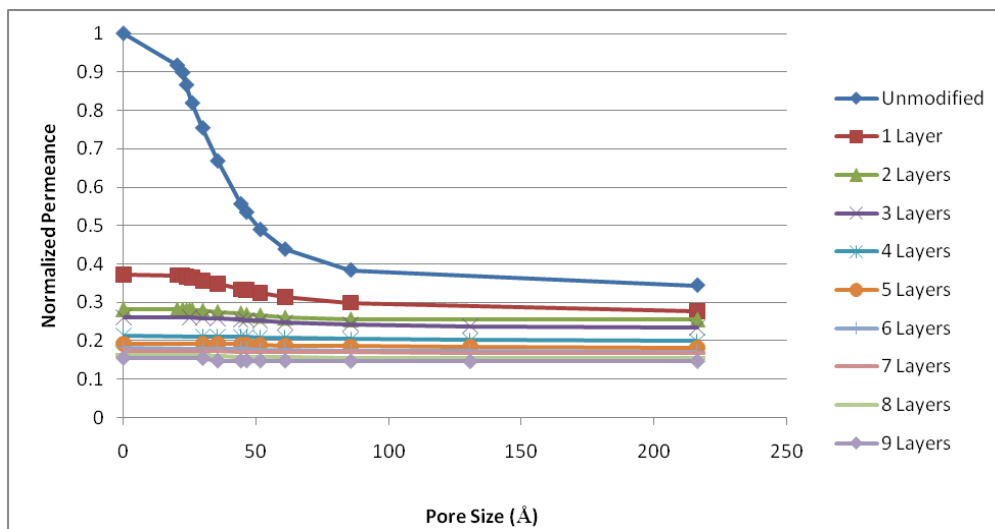


Figure 4 – Hexane Permporometry of CTAB membrane during Atomic Layer Deposition



# Annual Report 2010

## Summary

The highlights this year included the graduation of a doctoral candidate, Raymond Kennard, who successfully defended his Ph.D. thesis entitled, "Characterization of Mesoporous Materials via Fluorescent Spectroscopy Methods." His work has been published in Applied Physics Letters (Molecular diffusivity measurement through an alumina membrane using time-resolved fluorescence imaging). The final chapter of his thesis is currently under manuscript preparation. In addition, an undergraduate researcher, Abigail Siegfriedt, has completed her engineering capstone and Honors Thesis entitled, "Evaluation of Membrane Performance on Separating Acetic Acid from Water Compared to Competing Technologies," graduating with Highest Honors from the University of Maine with an undergraduate degree in Chemical Engineering. Abbie will take a position with Verso after graduation. David Cassidy continues progress toward his Ph.D. degree and has submitted one manuscript for review. Tyrone Ghampson was supported on a supplemental grant to travel to Concepcion, Chile, to work with Professor Nestor Escalona regarding catalytic activity of mesoporous silica supported catalysts for hydrodeoxygenation. This activity was initiated during my sabbatical spent in Concepcion with a Technology Development Unit in Chile focused on forest bioproduct and process development.

Included below are updates on these three activities as abstracts of publications.

# Atomic layer deposition modified ordered mesoporous silica membranes

David Cassidy<sup>1</sup> and William J. DeSisto<sup>\*1,2</sup>

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<sup>2</sup>*Laboratory for Surface Science and Technology, University of Maine, Orono, ME 04469*

## **Abstract**

Mesoporous silica membranes, prepared by surfactant-templating with a pore diameter of ~4 nm on a macroporous alumina support, were modified by atomic layer deposition (ALD) of aluminum oxide. ALD of aluminum oxide was achieved using trimethyl aluminum and water as reactants. Membranes modified with 50 ALD reaction cycles were characterized periodically during progressive reaction cycles to provide details of the pore modification process. A decrease in light gas permeance, pore size shift to lower pore sizes and a decrease in porosity provided evidence for pore size reduction through ALD. Further analysis of the data indicated that the ALD reaction favored larger pores and defects, and became less efficient as the pore size decreased. This is related to the constant reaction conditions used in this study as well as a decrease in intrinsic diffusivity of reactants into smaller pores.

# Molecular diffusivity measurement through an alumina membrane using time-resolved fluorescence imaging

Raymond Kennard<sup>1</sup>, William J. DeSisto<sup>1,2</sup> and Michael D. Mason<sup>1,3</sup>

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<sup>3</sup>Institute for Molecular Biophysics, University of Maine, Orono, ME 04469

We present a simple fluorescence imaging method for measuring the time-resolved concentration of a fluorescent molecule diffusing through an anodic alumina membrane with a pore diameter of 20 nm. From the concentration breakthrough curve, the molecular diffusivity of the fluorophore was extracted. The experimentally determined diffusivity was three orders of magnitude lower than reported bulk values. Due to the relative simplicity and ease of use this method can be applied to provide fundamental information for bio-molecular separations applications. One feature of this method is the high sensitivity at inter-cellular volumes broadening its application to drug delivery and controlled cell growth.

EVALUATION OF MEMBRANE PERFORMANCE ON SEPARATING ACETIC ACID  
FROM WATER COMPARED TO COMPETING TECHNOLOGIES

by  
Abigail Siegfriedt

A Thesis Submitted in Partial Fulfillment of the Requirements for a Degree with Honors  
(Biological Engineering)

The Honors College

University of Maine

May 2011

Advisory Committee:

William DeSisto, Associate Professor of Chemical and Biological Engineering, Advisor

Doug Bousfield, Professor of Chemical and Biological Engineering

Peter van Walsum, Associate Professor of Chemical and Biological Engineering

Mimi Killinger, PhD. **Honors Preceptor**

**Abigail Engelberth, Post Doctorate for Chemical and Biological Engineering**

## Abstract

Acetic acid is a byproduct of many biochemical processes and has considerable commercial value. In the state of Maine, a pulp mill with a production rate of 1000 tonnes of pulp per day will generate approximately 30 tonnes of acetic acid per day.<sup>1,2</sup> The most cost intensive portion of the separation of acetic acid from the pulp extracts is its separation from water. This paper will focus on one of the developing alternatives for this separation, membrane technology. A viable option for an industrial membrane would be silica-based. The research will include membrane synthesis and the comparison of a distillation column and liquid-liquid extraction to several membrane/ separation column hybrids using ASPEN Plus and MathCAD simulation models. The addition of pervaporation/vapor permeation will decrease the economic burden of some current separation techniques. The simulation results suggest that the combination of a stripping column with a hydrophobic and hydrophilic membrane has the lowest equivalent annual operating cost with a high recovery at a specified purity of 99wt% excluding the cost of the membrane itself. The laboratory results support the variability of polymerization and binding characteristics of Aminopropyltriethoxysilane (APTES), however suggest that there should be further testing on the stability of silica membranes. Other recommendations include testing membrane cascade, recycle streams, and the use of other functionalized membrane groups for a better separation factor.

# Annual Report 2011

## Summary

The highlights this year included the graduation of a doctoral candidate, David Cassidy, who successfully defended his Ph.D. thesis entitled, "Preparation and characterization of atomic layer deposition and molecular layer deposition modified mesoporous silica membranes." His work has been published in Chemical Vapor Deposition. The final chapter of his thesis is currently under manuscript preparation for submission to the Journal of Membrane Science. In addition, an undergraduate researcher, Ogechi Ogoke, has begun learning research techniques in membrane characterization within our laboratory. Tyrone Ghampson was supported on a supplemental grant to travel to Concepcion, Chile, to work with Professor Nestor Escalona regarding catalytic activity of mesoporous silica supported catalysts for hydrodeoxygenation. A paper entitled "Comparison of alumina- and SBA-15-supported molybdenum nitride catalysts for hydrodeoxygenation of guaiacol," has been accepted for publication in Applied Catalysis A: General. This activity was initiated during my sabbatical spent in Concepcion with a Technology Development Unit in Chile focused on forest bioproduct and process development. Included below are updates on these activities.

## Molecular layer deposition modification of mesoporous silica membranes

David E. Cassidy<sup>1</sup> and William J. DeSisto<sup>1,2,3</sup>

<sup>1</sup>Department of Chemical and Biological Engineering, University of Maine, Orono, ME 04469

<sup>2</sup>Laboratory for Surface Science and Technology, University of Maine, Orono, ME 04469

<sup>3</sup>Forest Bioproducts Research Institute, University of Maine, Orono, ME 04469

### Abstract

Mesoporous silica membranes dip-coated onto an alumina support with a mean pore radius of 2.5 nm, were subsequently modified using molecular layer deposition, MLD. An inorganic/organic material was deposited within the membrane resulting in a reduction in permeance values of light gases. The MLD reactions studied were trimethyl aluminum with oxalic acid (OA MLD) and with o-phthalic acid (PA MLD). The reactions took place in sequential order, similar to ALD, where a self-limiting process occurs that controls film deposition. The OA MLD modification of mesoporous silica resulted in a membrane that had its porosity reduced significantly (>95%) in the first deposition cycle and after 10 deposition cycles had a permeance value 233 times lower than the unmodified membrane. The PA MLD modification of mesoporous silica resulted in a membrane with a less pronounced decrease in porosity than the OA MLD membrane and a permeance of N<sub>2</sub> after 10 deposition cycles that was considerably higher (28 times) than the 10 cycle OA MLD membrane. Both modified membranes had a He/N<sub>2</sub> selectivity greater than the theoretical Knudsen value. Analysis of the permeance data for both membranes indicated that transport occurred largely by Knudsen diffusion. The permeance reduction in the MLD modified membranes was due to a combination of porosity and mean pore radius decrease. Molecular layer deposition provides an alternative synthesis technique for creating inorganic/organic membranes.

Note: Manuscript in preparation, published as David Cassidy's Ph.D. thesis

# Comparison of alumina- and SBA-15-supported molybdenum nitride catalysts for hydrodeoxygenation of guaiacol

I. Tyrone Ghampson<sup>a,b</sup>, Catherine Sepúlveda<sup>c</sup>, Rafael Garcia<sup>c</sup>, J.L. García Fierro<sup>d</sup>,  
Nestor Escalona<sup>c,\*</sup>, William J. DeSisto<sup>a,e,\*\*</sup>

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<sup>d</sup> Instituto de Catalisis y Petroquímica, CSIC, Cantoblanco, 28049 Madrid, Spain

<sup>e</sup> Forest Bioproducts Research Institute, University of Maine, Orono, ME 04469, United States

## Abstract

The hydrodeoxygenation of guaiacol (2-methoxyphenol) has been studied in a batch reactor over alumina- and SBA-15 silica-supported molybdenum nitride catalysts at 300 °C and 5 MPa of hydrogen pressure. The catalysts were prepared by nitriding supported Mo oxide precursors with ammonia gas or nitrogen–hydrogen mixtures via temperature-programmed reaction. The alumina-supported catalysts had a higher activity relative to the SBA-15 silica-supported catalysts which was essentially due to catechol production, an effect of the alumina support. The SBA-15 silica-supported catalysts transformed guaiacol directly to phenol by demethoxylation without noticeable catechol production. On both supports, nitridation by ammonolysis increased the activity by a factor of ~1.1 relative to nitridation by nitrogen–hydrogen. On SBA-15, ammonolysis preferentially produced the  $\gamma$ -Mo<sub>2</sub>N phase while the N<sub>2</sub>/H<sub>2</sub> mixture produced the  $\delta$ -Mo<sub>2</sub>N<sub>0.78</sub> phase. The incorporation of Co led to a marginal improvement in exposed Mo species but generally had a diminishing effect on HDO activity. The lack of catechol production using the SBA-15 silica support is important in minimizing coking reactions and also opens up possibilities for utilizing silica supports with highly controlled pore sizes to possibly influence product distribution in HDO of more diverse feed streams derived from biomass conversion processes.

Note: Manuscript accepted for publication in Applied Catalysis A: General



# Merging atomic layer deposition with membrane synthesis

**Dr William DeSisto** is a chemical scientist at the cutting edge of porous membrane research. He explains why Atomic Layer Deposition is so important to his work and the potential applications

**Can you outline the background from which your current research into silica membranes has emerged?**

This research originally came from our desire to merge atomic layer deposition with membrane synthesis. We knew that Atomic Layer Deposition (ALD) would be a good method for depositing a thin layer of material in a highly controlled manner within a porous structure. This is because in any membrane its performance will increase when it has a more homogeneous pore size distribution, a thin separating layer and controlled surface chemistry. ALD is ideally suited to address these issues in membrane fabrication. There has been a small amount of work published in this field of interest, but a lot of questions remain. For example, how much control over the process could we have? What happens when pores become very small? Could we take advantage of certain ALD chemistry to control pore size and pore homogeneity?

**For those who are unaware, could you describe what ALD is?**

ALD is an exciting method to fabricate a thin layer on a support. At its core is the ability to control the deposition of the material one atomic layer at a time. ALD achieves this by selecting appropriate chemicals for the deposition process and applying these chemicals to the surface in a sequential, controlled manner.

The overall atomic layer is synthesised by two half-reactions. Each one of these half-reactions is surface-limited. That is, the reaction stops when the surface is completely covered. This is achieved by selecting specific chemicals to react. For example, the first half-reaction takes place using chemical A that completely



covers the surface. Once the surface is covered with A, A will not continue to react with itself to build a thicker layer. Then, excess chemical A is removed from the reactor and A-terminated surface is exposed to chemical B. Again, chemical B chemically attaches itself to A forming an AB layer. Once all the surface is covered in one layer, B can no longer react with itself and is removed from the reactor. This process is repeated over as many AB cycles as is desired for the layer thickness needed. ALD has really emerged recently in microelectronics fabrication (computer chips).

**Why is ALD so significant in the context of this work?**

As devices continue to get smaller and smaller to aid faster, more efficient computing, the only place to go is vertically on the chip (similar to packing people into large cities with limited land). In order to achieve this, thin layers of materials must be formed in trenches and on dome-like structures. ALD

happens to have the unique ability to coat these odd-shaped structures uniformly. Since ALD can coat odd shaped structures uniformly, it makes sense that it could coat the inside of a pore within a porous material or membrane. ALD is a controlled deposition method, so it has the potential to reduce an existing pore size distribution in a membrane to a final desired pore size. This would allow molecular separation based on size differences. In addition, ALD can leave the surface of the pore with a specific chemical functionality that would allow molecular separation based on surface affinity.

**What range of skills is represented by the research group you are working with?**

I have had the good fortune to collaborate with a number of colleagues who have expertise which I do not have myself. These include experts in understanding diffusivity in porous materials and characterising materials with heterogeneities on a very small scale. I have also had the ability to work with several industrial researchers including the oil industry, lithium-ion battery industry and membrane industry.

**Will you be attempting to develop these materials for market once the fundamental research is complete?**

As an academic researcher I do not have a strong focus on market development. However, we do have some strategies in place to derive the maximum potential from our work. For example, I am currently working with a small company trying to develop membranes for biorefinery applications. Interestingly, one of the immediate benefits of this research might be to selectively remove defects – larger, unwanted pores – from existing membranes. Thus, in essence, we are able to make existing membranes more homogeneous.



# Stabilising membrane fabrication with **nano tools**

Researchers at the **University of Maine** are developing unique synthetic approaches and innovative nanotechnologies to modify porous structures, and reaching new levels of atomic control during material preparation

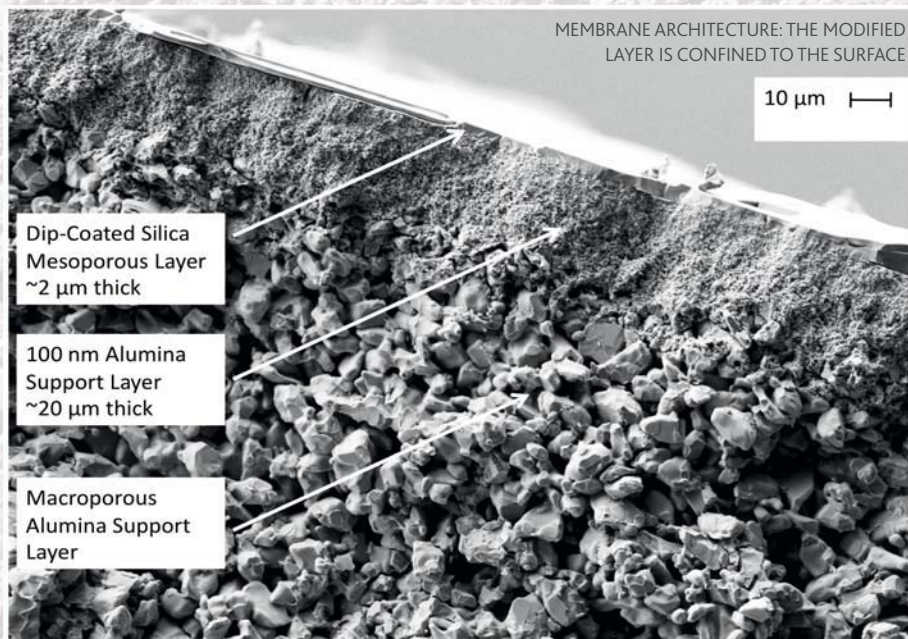
**MOTIVATED BY THE** desire to fill a gap in the world of membrane control, research being undertaken by a team of chemical engineers at the University of Maine's Department of Chemical and Biological Engineering is looking to address a 'pore size gap' in silica membranes. Funded by the U.S. National Science Foundation as a CAREER project, the intent of which is to offer stable support for researchers effectively integrating teaching, learning and discovery in their work, the research is focused on developing a new class of modified mesoporous silica membranes with controlled pore size and surface functionality through unique synthetic approaches. Principal Investigator, Dr William DeSisto is excited about the applications of this technology because, at this point in time, the only membrane sizes (controlled by templating or crystal structure) that are available on the market place are very small sizes around 0.5 nm, the size of permanent gases such as methane and carbon dioxide, or around 2 nm, which is the size found in ordered mesoporous silica membranes.

## **TRANSFORMING THE SEPARATIONS INDUSTRY**

The research group, which is made up of a number of different contributors from a range of backgrounds, including experts in diffusivity in porous materials, as well as several researchers working with industry, sees the

potential applications for membranes which have pore sizes controlled within this 'pore size gap' as being extensive. DeSisto expects many specific separation needs to arise as the renewable fuels and chemicals technologies continue to mature. He points out that there are researchers around the world who are increasingly focusing on how they can achieve and realise the efficient transformation of biomass into practical fuels and chemicals, all of which require separations of different mixtures through porous membranes: "Right now, many of these conversion technologies result in chemical mixtures of many different compounds in a range of dilute quantities and often mixed with water, which can be costly and resource-dependent to separate".

After the biomass is chemically transformed into these mixtures of chemicals, there are plenty of uses for the innovative technologies developed within the project: "In general, the motivation for developing membranes in molecular separations is to replace alternative technologies, such as distillation, which require significant amounts of energy and are limited by the thermodynamic properties of the mixture," affirms DeSisto. Another example for the potential of applications that he uses is where biorefineries are attempting the separation of valuable chemicals from mixes which can be costly and energy intensive. DeSisto is also excited about the potential for his work on





separation to find a home in the bio-molecular separation field, where many of the larger size molecules fall into the 'pore size gap' their research is targeting. He is now envisioning a wealth of possibilities in pharmaceutical separations and drug delivery materials as having every likelihood of becoming a reality.

### THE VALUE OF ATOMIC LAYER DEPOSITION

Through this work the team has successfully managed to show that pore size and surface chemistry control can be achieved using these new synthetic approaches. The aim is to use these novel techniques, called atomic layer deposition (ALD) to help prepare silica membranes and efficiently produce new membranes that are hybridised organic/inorganic. At the very heart of the group's techniques are the highly controlled surface chemistry reactions which are used to modify the mesoporous silica membranes. They control pore size reduction by starting with a template mesoporous silica membrane ( $d_{\text{pore}} = 3.6 \text{ nm}$ ) and they have found that the ALD of alumina and silica will decrease the pore diameter in a controlled manner. This means that as the pores become smaller, the average ALD growth rate decreases, delivering effective self-limiting pore size reduction. DeSisto explains that the ALD growth rate has a decreasing linear dependence on pore size consistent with Knudsen permeance of reactants into small pores. This diffusion limitation may also have benefits in keeping the modified separation layer confined to the surface, which would enhance flux through the membrane.

The team did not initially set out to solve one particular separation problem or application, rather to provide a new method for fabricating membranes that could be tailored for a specific application defined by the end user

Part of their work also requires controlling surface functionality of membranes. This component can be achieved by attaching functional silanes to silica and alumina surfaces through reaction with surface hydroxyls. DeSisto explains this by using an example of amino groups for selective adsorption of carbon dioxide. He says that a synthesis strategy for increasing free amino groups on a silica surface by 25 per cent led to increased carbon dioxide selective permeance through a membrane for separation from nitrogen. This means that during the materials preparation stage they have been able to confirm a level of atomic control that is not currently possible within industry today. In particular, DeSisto hopes

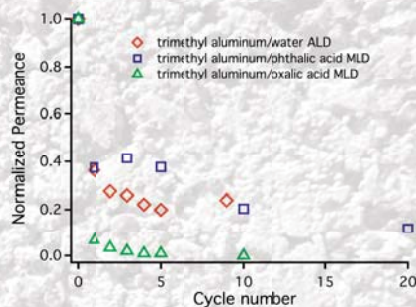


FIGURE 1. The sequential reduction in membrane permeance from modification by different ALD and MLD chemistries.

that their work will encourage new applications towards different classes of materials, and to potentially include adsorbents as well as other inorganic membranes.

### USING NOVEL CHARACTERISATION TOOLS TO UNDERSTAND ALD

The group has made some excellent progress since the project commenced in January 2006. They have been able to demonstrate under laboratory conditions that using ALD to reduce the pore size is actually self-limiting within specific ALD chemistries. From DeSisto's perspective, this is a motivating breakthrough as they can finally envision a heterogeneous membrane being able to transform into a more homogeneous membrane: "We have reasonable evidence that the ALD reaction favours larger pores within the heterogeneous membranes being modified. That is consistent with the increasing difficulty to diffuse ALD reactants into smaller and smaller pores". They have also made inroads into understanding how ALD reactants containing organic functionalities are able to create hybrid organic-inorganic layers within the pores of membranes. In addition, the researchers have been able to advance ways to encourage ALD in membranes to increase the pore surface coverage of reactants using supercritical fluids which target the diffusion barrier, essentially lowering this barrier to coverage.

While the team has made a number of significant findings, they are still struggling to definitively understand the ultimate limits of ALD in pore modification, particularly when the pores are approaching the molecular diameters of the ALD reactants states DeSisto: "This issue has been a bit elusive for us to date, mainly because of the limits of characterisation ability and the starting membranes used for modification". However, they have been able to demonstrate that ALD is used to modify nanoporous materials tailoring adsorptive and diffusive properties, that pore size reduction is self-limiting through precursor selection and reaction conditions and that surface functional groups change adsorptive properties and permeability in membranes. The next stage planned for this research is to work on developing some innovative characterisation tools, which DeSisto hopes will ultimately help the group to really improve their comprehension of what is actually going on during the process of ALD.

## INTELLIGENCE

### A NEW CLASS OF MODIFIED MESOPOROUS SILICA MEMBRANES WITH CONTROLLED PORE SIZE AND SURFACE FUNCTIONALIZATION THROUGH UNIQUE SYNTHETIC APPROACHES

#### OBJECTIVES

- To utilise the new synthesis technique, known as catalysed-atomic layer deposition, to prepare silica membranes with controlled pore sizes in the pore size range of 10-20 angstroms and create new hybrid organic/inorganic membranes
- To understand the chemical, microstructural, permeation, and separation properties of the new materials while quantitatively linking the synthesis procedure to material performance

#### KEY COLLABORATORS

- Dr David E Cassidy, Cerahelix, Inc
- Dr Scott R Higgins, Hawaii National Energy Institute
- Dr Benjamin McCool, Algenol
- Dr Raymond Kennard, Orono Spectral Solutions, Inc
- Abigail Siegfriedt, Verso Paper
- Professor Douglas Ruthven, University of Maine
- Professor Mike Mason, University of Maine
- Dr Joseph DiCarlo, BASF

#### FUNDING

National Science Foundation – contract no. 0547103

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**WILLIAM J DESISTO** received his undergraduate education at the University of Rhode Island in Chemical Engineering and his graduate education at Brown University in Engineering. Prior to his appointment at the University of Maine, he worked for 10 years at the U.S. Naval Research Laboratory as a research engineer.



We have prepared and characterized organically-modified mesoporous silica membranes using supercritical CO<sub>2</sub> fluid deposition. Supercritical CO<sub>2</sub> fluid deposition has been shown to increase both diffusion and concentration of the reactants at the reaction site, a particular advantage when the reaction site is inside a small pore, where access can be limited. The pre-modified mesoporous silica membranes were prepared by surfactant-templated synthesis on  $\alpha$ -alumina disk-shaped supports. These mesoporous silica supports had a mean pore size distribution of 5 nm. The alkyl modification of the silica membranes was achieved by the covalent attachment of trimethylchlorosilane (TMCS) and octadecyldimethylchlorosilane (ODMCS) using triethylamine (TEA) as a catalyst in supercritical-CO<sub>2</sub>. Successful attachment was confirmed through infrared spectroscopic identification of methyl and methylene groups and also a decrease in single gas permeance of light gases through the modified membrane. The synthesis process did not degrade the support membrane, was relatively efficient, and was free of organic solvents required for traditional synthesis. The dominant transport modes in the membranes were Knudsen and surface flow. Separation factors for methane and propane over nitrogen were not increased relative to the bare support, indicating that neither surface flow was enhanced nor size selectivity improved for the membrane system studied. Supercritical CO<sub>2</sub> fluid deposition was demonstrated an effective technique for reaction of functionalized silanes on the surface of silica membranes.

## Annual Report 2006

We have prepared and characterized organically-modified mesoporous silica membranes using supercritical fluid CO<sub>2</sub> fluid deposition. Supercritical CO<sub>2</sub> fluid deposition has been shown to increase both diffusion and concentration of the reactants at the reaction site, a particular advantage when the reaction site is inside a small pore, where access can be limited. The pre-modified mesoporous silica membranes were prepared by surfactant-templated synthesis on alpha-alumina disk-shaped supports. These mesoporous silica supports had a mean pore size distribution of 5 nm. The alkyl modification of the silica membranes was achieved by the covalent attachment of trimethylchlorosilane (TCMS) and octadecyldimethylchlorosilane (ODMCS) using triethylamine (TEA) as a catalyst in supercritical-CO<sub>2</sub>. Successful attachment was confirmed through infrared spectroscopic identification of methyl and methylene groups and also a decrease in single gas permeance of light gases through the modified membrane. The synthesis process did not degrade the support membrane, was relatively efficient, and was free of organic solvents required for synthesis. The dominant transport modes in the membranes were Knudsen and surface flow. Separation factors for methane and propane over nitrogen were not increased relative to the support, indicating that neither surface flow was enhanced nor size selectivity improved for the membrane system studied. Supercritical CO<sub>2</sub> fluid deposition was demonstrated an effective technique for reaction of functionalized silanes on the surface of silica membranes.

We have conducted experiments on the synthesis and characterization of mesoporous silica membranes used as supports for subsequent pore size and surface chemistry

modification. Surface chemistry modification experiments have been conducted using trimethylchlorosilane and octadecyldimethylchlorosilane. These experiments were carried out by reaction in supercritical CO<sub>2</sub> to explore this new method for membrane modification. Experimental characterization includes infrared spectroscopy of the membrane surface, single gas permeation measurements, and adsorption branch porosimetry measurements. Additional work was done on designing and fabricating an atomic layer deposition system for pore size reduction experiments. This work has included refurbishing used equipment, procuring new equipment, computer programming for automated control and general experimental planning.

Educational activities include incorporating current data collected from research and using this data as a teaching vehicle for my introduction to chemical engineering calculations class. Advising two graduate students in research, one undergraduate in research, and one high school student in developing a teaching module has also taken place.

## **Annual Report 2007**

### **ALD of porous silica membranes**

An ALD reactor has been constructed for depositing silica layers into mesoporous silica membranes. The reactor will deliver three reactants through a GC valve into a custom reactor chamber configured to hold porous disc supports. An additional reactor is being constructed for alumina deposition from trimethylaluminum and water. Experiments are expected to commence shortly in this area.

### **Functionalized silica membranes**

We have continued our research in functionalized silica membranes. Two papers have been submitted. The first paper entitled, Covalent attachment of monochlorosilanes to mesoporous silica membranes using supercritical fluid deposition, was submitted to a special edition of Separation and Purification Technology focused on functionalized membranes. The abstract for this paper follows below. We have prepared and characterized organically-modified mesoporous silica membranes using supercritical CO<sub>2</sub> fluid deposition. Supercritical CO<sub>2</sub> fluid deposition has the potential to increase both diffusion and concentration of the reactants at the reaction site, a particular advantage when the reaction site is inside a small pore, where access can be limited. The unmodified mesoporous silica membranes were prepared by surfactant-templated synthesis on  $\alpha$ -alumina disk-shaped supports. These mesoporous silica supports had a mean pore diameter of 5 nm. The alkyl modification of the silica membranes was achieved by the covalent attachment of octadecyldimethylchlorosilane (ODMCS) using triethylamine (TEA) as a catalyst in supercritical-CO<sub>2</sub>. Successful attachment was confirmed through infrared spectroscopic



identification of the removal of the band due to isolated silanols accompanied by the appearance of bands due to methyl and methylene groups. We also directly measured a ~90% reduction in permeance of light gases through the modified membrane. The synthesis process did not degrade the support membrane, was relatively efficient, and was free of organic solvents required for traditional synthesis. The dominant transport modes in the membranes were Knudsen and surface flow. Ideal separation factors for methane and propane over nitrogen were not increased relative to the bare support, indicating that neither surface flow was enhanced nor size selectivity improved for the membrane system studied. Supercritical CO<sub>2</sub> fluid deposition was demonstrated as an effective technique for reaction of functionalized silanes on the surface of silica membrane.

A second paper entitled, Diffusive transport through mesoporous silica membranes, was submitted to the Journal of Microporous and Mesoporous Materials. This paper provided a more thorough analysis of the permeance and separation data. The abstract is given below. The results of a detailed study of the permeation of several light gases through unmodified and modified mesoporous silica membranes are reported. The base membranes which were synthesized by dip-coating multiple layers of a templated silica onto a macroporous alumina support showed relatively high permeances with evidence of both support resistance and a contribution from viscous flow, in addition to Knudsen diffusion, through the active layer. The behavior of the modified membranes, which were prepared by silanation of the original membranes with octadecyldimethylchlorosilane, was more interesting. Permeances were lower and there was no evidence of support resistance or viscous flow. Permeation through the active layer appeared to occur by a Knudsen-like process. Permeance and permeance ratios measured in both single component and binary systems showed the characteristic



inverse dependence on the square root of the molecular weight (or the molecular weight ratio) but the temperature dependence was much stronger than expected for classical Knudsen flow. The behavior of CO<sub>2</sub> was somewhat anomalous yielding permeances that were about 25% larger than that for propane which has the same molecular weight.

## **Measurement of Intrinsic Pore Properties in Mesoporous Silica Membranes**

This work is the result of collaboration between Mike Mason and me. We are looking to measure intrinsic properties of mesoporous silica membranes using single molecule imaging spectroscopy. One paper has been accepted to the Journal of Chemical Physics. The abstract is given below. Mesoporous silica membranes fabricated by the surfactant templated sol-gel process have received attention because of the potential to prepare membranes with a narrow pore size distribution and ordering of the interconnected pores. Potential applications include ultrafiltration, biological separations and drug delivery, and separators in lithium-ion batteries. Despite advancements in synthesis and characterization of these membranes, a quantitative description of the membrane microstructure remains a challenge. Currently the membrane microstructure is characterized by the combination of results from several techniques, i.e. gas permeance testing, XRD, SEM, TEM, permoporometry. The results from these ensemble methods are then compiled and the data fitted to a particular flow model. Although these methods are very effective in determining membrane performance, general pore size distribution, and defect concentration, they are unable to monitor molecular paths through the membrane and quantitatively measure molecular interactions between the molecular specie and pore network. Single molecule imaging techniques enable optical measurements that probe materials on nanometer length scales through observation of individual molecules without the influence of averaging. Using single molecule imaging spectroscopy, we can quantitatively characterize the interaction between the probe

molecule and the interior of the pore within mesoporous silica membranes. This approach is radically different from typical membrane characterization methods in that it has the potential to spatially sample the underlying pore structure distribution, the surface energy, and the transport properties. Our hope is that this new fundamental knowledge can be quantitatively linked to both the preparation and the performance of membranes leading to the advancement of membrane science and technology. Fluorescent molecules, 1,1-dioctadecyl-3,3,3,3-tetramethylindo-carbocyanine perchlorate (DiIC-18), used to interrogate the available free volume in their vicinity, were loaded into the mesoporous silica membranes at subnanomolar concentrations. The mesoporous silica films were prepared using a non-ionic ethylene oxide-propylene oxide-ethylene oxide tri-block copolymer surfactant, Pluronic P123, on single crystal silicon substrates using dip-coating of a silica sol. Membranes were prepared resulting in an average pore diameter of approximately 5 nm as measured by helium, nitrogen permeance and porosimetry. Fluorescent images and time transient experiments were recorded using a custom built single molecule scanning confocal microscope at differing temperatures (10°C, 20°C, 30°C, 40°C, and 50°C). Time dependent polarization anisotropy was used to obtain the enthalpy of adsorption and Henry's law constant of the probe molecule.

## Educational Activities

Two graduate students and one undergraduate student were mentored and received experience in membrane synthesis and characterization. Data collected was used in an Introduction to Chemical Engineering Calculations course given to second semester first-year students. The material was well-received. Students enjoyed "real" examples as a basis for learning concepts. Of the three high

school students mentored so far, two have entered engineering (both females). One is in our department, Chemical and Biological Engineering, and the other is in Civil Engineering. The third student is expected to graduate from High School this spring.

## **Annual report 2008**

### **ALD of porous silica and alumina membranes**

Two ALD reactors are build and functional. A diffusion pump is being added to the systems to reduce pressure and increase pump down times. Initial experiments on the ALD of silica in mesoporous silica supports indicate that a significant defect reduction was accomplished. This was quantified using permeance measurements as a function of pressure drop. Initially, >90% of defects (defined as pores contributing to viscous flow) were eliminated after ALD modification. This work is being carried out by one Ph.D. candidate (David Cassidy) and two undergraduate students (Abby Siegfriedt and James Ecker). This work was presented at the Gordon Research Conference on Nanoporous Materials in June 2008. An international collaboration is being planned between the University of Edinburgh (Stefano Brandani) and University of Maine (DeSisto). Brandani has an interest in modeling adsorptive and diffusive properties of membranes and is a natural fit with DeSisto's background in synthesis.

Additional work has been initiated on ALD modification of mesoporous silica powders. The reasons for this include preparation and characterization of new materials for adsorbents and catalyst supports as well as gaining a more detailed understanding of ALD of the mesoporous materials. Advantages include controlling pore size and perhaps imparting hydrothermal stability of the silica materials through surface passivation.

Additional work is being conducted on preparing and characterizing mesoporous silica thin films on supports suitable for single-molecule imaging.

Functionalized silica membranes

The graduate student being supported on this portion of the grant has graduated with a Ph.D. in May 2008 and is planning to post doc in the area of fuel cells. The two papers that were submitted (as of the last writing) were accepted for publication and now in print. An additional paper is being submitted, entitled "Diffusion in Mesoporous Silica Membranes". This paper provides experimental evidence confirming Knudsen flow in mesoporous silica membranes and contradicts some recent papers published proclaiming deviations from Knudsen flow based on molecular modeling studies that were not backed up with experimental evidence.

## **Measurement of Intrinsic Properties in Mesoporous Silica Membranes**

One of the challenges in characterizing micro/nanostructures in membranes and porous materials is unpacking the heterogeneity inherent to these materials. Single molecule spectroscopy is one method for addressing this issue. Last year, in collaboration with Professor Mike Mason, we began looking at single molecule imaging methods to characterize properties of mesoporous silica membranes. Recently, we have focused our efforts on using fluorescence photoactivation localization microscopy (FPALM) to characterize the heterogeneity in mesoporous silica films. A caged dye molecule was loaded into the pores of a silica membrane. In the FPALM technique many dye molecules can be loaded and turned on/off at particular times, and located with very high precision (spatial resolution on the order of tens of nanometers). We have initial data on mesoporous films. We are currently in the process of collecting reference data (on non porous films and substrates). Our hope is that we can locate and quantify regions that have a high concentration of molecules that may indicate the presence of defects.

Combined with our ALD process for selective pore size reduction, we hope to observe defect healing in porous films. This has both fundamental and practical significance in the membrane field.

## **Educational Activities**

Two graduate students and two undergraduate students were mentored and received experience in membrane synthesis and characterization. One graduate student received his Ph.D. and has accepted a post-doctoral position in the area of fuel cells.

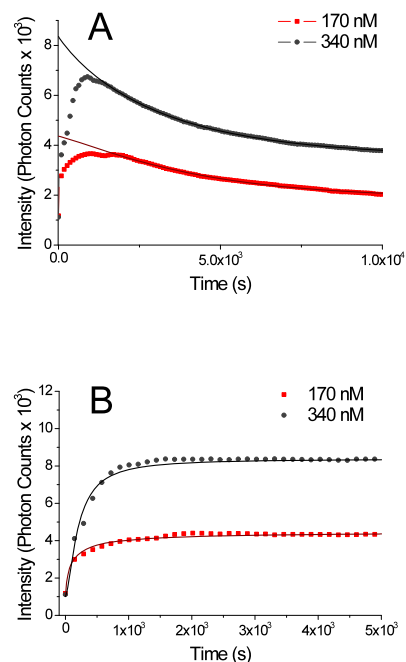
## Annual Progress 2009

### Characterization of mesoporous silica membranes

We are continuing to use a broad range of fluorescence-based techniques to obtain preliminary intrinsic kinetic and thermodynamic quantities in inorganic membranes. These include bulk measurements of diffusion on ideal membranes using time-resolved fluorescence, localized measurements of guest/host interactions within ordered mesoporous silica films using single molecule imaging (already published), and imaging heterogeneous structures within mesoporous silica films using Fluorescence Photoactivation and Localization Microscopy (FPALM). The preliminary data described below demonstrates our ability to make sensitive and meaningful fluorescence measurements in a mesoporous material system, a necessary first step toward achieving our vision of 2D mapping of heterogeneity in membranes and porous materials. As a result of these preliminary experiments, *Professor Mike Mason and I have submitted two proposals to NSF for continued funding.*

#### **Bulk Measurements of Diffusion**

We have carried out preliminary time-dependent fluorescence measurements of the diffusion of an organic dye through a model membrane (Anodisc™). By integrating over the entire sample area, the maximum possible signal-to-noise, and hence, time resolution was



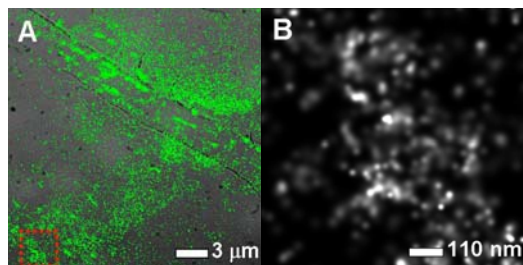
**Figure 1. Bulk molecular diffusion.** A) Comparison of raw fluorescence intensity data (points) versus time and expected effect due to photobleaching (solid) for two starting dye concentrations. B) Corrected data and fit to sigmoidal growth model for 170 nM and 340 nM initial dye concentrations.

achieved. The measurement of the entire parent distribution ensures the accuracy of the mean diffusivity. This data is necessary for calibrating collective single molecule data.

Time-dependent fluorescence data was collected in an inverted fluorescence microscope. A 200  $\mu\text{L}$  aliquot of nanomolar concentration fluorescein was added to one side of the 20nm pore diameter Anodisc<sup>TM</sup> membrane. Fluorescence data was collected on the opposite side of the membrane versus time and is plotted in Figure 2A (points) along with model generated data (solid lines) representing the expected dye photobleaching rate (the dye simultaneously diffuses and bleaches). In Figure 2B, the data shown has been corrected, removing the effects of photobleaching, and fit to a simple sigmoidal growth model showing the time-dependent dye concentration due to diffusion through the membrane for two initial dye concentrations.

### ***Fluorescence Photo-Activation Localization Microscopy (FPALM)***

Our work with single molecule imaging provided valuable local information, identification of probe molecules required separation between molecules, resulting in limited ability to map heterogeneity. In effect, we were required to undersample the pore network. As part of an ongoing high resolution imaging initiative, a new technique, Fluorescence Photo-Activation Localization Microscopy (FPALM) was developed. Recently, we have obtained preliminary FPALM data for  $\sim 500$  nm thick mesoporous silica membranes deposited on glass and loaded with photoactivatable fluorescein. FPALM images are shown in Figure



**Figure 2.** Mesoporous silica film FPALM data. A) Brightfield image localized single molecule positions superimposed (green). B) Expanded view of boxed region (red in A), where feature sizes are determined by localization precision.



2. A typical 30 x 30  $\mu\text{m}$  region of the membrane including a visible defect feature is shown in Fig 2A where the positions of approximately 100,000 single molecules, determined via FPALM, are superimposed in green. Qualitatively, in regions on either side of the crack feature, the probe molecules appear to be relatively homogeneously distributed. In stark contrast, molecules appear to aggregate along the crack feature, likely due to the high surface energy associated with these regions. A zoomed-in region of Fig 2A is shown in Fig. 2B, illustrating the dramatic improvement in image resolution and fluorescence labeling density possible with FPALM. The position of each molecule is plotted as a Gaussian spot with a width of  $\sim 5$  nm (approximately the localization precision in this sample).

In summary, FPALM measurements on membranes resulted in increased aerial coverage of probe molecules, thereby increasing our ability to map the heterogeneity of membrane properties. Because the dynamics of transport, obtained from the bulk measurements described above, are much slower than the time required for a typical FPALM measurement, it is now possible to observe molecular transport while simultaneously locating those molecules with extremely high spatial resolution and large aerial density. Hence, we now have the potential to two-dimensionally map transport properties. Intrinsic to this map will be the underlying heterogeneity and spatial distribution of membrane properties.

## **Atomic Layer Deposition Modification of Silica Membranes**

Last year's research was focused on two areas of Atomic Layer Deposition of Mesoporous Silica membranes. One part was on producing consistent mesoporous silica membranes and utilizing more characterization techniques of the produced

membranes. The other area was on Atomic Layer Deposition of one of the mesoporous membranes produced.

We are currently producing two different silica sol-gel membranes. One uses CTAB as the surfactant and the other with Pluronic-123. The membranes were produced using evaporated induced self-assembly in a humidity and temperature controlled environment. In order to confirm that we were producing highly porous membranes in the desired pore size range, nitrogen porosimetry was performed. We were able to repeatedly produce membranes, with the average pore size of 28Å for the CTAB membrane and 75Å for the P-123 membrane. Figure 1 shows the pore size distribution of the CTAB membrane collected.

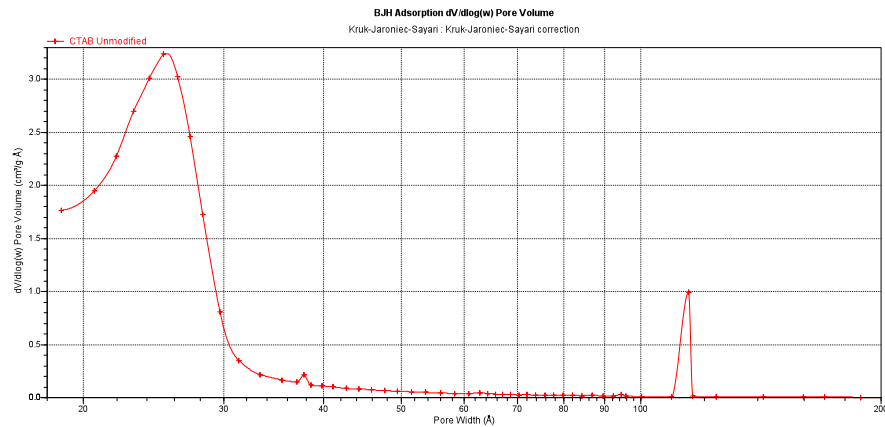


Figure 1 – Nitrogen Porosimetry of CTAB membrane

The membranes were examined for ordered pore structure and consistency for each sample produced. The order was examined using XRD of membranes on dip coated glass slides. For the CTAB membranes it was confirmed to have a highly ordered cubic structure. The XRD for CTAB is shown in Figure 2. The P-123 membrane produced a hexagonal order. We worked to change our procedure to produce a cubic structure for P-123 but were not successful.

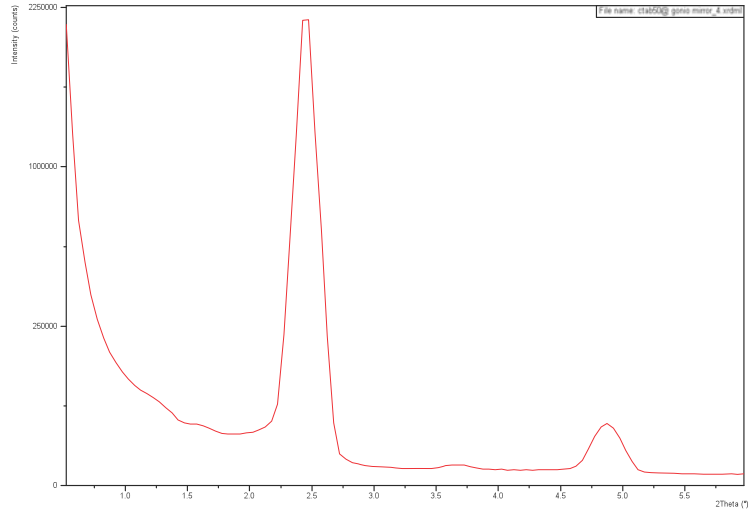


Figure 2 – XRD of CTAB membrane

The membranes characterization of the sol-gel was compared with the dip-coating the membranes on a ceramic support. The CTAB membranes produced a more consistent product and were analyzed using a hexane permoporometry setup. The hexane permoporometry measured a similar pore size distribution as the nitrogen porosimetry, around 25Å.

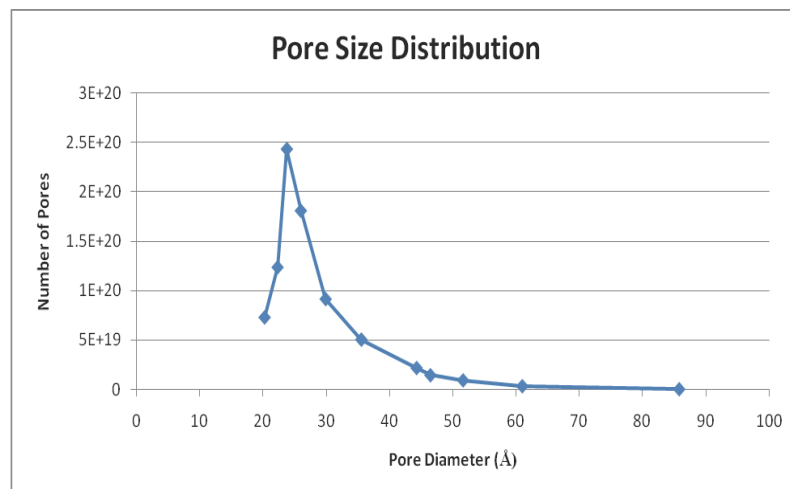


Figure 3 – Pore Size Distribution of CTAB Membrane

The membranes were finally modified using Atomic Layer Deposition using trimethyl alumina and water as precursors. The membranes were measured using the hexane permoporometry after each cycle of atomic layer deposition. Figure 4 shows the changes after each cycle. There was no observed shift in the pore size but we were able to fill the smallest pores and gradually reduce the larger pores after each cycle.

These results are significant. Under the given reaction conditions, the precursors were limited to diffusion and reaction in the larger pores. Qualitatively, this was successful in reducing the size of larger pores while leaving the smaller pores unchanged. These reaction conditions would prove useful in reducing defects in the membranes while leaving the pore size determined by the template unchanged.

Future work includes quantifying the pore size reduction in relation to individual layer thicknesses. We have also begun developing a model for relating the deposition conditions, precursor vapor pressure and exposure time, to the diffusion into pores with sizes on the order of 2-8 nm. Our initial calculations indicate that exposure times as well as evacuation times for unreacted precursors must be increased several orders of magnitude above those determined for flat surfaces. In addition, we will modify similar membranes under different reaction conditions in attempts to modify the smaller pores in the membranes.

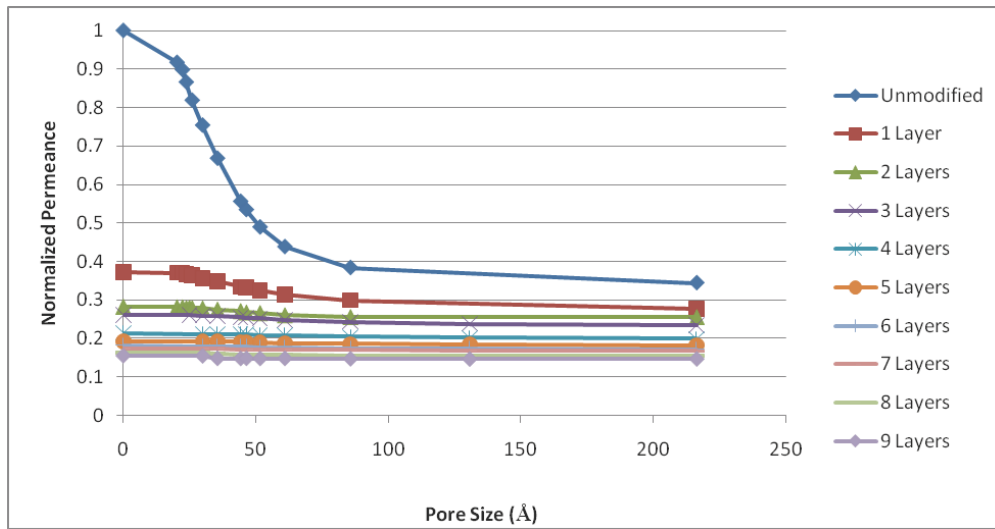


Figure 4 – Hexane Permporometry of CTAB membrane during Atomic Layer Deposition

## **Annual Report 2010**

### **Summary**

The highlights this year included the graduation of a doctoral candidate, Raymond Kennard, who successfully defended his Ph.D. thesis entitled, "Characterization of Mesoporous Materials via Fluorescent Spectroscopy Methods." His work has been published in Applied Physics Letters (Molecular diffusivity measurement through an alumina membrane using time-resolved fluorescence imaging). The final chapter of his thesis is currently under manuscript preparation. In addition, an undergraduate researcher, Abigail Siegfriedt, has completed her engineering capstone and Honors Thesis entitled, "Evaluation of Membrane Performance on Separating Acetic Acid from Water Compared to Competing Technologies," graduating with Highest Honors from the University of Maine with an undergraduate degree in Chemical Engineering. Abbie will take a position with Verso after graduation. David Cassidy continues progress toward his Ph.D. degree and has submitted one manuscript for review. Tyrone Ghampson was supported on a supplemental grant to travel to Concepcion, Chile, to work with Professor Nestor Escalona regarding catalytic activity of mesoporous silica supported catalysts for hydrodeoxygenation. This activity was initiated during my sabbatical spent in Concepcion with a Technology Development Unit in Chile focused on forest bioproduct and process development.

Included below are updates on these three activities.

Note: Manuscript submitted to Chemical Vapor Deposition

# Atomic layer deposition modified ordered mesoporous silica membranes

David Cassidy<sup>1</sup> and William J. DeSisto<sup>\*1,2</sup>

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## **Abstract**

Mesoporous silica membranes, prepared by surfactant-templating with a pore diameter of ~4 nm on a macroporous alumina support, were modified by atomic layer deposition (ALD) of aluminum oxide. ALD of aluminum oxide was achieved using trimethyl aluminum and water as reactants. Membranes modified with 50 ALD reaction cycles were characterized periodically during progressive reaction cycles to provide details of the pore modification process. A decrease in light gas permeance, pore size shift to lower pore sizes and a decrease in porosity provided evidence for pore size reduction through ALD. Further analysis of the data indicated that the ALD reaction favored larger pores and defects, and became less efficient as the pore size decreased. This is related to the constant reaction conditions used in this study as well as a decrease in intrinsic diffusivity of reactants into smaller pores.

## Introduction

A superior gas separation membrane will be ultra thin for high throughput, and homogeneous in pore size with a high porosity/low tortuosity for maximum molecular sieving. In addition, many separation applications require thermo-chemical stability provided by inorganic membranes. Mesoporous silica membranes, prepared using surfactant templates and evaporation induced self-assembly, are highly porous with a majority of pores of 3-10 nm diameter.<sup>[1,2]</sup> Therefore, to be utilized in gas and small molecule separations, pore size reduction techniques, such as atomic layer deposition (ALD) must be applied to reduce pore dimensions for molecular sieving.

ALD is routinely utilized for preparing conformal coatings on high aspect ratio, non-planar supports in semi-conductor manufacturing.<sup>[3]</sup> ALD has also been applied to reduce the pore size of  $\gamma$ -alumina membranes<sup>[4-6]</sup>, anodic aluminum oxide membranes<sup>[7-11]</sup>, mesoporous silica membranes<sup>[12-14]</sup> and powders<sup>[15]</sup>, porous substrates<sup>[16,17]</sup> and organic membranes<sup>[18]</sup>. In all cases, ALD has proven a successful method for controlled pore size reduction using several reaction chemistries including  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and others.

In applying ALD to membrane synthesis, the ultimate goal is achieving highly effective molecular separations. This is achieved by tuning the final pore size and surface functionality. As the pore diameter shrinks down to molecular dimensions, the final ALD processing parameters can become highly sensitive to diffusivity reduction of reactants into the pores<sup>[19,20]</sup>. In addition, ceramic membranes have a heterogeneous pore size distribution that contributes to the final pore size distribution in the modified membranes. Therefore, it is important to understand the effect of ALD parameters, such as temperature, reactant exposures and reactant purging, as well as support heterogeneity, have on the pore size distribution after modification.



In this paper, we applied ALD of  $\text{Al}_2\text{O}_3$  to reduce the pore size in surfactant-templated mesoporous silica membranes prepared by dip-coating onto macroporous alumina supports. The membranes were characterized at various stages of ALD-modification, up to 50 ALD cycles, using light gas permeance and perm-porosimetry. Under constant ALD reaction conditions, the deposition efficiency was reduced as the ALD cycles increased. This resulted in favorable conditions for coating larger pores within the heterogeneous support. Between 30-50 ALD cycles, the ideal separation factor for light gases was limited to that predicted by Knudsen diffusion, indicating that a significant number of remaining pores were not reduced to the molecular dimensions of the light gases probed. This can be correlated to the heterogeneity of the support as well as the observed reduced deposition efficiency as the number of ALD cycles increased.

## Results

Mesoporous silica membranes were formed on alumina supports via dip-coatings and subsequent thermal treatments to remove the surfactant template, leaving behind a porous layer. Membranes were formed with four dip/fire cycles to minimize large cracks, commonly formed from film shrinkage and the unevenness of the alumina support. Figure 1 is a cross-sectional view of a fractured, fabricated membrane. This view reveals the asymmetric support that consisted of two layers; a thicker, highly porous layer that supported a 20  $\mu\text{m}$  thick layer with 100 nm pores. This asymmetric support provided a relatively smooth layer for dip-coating the thin, mesoporous silica membrane with pore diameters less than 5 nm. The thin, 1-3  $\mu\text{m}$ , top mesoporous silica layer, prepared by dip-coating is also viewed in Figure 1. This design allowed for minimizing the thickness of the separation layer required for high-flux membranes.

Evidence for pore size reduction via ALD of alumina is provided in Figure 2 showing the continued reduction of He permeance as the number of ALD cycles was increased. Overall, the He permeance reduced from  $4.0 \times 10^{-6}$  to  $6.6 \times 10^{-8}$   $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$  after 50 ALD cycles. Figure 3

shows the pore size distributions calculated from perm-porosimetry data taken at different stages of ALD modification. The unmodified mesoporous silica membrane had a majority of pores with ~4 nm diameter. The unmodified membrane also had a 20% residual He permeance through pores larger than 50 nm, indicative of defects in the membrane. As shown in Figure 3, the pore size distribution shifted to lower pore diameters along with a porosity decrease as the number of ALD cycles increased.

Improvement in membrane performance after ALD modification is shown in Figure 4. The experimental ideal separation factor,  $\alpha$ , for He/N<sub>2</sub> (ratio of single gas permeance values) is compared to the theoretical Knudsen separation factor of 2.65, calculated from

$\alpha = \sqrt{M_1/M_2}$  where  $M_1$  and  $M_2$  are the molecular weights of N<sub>2</sub> and He, respectively. For pore diameters between 2-10 nm and at atmospheric pressure, molecule-pore wall interactions become significant, and the transport mechanism is largely Knudsen flow. The Knudsen permeance is proportional to the inverse root of molecular weight of the permeating molecule. Initially, the ideal separation factor was lower than the theoretical separation factor, indicating that there were larger pores and defects present in the membrane.<sup>[21]</sup> This was consistent with the perm-porosimetry data shown in Figure 3. Between 20 and 30 ALD cycles, the ideal separation factor increased to a value slightly greater than the Knudsen value indicating that the majority of defects had been reduced to pores with diameters where Knudsen flow is dominant. From 30 to 50 ALD cycles, the ideal separation factor was constant, suggesting that while pore sizes continued to reduce, a significant fraction of sub-Knudsen sized pores were not present.

## Discussion

The decrease in measured He permeance with subsequent ALD cycles provides evidence for film growth within the pores of the membrane. Initially, the He permeance decreased

significantly and gradually tapered off. This large initial decrease in permeance was also reported by George's group.<sup>[5]</sup> As the pore size decreased through film growth, the porosity also decreased.

Porosity is defined as the volume fraction of the membrane available for molecular transport. In the perm-porosimetry measurement, only active pores contribute to the pore size distribution. Therefore, the pore size distribution, calculated at a fixed membrane thickness, provides a measure of the two-dimensional porosity of the membrane. This porosity, normalized against the unmodified membrane, is plotted against ALD cycles in Figure 5. The porosity data is similar to the permeance data in Figure 2.

Starting with the pore size distribution for the unmodified membrane, the reduction in two-dimensional porosity per ALD cycle was modeled using a constant ALD growth rate per cycle, applied to the pore size distribution. The resulting reduction in pore area per ALD cycle can be compared to the porosity decrease with a constant ALD growth rate. Over the complete range of data, it was clear that one ALD growth rate was not adequate for describing the pore size reduction. As shown in Figure 5, for the first 7 ALD cycles, the data compared to a porosity decrease predicted with a 1.5 Å per cycle growth rate. For the subsequent ALD cycles, the data compared to a porosity decrease predicted with a 0.7 Å per cycle growth rate, indicating a decrease in growth rate as the pore size decreased. The 0.7 Å per cycle growth rate is well below the 1.3 Å per cycle growth rate cited for planar substrates.<sup>[19]</sup>

There are several reasons for the decrease in growth rate under constant reaction conditions as the ALD layer grows within the pores. In order for reaction to occur, the reactants must diffuse into the membrane pore network. The intrinsic diffusivity of reactants into the pores will decrease as the radius decreases. In our membranes, diffusion through the intrinsic pores will largely occur by Knudsen diffusion and the diffusion through the larger, defect pores will have some pressure-driven diffusion. These diffusivities both are dependent upon pore radius ( $D_K \sim r$

and  $D_p \sim r^2$ ) and are additive.<sup>[21]</sup> In addition, it is expected that due to curvature, the number of surface sites available for reaction will be reduced in greater proportion to reduced surface area because of steric hindrance.

The ALD reaction under our reaction conditions clearly favored larger pores. This is evident from the data in Figures 3-5. The data indicate that there may be a limit to pore reduction above the kinetic diameters of the reactants. Figure 3 indicates that larger pores are favorable reaction sites for ALD. Figure 4 indicates that the final pore size distribution results in permanent gas transport characterized by Knudsen flow. If pore closure were to continue below 10Å, we would expect configurational flow (characterized by significant molecule-pore interactions) to occur, resulting in ideal separation factor significantly greater than that of Knudsen flow.<sup>[22]</sup> The data above also suggest that pore modification can be controlled, to some degree, based on controlling the reaction conditions during modification. If larger pore removal is desired, for example, reactant exposure conditions can be reduced to limit modification of the smaller pores.

## **Conclusion**

We have modified ordered mesoporous silica membranes, prepared by dip-coating surfactant-templated silica sols onto porous alumina disks, by atomic layer deposition of aluminum oxide layers within the porous network of the membrane. Light gas permeance measurements taken at different stages (up to 50 ALD cycles) of modification provide evidence for pore modification. Perm-porosimetry data taken at different stages of modification provided information regarding the pore size shift and porosity changes in the membranes. The porosity change per ALD cycle deviated from one predicted assuming a constant growth rate per ALD cycle. Our data indicated that after 7 ALD cycles, the growth rate per cycle significantly decreased. This is possibly explained by limited diffusivity of reactants into the pores and decreasing reaction sites. This data indicates that membrane modification by ALD is very

sensitive to ALD reaction conditions. Applications include controlled defect reduction and controlled deposition layer thickness in membranes.

## **Experimental**

### *Membrane Synthesis*

Mesoporous silica membranes were prepared with tetraethylorthosilicate (TEOS, Sigma Aldrich) as the silica source and cetyl trimethylammonium bromide (CTAB, Sigma Aldrich) as the surfactant template. To prepare the mesoporous silica films a solution of 7.5 ml of TEOS, 4.73 g of EtOH, 0.617 g of H<sub>2</sub>O, and 0.057 ml of 0.03 M HCl were combined and refluxed at 60 °C for 1 hour. Following this, 10 ml of the refluxed solution was combined with 1.3 g of CTAB, 20.24g of EtOH, 1.75 g of H<sub>2</sub>O, and 0.1 ml of 1M HCl forming a final molar ratio of 1 TEOS:20.52 EtOH:5.25 H<sub>2</sub>O:0.144 CTAB:0.00409 HCl. This solution was allowed set for 1 week at ≈3°C in a sealed container.

Inside a controlled environment chamber at 30°C and 50% humidity, an asymmetric alpha alumina support disk with a 20 μm top layer of 100 nm pore size (HiTK, Germany) was dipped into the solution for 15 seconds, using a dipping apparatus. The membrane was allowed dry inside the chamber for 24 hr. The surfactant was removed by sintering at 500°C for 4 hr in air with a ramp rate of 1°C/min. The dip and calcination procedure was repeated 3 additional times to build up membrane thickness to cover the support.

### *Atomic Layer Deposition Modification*

The membrane/support disc was placed in a custom-built stainless-steel cell that sealed the membrane using Viton O-rings, allowing both membrane modification and characterization without membrane removal. ALD was carried out at 100°C and ≤5 mtorr using trimethyl aluminum (TMA, Sigma Alrich) and H<sub>2</sub>O as reactants. The TMA and H<sub>2</sub>O were held at 0°C,

producing a vapor pressures of 2.56 and 4.60 torr, respectively. The membrane was dosed to each precursor for 1 second over the top of the membrane. Here, our goal was to provide a thin separation layer confined to the surface of the membrane. The exposure times used in this study approach the minimal for alumina ALD.<sup>[19]</sup> To evacuate the cell, it was first held under vacuum for 10 minutes on both sides of the membrane. Then, N<sub>2</sub> was purged for 30 seconds at 30 sccm over the top of the membrane. This purge cycle was repeated to remove all non-adsorbed reactant from the pore network. The typical coating cycle sequence was: dose TMA, evacuate excess TMA, N<sub>2</sub> purge, evacuate, N<sub>2</sub> purge, evacuate, dose H<sub>2</sub>O, evacuate excess H<sub>2</sub>O, N<sub>2</sub> purge, evacuate, N<sub>2</sub> purge, and evacuate. This complete cycle resulted in one monolayer of Al<sub>2</sub>O<sub>3</sub> deposited within the pores. Up to 50 complete cycles were applied to modify the support membranes.

### *Characterization*

The membranes were characterized using single gas permeation and perm-porosimetry. Single gas permeation was measured with helium and nitrogen at 25°C at pressure drops between 300 and 1800 torr. The hexane perm-porosimetry measurement apparatus and procedure is described in greater detail elsewhere.<sup>[23]</sup> Briefly, as the hexane vapor pressure is exposed to the membrane, capillary condensation occurs in the pores governed by the Kelvin equation. As the activity of hexane is increased, successively larger pores are blocked, and the He permeance through the membrane is reduced. From this data, a pore size distribution can be calculated.<sup>[24]</sup> The hexane perm-porosimetry was carried out with the membrane and hexane bubbler at 25°C and a pressure drop of 300 torr. These measurements were completed on an unmodified membrane and after 1, 2, 3, 4, 5, 10, 15, 20, 30, 40, and 50 cycles of ALD.

### **Acknowledgements**

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#### Figure Captions

Figure 1. Cross-sectional view of the asymmetric alumina membrane support coated with a mesoporous silica membrane.

Figure 2. He permeance reduction in a mesoporous silica membrane during alumina ALD modification.

Figure 3. Pore size distributions calculated from perm-porosimetry measurements on ALD modified mesoporous silica membranes.

Figure 4. The effect of ALD cycles on the measured ideal separation factor compared to the ideal Knudsen separation factor for He/N<sub>2</sub>.

Figure 5. Normalized porosity decrease with increasing ALD cycles: data (closed circles) shown with the decrease predicted using a constant growth rate model indicating a decrease in growth rate with increasing pore closure.



Figure 1.

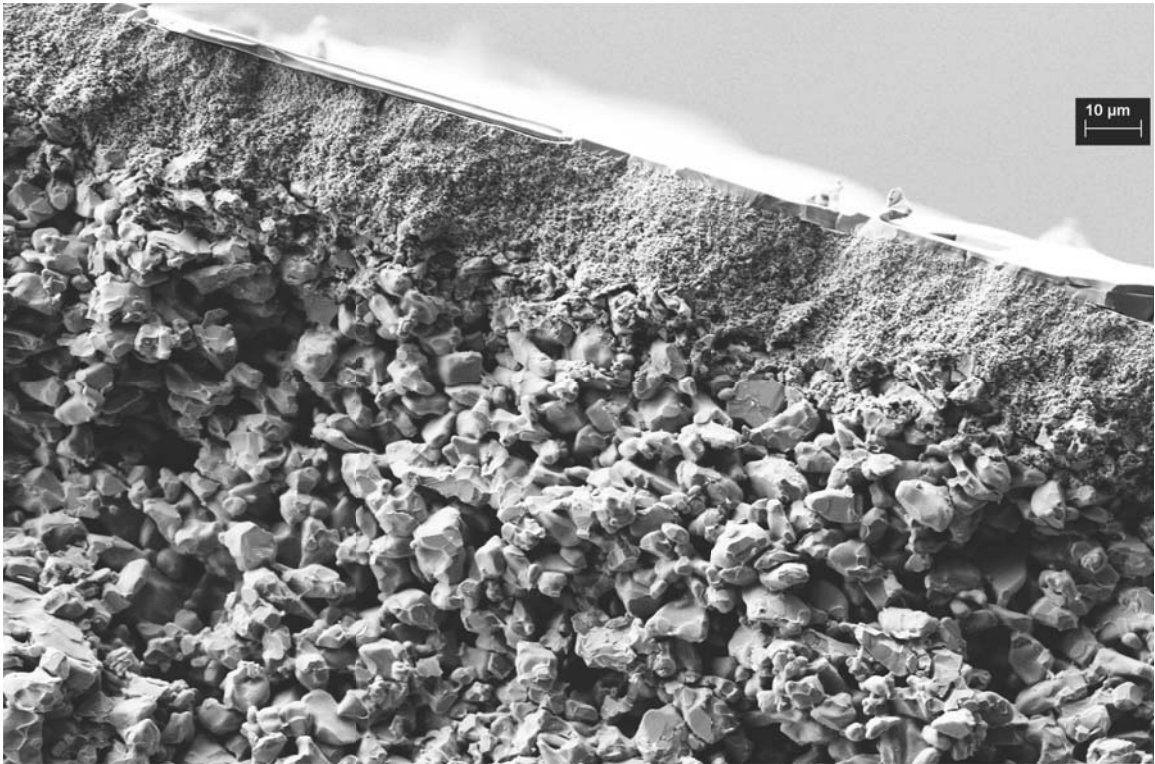


Figure 2.

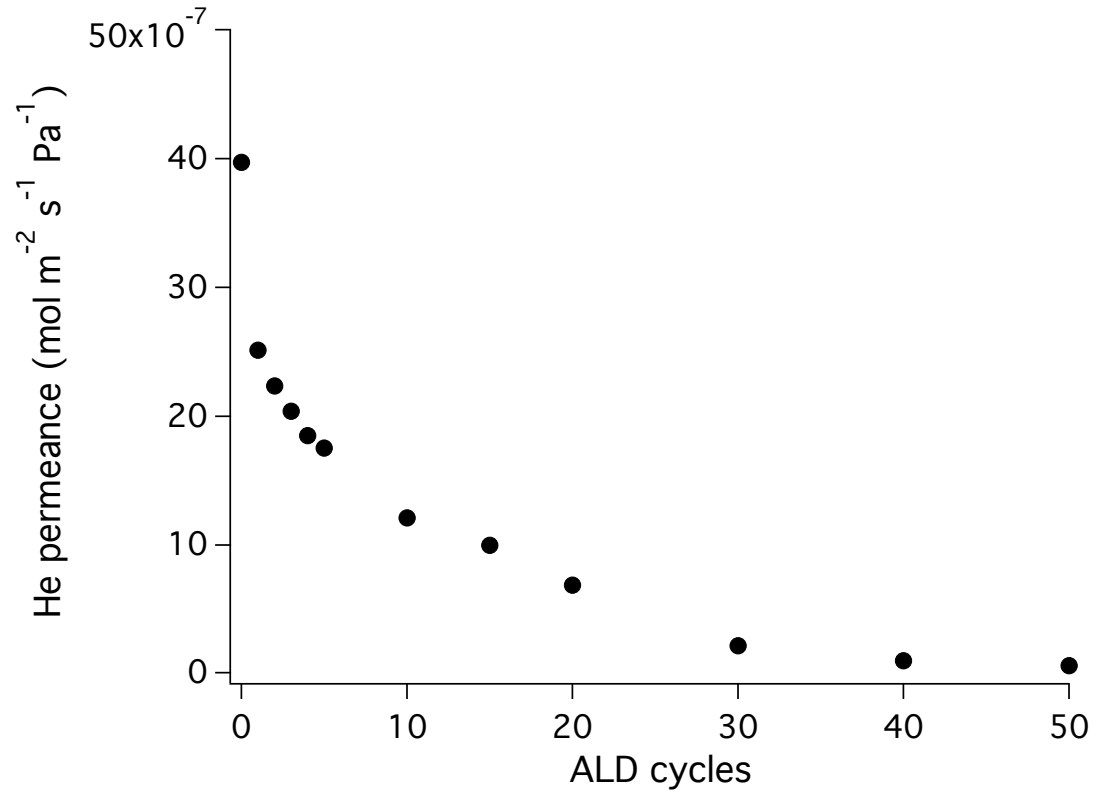


Figure 3.

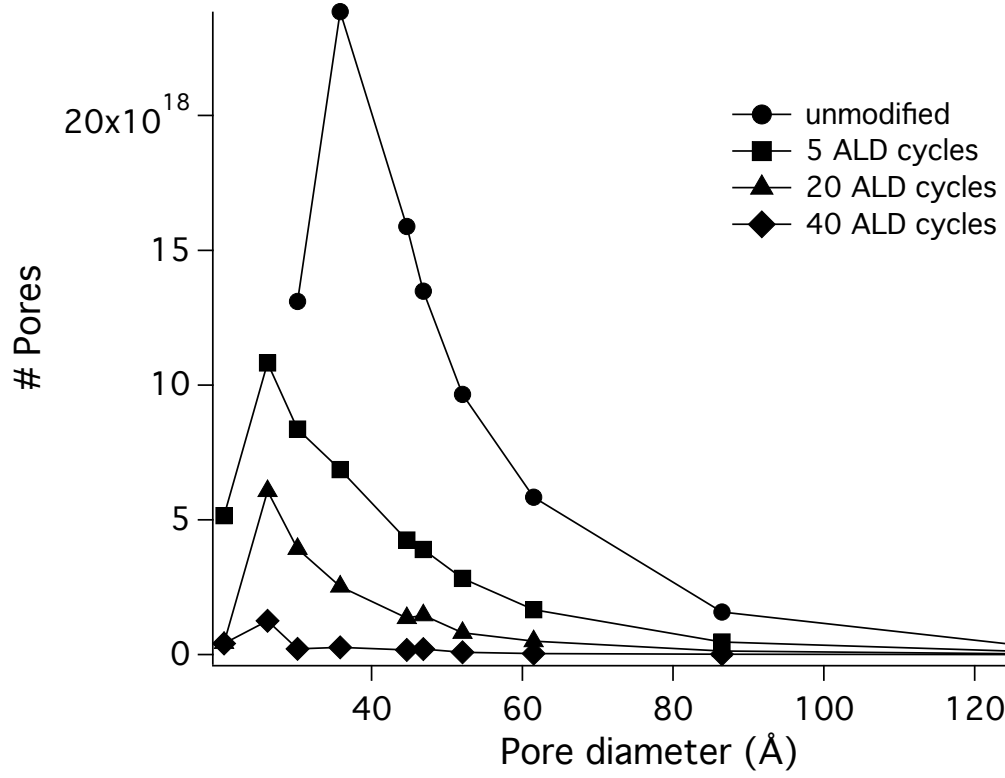


Figure 4.

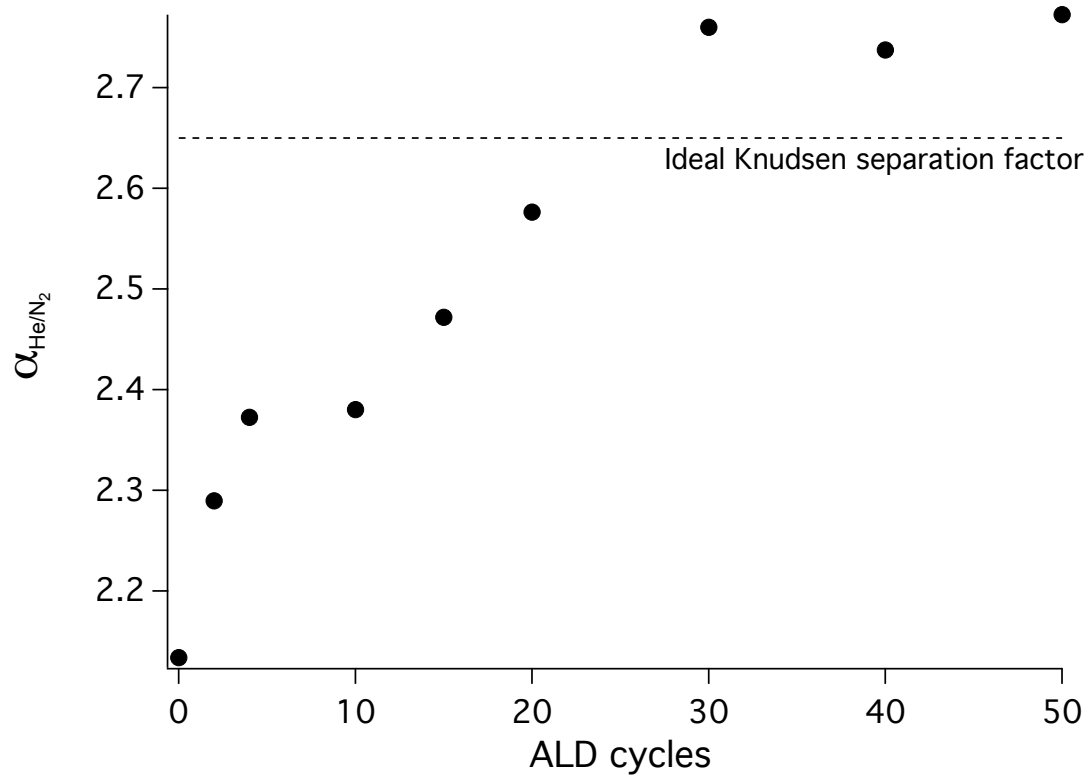
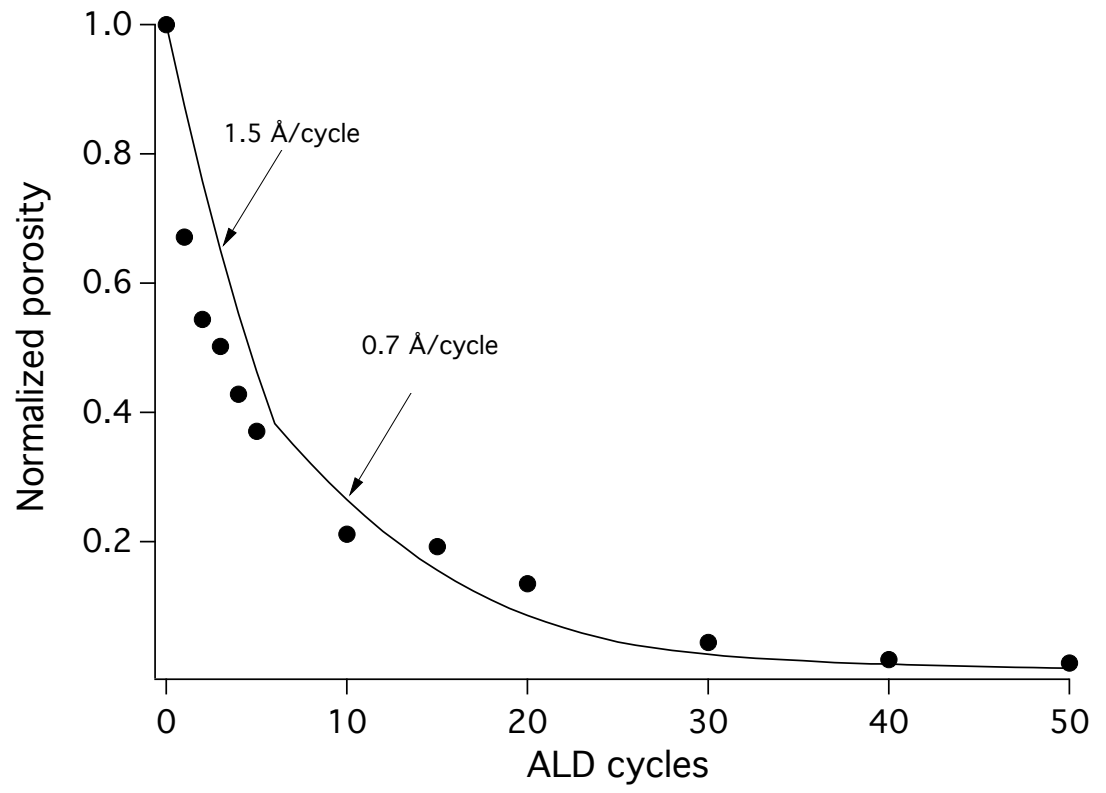


Figure 5.



# Molecular diffusivity measurement through an alumina membrane using time-resolved fluorescence imaging

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We present a simple fluorescence imaging method for measuring the time-resolved concentration of a fluorescent molecule diffusing through an anodic alumina membrane with a pore diameter of 20 nm. From the concentration breakthrough curve, the molecular diffusivity of the fluorophore was extracted. The experimentally determined diffusivity was three orders of magnitude lower than reported bulk values. Due to the relative simplicity and ease of use this method can be applied to provide fundamental information for bio-molecular separations applications. One feature of this method is the high sensitivity at inter-cellular volumes broadening its application to drug delivery and controlled cell growth.

The time-dependent concentration measurement of a molecule diffusing through a porous medium provides fundamental information for the design of separation and transport systems/devices. In the case of solute diffusion, practical applications include drug delivery<sup>1, 2</sup>, cell growth via controlled nutrient delivery<sup>3</sup> and molecular separations<sup>4-6</sup>. Recently optical methods, such as Fluorescence Recovery After Photobleaching (FRAP), have been successfully applied to measure the diffusivity in a variety of material systems including: biofilms, fibers and membranes.<sup>7-10</sup> In FRAP, the fluorophore is photobleached in a known area and the time-dependent migration of non-bleached fluorophores is measured.<sup>10</sup> Unfortunately, with this technique, it is difficult to ensure concentration-driven diffusion is observed because the photobleached molecules remain within the volume of interest. More recently, single-molecule imaging techniques have been applied to study diffusive transport through membranes, providing a highly-sensitive, spatially-correlated picture of molecular movement through porous media.<sup>11</sup> Owing to the low signal levels present specific and often very costly instrumentation is required. Strict sample preparations are mandated, and significant limitations on sample type and geometry exist. In this letter we present what we believe to be a new and relatively simple fluorescence imaging method to measure molecular breakthrough from an inorganic membrane. This method avoids many of the limitations of single-molecule methods, but still provides femto-molar sensitivities at the inter-cellular volumetric scale.

The system we studied was the transport of fluorescein through a commercial anodic alumina porous disc (Anodisc<sup>TM</sup>). These membranes are characterized by a high pore density ( $10^9$  pores/m<sup>2</sup>), uniform pore size (range 20-200nm) and straight channel pores (tortuosity,  $\tau = 1$ ). In this study, we used anodic alumina membranes with a total diameter of 13 mm, mean pore diameter of 20 nm, thickness of 60  $\mu$ m and porosity of 25-50%.

Figure 1 shows a diagram of the experimental set-up used to collect breakthrough data for fluorescein through our membranes. This geometry allowed for concentration-driven solution diffusion from a large bulk volume into a vessel of approximately 150 nL.

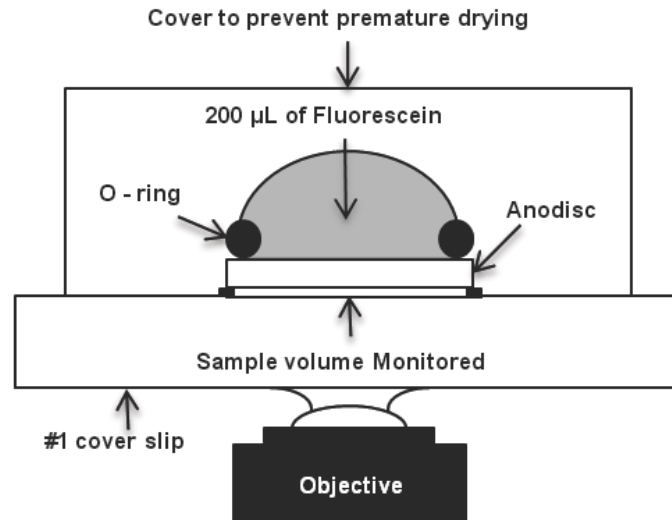


Figure 1.

Prior to sealing in the cell, the membranes were soaked in bleached nanopure water for 24 hrs to ensure pore filling. To load the cell, 200  $\mu\text{L}$  aliquots of fluorescein at concentrations of 170 and 340 nM were added to the top side of the prepared sample.

Fluorescence was recorded using an inverted laser microscope (Olympus IX71) and a CCD camera. Images were recorded at 4 different excitation energies ( $\approx 0.4$ ,  $\approx 0.8$ ,  $\approx 1.9$ , and  $\approx 3.0$  mW) and two different fluorescein concentrations (170nm and 340nm) for exposures of 200ms with a 15.3 second delay between each image acquisition. Measurements at different incident power levels eliminated effects of instrumentation on the breakthrough curves. The camera and power meter were run simultaneously and continuously for 155 minutes (600 images), until steady state intensity was reached, indicating no further change in fluorescein concentration. The raw collected data is shown in Figure 2 for the four different excitation energies and includes photobleaching effects.



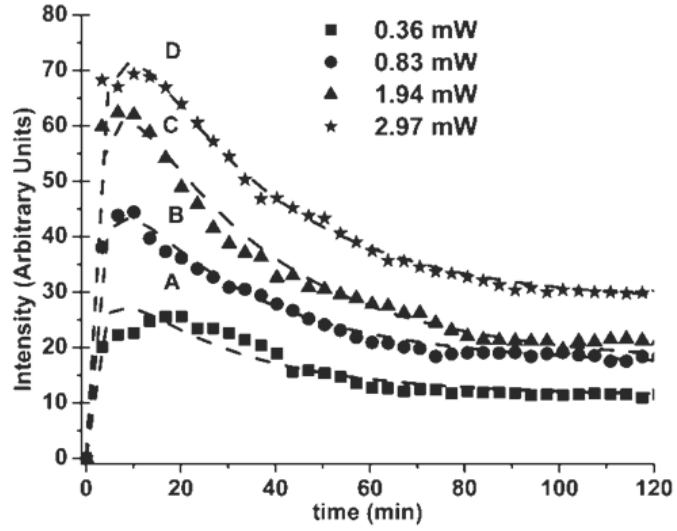


Figure 2.

The experimental set-up in Figure 1 was modeled by applying a mass balance to across the membrane. For a membrane with a porosity  $\epsilon$  and cross-sectional area  $A$  the balance is:

$$V_i \frac{dC_i}{dt} = J\epsilon A \quad (1)$$

where  $V_i$  is the collection volume at the exit of the membrane,  $C_i$  is the concentration and  $J$  is the flux leaving the membrane. The flux in the membrane can be expressed by Fick's first equation:

$$J = -\frac{D}{\tau_r} \frac{dC}{dx} \quad (2)$$

where  $D$  is the diffusivity and  $\tau_r$  the tortuosity of the pore network. Integrating the flux over the membrane thickness,  $\ell$  and the bulk concentration,  $C_0$  to  $C_i$  and solving Eq. 1, yields a model for transport through the membrane:

$$\frac{C_i(t)}{C_o} = 1 - \exp\left[-\left(\frac{\varepsilon DA}{\tau_r V_i \ell}\right)t\right] \quad (3)$$

In addition to transport, photobleaching of the molecules must be accounted for as described by equation 4.

$$I(t) = I_0 \Phi_{ext} C_i \left[ A_0 \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] + y_0 \right] \quad (4)$$

Here,  $I(t)$ , the emission intensity observed at time  $t$ , which is the product of excitation energy,  $I_0$ , the collection efficiency,  $\Phi_{ext}$ , and the concentration of the fluorescent species,  $C_i$ .  $A_0$  is the molecular quantum efficiency,  $\tau$  is the lifetime,  $\beta$  is a fitting parameter for a stretched exponential (ideally 1), and  $y_0$  is the background fluorescence of the system. The time-dependent extent of bleaching,  $EB(t)$ , in our continuous system is then:

$$EB(t) = I(t)/I(0) \quad (5)$$

The final expression for transport as measured by the fluorescence signal, including photobleaching effects is given as:

$$I(t) = I_0 \Phi_{ext} C_i(t) EB(t) \quad (6)$$

The raw data shown in Figure 2 were fitted to the model above. The defined parameters were  $I_0$ , the excitation energy used to produce the raw data and  $C_0$ , the loading concentration of fluorescein. The shared, undefined parameters between all experiments were  $\Phi_{ext}$ , the excitation efficiency of the system,  $D$ , the effective diffusion constant,  $\tau$ , and  $\beta$ . The parameters allowed to freely flow for each data set were  $\varepsilon$ , the porosity of the alumina membranes (bounded by 20% to 50% as reported by Whatman);  $A$ , the area accessible to the fluorescent molecules,  $\ell$ , the thickness of the disc (reported by Whatman),  $V_i$ , the volume between the alumina membrane and

glass slide shown in Figure 1; and,  $y_0$  and  $A_0$ , the mathematical representation of the background fluorescent signal from equation 6. Figure 3 shows the breakthrough curve for the alumina membrane determined from the averaging of the data shown in Figure 2, normalized by excitation energy for each initial concentration of fluorescein. The experimental breakthrough curve is similar to data obtained from molecules diffusing from porous media.

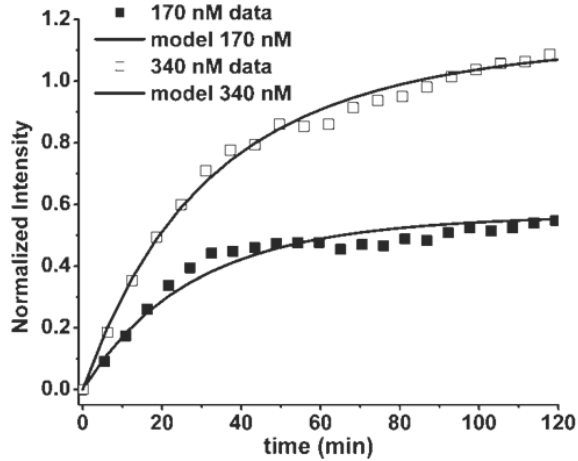


Figure 3.

The diffusivity of fluorescein determined from our data and model in anodic alumina membranes was  $(1.0 \pm 0.1) \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ; considerably slower than the bulk diffusivity measured in pure water ( $5.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ).<sup>7</sup> Our results compare favorably to those of Jiang, et al.<sup>2</sup> who measured diffusivities of caffeine, methyl orange and malachite green oxalate through 40 nm porous anodic alumina membranes. In addition, our results compare to the diffusivity of fluorescein measured by FRAP in collagen fibrils with an estimated interstices of 1.6 nm ( $D = 1 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ )<sup>7</sup> nylon 66 ( $D = 6.9 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ )<sup>12</sup> and biofilms ( $D = 7.7 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ )<sup>9</sup>. Here, binding of the fluorescein to the fiber surface also contributed to the reduced diffusivity. In addition, Fowlkes, et al.<sup>8</sup> measured a diffusivity of fluorescein isothiocyanate through a carbon nanofiber membrane using FRAP ( $D = 7.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ ). The decrease in diffusivity of fluorescein in our alumina membranes could result from either size effects or surface effects. The

hydrodynamic radius of fluorescein has been estimated at 0.4 nm<sup>7</sup>, smaller than the pore diameter of 20 nm, yet still close enough to the pore diameter to have significant interaction with the pore walls. Since the isoelectric point of alumina is 8, membranes in our experiments had a positive surface charge. The pKa of Fluorescein is 6.4<sup>13</sup>, leaving the molecule with a small negative charge. Therefore electrostatic interactions could also play a role in decreasing diffusivity relative to bulk diffusivity.

In conclusion, we have demonstrated a relatively simple fluorescence imaging method for measuring the time-resolved concentration profile of a fluorescent molecule diffusing through an alumina membrane. The integrated system allowed for the imaging of highly dilute concentrations at inter-cellular volumes, applicable to many biological applications including drug delivery and controlled cell growth. In addition, this system provides a relatively simple method for determining fundamental information useful for designing separation systems. While not specifically addressed here, fluorescence imaging the sample area allows for direct correlation between measured diffusivities and local macroscopic morphology. In this way, defect areas can be measured separately (or excluded completely) during analysis providing additional information of membrane integrity.

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EVALUATION OF MEMBRANE PERFORMANCE ON SEPARATING ACETIC ACID  
FROM WATER COMPARED TO COMPETING TECHNOLOGIES

by

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## Abstract

Acetic acid is a byproduct of many biochemical processes and has considerable commercial value. In the state of Maine, a pulp mill with a production rate of 1000 tonnes of pulp per day will generate approximately 30 tonnes of acetic acid per day.<sup>1,2</sup> The most cost intensive portion of the separation of acetic acid from the pulp extracts is its separation from water. This paper will focus on one of the developing alternatives for this separation, membrane technology. A viable option for an industrial membrane would be silica-based. The research will include membrane synthesis and the comparison of a distillation column and liquid-liquid extraction to several membrane/ separation column hybrids using ASPEN Plus and MathCAD simulation models. The addition of pervaporation/vapor permeation will decrease the economic burden of some current separation techniques. The simulation results suggest that the combination of a stripping column with a hydrophobic and hydrophilic membrane has the lowest equivalent annual operating cost with a high recovery at a specified purity of 99wt% excluding the cost of the membrane itself. The laboratory results support the variability of polymerization and binding characteristics of Aminopropyltriethoxysilane (APTES), however suggest that there should be further testing on the stability of silica membranes. Other recommendations include testing membrane cascade, recycle streams, and the use of other functionalized membrane groups for a better separation factor.