Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 37 (2013) 1030 – 1038

Energy Procedia

GHGT-11

Dense membranes for oxygen and hydrogen separation (DEMOYS): project overview and first results

P. Pinacci[a]*, E. Louradour[b], L. Wimbert[c], M. Gindrat[d], M. O. Jarligo[e], R. Vassen[e], A. Comite[f], J. M. Serra[g], J. Jewulski[h], L. Mancuso[i], P. Chiesa[j], M. Prestat[k], E. Ivers-Tiffée[l]

[a]RSE S.p.A., Via Rubattino 54, 20134 Milano, Italy
[b] Céramiques Techniques Industrielles SA, 382 Avenue du Moulinas, 30340 Salindres, France
[c]GKN Sinter Metals Engineering GmbH, Krebsöge 10, 42477 Radevormwald, Germany
[d]Sulzer Metco AG, Rigackerstrasse 16, 5610 Wohlen, Switzerland
[e]Forschungszentrum Jülich GmbH, IEK-1, 52425 Jülich, Germany
[f]Dipartimento di Chimica e Chimica Industriale - Università di Genova , Via Dodecaneso31, 16146 Genova , Italy
[g] Instituto de Tecnología Química (Universidad Politécnica de Valencia - Consejo Superior de Investigaciones Científicas) Avenida de los Naranjos s/n.46022 Valencia, Spain
[h] Instytut Energetyki, Augustowka 36, 02-981 Warszawa, Poland
[i]Foster Wheeler Italiana S.r.l, Via S.Caboto, 20094 Corsico (Mi) Italy.
[j] Politecnico di Milano, via Lambruschini 4, 20156, Milan, Italy
[k]ETH Zurich, Nonmetallic InorganicMaterials,Wolfgang-Pauli-Strasse 10,CH-8093 Zurich, Switzerland
[l]Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany

Abstract

This paper provides an overview of objectives, structure and first results of the DEMOYS project, financially supported by the European Commission in the frame of the 7th FP – Energy. The project started on May 1, 2010 and brings together fifteen Partners, including three Universities, five Research Organizations and seven Industries. The objective of DEMOYS is the development of thin mixed conducting membranes for O_2 and H_2 separation by using a new deposition technique "Plasma Spraying – Thin Film" (PS-TF) in combination with nano-porous, highly catalytic layers.

Keywords:oxygen transport membranes;hydrogen membranes ;mixed conductors; plasma sprayng; PVD; CO_2 capture.

* Corresponding author. Tel.: +390239925865; fax: +390239925620.
E-mail address: pietro.pinacci@rse-web.it

doi:10.1016/j.egypro.2013.05.199

1. Introduction

Membranes for oxygen and hydrogen separation are expected to play a key-role in the development of CO_2 emission-free coal or natural gas power plants. In addition, cost-effective oxygen and hydrogen production processes are urgently needed in gas supply industry. The most promising oxygen membranes are based on mixed ionic electronic conducting oxides such as perovskites which give sufficiently high oxygen fluxes only at high temperatures (>800°C). Similarly ceramic-metal materials (cermets) have been recently studied in order to obtain H_2 separation from CO_2 in Water Gas Shift (WGS) reactors. However the above membranes, which are usually produced by sintering techniques using ceramic cylindrical porous substrates, are not able to meet the requirements for an economical use because of the high costs in combination with limited permeability values and long-term stability in the operating environment. Hence, world-wide activities are focused on the development of more efficient membranes in combination with cost-effective supporting concepts.

More specifically, an increase in membrane permeation can be achieved by two routes:

- reduction of the membrane thickness;
- improvement of the catalytic performance of the membrane surface where adsorption, dissociation, and reduction of oxygen (hydrogen) and the charge transfer takes place and become rate limiting.

The main objective of this project is, therefore, the development of thin mixed conducting membranes for O_2 and H_2 separation by using a new deposition technique "Low Pressure Plasma Spraying – Thin Film" (PS-TF) in combination with nano-porous, highly catalytic layers.

PS-TF is a proprietary technology developed by Sulzer, which stands between the conventional thin film technologies, such as PVD and CVD, and the conventional thermal spray technologies (see Fig. 1). PS-TF (also LPPS-TF) represents a refinement of the well-know LPPS technique. It operates at a lower pressure (around 1-2 mbar), thus allowing the fast depositions (faster than in the common PVD or CVD spraying technique) of large areas (up to 1 m), larger than in conventional LPPS deposition [1-3].

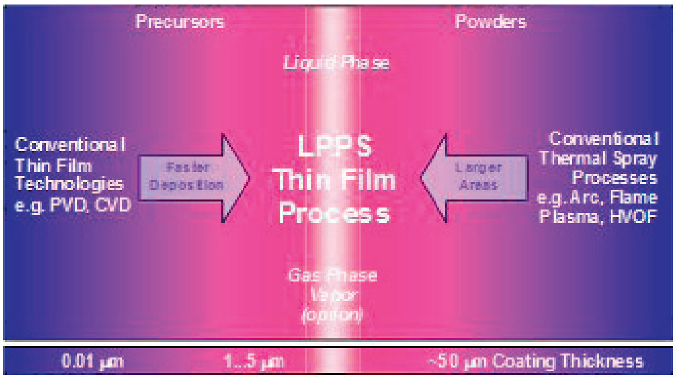


Fig. 1 Comparison of the main characteristics of thin film and thermal spray deposition technologies

It is expected that, by using the PS-TF process, a dense, stable deposit with thickness lower than 20 micron can be obtained. This would allow increasing membrane performances while decreasing their manufacturing costs. Catalytic layers will be also applied to enhance the surface reactions becoming rate limiting for thin membranes. Specific goals are the following:

- development of O_2 membranes with a flux > 8 ml/cm^2/min and a selectivity > 99%;
- development of H_2 membranes with a flux > 10 ml/cm^2/min and a selectivity >99.5%;

- remove more than 90% of CO_2 emissions by integration of the developed membranes in power generation and/or hydrogen production plants;

Accordingly the main expected impacts of the project are:

- Approach the CO_2 capture cost of 15 €/ton in power and/or H_2 generation plants.
- Increase the competitiveness of European Industry. PS-TF is, in fact, a proprietary technology developed by a European company (Sulzer).

1. Project Structure

R&D activities of DEMOYS are developed in six work packages. The first part of the project (WP1-4) is mainly focused on development of materials and process, in order to evaluate the feasibility of preparing dense membranes for O_2 and H_2 separation by using the PS-TF process and evaluating their integration in power generation and/or hydrogen production plants. The second phase (WP 5-6) is more focused on application in operating environment and on process scale-up and cost evaluation.

The Consortium includes 15 Partners from 6 European countries, with specific skill and roles, as indicated in table 1.

Table 1 Partners of DEMOYS and main role in the project

Organization	**Country**	**Main role in the project**
RSE	I	Project management H_2 membrane testing in laboratory pilot
CTIsa	FR	Development of membrane ceramic supports
GKN	DE	Development of membrane metallic supports
ETH Zurich	CH	Powders development
Sulzer Market & Technology and Sulzer Metco	CH	Manufacture of powders for PS -TF processes; PS-TF deposition tests and membrane scale-up
Forschungszentrum Jülich GmbH	DE	PS-TF process development for membrane preparation
Università degli Studi di Genova	I	H_2 Membrane development: Catalytic layer deposition & membrane characterization
CSIC	ES	O_2 Membrane development - catalytic layer deposition & membrane characterization
Karlsruher Institut fur Technologie (KIT-U)	DE	Modelling of membrane transport properties
Instytut Energetyki (IEn)	Pol	O_2 membrane testing in laboratory pilot
SOL S.p.A	I	H_2 membrane testing with industrial gas stream
Foster Wheeler Italiana (FWI)	I	Process scale-up & cost evaluation of power & H_2 generation plants
Politecnico di Milano	I	Modelling of power and H_2 generation plants
Rezia Power	I	Collection & elaboration of data on power and CO_2 emission credit markets

2. Main results

3.1 Material selection and optimization (WP1)

WP1 activity is focused on:

- defining geometry, type of material, physical and chemical characteristics of membrane supports in order to meet requirements for deposition with PS-TF process;
- select, manufacture and characterize powders to be used for PS-TF process.

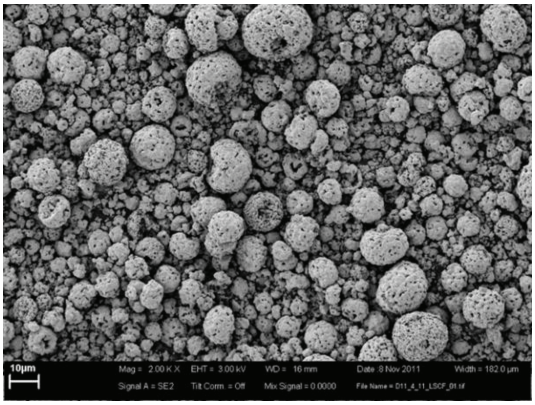
Concerning membrane supports, both metallic and ceramic materials have been considered.

Porous Hastelloy X, symmetric, 0.5 grade, has been first selected as reference material for metallic supports. Several batches of disk samples (up to 110 mm in diameter) have been manufactured by GKN Sinter Metals and used for spraying trials. Permeation tests with membranes after, however, indicate a lack of O_2 permeation, due to a densification of the metallic support which occurs, during spraying process, in the region underneath the dense coating spraying (see section 3.2). For this reason a new porous support material based on NiCoCrAlY-alloys has been prepared. Such a material exhibits an higher creep resistance and stability in oxygen atmosphere under spraying conditions [4, 5].

The selected material for ceramic supports is porous zirconia-yttria with a top layer of cerium gadolinium oxide CGO applied in order to limit inter-diffusion problem between zirconia and the dense conductive membrane. LSCF deposited layers on ceramic supports show good adhesion. Vertical cracks, however, have developed in the deposited layer due to thermal stresses. Development of appropriate spraying procedures which include a better heat management has been defined. At the same time improved formulations of zirconia-yttria and synthesis of other ceramics, which have higher thermal shock resistance, are in progress at CTIsa.

$La_{0.58}Sr_{0.40}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and a proton conducting ceramic (patent pending) have been selected as reference materials for O_2 and H_2 separation membranes, respectively.

Several batches of LSCF and proton conductor ceramic powders have been manufactured by Sulzer in a prototype plant (up to 50 kg for a single batch). ICP and XFS have been used to determine the elemental composition of the powders, while structural and morphological characterization has been carried out by XRD and SEM analysis. Results indicate that synthesized powders meet specification requirements and show sufficient phase purity (fig. 2).



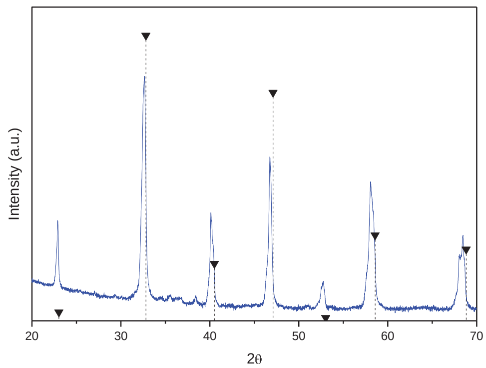


Fig. 2 SEM micrograph (left) and XRD pattern (right) of LSCF powders manufactured by Sulzer. Triangle symbols show the reported diffraction peaks in the reference LSCF pattern.

An improved formulation for LSCF powders (selective doping with Cu) has been defined and synthetized by ETHZ. The introduction of Cu in the LSCF helps to get a more stable perovskite with cubic phase (beneficial to avoid crack formation in heating/cooling cycles) [6,7]. Moreover, Cu^{2+} substitution on the B-site of the perovsikte (instead of Co and Fe that exhibit effective charge between 4+ and 2+) is expected to generate oxygen vacancies and be beneficial for the oxygen transport through the membrane.

Concerning proton conducting ceramic, DC conductivity measurements using the 4-probe bar configuration have been performed in hydrogen as a function of temperature, at CSIC laboratories. Results indicate that the synthesized powders are good proton conductors and present certain electronic conductivity while they remain structurally stable in wet CO_2 at high temperatures. In principle, it is expected that their ambipolar conductivity should be adequate for hydrogen separation at high temperatures.

3.2 Membrane development and basic characterization (WP2)

The WP activity has been mainly addressed to obtain dense membranes for O_2 and H_2 separation by the PS-TF process.

Several spray sessions have been performed both at Jülich and at Sulzer Metco. Jülich performed spray trials using Sulzer Multicoat facility and intensive activities were conducted to determine the best process parameters, such as torch power, carrier gas, plasma jet velocity as well as understanding of the dominant deposition mechanisms [8]. Sulzer also made deposition tests in a prototype plant (fig. 3), where large samples can be sprayed.

Both LSCF and proton conducting ceramic powders have been deposited on Hastelloy X porous supports. Process parameters have been optimized in order to obtain target composition and crack-free structure [9,10]. Their characterization has been performed both at UNIGE and at CSIC. Deposited layers show good adhesion to the supports and their thicknesses typically range from 30 to 50 microns (fig. 4a).

Fig. 3 Prototype plant for PS-TF at Sulzer Metco.

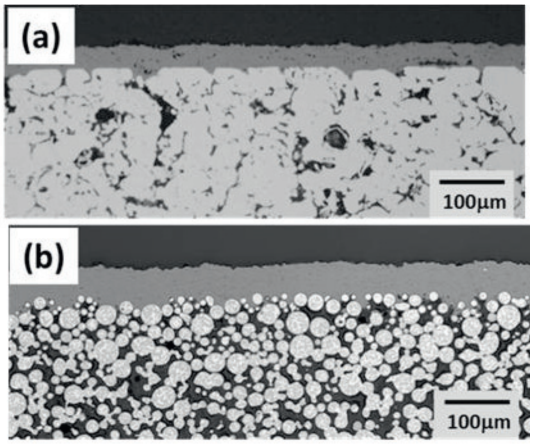


Fig. 4 Micrograph of LSCF coating deposited on porous Hastelloy X (a) and NiCoCrAlY (b) supports.

Permeation tests at room temperature low indicated low leakage rates; the best membranes have been pressurized up to 8 bar without exhibiting any leakage. Permeation tests at high temperature (750-950°C), however, indicate a lack of O_2 permeation. In the micrographs of the sprayed membranes a densified layer in the metallic support underneath the membrane was observed. This has been quantified with an image analysis, where the ratio of porosity between a first (top) layer and a second (50 μm under the surface) layer and the bulk substrates was determined.

These results led to several trials with new substrate materials based on NiCoCrAlY-alloys. Optimized fabrication of these substrates produced highly porous microstructures (fig. 4b), that ultimately led to much improved oxygen flux across the membrane, as shown in Fig. 5.

Two patents on membrane preparation and use of improved metallic substrates have been filed [11,12].

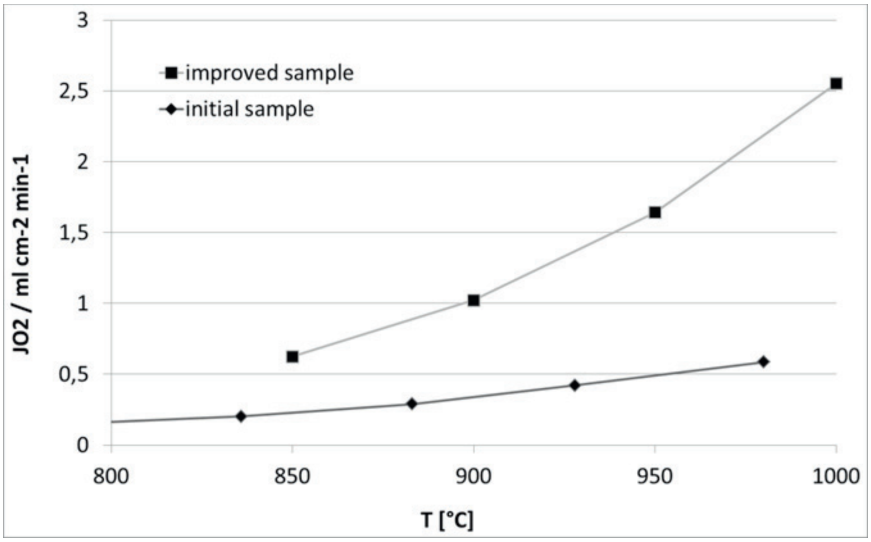


Fig. 5 Permeation tests with a LSCF membranes (feed: air; sweep: argon; at atmospheric pressure)

A three-dimensional finite element method (FEM) model for mixed ionic/electronic conducting (MIEC) materials has been developed by KIT-U. The model is based on the commercial software package COMSOL Multiphysics® which includes a representation for the actual microstructure of a multiphase material. The subsiding processes (1) gas diffusion, (2) oxygen incorporation, (3) bulk diffusion and (iv) oxygen excorporation are taken into account in the model at a constant temperature T. The model is able to predict the performance of a dense mixed conducting membrane with an (optional) porous functional layer functional layer on the top.

From the results it can be shown that the consideration of a porous functional layer on top of the dense membrane strongly improves the performance of the membrane, as the additional surface area results in a higher oxygen flux, in agreement with previous experimental results [13].

The influence of the functional layer on the membrane performance strongly depends onto which side of the dense membrane it is applied (Fig. 6). Whereas on the feed side it facilitates an enhanced oxygen incorporation into the membrane, on the permeate side it improves the oxygen release strongly (especially under the assumption that the free membrane surface area on the permeate side is significantly restricted due to the porous support structure that partly blocks the membrane surface and is thus inert with respect to oxygen exchange).

Accordingly, activities for the application of a functional layer on the membranes are in progress at Jülich and CSIC. Catalyst deposition/impregnation on both sides of the membranes is also performed at

CSIC and UNIGE in order to enhance in order the surface reactions which are rate limiting for thin membranes.

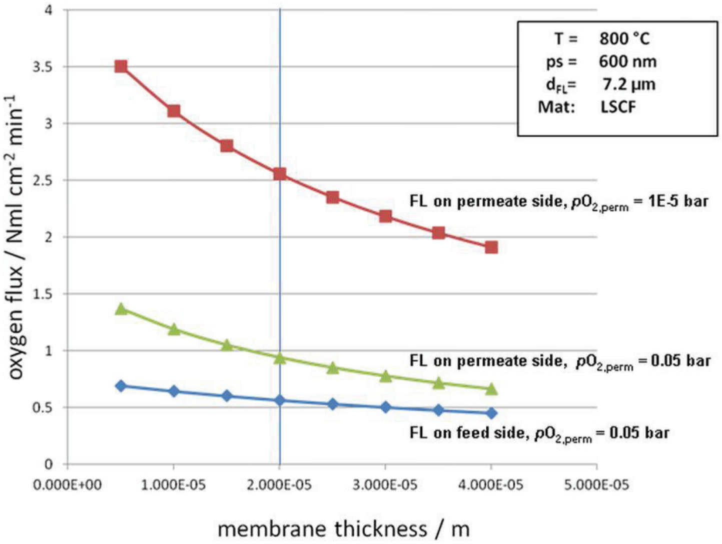


Fig. 6 FEM modeling results: influence of a functional layer (FL; 7.2 µm thickness, particle size 600 nm, porosity 30 %) applied onto either the feed side (pO_2,feed = 1 bar, pO_2,permeate = 0.05 bar,) or the permeate side (pO_2,feed = 1 bar, pO_2,permeate = 0.05 bar or 10-5 bar, respectively) of a dense membrane.

3.3 Membrane integration in power generation plants (WP4)

The main objectives of WP 4 are:

- provide an assessment concerning membrane integration in plants for power generation and/or hydrogen production in order to reduce the cost of CO_2 capture and product output;
- evaluate potential thermodynamic advantages allowed by membranes integration in comparison with other commercially ready technologies.

To this purpose an accurate review of the benchmark technologies with and without CO_2 capture for electricity and hydrogen production from coal and natural gas has been carried out by FWI , Polimi and Ien, in order to map all the possible options to implement membranes in these plants [14]. A reasoned selection led to exclude those solutions where membrane operating conditions (temperature in particular) are not compatible with the ones studied in DEMOYS. More plant configurations based on components now commercially unavailable were neglected. The conclusions of this analysis are summarized in table 2, where the list of the membrane based plant configurations selected for more detailed performance investigation are reported.

To perform consistent evaluation of the mass and energy balance of plants, a set of assumptions based on the EBTF (European Benchmark Task Force) work was prepared. Selected plant configurations were then modeled and energy balance simulated by means of proper methodology. Relevant results of this activity are reported in another paper of this conference focused of natural gas fired plants for electricity production [15]. Moreover the estimated plant performances will be the input for equipment sizing and economic evaluation performed in WP6.

Table 2 Membrane based plants selected for further evaluation in the project

Plant		Output	O_2 Membranes	H_2 Membranes
COAL	IGCC	Power / H_2	Provide O_2 to the gasifier	--------
	Oxy-fuel Boiler	Power	Provide O_2 to the boiler	--------
NATURAL GAS	Steam Methane Reformer	Power / H_2	--------	H_2 separation membrane-reformer
	Auto Thermal Reformer	Power / H_2	Provide O_2 to the reforming reactor	--------
		Power / H_2	Provide O_2 to the reforming reactor	H_2 separation membrane-reformer

3. Conclusions

In this paper objectives, structure and main results of DEMOYS have been described. The project is now entering in a second phase where performances of both H_2 and O_2 membranes will be evaluated in laboratory pilot loops. in order to provide elements for process scale-up and cost evaluation.

Acknowledgements

DEMOYS receives funding from the European Community's Seventh Framework Programme, FP7/2007-2013, under grant agreement no 241309.

References

[1] Refke A, Hawley D, Doesburg J, Schmid R, LPPS Thin Film Technology for the Application of TBC Systems, International Thermal Spray Conference 2005, p. 438 -443.

[2] Refke A, Barbezat G, Hawley D, Schmid R., Low Pressure Plasma Spraying (LPPS) as a Tool for the Deposition of Functional SOFC Components, International Thermal Spray Conference 2004: Advances in Technology and Application, ASM International, May 10-12, 2004 (Osaka, Japan), ASM International, 2004, p-1129-1134.

[3] Dorier J.L, Gindrat M., Hollenstein C., Loch M, Refke A, Salito A, Barbezat G, Plasma Jet Properties in a New Spraying Process at Low Pressure for Large Area Thin Film Deposition, Thermal Spray 2001, New Surface for a New Millenium (Ed.) C.C. Berndt, K.A. Khor and E.F. Lugscheider, Published by ASM International, Material Park, Ohio, USA, 2001, p. 759-763.

[4] Muelenberg W.A, Baumann S, Ivanova M, Van Gestel T, Bram M, Stover D, Ceramic membranes for gas separation in advanced fossil power plants, 9th Liege Conference: Materials for Advanced PowerPower Enginnering, 2010.

[5] Baumann S, Xing Y, Muelenberg W. A., Ruttinger M, Metal supported oxygen transport membranes, 12 Julicher Werktoffsymposium, October 5-6, 2011.

[6] Yang Z, Martynczuk J, Efimov K, Harvey A.S, Infortuna A, Kocher P, Gauckler L.J, Oxygen-Vacancy-Related Structural Phase Transition of $Ba_{0.8}$ $Sr_{0.2}Co_{0.8}Fe_{0.2}O_{3-\delta}$, *Chemistry of Materials* 2011; 23 13: 3169-3175.

[7] Yang Z, Harvey A.S, Infortuna A, Gauckler L.J, Phase relations in the Ba-Sr-Co-Fe-O system at 1273 K in air, *J of Appl. Crystallography* 2009; 42: 153-160.

[8] Zotov N, Hospach A, Mauer G, Sebold D, Vassen R, Deposition of $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ coatings with different phase compositions and microstructures by Low-Pressure Plasma Spraying-Thin Film (LPPS-TF) processes, *J. Thermal Spray Technol.* 2012; 21: 441-447.

[9] Haering J, LPPS hybrid technologies for emerging energy applications –recent developments, 3rd European conference on CCS research development and demonstration, London , May 25, 2011.

[10] Azzurri F, Capannelli G, Comite A, Damani R, Drago F, Gindrat M, Vassen R, Zotov N, Characterization of defectiveness of oxygen transport membranes deposited by Low Pressure Plasma Spraying - Thin Film Processes, Euromembrane 2012, London, October 23-27, 2012.

[11] Sulzer Markets and Technology AG, Plasmaspritzverfahren zum Herstellen einer ionenleitenden Membran und ionenleitende Membran, EP12161868.0, filed on 28 March, 2012.

[12] Forschungszentrum Juelich, Beschreibung Gemischt Ionen und Elektronen leitende Membran zur Gastrennung sowie Verfahren zur Herstellung derselben, Patent application number 10 2012 006 744.5, filed on 4 April, 2012.

[13] Baumann S, Serra J.M, Lobera P, Escolástico S, Schulze-Küppers F, Meulenberg W. A.., Ultrahigh oxygen permeation flux through supported Ba0.5Sr0.5Co0.8Fe0.2O3−δ membranes, *J. Membr. Sci.* 2011; 377: 198-205.

[14] Mancuso L, Fazi F, Chiesa P, Romano M, Spallina V, Jewulski J, Blesznowski M, Preliminary definition of plant configurations and specifications of membrane operating conditions, October 2010, available at http://demoys.rse-web.it.

[15] Chiesa P, Romano M. C, Spallina V, Turi D. M, Mancuso L, Efficient low CO_2 emissions power generation by mixed conducting membranes, GHGT 11, Kyoto, November 18-22, 2012.