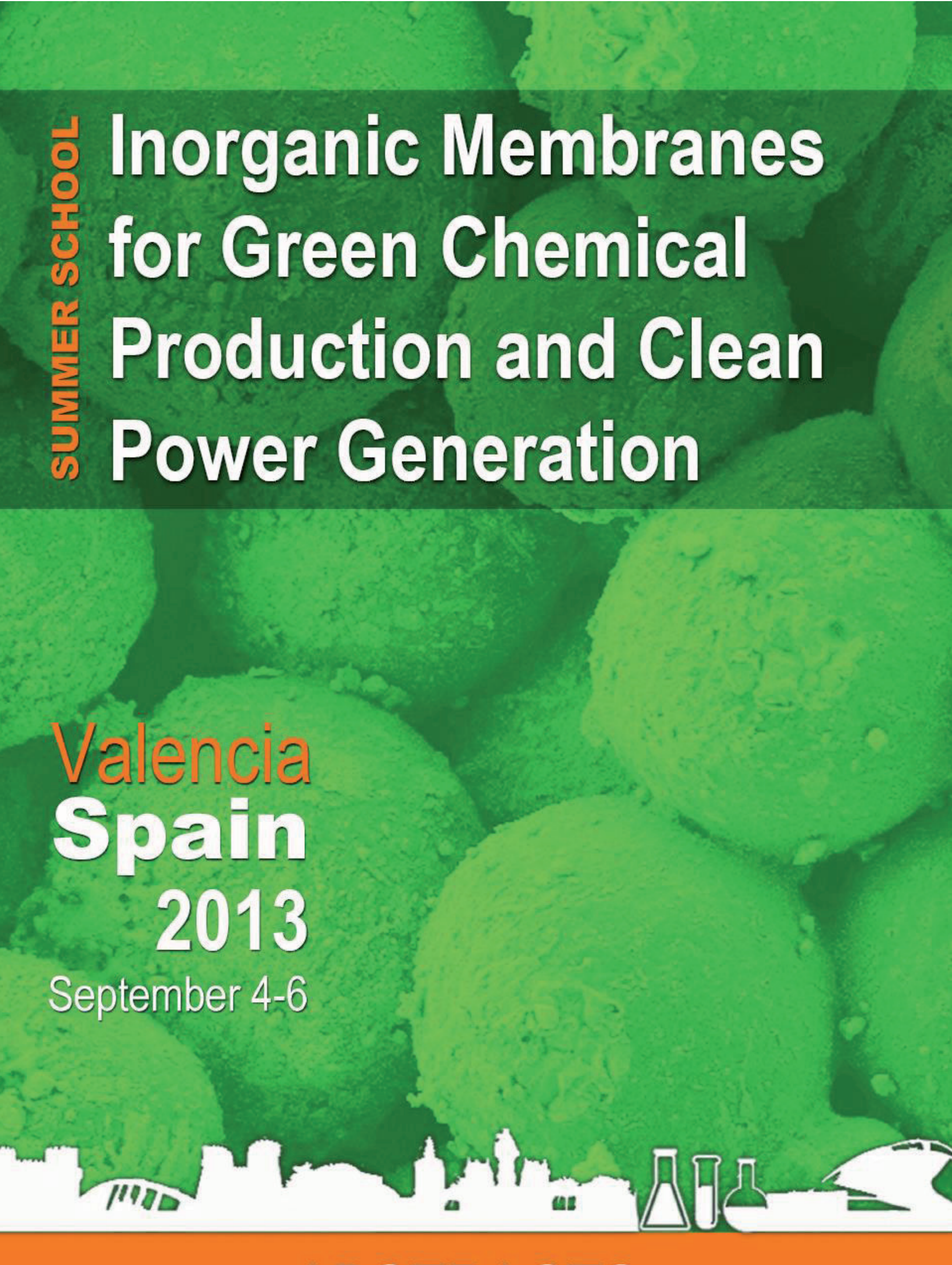


SUMMER SCHOOL

Inorganic Membranes for Green Chemical Production and Clean Power Generation

Valencia
Spain
2013
September 4-6

ABSTRACTS

CHAIR-SCIENTIFIC COMMMITTEE

Dr. José M. Serra
Prof. Rune Bredesen
Prof. Peter Vang Hendriksen
Dr. Pietro Pinacci
Dr. W. A. Meulenberg

ORGANIZING COMMITTEE

Dr. Cecilia Solís
María Fabuel
Dr. María Balaguer
Dr. Sonia Escolástico
Laura Navarrete
Dr. Vicente B. Vert
Dr. Cyril Gaudillere
Julio García-Fayos
Raquel Zanón
Clara Fornés
Fidel Toldrá
David Catalán
Paula Pla
Elena Palafox
Mateusz Tarach

The contents of this publication have been subject to revision by Chair-Scientific Committee

First edition, 2013

Dr. José M. Serra
Prof. Rune Bredesen
Prof. Peter Vang Hendriksen
Dr. Pietro Pinacci
Dr. W. A. Meulenberg

Distribution:
Telf. 963 877 012 / http://www.lalibreria.upv.es / Ref.: 6137

ISBN: 978-84-9048-111-0 (Versión impresa)

Print on demand

INDEX

WELCOME

Welcome to the NASA-OTM, MEM-BRAIN, DEMOYS, CARENA and HETMOC Summer School held in Valencia from 4th to 6th of September 2013. In this occasion, the Summer School entitles "Inorganic membranes for green chemical production and clean power generation". We all are concerned by the importance of developing means to reduce global warming and increasing the energetic efficiency in electricity production and chemical production. Membranes can be part of the solution by minimizing greenhouse gas emissions and allowing process intensification.

The school is organized by the ***I****nstituto de* ***T****ecnología* ***Q****uímica (joint center of the Universidad Politécnica de Valencia and Spanish Research Council CSIC). This event is organized in the frame of five public funded projects: (1) NASA-OTM 7FP Project, which aims to develop ultra-thin supported oxygen transport membranes (OTM); (2) DEMOYS 7FP Project, which develops supported ceramic H2/O2 permeable membranes by means of plasma spraying (LPPS) ; (3) CARENA 7FP Project promotes catalytic membrane reactors in the European chemical industry to reduce the dependency of the European community on imported oil ; (4)* HETMOC will develop and demonstrate Highly Efficient Tubular Membranes for Oxy-Combustion; and (5) MEM-BRAIN Portfolio (Helmhotz Assoc. Funds) supports membrane technology R&D for clean coal-burning power plants. *The school tackles from transport fundamentals through synthesis/manufacturing to final applications of gas separation membranes. Specifically the topics addressed along the different sessions are: (1) oxygen transport membranes; (2) hydrogen permeable membranes; (3) theoretical modeling and characterisation of transport and surface chemistry; (4) advanced manufacturing techniques; (5) European research projects and consortia; (6) microporous membranes; and (7) application to chemical processes and advanced separations. A special session for students has been allocated in order to give the opportunity to several students to show a brief summary of their PhD research work. Finally, the organizers are very thankful for the willingness of all speakers to contribute to the school and enjoy this scientific summer time with the rest of the European membrane community.*

We hope you all enjoy this Summer School and your stay in Valencia.

The Organizing Committee

SCIENTIFIC PROGRAMME

Wednesday, 04.09.2013

14^{00} **Welcome** – Registration

Session 1: Oxygen transport membranes
Chairmen: J. A. Kilner and J. da Costa

14^{30} Oxygen separation using mixed conducting oxide membranes
H.J.M. Bouwmeester - University of Twente (The Netherlands)
15^{00} Ceria based oxygen transport membranes
M. Søgaard - Risø National Laboratory (Denmark)
15^{20} Defects and transport of mixed conducting membranes
M. Schröder - RWTH Aachen University (Germany)
15^{40} Assessment of mechanical stress inside MIEC membranes depending on geometry and operating conditions
R. Kriegel– Fraunhofer IKTS (Germany)
16^{00} Mechanical testing and analysis of inorganic membranes
H. L. Frandsen – DTU (Denmark)
16^{20} **Coffee Break**

Session 2: Hydrogen permeable membranes
Chairmen: M.-L. Fontaine and J. M. Serra

16^{40} Characterisation of concentration and transport of protons in oxides
T. Norby – University of Oslo (Norway)
17^{10} Composite membranes for hydrogen separation
N. Bonanos – DTU (Denmark)
17^{30} Hydrogen permeable membranes based on mixed protonic-electronic conductors
S. Escolástico – CSIC-ITQ (Spain)
17^{50} Preparation and characterization of palladium membranes for hydrogen separation
A. Pacheco-Tanaka -Tecnalia (Spain)
18^{10} Development of ITM-based palladium membranes
W. Schafbauer – Plansee (Austria)

18^{30} **Poster session**

Thursday, 05.09.2013

Session 3: Theoretical modelling and Characterisation of transport and surface chemistry

Chairmen: H.J.M. Bouwmeester and M. Schroeder

09^{00}	The application of ion beam analysis to mass transport studies in mixed electronic ionic conductors (MEICs) *J.A. Kilner* - Imperial College (Great Britain)
09^{20}	MIEC materials for membrane applications: electrochemical characterization and performance modelling *S. Wagner – Karlsruhe Institute of Technology (Germany)*
09^{40}	Structural investigations on ceramic membranes by transmission electron microscopy *S. Roitsch – RWTH Aachen University (Germany)*
10^{00}	Evaluation of the porous support influence on the permeation of asymmetric membranes *F. Drago –RSE S.p.A. (Italy)*
10^{20}	Multiphysics modelling of oxygen transport in MIEC membranes placed in an axis-symmetric experimental set-up *J.M. Gozalvez-Zafrilla – Universitat Politecnica de València (Spain)*
10^{40}	Atomistic Modeling of MIEC membrane materials *M. Gillessen – RWTH Aachen University (Germany)*
11^{00}	**Coffee Break**

Session 4: Advanced manufacturing techniques

Chairwoman/man: P. V. Hendriksen and H.-P. Buchkremer

11^{20}	Plasma spray-physical vapor deposition (PS-PVD) of thin film oxygen and proton conducting membranes on porous metallic supports *R. Vaßen – Forschungszentrum Jülich (Germany)*
11^{40}	New pathways for ceramic supports and membrane manufacturing: from powders and colloids to functional membranes *C. Guizard – Saint-Gobain (France)*
12^{00}	Development of thin film supported tubular membranes for high temperature gas separation *M.-L. Fontaine – SINTEF (Norway)*
12^{20}	Thin-film manufacturing of inorganic oxygen transport membranes by physical vapor deposition *S. Uhlenbruck – Forschungszentrum Jülich (Germany)*
12^{40}	Advanced deposition techniques for thin films and membranes *G. Garcia – Universitat Autònoma de Barcelona (Spain)*
13^{00}	Advances in the synthesis of dense hollow fiber/capillaries for oxygen and hydrogen separation *F. Snijkers – VITO (Belgium)*
13^{20}	**Lunch**

Session 5: European Research Projects and Consortia

Chairmen: J.A. Kilner – N. Bonanos

14^{30} Graded membranes for energy efficient new generation carbon capture process – GREEN CC
W.A. Meulenberg - Forschungszentrum Jülich (Germany)

14^{45} Highly efficient tubular membranes for oxy-combustion
P. Hendriksen – HETMOC Coordinator- DTU (Denmark)

15^{00} Dense membranes for efficient oxygen and hydrogen separation
P. Pinacci – DEMOYS Coordinator – RSE S.p.A (Italy)

15^{15} Advanced Materials and Processes for Energy Application (AMPEA)
Frédéric Chandezon – EERA – AMPEA Coordinator

15^{35} Catalytic membrane reactors based on new materials for C1-C4 valorization
A. de Groot- CARENA Coordinator – ECN (The Netherlands)

15^{50} Design and manufacturing of catalytic membranes reactors (DEMCAMER) and advanced multi-fuel reformer for CHP-fuel cell systems (REFORCELL)
J.L. Viviente – Projects Coordinator – Tecnalia (Spain)

16^{10} **Coffee Break**

Session 6: Student session

Chairmen: W. A. Meulenberg – N. Bonanos

16^{35} Electrical conductivity relaxation on the $SrTi_xFe_{1-x}O_{3-\delta}$ system.
Sebastiaan F.P. ten Donkelaar and Henny J.M. Bouwmeester

16^{45} Experimental surface characterization of oxygen ion transport membranes for flux model development under oxy-fuel combustion conditions
Anton Hunt, Giorgos Dimitrakopoulos, Prof. Patrick Kirchen and Prof. Ahmed Ghoniem

17^{55} Inorganic porous hollow fibers for intensified fractionation and filtration
Patrick de Wit, Arian Nijmeijer, Nieck E. Benes

17^{05} $Ni-Al_2O_3$ composite membrane for hydrogen separation
Stefano Fasolin, Cecilia Mortalò, Monica Fabrizio and Simona Barison

17^{15} Studies of the inhibition influence of other gases such as H_2O, CO, CO_2, N_2 on the H_2 permeation using a Pd-based membrane
M. M. Barreiro, M. Maroño, J. M. Sánchez

17^{25} Tubular solid oxide electrolysers for CO_2 / H_2O reduction
L Kleiminger, G.H. Kelsall

17^{45} Poster session

19^{00} Tour & Banquet

Friday, 06.09.2013

Session 7: Porous materials and membranes
Chairmen: F. Snijkers and K. Haas-Santo

09^{30} Metal-silica membranes for hydrogen separation
J. Diniz da Costa - University of Queensland (Australia)
09^{50} Non-oxide molecular sieve membranes for gas separation
A. Julbe – Université Montpellier (France)
10^{10} Zeolite membranes for energy efficient separations in bio processes and power generation
H. Richter – Fraunhofer IKTS (Germany)
10^{30} Taylor-made zeolites for gas separation processes
S. Valencia – CSIC-ITQ (Spain)
10^{50} Coffee break

Session 8: Application to chemical processes and advanced separations
Chairmen: M. Modigell – V. Scherer

11^{20} Catalytic membrane reactors based on mixed conducting oxide membranes
J.M. Serra – CSIC-ITQ (Spain)
11^{40} Integration of Pd-membranes in catalytic micro reactors for hydrogen production: Concepts & applications
K. Hass-Santo – Karlsruhe Institute of Technology (Germany)
12^{00} OTM: market application
I. Moriña- Inabensa – Abengoa (Spain)
12^{20} CCS membrane development at CIUDEN´s technology development centre for CO_2 capture
J. A. Gutierrez-Bravo- CIUDEN (Spain)
10^{25} Catalytic membrane reactors - perspectives and challenges
J. Caro - University Hannover (Germany)
10^{55} Selective oxidative conversion of light hydrocarbons using catalytic modified dense ionic oxygen conducting membranes
C. Mirodatos - IRCELYON-CNRS, France
12^{40} Lunch

14^{20} Membrane developments for hydrogen separation
A. Nijmeijer – Shell Global Solutions International BV (The Netherlands)
14^{40} R&D strategies for the reduction of CO_2 emissions from fossil fuel-fired power generation
M. Modigell – RWTH Aachen University (Germany)
15^{00} Integration of oxygen transport membrane in an oxyfuel circulating fluidized bed boiler coal plant
P. Chiesa – Politecnico di Milano (Italy)

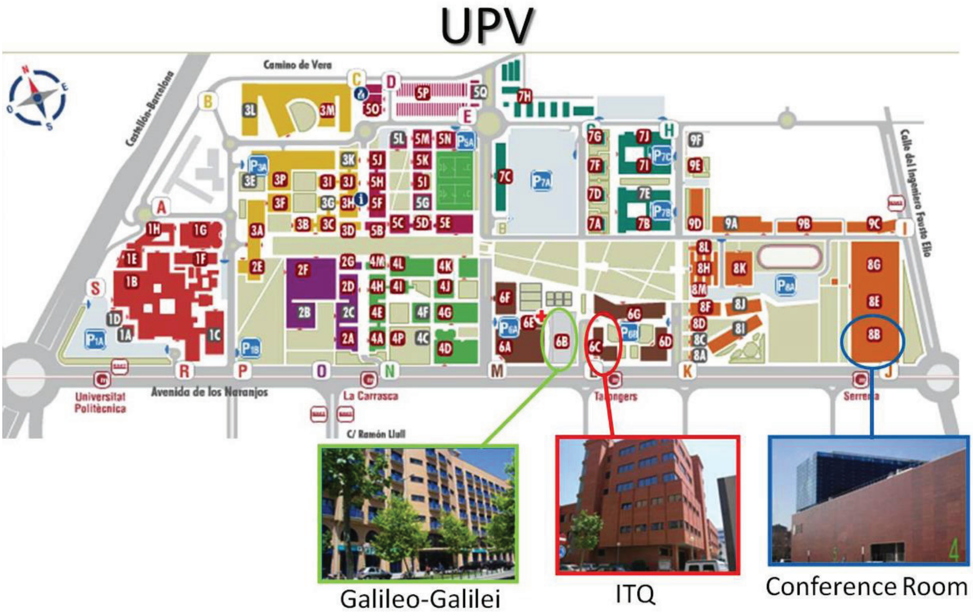
15^{20} Membrane based CO_2 capture in coal fired integrated gasification combined cycles
V. Scherer – Ruhr University Bochum (Germany)

15^{40} Concluding Remarks
18^{30} Students Event on the Beach

Summer School organized in the frame of NASA-OTM, DEMOYS, CARENA and HETMOC FP7 European Projects.

Conference Room

The Summer School will be held in the building 8B (blue cube) of the “Ciudad Politécnica de la Innovación, CPI” in the University Polytechnic of Valencia (UPV) campus (Camino de la Vera, s/n, 46022 Valencia). It is located inside the UPV campus, close to the *Serreria* tram stop (tram lines 4 and 6) and 5 minutes walking from Galileo-Galilei and Reuniver residences.



PLENARY LECTURES

Session 1: Oxygen transport membranes

L-1 Oxygen separation using mixed conducting oxide membranes
H.J.M. Bouwmeester - University of Twente (The Netherlands)

L-2 Ceria based oxygen transport membranes
M. Søgaard - Risø National Laboratory (Denmark)

L3 Defects and transport of mixed conducting membranes
M. Schröder - RWTH Aachen University (Germany)

L-4 Assessment of mechanical stress inside MIEC membranes depending on geometry and operating conditions
R. Kriegel– Fraunhofer IKTS (Germany)

L-5 Mechanical testing and analysis of inorganic membranes
H. L. Frandsen – DTU (Denmark)

Session 2: Hydrogen permeable membranes

L-6 *Characterisation of concentration and transport of protons in oxides*
T. Norby – University of Oslo (Norway)

L-7 Composite membranes for hydrogen separation
N. Bonanos – DTU (Denmark)

L-8 Hydrogen permeable membranes based on mixed protonic-electronic conductors
S. Escolástico – CSIC-ITQ (Spain)

L-9 Preparation and characterization of palladium membranes for hydrogen separation
A. Pacheco-Tanaka -Tecnalia (Spain)

L-10 Development of ITM-based palladium membranes
W. Schafbauer – Plansee (Austria)

Session 3: *Theoretical modelling and Characterisation of transport and surface chemistry*

L-11 The application of ion beam analysis to mass transport studies in mixed electronic ionic conductors (MEICs)
J.A. Kilner - Imperial College (Great Britain)

L-12 MIEC materials for membrane applications: electrochemical characterization and performance modelling
S. Wagner – Karlsruhe Institute of Technology (Germany)

L-13 Structural investigations on ceramic membranes by transmission electron microscopy
S. Roitsch – RWTH Aachen University (Germany)

L-14 Evaluation of the porous support influence on the permeation of asymmetric membranes
F. Drago –RSE S.p.A. (Italy)

L-15 Multiphysics modelling of oxygen transport in MIEC membranes placed in an axis-symmetric experimental set-up
J.M. Gozalvez-Zafrilla – Universitat Politecnica de València (Spain)

L-16 Atomistic Modeling of MIEC membrane materials
M. Gillessen – RWTH Aachen University (Germany)

Session 4: *Advanced manufacturing techniques*

L-17 Plasma spray-physical vapor deposition (PS-PVD) of thin film oxygen and proton conducting membranes on porous metallic supports
R. Vaßen – Forschungszentrum Jülich (Germany)

L-18 New pathways for ceramic supports and membrane manufacturing: from powders and colloids to functional membranes
C. Guizard – Saint-Gobain (France)

L-19 Development of thin film supported tubular membranes for high temperature gas separation
M.-L. Fontaine – SINTEF (Norway)

L-20 Thin-film manufacturing of inorganic oxygen transport membranes by physical vapor deposition
S. Uhlenbruck – Forschungszentrum Jülich (Germany)

L-21 Advanced deposition techniques for thin films and membranes
G. Garcia – Universitat Autònoma de Barcelona (Spain)

L-22 Advances in the synthesis of dense hollow fiber/capillaries for oxygen and hydrogen separation
F. Snijkers – VITO (Belgium)

Session 5: *European Research Projects and Consortia*

L-23 Graded membranes for energy efficient new generation carbon capture process – GREEN CC
W.A. Meulenberg - Forschungszentrum Jülich (Germany)

L-24 Highly efficient tubular membranes for oxy-combustion
P. Hendriksen – HETMOC Coordinator- DTU (Denmark)

L-25 Dense membranes for efficient oxygen and hydrogen separation
P. Pinacci – DEMOYS Coordinator – RSE S.p.A (Italy)

L-26 Advanced Materials and Processes for Energy Application (AMPEA)
Frédéric Chandezon – EERA – AMPEA Coordinator

L-27 Catalytic membrane reactors based on new materials for C1-C4 valorization
A. de Groot- CARENA Coordinator – ECN (The Netherlands)

L-28 Design and manufacturing of catalytic membranes reactors (DEMCAMER) and advanced multi-fuel reformer for CHP-fuel cell systems (REFORCELL)
J.L. Viviente – Projects Coordinator – Tecnalia (Spain)

Session 7: *Porous materials and membranes*

L-29 Metal-silica membranes for hydrogen separation
J. Diniz da Costa - University of Queensland (Australia)

L-30 Non-oxide molecular sieve membranes for gas separation
A. Julbe – Université Montpellier (France)

L-31 Zeolite membranes for energy efficient separations in bio processes and power generation
H. Richter – Fraunhofer IKTS (Germany)

L-32 Taylor-made zeolites for gas separation processes
S. Valencia – CSIC-ITQ (Spain)

Session 8: *Application to chemical processes and advanced separations*

L-33 Catalytic membrane reactors based on mixed conducting oxide membranes
J.M. Serra – CSIC-ITQ (Spain)

L-34 Integration of Pd-membranes in catalytic micro reactors for hydrogen production: Concepts & applications
K. Hass-Santo – Karlsruhe Institute of Technology (Germany)

L-35 OTM: market application
I. Moriña- Inabensa – Abengoa (Spain)

L-36 CCS membrane development at CIUDEN´s technology development centre for CO_2 capture
J. A. Gutierrez-Bravo- CIUDEN (Spain)

L-37 Catalytic membrane reactors - perspectives and challenges
J. Caro - University Hannover (Germany)

L-38 Selective oxidative conversion of light hydrocarbons using catalytic modified dense ionic oxygen conducting membranes
C. Mirodatos - IRCELYON-CNRS, France

L-39 Membrane developments for hydrogen separation
A. Nijmeijer – Shell Global Solutions International BV (The Netherlands)

L-40 R&D strategies for the reduction of CO_2 emissions from fossil fuel-fired power generation
M. Modigell – RWTH Aachen University (Germany)

L-41 Integration of oxygen transport membrane in an oxyfuel circulating fluidized bed boiler coal plant
P. Chiesa – Politecnico di Milano (Italy)

L-42 Membrane based CO_2 capture in coal fired integrated gasification combined cycles
V. Scherer – Ruhr University Bochum (Germany)

L-1

Oxygen separation using mixed conducting oxide membranes

Henny J.M. Bouwmeester
Faculty of Science and Technology, Organization
Drienerlolaan, 7522 NB Enschede, The Netherlands
Email: h.j.m.bouwmeester@utwente.nl
Keywords: mixed conductors, perovskites, defect chemistry, Wagner equation, oxygen surface exchange

Mixed oxide ionic-electronic conductors hold promise for use as oxygen separation membrane for direct oxygen production or integrated in, e.g., an oxyfuel power plant design. Besides the obvious requirement of fast oxygen transport kinetics, the challenge to materials scientists is to design membrane materials and systems, showing sufficiently long-term performance stability under actual operation conditions. Many of the research efforts in the field are focused on acceptor-doped oxygen-deficient perovskite oxides, such as $La_{1-x}A_xCo_{1-y}B_yO_{3-\delta}$ (A = Sr, Ba; B = Fe, Cr), or oxides with closely related structures. This tutorial lecture gives an introduction into the equilibrium defect chemistry of the mixed conducting perovskite oxides, and discusses underlying concepts and limitations in defect-chemical modelling. Also covered are oxygen transport kinetics, oxygen diffusion versus oxygen surface exchange, and asymmetric (supported) membranes. Data from measurements on different mixed conductors are used for illustration.

L-2

Ceria based oxygen transport membranes

Martin Søgaard
Department of Energy Conversion and Storage, Technical University of Denmark
Frederiksborgvej 399, DK-4000, Denmark
Email: msqg@dtu.dk

Oxygen Transport Membranes are of interest for high purity oxygen production and for integration into membrane reactors where high temperature oxygen is required. Additionally, for future power plants with carbon capture and storage, OTMs can possibly be used for the production of the required oxygen with an anticipated smaller energy penalty, than for the competing technologies such as cryogenic distillation. Even though the technology is expected to be competitive, the technology has at present not entered the market. The reasons for this are among others lack of stability of the materials used as membranes.

The present talk will focus on gadolinia doped ceria (CGO) as a membrane material. CGO has a very high oxide ion conductivity, high stability and at temperatures above 600°C and at reducing conditions (pO2 < 10-10 atm) also a fairly high n-type electronic conductivity. Oxygen fluxes of more than 10 Nml min-1 cm-2 have been reported for 30 µm thick Ce0.9Gd0.1O1.95-δ membranes at 850°C between wet methane as permeate gas and air as feed gas. Fluxes have also been shown to be fairly stable over test periods exceeding 300 hours. In order to understand the results obtained for the 30 µm thick CGO10 membrane a detailed model that includes the ionic and electronic conductivity of CGO10, the polarization resistance of the activation layers (electrodes), gas diffusion and conversion has been developed. Based on the model and literature it is shown that one of the limiting factor for oxygen transport through the membrane is a low electronic conductivity of CGO10. Based on the developed model it will be shown that with an enhancement of the electronic conductivity of CGO10, fluxes of more than 10 Nml min-1 cm-2 can be anticipated at 600°C. Different ways of introducing electronic conductivity into CGO will then be discussed and it will be shown that composite membranes of CGO10 and mixed ionic electronic conductors seems to be a promising option for introducing electronic conductivity.

L-3

Defects and transport in mixed conducting membranes

Michael Schroeder
Institute of Physical Chemistry, RWTH Aachen, Landoltweg 2, 52074 Aachen, Germany
E-mail: schroeder@rwth-aachen.de

Permeation through dense metal oxide membranes involves simultaneous migration of ionic and electronic charge carriers in the bulk. Ionic charge carriers may be oxide ions (in the case of oxygen permeable membranes), or protons (in the case of hydrogen permeable membranes). However, bulk migration constitutes only one part of the overall permeation process. Other parts are the exchange reactions at the gas/solid interfaces of the membrane, where gas molecules are transformed into ions and vice versa, and the gas-phase transport in the feed and sweep gas stream, of the gas component to be separated. A typical laboratory permeation experiment may simply aim at determining the permeation flux, however, if combined with defect and transport modelling of the membrane, it may also assist in identifying the rate limiting step of the overall permeation process.

This contribution will focus on the experimental details of permeation measurements, and the pitfalls that need to be considered when designing a permeation experiment. It will be demonstrated, how permeation of dense ceramic membranes of various geometries can be modelled, and how surface exchange reactions can be taken into account in the modelling. Furthermore, it will be discussed which additional data, e.g. obtained with experimental techniques other than membran permeation, are necessary to carry out and validate the modelling.

L-4

Assessment of mechanical stress inside MIEC membranes depending on geometry and operating conditions

Ralf Kriegel, Matthias Schulz
Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Hermsdorf branch of the Institute, Michael-Faraday-Str. 1, Hermsdorf D-07629, Germany
Email: ralf.kriegel@ikts.fraunhofer.de

Keywords: oxygen membrane, BSCF, mechanical stress, simulation

Mixed ionic electronic conductors (MIEC) are able to separate oxygen from oxygen containing gases at high temperatures. The enormous application potential of these oxide ceramics includes optimized firing processes, gasification of coal or biomass, syngas production by partial oxidation or the local production of oxygen. However, the gradient of temperature T and/or oxygen partial pressure p_{O2} at application conditions generates several mechanical loads entailed frequently by cracking of the brittle materials.

MIEC membranes behave much more complicated than inert membranes. The oxygen content δ of the generalized material formula $ABO_{3-\delta}$ depends significantly on p_{O2} of the dominating gas phase and also on temperature. Besides, important physical properties like thermal expansion, lattice constants, electrical and thermal conductivity, the apparent specific heat, Young's modulus and compressive or tensile strength are remarkably influenced by δ. Additionally, the exothermic oxidation of the membrane material at the feed gas side and the endothermal reduction at the permeate side generate temperature gradients. Therefore, usual loads generated by outer forces like absolute pressures are superposed by chemically induced stress resulting from the lattice expansion and by thermal stress too [1]. This could result in crack formation as illustrated schematically in Fig. 1. Corresponding cracks were proven for BSCF membrane tubes used in a portable demonstration unit for 1500 hours [2].

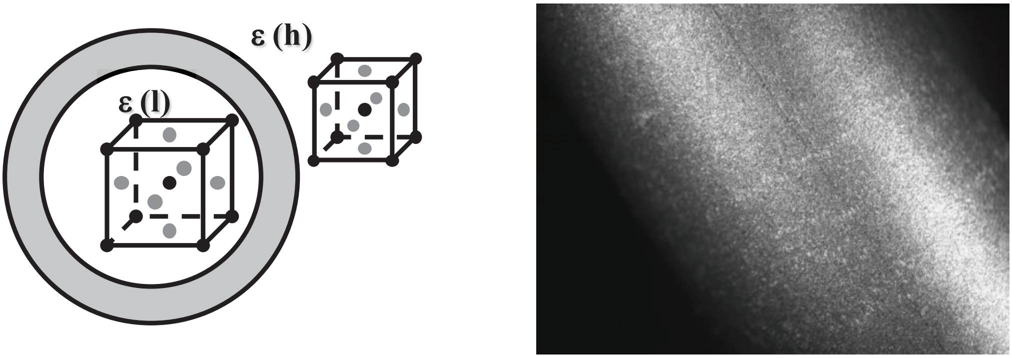


Fig. 1. Left: Scheme of chemical expansion in a working MIEC membrane, lower p_{O2} inside; Right: Axial crack at the outer side of a BSCF membrane tube [2]

Modelling of the whole stress situation reveals the dominating role of chemical induced stress compared to stress generated by thermal gradients and mechanical loads. Correspondingly, the whole stress inside a MIEC membrane depends mainly on the chemical expansion coefficient of the material, on the change of the oxygen stoichiometry caused by the O_2 partial pressures applied and by the membrane geometry. A minimization of the tensile stress seems to be possible for a given material by the use of low driving forces, by application of low outer loads and by optimized membrane geometry [3]. The superposition of separate load-cases results in some universally valid conclusions for material properties and reactor design.

References

[1] Schulz, M., Kriegel, R., Kaps, Ch.: Simulation of the complex loads of ceramic membranes used for oxygen separation. in: Proceedings. A global roadmap for ceramics, 1St Intern. Conf. on Ceramics, Toronto, Kanada 2006
[2] Kriegel, R.: Einsatz keramischer BSCF-Membranen in einem transportablen Sauerstoff-Erzeuger. in: J. Kriegesmann (Ed.), DKG Handbuch Technische Keramische Werkstoffe, HvB-Verlag Ellerau, 119. Delivery complement, Nov. 2010, Chapter 8.10.1.1, p. 1-46
[3] Kriegel, R., Schulz, M., Ritter, K., Kiesel, L., Pippardt, U., Stahn, M., Voigt, I.: Advanced membrane design for oxygen separation. in: Efficient Carbon Capture for Coal Power Plants, Book of Extended Abstracts, Dechema, Frankfurt a.M., 2011, p. 114-117

L-5

Mechanical testing and analysis of inorganic membranes

Henrik Lund Frandsen, Kawai Kwok, Martin Sogaard and Peter Vang Hendriksen
Department of Energy Conversion and Storage, Technical University of Denmark
Frederiksborgvej 399, Roskilde 4000, Denmark
Email: hlfr@dtu.dk

Keywords: Strength measurement, Weibull theory, Stress analysis, Failure theories

This lecture will cover the basic theories and testing needed for the mechanical design of an in-organic membrane based on functional ceramics in particular.

In the design of ceramics two approaches can be followed; the statistical 'Weibull approach' or the fracture mechanical approach. A brief introduction will be given to both approaches, and the advantages and disadvantages for both methods will be discussed. Although the statistical approach has suffered some criticism, since Weibull formulated it in 1939, it is still recognized to be applicable for the most flaw distributions in ceramics [1]. Furthermore, it offers a functional and operational alternative to the computational heavy and mathematical complex fracture mechanical approach.

In the lecture the basics of the Weibull theory will be presented and exemplified by application on an in-organic membrane system, i.e. *measurement of material parameters*, *analytical and numerical stress analysis*, *size effects*, and *failure theories for multi-axial stress* will be covered.

The material parameters needed for the evaluation of the probability of failure are the so-called Weibull strength and Weibull modulus. For a proper statistical determination of these, testing more than 30 samples are typically prescribed by different standards. Also it is essential to test the materials at the relevant temperature and atmosphere as various phase changes and temperature will influence the strength [2]. Strength measurement is thus in general time consuming, and efficient methods are needed for general development of functional ceramic components. In the lecture an experimental method allowing for multiple samples to be tested at high temperature with high throughput will be presented [3,4].

To apply the material data for evaluation of the probability of failure, the stress distribution in the membrane components must be known as well. The stress distribution in multi layer systems exposed to mechanical loads, chemical and thermal expansions can be determined by analytically methods or numerical methods. In the lecture a recent simple and accurate analytical model for tubular bi-layered membranes [5] and a numerical computational study [6] will be presented. In the latter the effect of geometric imperfections from the production will be discussed (see Fig. 1).

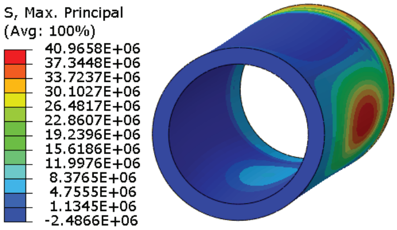


Fig. 1. Stress field in a BSCFZ membrane with uneven wall thickness [6].

For ceramic materials it is well known that the strength scales with amount of the volume of the specimen or component exposed to tensile stress, i.e. a size effect is present. Thus, in order to apply the results from the strength measurements in the stress distribution models, the strength has to be scaled to the relevant size. In thee final part of the lecture the scaling laws for the Weibull theory and other multi-axial failure theories [7] will touched upon and exemplified in terms of a in-organic membrane system.

References

[1] R. Danzer, P. Supancle, J. Pascual and T. Lube, 'Fracture statistics of ceramics - Weibull statistics and deviations from Weibull statistics,' *Eng. Fract. Mech.*, 74 [18] 2919-2932 (2007).

[2] B. X. Huang, J. Malzbender, R. W. Steinbrech and L. Singheiser, 'Discussion of the complex thermo-mechanical behavior of Ba0.5Sr0.5Co0.8Fe0.2O3-delta,' *J. Membr. Sci.*, 359 [1-2] 80-85 (2010).

[3] H. L. Frandsen, D. Curran, S. Rasmussen and P. V. Hendriksen, 'A method for high throughput measurement of strength at temperature in controlled atmosphere,' (To be submitted).

[4] K. Kwok, H. L. Frandsen, M. Sogaard and P. V. Hendriksen, 'Strength characterization of tubular ceramic materials using semi-cylindrical test specimens,' (To be submitted).

[5] K. Kwok, H. L. Frandsen, M. Sogaard and P. V. Hendriksen, 'Chemical and Mechanical Stresses in Tubular Supported Ceramic Membranes,' (To be submitted).

[6] K. Kwok, H. L. Frandsen, M. Sogaard and P. V. Hendriksen, 'Effects of geometric imperfections in ceramic membranes supported on tubular substrates,' (To be submitted).

[7] H. L. Frandsen, 'Weibull statistics effective area and volume in the ball-on-ring testing method,' (To be submitted).

L-6

Characterisation of concentration and transport of protons in oxides

Truls Norby
Department of Chemistry, University of Oslo
FERMiO, Gaustadalleen 21, NO-0349 Oslo, Norway
Email: truls.norby@kjemi.uio.no
Keywords: protons, oxides, hydrogen, conductivity, thermogravimetry

Oxides may take up protons at high temperatures from surrounding H_2O and H_2. Protons are located in effectively positive OH^- ions substituting O^{2-} ions. These protons may be seen also as interstitial species located on oxide ions. They typically charge compensate acceptors or electrons. They move by free H^+ jumps between the O^{2-} ions hosts giving rise to proton conductivity. Depending on transport numbers, materials with proton conductivity may be used as high temperature solid electrolytes for proton ceramic fuel cells (PCFCs) and electrolyser cells (PCECs) or mixed conducting hydrogen transport membranes (HTMs) for pre-combustion CO_2 and H_2 separation. Proton conducting oxides may also be used in catalytic membrane reactors for valorisation (dehydrogenation) of light hydrocarbons.

As temperature increases and kinetics becomes faster, proton conducting oxides will however start to lose water. Protons are replaced by oxygen vacancies, and the ionic conductivity shifts from protonic to oxide ionic. The membranes can thus be mixed proton and oxide ion conducting for use in co-ionic fuel cells and electrolysers as well as membranes permeable to water vapour. If the electronic transport number is also high they can be permeable to both hydrogen, oxygen, and water, depending on the driving forces. It is thus often important – but also complicated – to quantifiy the transport of all three charge carriers in proton conducting oxides. Here, however, we will concentrate on protons and proton conductivity; the product of their charge, concentration, and mobility.

The oxides studied today as proton conducting electrolytes or mixed proton electron conducting membranes are mainly acceptor doped or with inherently disordered oxygen deficiency. Examples of the two classes comprise $BaCe_{0.8}Y_{0.2}O_{2.9}$ and $La_{27}W_5O_{55.5}$, both having oxygen vacancies in the dry state and/or at high temperatures. In wet atmospheres and lower temperatures they hydrate. Thermogravimetry in wet atmosphere vs temperature provides a complete analysis of the amount of protons and the thermodynamic parameters of hydration. Weighing the *in situ* isotope exchange between H_2O and D_2O provides a direct second measure of the total proton/deuteron content. This is best done in the fully hydrated state, otherwise several secondary isotope effects come into play. Simultaneous TG-DSC provides directly the enthalpy of hydration. Several other methods – e.g. based on desorption gas analysis or IR spectroscopy – can also be used, each with advantages and challenges.

The mobility or diffusivity of protons can be studied independently by some methods, like PFG-NMR or H/D isotope exchange using SIMS or transient thermogravimetry or conductivity.

From the total conductivity, the partial protonic conductivity may be obtained by transport number measurements. Unlike oxygen transport membranes – where the oxide ion transport number is usually too small to be measured by the EMF method – hydrogen transport membranes so far have comparable protonic and electronic transport numbers, and the EMF method with gradients in hydrogen (and water) activity may give useful first insight. One must be careful, though, to apply corrections for electrode polarization. Total and partial conductivity studies vs pO_2, pH_2O, and T are in much use to give whole sets of thermodynamic and mobility parameters provided the results and assumptions match the number of unknowns. Flux measurement through membranes is the ultimate way to measure the effective ambipolar proton electron conductivity and the application of the materials with its surface limitations. However, also here, there are pitfalls, notably hydrogen generation by oxide ion transport and water splitting. The use of D_2 as hydrogen feed can circumvent this.

Both concentration, mobility, flux, and conductivity studies of protons in oxides require consideration of various microstructural pathways and obstructions: bulk (grain interior), grain boundaries, pores, electrodes, and surfaces. Variation in sample dimensions, electrode configurations, surface catalysts, variations in grain size from single crystals to nanograined ceramics, use of impedance spectroscopy and diffusion profiles, and application of space charge layer theory and brick layer models are among the many tools one may have to apply to resolve this fascinating and challenging issue, which is critical to proper scientific interpretation of experimental results and to technological development.

Computational techniques are making leaps of progress – also in defect chemistry and transport of protons in oxides. Agreement with experiment on for instance hydration thermodynamics is satisfactory. The next level will be to help interpret experiments on the complex matters of grain boundary and surface transport.

L-7

Composite membranes for hydrogen separation

Nikolaos Bonanos
Department of Energy Conversion and Storage, Technical
University of Denmark DTU, DK-4000 Roskilde, Denmark.
Email: nibo@dtu.dk

Robust inorganic hydrogen permeation membranes would find applications in the chemical industry, namely for the recovery of hydrogen from impure gas streams produced during biomass gasification and oil refining; the hydrogen can then be used to make chemicals or to generate electrical power. Competing technologies are membrane separation using palladium alloys or microporous inorganic membranes, and also pressure swing absorption. In dense inorganic membranes, the carriers move by ambipolar conductivity, that results in the transport of hydrogen from a compartment with high to a compartment of low pressure. Temperatures of 600°C and above are envisaged, which are compatible with temperatures of biomass gasification.

Work is in progress in several laboratories to produce oxide-based materials with electronic conductivity, in addition to protonic conductivity. Due to the reducing environment of hydrogen, this electronic conductivity should preferably be n-type. An alternative approach is to develop inorganic composites of protonically and electronically conducting oxides. This, however, requires oxides of different compositions to be co-sintered, without significant reaction or interdiffusion- a challenge. The presentation describes the preparation of composites of a protonic conductor $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{\xi}$ (BCZY27) and an electronic conductor $Sr_{0.95}Ti_{0.9}Nb_{0.1}O_{\xi}$ (STN95) by spark plasma sintering, and investigations of the resulting microstructure and electrical properties [1].

References:

[1] J.S. Fish, S. Ricote, T. Holgate, F. Lenrick, L.R. Wallenberg, R. O'Hayre and N. Bonanos, Synthesis by spark plasma sintering of novel protonic/electronic conductor composite: $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}/Sr_{0.95}Ti_{0.9}Nb_{0.1}O_{3-\delta}$ (BCZY27/STN95), *Journal of Materials Science* (in press).

L-8

Hydrogen permeable membranes Hydrogen permeable membranes based on mixed protonic-electronic conductors

S. Escolástico, C. Solís, J.M. Serra
[2]Instituto de Tecnología Química, UPV-CSIC, C/ Camino de Vera, s/n, Valencia 46022, Spain
Email: soesro@itq.upv.es

Dense mixed protonic and electronic membranes allow producing high-purity hydrogen due to the high selectivity of the proton-transport mechanism and the advantage of operating at high temperature and high pressure. This kind of membranes could be integrated in CCS processes [1] and in catalytic membrane reactors for reactions such as non-oxidative olefin and aromatics production, syngas production and hydrocarbon reforming. Among the different proton conducting oxides, tungstates based materials (Ln_6WO_{12}) are presented as the most promising oxides for hydrogen permeable membranes at high temperature due to their important mixed conductivity (protonic and electronic) and their stability in CO_2-rich and sulphur-containing environments [2,3,4]. This work presents a broad study of the transport properties of $Ln_{5.5}WO_{11.25-\delta}$ materials and the improvement of their hydrogen permeation by doping using different lanthanides and transition metals.

Materials were synthesized by solid state reaction and modified sol-gel method [3]. Transport properties were studied by standard four-point DC conductivity measurements as a function of temperature for different environments. These measurements were focused on the study of the isotopic and hydration effect.

Permeation measurements were performed on a double chamber quartz reactor and hydrogen was separated from a mixture of H_2-He (dry or saturated in water at 25 ºC) using argon as sweep gas. The influence of three different parameters on the hydrogen separation was studied: operation temperature, hydrogen feed concentration and hydration degree of the membrane. $Ln_{5.5}WO_{11.25-\delta}$ membranes used consisted of a gastight thick disc with a diameter of 15 mm sintered at 1550 ºC. Both disk sides were coated by screen printing with a 20 μm layer of a Pt ink (Mateck, Germany) in order to improve the catalytic activity of the sample

Hydrogen flow for $Nd_{5.5}WO_{11.25-\delta}$ was improved by doping with different lanthanides and transition metals [4]. On the other hand, no improvement was obtained by doping in the A position in $La_{5.5}WO_{11.25-\delta}$, whereas an important improvement was obtained using transition metals as dopants in the B-position at low temperatures [5]. H_2 flow values for $La_{5.5}WO_{11.25-\delta}$ range from 0.005 $mL\cdot min^{-1}\cdot cm^{-2}$ up to 0.136 $mL\cdot min^{-1}\cdot cm^{-2}$, depending on the feed composition and hydration degree. By doping of $La_{5.5}WO_{11.25-\delta}$, H_2 flow values up to 0.095 $mL\cdot min^{-1}\cdot cm^{-2}$ at 700 ºC were reached depending on the feed composition, H_2O % and the dopant element. In general, all the studied compounds exhibit similar overall permeation behavior depending of the hydration configuration. The hydrogen flow obtained is very low when the permeation is measured in dry atmospheres, due to the lack of proton charge carriers concentration. However, when feed side is humidified the hydrogen flow increases due to the hydration of the membrane. When both sides are humidified, the hydrogen flow increases notably. This increase is ascribed to two different processes: (1) transport of protons through the membrane from the higher pH_2 (feed) to the lower pH_2 side (sweep) and (2) hydrogen production by water splitting in the sweep side which is favored at high temperatures by the predominant oxygen-ion transport that the materials present.

Finally, all the studied compounds remained stable under CO_2 containing environments as it was checked by XR-diffraction.

References

[1] K. Jordal, R. Bredesen, H.M. Kvamsdal and O. Bolland. Energy 9 (2004) 1269.
[2] R. Haugsrud. Solid State Ionics 178 (2007) 555.
[3] S. Escolástico, V. B. Vert and J. M. Serra. Chem. Mater. 21 (2009) 3079.
[4] S. Escolástico, C. Solís and J. M. Serra. Int. J. Hydrog. Energy 36 (2011) 11946
[5] S. Escolastico, J. Seeger, S. Roitsch, M. Ivanova, W. A. Meulenberg, J. M. Serra et al. ChemSusChem in press (2013) (doi: 10.1002/cssc.201300091)

L-9

Preparation and characterization of palladium membranes for hydrogen separation

David A. Pacheco Tanaka
Materials for Energy & Environment Department, Tecnalia Research & Innovation.
Mikeletegi 2, Donostia-San Sebastian, E-20009, Spain.
Email: alfredo.pacheco@tecnalia.com

Keywords: Pd membranes, Hydrogen separation, Electroless plating, High temperature hydrogen permeation.

Palladium-based membranes have received a growing interest for the separation and purification of hydrogen from various resources. In addition, Pd membranes can be used as an integrated membrane reactor where the separation process is coupled with catalytic reactions. Pd membranes have advantages of high hydrogen flux and exclusive perm-selectivity for hydrogen due to the unique permeation mechanism. However, pure Pd membranes suffer from hydrogen embrittlement at low temperature, it can be poisoned by sulphur and prone to become contaminated and mechanically damaged. Since the permeation flux is inversely proportional to the membrane thickness, development of composite membranes with a thickness of less than 5 μm have been intensively studied in order to attain high hydrogen flux and to minimize the material cost. The choice of support is of critical importance in the preparation of thin and defect-free palladium membranes. Surface roughness and the presence of large pores inhibit the deposition of thin palladium membrane. A very important issue to be considered is the strong interaction between the Pd membrane and the support at high temperature.

The presentation will be divided in three parts:

1.- Preparation of Pd-Ag and Pd-Au membranes by electroless plating.- Pd-Ag alloys membranes are more resistant againt hydrogen embritlement and have more hydrogen permeation; Pd-Au membranes are more resistant to sulphur poisoning [1][2].

2.- Preparation of Pd “Pore Filled” membranes.- In this configuration Pd is located inside the pores of a nano-porous ceramic. These membranes use less Pd than conventional membranes, are resistant against hydrogen embrittlement and are mechanically stronger [3][4].

3.-Effect of the support in Pd membranes.- It is important to consider the thermal compatibility of Pd and the supports for practical applications in hydrogen recovery using Pd membranes for reactions carried out at more than 650 °C such as methane steam reforming. The effect of the support in hydrogen permeation at high temperature will be described[5][6].

References

[1] D.A. Pacheco Tanaka, M. Llosa Tanco, S. Niwa, Y. Wakui, F. Mizukami, T. Namba, et al., Preparation of palladium and silver alloy membrane on a porous α-alumina tube via simultaneous electroless plating, Journal of Membrane Science. 247 (2005) 21–27.

[2] J. Okazaki, D.A. Pacheco Tanaka, M.A.L. Tanco, Y. Wakui, T. Ikeda, F. Mizukami, et al., Preparation and Hydrogen Permeation Properties of Thin Pd-Au Alloy Membranes Supported on Porous α-Alumina Tube, Materials Transactions. 49 (2008) 449–452.

[3] D.A. Pacheco Tanaka, M. Llosa Tanco, T. Nagase, J. Okazaki, Y. Wakui, F. Mizukami, et al., Fabrication of Hydrogen-Permeable Composite Membranes Packed with Palladium Nanoparticles, Advanced Materials. 18 (2006) 630–632.
[4] D.A. Pacheco Tanaka, M.A. Llosa Tanco, J. Okazaki, Y. Wakui, F. Mizukami, T.M. Suzuki, Preparation of “pore-fill” type Pd–YSZ–γ-Al2O3 composite membrane supported on α-Al2O3 tube for hydrogen separation, Journal of Membrane Science. 320 (2008) 436–441.
[5] J. Okazaki, T. Ikeda, D.A. Pacheco Tanaka, M.A. Llosa Tanco, Y. Wakui, K. Sato, et al., Strong Interaction at the Palladium/Alumina Interface of Membrane during Hydrogen Permeation at Elevated Temperature, Chemistry Letters. 37 (2008) 1004–1005.
[6] J. Okazaki, T. Ikeda, D. a Pacheco Tanaka, M. a Llosa Tanco, Y. Wakui, K. Sato, et al., Importance of the support material in thin palladium composite membranes for steady hydrogen permeation at elevated temperatures., Physical Chemistry Chemical Physics: PCCP. 11 (2009) 8632–8.

L-10

Development of ITM-based Palladium Membranes

Wolfgang Schafbauer, Th. Franco, M. Haydn, A. Venskutonis, and L. S. Sigl
Innovation Services – Plansee SE, Metallwerk-Planseestr. 71, 6600 Reutte, Austria
Email: wolfgang.schafbauer@plansee.com

Keywords: hydrogen, membrane, palladium, PVD

With respect to taking care of the limited resources for energy conversion, hydrogen plays a more and more important role for increasing demand of decentralized power generation. As hydrogen generation by steam electrolysis is still very expensive due to high costs for electricity and low efficiency, steam reforming of natural gas is one of the most promising ways for gaining hydrogen efficiently from fossil fuels. While hydrogen by methane steam reforming and following pressure swing adsorption (PSA) is widely established in large scale production, the scale down of PSA is economically not reasonable for systems generating < 500 m³/h H_2. For this market of decentralized hydrogen generation, inorganic asymmetric membranes offer high potential for industrialization.

In this contribution, a manufacturing process for the production of inorganic asymmetric supported palladium membranes for hydrogen separation is presented. The manufacturing is designed with respect to scalable processes for high volume membrane production. After the production of this type of membranes, tests are performed at project partners in order to verify feasibility.

At Plansee SE, a highly corrosion resistant ferritic steel alloy, called ITM, has been developed for high temperature applications. In the case of gas separation membranes, metal supports offer easy sealing to dense parts in the system together with lower manufacturing costs. In the presented system, tailored porous tubular metal parts with dense connectors are used as support for the pure palladium membrane. Because of interdiffusion of Pd into the steel matrix and therefore destruction of the gas separation membrane, ceramic diffusion barrier layers have to be applied on the steel support before coating with Pd. All the materials in the asymmetric membrane structure are chosen in order to obtain minimum differences in thermal expansion and maximum chemical compatibility.

The thin palladium layer is applied via an industrial thin film deposition directly on the support structure. In order to get dense Pd layers with a minimum thickness, the surface quality of the ceramic interlayers has to be as high as possible targeting surface roughness and defect size. Gas separation membrane flux of Pd membranes and hydrogen selectivity are the key issues for the future industrial scale application of this type of membrane and mainly influenced by the surface that has to be coated.

Together with industrial partners, such type of hydrogen separating membranes was developed at Plansee SE. The tubular membranes were successfully tested under H_2/N_2 but also real reformate gas compositions. The membranes showed excellent selectivity and stability against thermal cycling. With single tubes, values for the selectivity up to 9000 at 600 °C operation temperature were demonstrated. The membranes will be tested under real conditions in a demonstration unit project starting in 2013.

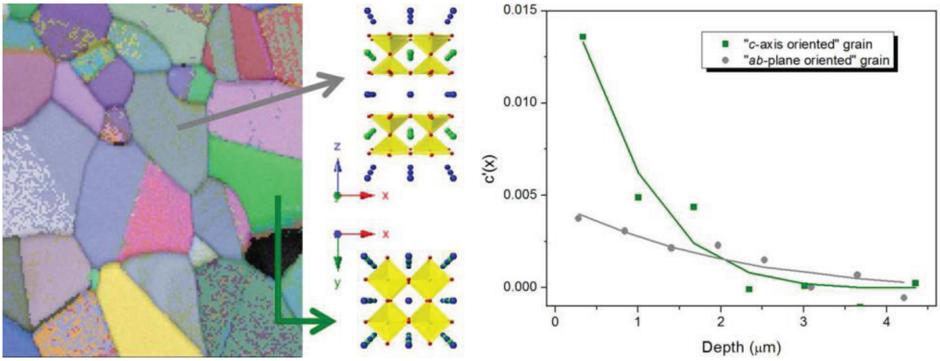
L-11

The application of ion beam analysis to mass transport studies in mixed electronic ionic conductors (MEICs)

J A Kilner[1,2], H.Tellez Lozano[1], M.Burriel[1] and J. Druce[2]
[1]Department of Materials, Imperial College, London, SW7 2AZ, UK.
[2] International Institute for Carbon-Neutral Energy Research, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan
Email: j.kilner@imperial.ac.uk
Keywords: Ion Beam Analysis, Isotopic Exchange, Secondary Ion Mass Spectroscopy, Low Energy Ion Scattering

Dense ceramic membranes composed of oxygen ion conducting MEICs have been proposed for a number of applications. Examples include membranes for the separation of oxygen from air and in partial oxidation reactors for the production of syngas. In order to optimize these materials it is important to have a fundamental understanding of the kinetics of the mass transport of oxygen in the bulk and grain boundaries as well as the details of the gas/solid exchange at the surface. This latter topic of surface exchange has become increasingly important, as recent studies have shown that the durability of these materials in commercial applications can be severely curtailed due to the degradation of surfaces by the interaction with water vapour and carbon dioxide in the air [1].

The measurement of the kinetics of oxygen exchange in MEICs has been greatly aided by the use of ion beam analysis techniques. In particular this has focused on the use of Secondary Ion Mass Spectrometry (SIMS) to measure the gas/solid exchange of oxygen 18. In recent years there have been significant improvements in commercially available instrumentation for SIMS which have extended the capabilities to allow much more detailed studies. An example is shown in the figure below where analysis of diffusion profiles within individual grains of $PrBaCo_2O_{5+\delta}$ has allowed the measurement of the anisotropy of oxygen transport parallel and perpendicular to the c axis [2].



In addition to the SIMS technique a second ion beam technique, Low Energy Ion Scattering (LEIS) has been benefited from recent instrumental developments and is now suitable for the study of the surface chemistry of these important materials. The advantage of LEIS is that it gives information about the composition of the outermost atomic layer where the exchange process is taking place [3]. The two techniques are synergistic; their combined use can provide a detailed insight of the development of the near surface regions and its effect upon membrane performance.

In this presentation details will be given of the use of both SIMS and LEIS in determining the factors affecting the kinetics of oxygen transport in a number of oxide MEIC materials used as ceramic membranes or SOFC/SOEC electrodes.

References

[1] E. Bucher, W. Sitte, *Solid State Ionics* 192 (2011) (1) 480.
[2] M. Burriel, J. Pena-Martinez, R.J. Chater, S. Fearn, A.V. Berenov, S.J. Skinner, J.A. Kilner, *Chemistry of Materials* 24 (2012) (3) 613.
[3] J.A. Kilner, S.J. Skinner, H.H. Brongersma, *Journal of Solid State Electrochemistry* 15 (2011) (5) 861.

L-12

MIEC materials for membrane applications: electrochemical characterization and performance modeling

Stefan F. Wagner, Andreas Häffelin, Christian Niedrig, Wolfgang Menesklou and Ellen Ivers-Tiffée
Institut für Werkstoffe der Elektrotechnik, Karlsruhe Institute of Technology
Adenauerring 20 b, 76131 Karlsruhe, Germany
Email: stefan.wagner@kit.edu
Keywords: gas separation, transport properties, computational modeling, MIEC

Mixed ionic-electronic conducting (MIEC) materials are of great interest for a variety of high-temperature applications, such as dense ceramic membranes for gas separation. This presentation focusses on two main issues:

(I) Electrochemical Characterization

Several MIEC perovskite oxides, namely of the composition $A_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ (A = La, Ba), are known to exhibit excellent oxygen-ionic and electronic transport properties, making them very promising candidates for a high-permeation oxygen transport membrane (OTM).

Electrochemical properties of these materials as well as their chemical stability as a function of oxygen partial pressure pO_2 and temperature T can be analyzed in an “oxygen pump” setup [1] facilitating precise and *continuous* pO_2 control in the entire range between $pO_2 = 10^{-20}...1$ bar above 700 °C. The electrical properties and oxygen equilibration kinetics of an oxide sample can thus be assessed as a function of ambient pO_2 and T. These data can then be employed for modeling the oxygen flux through an OTM, cf. (II) below.

(II) Performance Modeling

A 3D finite element method (FEM) model [2] has been developed to calculate the flux through a dense MIEC membrane depending on the material properties (derived, *e.g.*, from (I), s. above), on operating conditions and microstructure. For sufficiently thin membranes, an enhancement of the permeation can be achieved by modifying the surfaces with a porous “functional” layer. This model is applied to OTMs made of state-of-the-art high-flux materials, *e.g.*, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) or $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), as well as to hydrogen-permeation membranes.

The basic physico-chemical processes i) gas diffusion in the porous functional layer, ii) surface exchange between gas phase and MIEC material, and iii) ambipolar diffusion through the solid membrane are implemented in this model. Furthermore, microstructure modifications such as particle size, tortuosity, thickness and porosity of the functional layer are realized by using a geometry generator.

Fig. 1 shows the simulated oxygen flux through an OTM made of LSCF for varying geometrical properties of the functional layer. The simulations give a detailed view of the concentration profiles and flux distributions in a 3D microstructure of the MIEC membrane. The calculations are validated with measured permeation data, e.g. [3], for different operating temperatures and membrane thicknesses. The developed 3D model enables an optimization of the parameters for membrane design, depending on chemical composition and operating conditions.

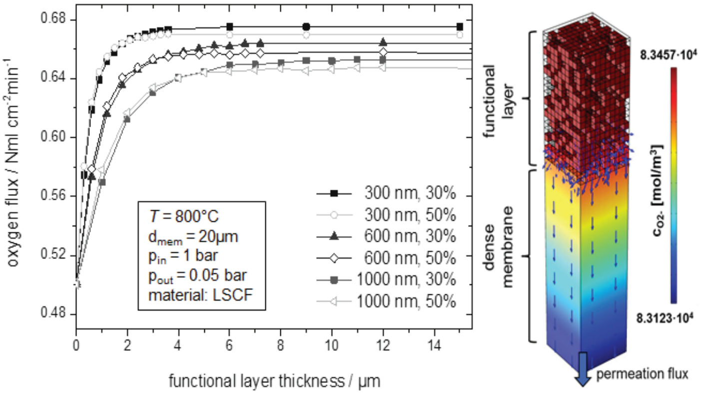


Fig. 1. Simulated oxygen flux across a dense LSCF OTM, enhanced by a porous functional layer with various particle sizes between 300 - 1000 nm and different degrees of porosity

References:

[1] C. Niedrig, W. Menesklou, S. F. Wagner, E. Ivers-Tiffée, *J. Electrochem. Soc.* **160** (2013) F135.

[2] A. Häffelin, C. Niedrig, S. F. Wagner, E. Ivers-Tiffée, *manuscript in preparation*.

[3] M. Betz, F. Schulze-Küppers, S. Baumann, W. A. Meulenberg, D. Stöver, *Adv. Sci. Tech.* **72** (2010) 93.

L-13

Structural investigations on ceramic membranes by transmission electron microscopy

Stefan Roitsch, Juri Barthel, and Joachim Mayer
GFE, RWTH Aachen University
Ahornstraße 55, 52074 Aachen, Germany
Email: sroitsch@uni-koeln.de

Keywords: carbon capture and storage, gas-separation membranes, transmission electron microscopy

Inorganic membranes can be applied in several industrial processes and are heavily discussed for seperation applications in chemical industry and the implementation of CO_2-sequestration strategies in power plants [1,2]. However, the thermal and chemical stability of the membrane materials under application conditions is a critical point for a possible implementation. For such applications, the long-term stability of the functional materials under realistic conditions is of extreme economic relevance and is therefore investigated thoroughly. Transmission electron microscopy (TEM) is a valuable tool for structural investigations of these materials. On the one hand TEM investigations can help to clearify distinct structural details and, hence, to understand and optimize transport mechanisms, on the other hand structural changes which emerged during operation within the materials and which may reduce the membrane's life time can be identified.

In this presentation examples of TEM investigations on microporous membranes, oxygen transport membranes, and proton conducting membranes will be shown. The talk will focus on structural transformations of the prominent oxygen transport material $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\square}$ (BSCF) under specific exposure conditions. As an example, Fig.1 shows two TEM micrographs of a BSCF sample which exhibit transformations from the cubic to a hexagonal crystal strucutre.

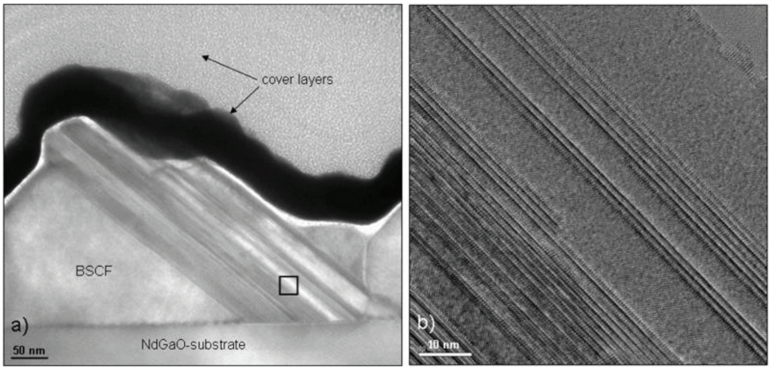


Fig. 1. TEM micrographs of an epitaxially grown BSCF thin layer which was annealed for 10 h at 900 °C. In (a) a secondary hexagonal phase can be observed as broad diagonal stripes. The black square indicates a region which is shown in (b) with higher magnification

References

[1] R. Haugsrud, Solid State Ionics **178** (2007), 555-560
[2] J. Vente *et al*, J. Solid State Electrochem. **10** (2006), 581

L-14

Evaluation of the porous support influence on the permeation of asymmetric membranes

Francesca Drago, Pietro Pinacci
RSE S.p.A., Via Rubattino 54, 20124 Milano, Italy
Email: francesca.drago@rse-web.it

Keywords: asymmetric membranes, dusty gas model, porous media, binary diffusion

Hydrogen and oxygen separation membranes are extensively studied for their application in the CO_2 emission-free coal or natural gas power plants. Due to the lower cost and higher permeation, research is now focused on the development of asymmetric membranes, where a thin dense membrane layer is deposited on cheaper porous supports, which is needed to increase the membrane mechanical stability. Gas transport mechanism in the porous media can play an important role on the gas separation, depending on porous support characteristics, in particular when a multicomponent mixture, in the process side or in the permeation side, is present.

Literature data show an increase of the permeation of supported membranes for oxygen separation, when pure oxygen is used instead of air as process gas on the support side [1]. Same results have been obtained by testing a Pd membrane for hydrogen separation in absence of sweep gas on the support side [2].

Hydrogen permeation tests have been performed on a supported Pd membrane, at 400°C by feeding N_2 as sweep gas on the support side, in the flow rate range of 0 – 100 Nl/h. The feed pressure has been increased up to 7 bar, while the permeate side has been kept at atmospheric pressure.

By considering experimental data, the gas transport trough the support has been modeled. Results show that in absence of sweep gas, the support resistance, estimated by considering the combination of the viscous flux and the Knudsen diffusion, leads an increase of the hydrogen partial pressure at the interface Pd layer/support and a consequent flux reduction of less than the 10%. In presence of sweep gas the hydrogen permeation is lower than expected and the flux reduction is up to the 30% at the higher sweep gas flow rate. The support resistance, when the binary mixture is present in the support, has been evaluated according to the theory of gas mass transport in porous media through a stagnant gas [3], which combines the Knudsen diffusion flow, the viscous flow and the binary diffusion.

The evaluated pressure gradient across the membrane is higher than the value estimated in absence of sweep gas and also the interface H_2 partial pressure is higher than the H_2 partial pressure measured in the permeate side. Such an increase is due to the binary diffusion term which determines an increase of the resistance of hydrogen transport through stagnant nitrogen.

It can be noted that the approach used in this work can be applied to evaluate the influence of any type of support of asymmetric membranes separating different type of gases. The binary diffusion coefficient, in fact depends on the gas involved in the permeation and on the support characteristics, as porosity, tortuosity, thickness and mean pore radius. Moreover the developed methodology, combined with a parametric study, provides the guide lines to minimize the support influence and to improve the membrane permeation.

References

[1] S. Baumann, J. M. Serra, M. P. Lobera, S. Escolático, F. Schulze-Küppers, W. A. Meulenberg, Journal of Membrane Science **377** (2011) 198 - 205
[2] P. Pinacci, F. Drago, Catalysis Today **193** (2012) 186 - 193.
[3] A. Ünal, Ind. Eng. Chem. Res. **26** (1987) 72 - 77

L-15

Multiphysics modeling of oxygen transport in MIEC membranes placed in an axis-symmetric experimental set-up

José M. Gozálvez-Zafrilla[1], José M. Serra-Alfaro[2], Asunción Santafé-Moros[1]
[1]Institute for Industrial, Radiophysical and Environmental Security, Universitat Politècnica de Valencia
[2]Instituto de Tecnología Química, UPV-CSIC, C/ Camino de Vera, s/n, Valencia 46022, Spain
Email: jmgz@iqn.upv.es

Mixed ionic–electronic conducting ceramic membranes (MIEC) working at high temperature are potentially able to obtain oxygen fluxes of high purity. The use in fossil fuel power plants of the Oxyfuel process [1] would allow minimizing CO_2 emissions since the final flue gas stream consists principally of moist CO_2, which can be readily liquefied and transported. In this case, the ceramic oxygen transport membrane modules can be thermally integrated and make possible to match the desired oxygen production due to the intrinsic modularity of these systems. Besides, they can be used in catalytic membrane reactors to achieve high selectivity in reactions of high industrial interest.

Crystalline transport by the oxygen vacancies takes place at high temperature with simultaneous transport of electrons and vacancies. This complex mechanism is usually modeled by the integral form of the Wagner's equation using directly the difference in oxygen chemical potential which is the driving-force of the transport. However, this approach is only valid when the only limiting step is the diffusion in the crystal network and the oxygen concentration is homogenous in both membrane sides. Undoubtedly, the inclusion of the effects of polarization and surface reaction improves the accuracy of the solution obtained. Nevertheless, considering a one-dimensional approach of the transport can be inadequate as the effects of module geometry on the flow and gradients are significant. This justifies the use of multiphysics program able to couple Fluid Dynamic calculations with component transport. A suitable technique for this purpose is Finite Element Analysis (FEA) which is experiencing an increasing application in several fields of engineering. Modern FEA solvers are able to manage differential equation systems, usually coupled and with complex boundary conditions [2].

The development of ceramic materials requires O_2 permeation studies at high temperatures, which are usually carried out in lab-scale permeation set-ups. In these set-ups, an averaged effective diffusion coefficient through the membrane can be obtained. However, the occurrence of gas transport limitations derived from the membrane set-up, operating conditions and porous supporting structures yields to difficulties in the evaluation of the intrinsic material properties (diffusion and O_2 exchange parameters).

In this work we explain different modeling issues of a MIEC membrane (BSCF) placed on an experimental set-up of cylindrical geometry. The model was carried out using the FEA platform COMSOL Multiphysics including: oxygen convection and diffusion in both the air and permeate chambers, vacancy diffusion in the membrane, equilibrium and kinetic interfacial resistance on the membrane interfaces. The coupling conditions between the air and membrane subdomain and between the permeate and membrane subdomains were defined considering the identity between the different fluxes. Using the model the effects of temperature, geometry and gas flow on the different resistances can be evaluated.

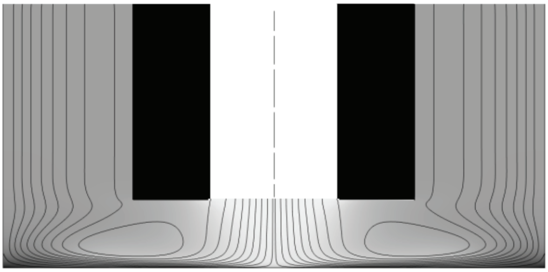


Fig. 2. Flow streamlines in the permeate of the experimental set-up (membrane is placed below)

References

[1] I. Pfaff, A. Kather, Energy Procedia **1** (2009) 495–502.

[2] J. M. Gozálvez Zafrilla, A. Santafé Moros, CFD Applications of Membrane Technology by Finite Element Analysis. Engineering Applications of Computational Fluid Dynamics, International Energy and Environment Foundation, 2011).

L-16

Atomistic modeling of MIEC membrane materials

Michael Gilleßen
RWTH Aachen University, Institute of Inorganic Chemistry, Landoltweg 1, 52056 Aachen, Germany
Email: Michael.Gillessen@ac.rwth-aachen.de

Keywords: density-functional theory, BSCF, nudged elastic band

At present, a number of atomistic structural properties can be routinely accessed by quantum-chemical calculations of density-functional theory (DFT) quality [1,2]. Electronic structures of known compounds may be numerically investigated, and unknown phases have been correctly predicted [3]. In addition, tools such as the COHP (Crystal Orbital Hamilton Population) analysis [4] help in explaining various bonding properties. To estimate preferred atomic pathways, the NEB (nudged elastic band) method is the right choice, in particular for looking at the anions in oxygen-conducting materials [5]. Finally, thermochemical properties may be calculated from first principles but only with a large computational load [6].

For example, we have investigated the properties of the oxygen conductor $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF). The role of the cation arrangements and the location of the oxygen vacancies have been evaluated by bond-analytical tech-niques. The latter are preferentially located close to cobalt instead of iron due to different oxygen affinities. These findings mirror results from XANES measurements [5]. Moreover, it could be shown that the cations in BSCF in-deed prefer a specific arrangement. By comparing the activation energies of possible different hopping processes, it is possible to identify a preferred minimum-energy oxygen pathway in orthorhombic BSCF. This path is character-ized by a correlation between the effective coordination number (ECoN) and the calculated energy: the lower the ECoN and the weaker the chemical bonding of the migrating oxygen atoms, the higher the energy. Also, the energy barriers appear to be slightly smaller when the oxygen atom passes an iron atom instead of a cobalt atom.

At last we have examined the structural stability of BSCF via phonon calculations. These were carried out to achieve a thermodynamic analysis of B-site substituted BSCF as a function of temperature.

References

[1] J Solid State Chem 176(2), (2003), Special issue on The Impact of Theoretical Methods on Solid-State Chem-istry.
[2] J Comput Chem 29(13), (2008), Special Issue: Computational Solid State Chemistry.
[3] R. Dronskowski, Computational Chemistry of Solid State Materials, Wiley-VCH, Weinheim, New York 2005.
[4] R. Dronskowski, P. E. Blöchl, *J. Phys. Chem.*, 97, (1993), 8617.
[5] M. Lumeij, J. Koettgen, M. Gilleßen, T. Itoh, R. Dronskowski, Solid State Ionics 222-223 (2012), 53.
[6] R. Stoffel, C. Wessel, M.-W. Lumey, R. Dronskowski, Angew. Chem. Int. Ed. 49, (2010), 5242.

L-17

Plasma Spray-Physical Vapor Deposition (PS-PVD) of thin film oxygen and proton conducting membranes on porous metallic supports

R. Vaßen[1], M. O. Jarligo[1], A. Comite[2], P. Pinacci[3], J. Serra[4], L. Wimbert[5]
[1]*Institut für Energie- und Klimaforschung (IEK-1), Forschungszentrum Jülich GmbH, Jülich, Germany*
[2]Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, 16146 Genoa, Italy
[3] RSE SpA, Via Rubattino 54, 20134 Milan, Italy
[4]Instituto de Tecnología Química, UPV-CSIC, C/ Camino de Vera, s/n, Valencia 46022, Spain
[5]GKN Sinter Metals Engineering GmbH, Krebsöge 10, 42477 Radevormwald, Germany
E-mail: r.vassen@fz-juelich.de

Keywords: Plasma Spray – Physical Vapor Deposition, gas separation membranes, metallic supports

Dense oxygen and proton-conducting ceramic membranes allow ion diffusion through a solid ceramic lattice, resulting in high selectivity. Oxygen and proton transport membranes are attractive due to their potential applications for high-purity oxygen and hydrogen production and for carrying out catalytic reactions at elevated temperatures. In addition, these membranes have the possibility to be integrated into power generation cycles in order to improve the energy efficiency and to address the carbon dioxide zero emission challenge.

Thin membranes need a support structure which is often made of porous ceramics manufactured by conventional ceramic processes. Also the use of metallic supports has recently been investigated as they show several advantages such as higher ductility and the use of potentially easier sealing technologies. However, the fabrication of dense membranes on metallic supports is rather difficult via conventional sintering routes due to the typically non-shrinking substrates and the limited available sintering conditions. In the frame of the 7FP European project DEMOYS "Dense membranes for Oxygen and Hydrogen transportation" a new deposition technique, "Plasma Spray – Physical Vapor Deposition (PS-PVD)" is investigated as a new deposition route for the thin membranes on porous metallic supports. The presentation will give an introduction to the process and will show the promising results obtained with this route. Highly dense oxide conduction membranes based on a $La_{1-x}Sr_xFe_{1-y}Co_yO_3$ perovskite with good permeation rates could be produced by the process.

L-18

New pathways for ceramic supports and membrane manufacturing: from powders and colloids to functional membranes

Christian Guizard
Institut Européen des Membranes (UMR CNRS/UM2/ENSCM)
Université de Montpellier2, Place Eugène Bataillon, 34095 Montpellier cedex 5, France

Since their early development, the geometrical and structural characteristics of ceramic membrane elements have changed significantly. Originally, they were prepared as single tubes with an inside diameter ranging from ~6 to 15 mm and a wall thickness of about 2 mm. The main handicaps with such tubular geometry are the high element volume to membrane surface ratio and the high liquid flow required for module feeding. The problem was solved by developing multichannel geometries. Actually, channels of a few millimetres in diameter minimize both the volume to membrane surface ratio and the feed flow inside the modules. Recently, monolithic structures with a high density of cells and thin walls led to much larger hydraulic section and high membrane surface per element. Such an evolution of element geometry has resulted in a significant improvement of the filtration capability of ceramic membranes. The structure of these membranes results from the extrusion and sintering of a ceramic paste for the substrate and coatings of powder slurries or colloidal suspensions for the supported membrane. Volume flux with these membranes can be consistently described by the Kozeny-Carman relationship, which corresponds to a system of close packed spheres. However this multi-layers structure do not fully satisfy the requirements of new applications areas for ceramic membranes such as nanofiltration, gas and vapor separation, catalytic membrane reactors, contactors and distributor. Specific substrate and membrane structures are needed, and subsequently adaptation of manufacturing technologies.

A number of hurdles still need to be overcome in order to develop efficient and robust ceramic membranes for applications other than liquid filtration. The conventional structure of ceramic membranes made of the superposition of different sintered layers on a porous substrate becomes problematic where high temperature processes are required, mainly because of thermal and chemical expansion coefficients. Moreover the porous structure of the substrate can be a limitation to gas diffusion for dense ion conducting supported membranes. In other respects, supported membranes with a microporous or dense structure must be produced which cannot be obtained from powder suspensions. Chemical modification of membrane layers is also of interest to control solid/liquid or gas interactions in membrane contactors or distributors. All this means that new technologies have been or will be introduced in the short term for ceramic membrane manufacturing.

The presentation will seek to identify recent progress in ceramic membrane preparation with relevant examples of new manufacturing pathways. Ceramic hollow fibers and capillaries prepared from ceramic pre-polymers offer a real opportunity for non-oxide membranes development in view of gas separation at high temperature. Ice templating is a very innovative technique allowing the creation of a hierarchical porosity in homogeneous ceramic materials, thus minimising the problem of multiple expansion coefficients encountered with multilayers ceramic structures. The supported membranes itself can also take advantage of a number of coating techniques such as CVD, self-assembled layer deposition, supercritical CO_2 assisted sol-gel deposition or microwave assisted zeolite layer growth.

L-19

Development of thin film supported tubular membranes for high temperature gas separation

Marie-Laure Fontaine, Paul Inge Dahl, Xing Wen, Jonathan Polfus, Yngve Larring, Ove Paulsen,
Christelle Denonville, Partow P. Henriksen and Rune Bredesen
SINTEF Materials and Chemistry, Sustainable Energy Technology,
POB 124 Blindern, NO-0134 Oslo Norway
Email: marie-laure.fontaine@sintef.no
Keywords: gas separation membranes, extrusion, sintering, fillers

Dense inorganic membranes are prospected for the selective separation of oxygen from air for power generation. Transport of oxygen from one side of the membrane to the other occurs through bulk diffusion in the lattice of the mixed oxygen ion and electronic conducting material. Both membrane thickness and kinetics of oxygen surface exchange contribute to determine the oxygen flux across the membrane. The membrane is therefore typically designed as an asymmetric structure with a thin dense layer coated on a mechanically strong porous support. For commercial deployment of this technology, low cost reliable membrane processing and compatible sealing technology for module fabrication should be developed.

The present work reports on the fabrication of asymmetric membranes with length up to 45 cm after sintering. Another part of the work not described here, is focused on the optimization of the flux of the oxygen membrane materials.

Porous ceramic tubes of $CaTi_{0.9}Fe_{0.1}O_{3-\delta}$ (CTF) perovskite oxide are produced by water-based extrusion with ca. 50 cm length and 1.5 mm wall thickness. Pyrolyzable pore formers are used to tailor their porosity. The green tubes are heat-treated in air with careful monitoring of the debinding step to achieve sufficient mechanical strength. The thin selective layer is then deposited by dip-coating using a colloidal ceramic suspension. A final sintering step is carried out to obtain the desired asymmetric membranes with length ranging from 30 cm to 45 cm (Fig. 1). Within this manufacturing route, several parameters are adjusted to monitor thickness, grain size, porosity (pore size, volume and distribution) and texture of the two layers. This will be illustrated by means of several structural and microstructural techniques applied for the thorough characterization of the produced membranes.

In order to evaluate the oxygen flux of the membranes, a sealing procedure has been developed which entails the preparation of dense CTF caps for closing off one side of the membranes and the development of a glass ceramic seal compatible with CTF materials and the support tubes of the permeation modules. The latter are made of alumina or various steels (Kanthal APM, C454…).

Flux measurements are carried out in various atmospheres in order to study the transport properties of the produced membranes under relevant operating conditions.

The results of these studies are used to establish correlations between membrane characteristics and oxygen flux which will be discussed and summarized in this presentation.

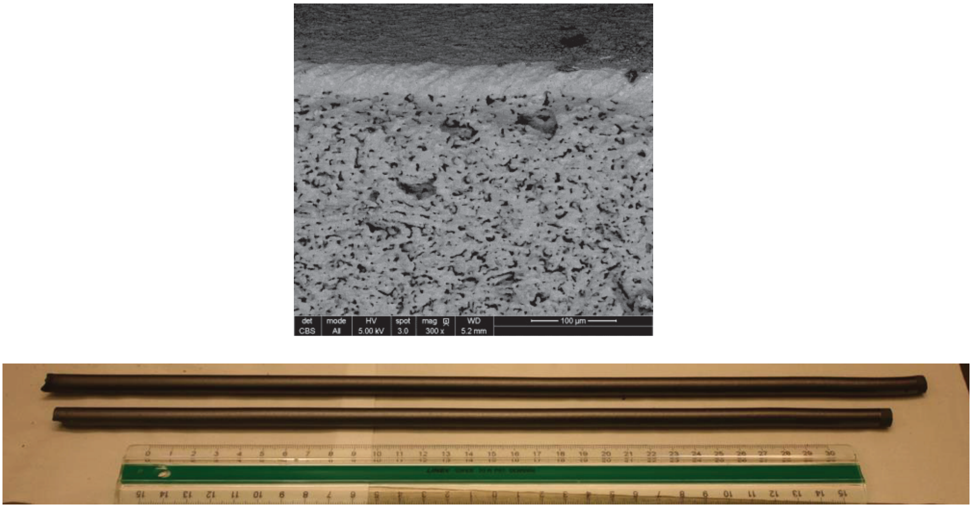


Fig. 3. SEM micrograph in cross-section view of asymmetric membrane (top). Camera picture of asymmetric membranes (bottom).

L-20

Thin-film manufacturing of inorganic oxygen transport membranes by physical vapor deposition

S. Uhlenbruck, S. Baumann, D. Sebold, H.P. Buchkremer
Institute of Energy and Climate Research (IEK-1), Forschungszentrum Jülich GmbH
52425 Jülich, Germany
Email: s.uhlenbruck@fz-juelich.de

Keywords: oxygen transport membrane, physical vapor deposition

Gases with high oxygen content or even pure oxygen can be used in certain future power plants for the combustion process (e.g. so-called OXYFUEL process), or in e.g. production processes in glass and cement industry. Inorganic membrane systems are considered as an efficient way to separate oxygen from air. It is evident that – as long as materials with extremely high oxygen permeation are not available – high oxygen fluxes through a membrane require *thin* membranes.

This paper discusses the manufacturing of thin inorganic oxygen transport membranes by physical vapor deposition (PVD). After a short review of the technology in general, the focal point of the presentation are ion-assisted techniques for the deposition of ceria-, zirconia- and perovskite-based oxygen transport membranes. Ion-assisted processes lead to layers with high density but also to higher compressive stresses, which the entire arrangement has to sustain. As a major finding from the experiments, a balancing of layer density and mechanical stress is necessary. Moreover, it is illustrated that the surface morphology of the substrate crucially determines the morphology of the PVD layers.

L-21

Advanced deposition techniques for thin films and membranes

Gemma Garcia
Department of physics, Universitat Autònoma de Barcelona
Campus UAB, 080193 Bellaterra
Email: gemma.garcia@uab.cat

Keywords: thin films, deposition techniques, vapor phase

In this lecture we will review general concepts in thin film growth as well as recent advances in deposition techniques, mainly from the vapour phase, physical (PVD) and chemical (CVD) vapour deposition techniques.

Description of the experimental parameters involved in thin films microstructure control, from amorphous to epitaxial films, will be discussed and compared as a function of the selected process.

Particular emphasis will be put in summarising processes used for preparing thin films and membranes in gas conductive and/or permeating applications.

L-22

Advances in the synthesis of dense hollow fiber/capillaries for oxygen and hydrogen separation

Frans Snijkers, Vesna Middelkoop, Marijke Jacobs, Marijn Gysen, Ivo Thijs, Steven Mullens and Bart Michielsen
Unit Sustainable Materials Management,
Flemish Institute for Technological Research (VITO)
Boeretang 200, 2400 Mol, Belgium
Email: frans.snijkers@vito.be
Keywords: hollow fiber, capillary, gas separation, oxygen separation, MIEC

Dense ceramic membranes with mixed oxygen-electronic or mixed proton-electronic conductivity at high temperatures have a significant potential in gas separation or catalytic membrane reactors in energy or basic chemicals production. Shaping of these membranes in the form of hollow fibers or capillaries offers interesting advantages over other mem-brane geometries in view of their surface to volume ratio.

The presentation will give a short overview of the phase inversion technique and the process parameters that are im-portant to make high-quality hollow fiber/capillary membranes. Up to now the typical binder used world-wide in this process is polysulphone or polyether sulphone. Research at VITO has shown that this binder reacts with typical ele-ments of many of the mixed ion electron (MIEC) conducting ceramics (e.g. La, Ba, Sr) producing sulphates. These sulphates create considerable surface exchange limitations in capillaries made with the traditional phase inversion pro-cess. So, it is preferred to use a phase inversion process with a sulphur-free binder. Oxygen permeation measurements of hollow fibers and capillaries synthesized with the S-free binder, show clearly bulk performance (>850°C), which is also very similar to the performance of pressed pellets. [1,2] Further research has been devoted to the effect of activation layers applied on the capillary wall. The effects of surface enhancement by spray coating of such activation layers are shown by comparative oxygen permeation measurements. [3,4]

References

[1] C. Buysse, A. Kovalevsky, F. Snijkers, A. Buekenhoudt, S. Mullens, J. Luyten, J. Kretzschmar, S. Lenaerts, "Development, performance and stability of sulfur-free, macrovoid-free BSCF capillaries for high temperature oxygen separation from air", *Journal of Membrane Science*, *Vol. 372, Iss. 1–2*, *15 April 2011*, *p. 239-248.*

[2] Jasper Van Noyen, Vesna Middelkoop, Cédric Buysse, Andrei Kovalevsky, Frans M.M. Snijkers, Anita Buekenhoudt, Steven Mullens, Jan Luyten, Jan Kretzschmar, Silvia Lenaerts, "Fabrication of perovskite capillary mem-branes for high temperature gas separation", *Catalysis Today*, *Vol.193, Iss. 1*, *15 October 2012*, *p. 172-178.*

[3] A.V. Kovalevsky, A.A. Yaremchenko, V.A. Kolotygin, A.L. Shaula, V.V. Kharton, F.M.M. Snijkers, A. Buekenhoudt, J.R. Frade, E.N. Naumovi; "Processing and oxygen permeation studies of asymmetric multilayer $Ba0.5Sr0.5Co0.8Fe0.2O3-\delta$ membranes", *Journal of Membrane Science*, *Vol. 380, Iss.1–2*, *15 September 2011*, *p. 68-80.*

[4] Bart Michielsen, Marijke Jacobs, Marijn Gysen, Ivo Thijs, Vesna Middelkoop, Steven Mullens and Frans Snijkers, *to be published.*

L-23

Graded membranes for energy efficient new generation carbon capture process – GREEN CC

Wilhelm A. Meulenberg,
Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research IEK-1, D-52425 Jülich, Germany
Email: w.a.meulenberg@fz-juelich.de

Major sources for human made CO_2 emissions comprise the energy and the industrial sector including cement production. One of the most appropriate concepts to capture CO_2 from such point sources is the oxyfuel combustion. The main energy demand for this method results from the O_2 generation, which is usually done by air liquefaction. This energy demand can substantially be lowered using thermally integrated separation modules based on ceramic oxygen transport membranes (OTM). It is least if the OTM is integrated in a 4-end mode, which entails that the permeating oxygen is swept and directly diluted using recirculated flue gas. Up to 60% reduction in capture energy demand compared to cryogenic air separation and up to 40% reduction compared to post-combustion capture approaches can be achieved.

The EC FP-7 funded Project GREEN-CC (01.09.2013 - 31.08.2017) is coordinated by Forschungszentrum Jülich. The project is carried out by the scientific organisations Forschungszentrum Jülich (Germany), Consejo Superior de Investigaciones Científicas Valencia (Spain), Imperial College London (Great Britain), ISSP, University of Latvia (Latvia), Ricerca sul Sistema Energetico – RSE S.P.A. (Italy), RWTH Aachen University (Germany), Technical University of Denmark (Denmark), University of Twente (Netherlands), University of Queensland (Australia) and the industrial companies H.C. Starck Ceramics GmbH (Germany), Instalaciones Inabensa, S.A. (Spain), Shell (Netherlands), Linde AG (Germany), Thyssen Krupp Resource Technology (Germany) and Elcogas (Spain).

GREEN-CC will provide a new generation high-efficiency capture process based on oxyfuel combustion. The focus lies on the development of clear integration approaches for OTM-modules in power plants and cement industry considering minimum energy penalty related to common CO_2 capture and integration in existing plants with minimum capital investment. This will be attained by using advanced process simulations and cost calculations. GREEN-CC will also explore the use of OTM-based oxyfuel combustion in different highly energy-demanding industrial processes, e.g. oil refining and petrochemical industry.

However, highly permeable membrane materials show a chemical instability against CO_2 and other flue gas components. One major challenge faced by GREEN-CC is therefore to identify and develop stable membrane materials, components, and a PoC-module for the 4-end mode OTM integration. The desired membrane assembly will consist of a thin membrane layer supported on substrates with engineered porosity and oxygen reduction catalysts with high and stable activity in flue gas. As proof of concept, a planar membrane module will be developed which involves technical hurdles like joining technology.

L-24

Highly efficient tubular membranes for oxy-combustion; highlights from the EU-FP7 project HETMOC

Peter Vang Hendriksen
Department of Energy Conversion and Storage, Technical University of Denmark
Frederiksborgvej 399, DK-4000, Roskilde, Denmark
Email: pvhe@dtu.dk

Keywords: Oxygen separation membrane, HETMOC, tubular membranes

In the EU-FP7funded project “HETMOC” five academic partners and three industries have teamed up to develop and demonstrate improved tubular membranes for oxy-combustion. The partners of the consortium are; DTU Energy Conversion (DTU, Denmark), Forschungszentrum Jülich, (JÜLICH, Germany), Fraunhofer-Institut für Keramische Technologien und Systeme (FRAUNHOFER IKTS, Germany), Foundation for Scientific and Industrial Research at the Norwegian Institute of Technology (SINTEF, Norway), Flemish Institute for Technological Research, (VITO, Belgium), AIR LIQUIDE, (AIR LIQUIDE, France), Saint Gobain CREE, (SAINT GOBAIN CREE, France), Installaciones Inabensa, S.A., (INABENSA, Spain).

The project focuses on up-scale and demonstration of tubular asymmetric thin film membranes from the current lab-scale level to a level, where the membranes are manufactured by up-scalable techniques at industrial partners on a pre-pilot scale. Further, a multi-tube medium sized Proof-of-concept module is being constructed for high pressure test of the membranes. In this module critical issues such as sealing are in focus. The project further involves design studies, a cost assessment and a safety analysis. An engineering design of a 100 TPD module will be prepared.

At this time the project is close to mid-term. Tubular membranes based on two very different candidate membrane materials have been developed and tested in the consortium; Line 1 is based on Zr-doped-$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ and Line 2 on an Fe-doped calcium-titanate. These materials represent in a sense “extremes” among membrane materials currently under study; the line one material is characterized by very good transport properties but ensuring sufficient mechanical robustness is a challenge. Moreover, human safety issues with handling of Co must be observed during manufacture. The latter material is based on abundant (cheap) elements and poses no problems in terms of human safety during handling and manufacture. However, the ionic conductivity in the material is limited and hence the challenges with membranes in this material are very stringent requirements to membrane thickness and to the module design, which has to allow for high temperature operation.

The talk will present the strategy behind the project as well as technical and scientific highlights from the project.

L-25

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

Pietro Pinacci
RSE S.p.A.
Via Rubattino 54, Milano 20134, Italy
Email: pietro.pinacci@rse-web.it

Keywords: oxygen transport membranes; mixed conductors; plasma spraying; CO_2 capture.

This lecture provides an overview of objectives, structure and main 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 fourteen Partners, including three Universities, five Research Organizations and six 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, catalytic layers.

PS-TF is a proprietary technology developed by Sulzer, which stands between the conventional thin film technologies, such as Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD), and the conventional thermal spray technologies (see Fig. 1). PS-TF (also LPPS-TF) operates at a low pressure (around 1-2 mbar), thus allowing the fast deposition (faster than in the common PVD or CVD spraying techniques) of large areas (up to 1 m).

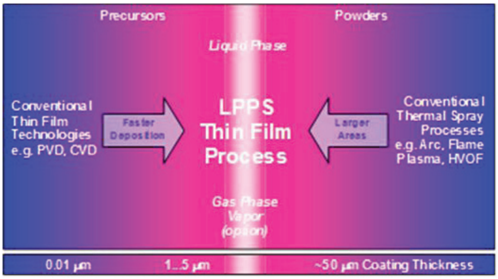


Fig. 1 Comparison of the main characteristics of thin film and thermal spray deposition technologies.

In DEMOYS both ceramic and metallic substrates are used for deposition. it is expected that, by using the PS-TF process, a dense, stable deposit with thickness below 30 µm can be obtained.

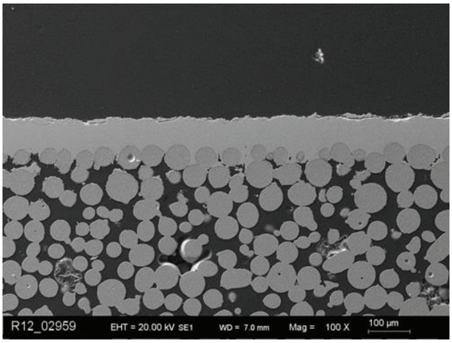


Fig. 2 Micrograph of LSCF deposited on a porous metallic substrate.

This would allow increasing membrane performances while decreasing their manufacturing costs. Catalytic layers are also applied to enhance the surface reactions becoming rate limiting for thin membranes. Membrane performances are assessed in pilot loops in order to meet specific targets in terms of permeability and stability at temperature. A modeling study concerning the integration of the developed membranes in power and hydrogen production plants is also performed. This provides inputs for process scale-up and cost evaluation in the selected plant configurations in order to approach zero CO_2 emission and lower CO_2 capture cost.

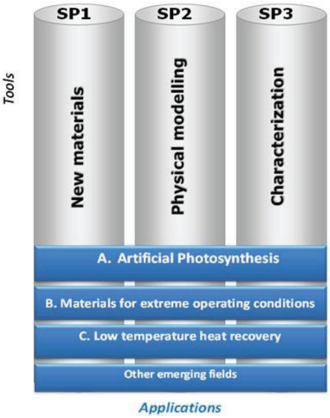
Acknowledgements
DEMOYS receives funding from the European Community's Seventh Framework Programme, FP7/2007-2013, under grant agreement n^o 241309.

L-26

Advanced Materials and Processes for Energy Applications (AMPEA) A joint programme from the European Energy research Alliance (EERA) focussed on basic science for energy

Frédéric Chandezon
Institute For Nanoscience and Cryogeny (INAC)/SPrAM (UMR 5819 CEA-CNRS-Univ. J. Fourier-Grenoble) CEA Grenoble - 17 Rue des Martyrs - F- 38054 Grenoble Cedex 9 - France
E-mail: frederic.chandezon@cea.fr

Implementing a basic science programme for energy is one of the key roles assigned to EERA by the European Commission in the frame of the European Strategic Energy Technology Plan (SET-Plan). The EERA comprises 15 Joints Programmes (JP) of areas relevant to energy challenges. Basic science is often presented as crucial in generating the breakthroughs needed to bring new generations of technologies to the market. The aim of the EERA-JP AMPEA is to foster a truly multi-disciplinary approach to develop enabling tools and new concepts for future emerging energy technologies.



The mission statement of AMPEA states that it has to develop new horizons for science for energy, visible in Europe at the industrial and political level. Thus the main objective is to harness and integrate materials science and process innovation for high performance sustainable energy technologies, in order to enhance the long-term competitiveness of European Industry. AMPEA will work in close coordination with other EERA-JPs and with Universities (European Platform Of Universities Engaged In Energy Research - EPUE) to bridge fundamental and applied research fields. AMPEA presently gathers approximately 43 public research organizations and universities from 154 European countries.

In order to fulfill this mission, AMPEA is organized in a matricial way with the aim of applying the capacity of 3 "tools" sub-programmes (SPs) corresponding to generic research areas to "applications" SPs related to known emerging energy challenges and domains (see Figure). There are presently 3 identified "applications" SPs, the first being artificial photosynthesis, *i.e.* the ability to efficiently convert large amounts of solar energy into easily usable and storable chemicals, by mimicking nature or by plain engineering. Other "applications" SPs will be added as they are identified and defined by the AMPEA and more generally by the EERA members.

References :

Web page SET-Plan : http://ec.europa.eu/energy/technology/set_plan/set_plan_en.htm
Web page of EERA : www.eera-set.eu

L-27

CARENA -Catalytic membrane reactors based on new materials for C1-C4 valorization

Arend de Groot,
Biomass and Energy Efficiency, ECN
Westerduinweg 3, 1755 LE Petten, The Netherlands
Email: a.degroot@ecn.nl

Keywords: membrane reactors, process integration, chemical industry, alkanes

There is a widening gap between the predicted demand for oil and known oil reserves driven amongst other by the growth of new economies like China and India. The chemical industry in Europe, relying for more than 70% on imported oil, may be particularly affect by the increasing demand. Europe actively considers novel feeds such as natural gas, coal and biomass to stay competitive. The chemical industry needs technologies that are able to use as feedstocks light alkanes and CO_2. However, light alkanes and CO_2, in contrast to long-chain hydrocarbons from oil, are stable molecules that are difficult to activate and transform directly and selectively to added value products.

One of the most promising technologies to innovate the chemical industry are membrane reactors. Within the CARENA project 17 partners work together to create breakthroughs on a number of routes from C1-C4 alkanes to platform chemicals. Advances in nanotechnologies are used to improve membranes, catalysts and membrane reactors. Three different feedstocks are considered.

- **Methane** is used in the current chemical industry as a feedstock for production of hydrogen and base chemicals such as methanol and ammonia. However, converting methane into more reactive molecules such as methanol and ammonia requires energy intensive processes. Two routes towards more efficient processing are investigated within the project:
    - The project aims to demonstrate on a scale of several Nm^3/h a fully integrated membrane reactor for hydrogen production using palladium membranes. Innovative proton conducting membranes are developed and tested for this application as well
    - Direct routes from methane investigated in the project include oxidative coupling and direct methane-to-methanol conversion.
- A very innovative scheme from **propane** to acrylic acid is investigated. In this scheme a membrane reactor for propane dehydrogenation is used to produce a propane/propylene mixture which is fed to an propylene oxidation reactor thus avoiding the use of a very energy consuming P/P splitter. Many innovative process steps are developed, including for the selective oxidation of carbon monoxide.
- Reuse of **carbon dioxide** receives much attention. CARENA investigates two routes which could greatly enhance reuse of CO_2 in the chemical industry: direct conversion of CO_2 into dimethyl carbonate (DMC) and methanol (MeOH). As both reactions are strongly limited by equilibrium, the use of membrane reactors is of special interest. Through lab-scale testing of a system integrating both catalyst and membranes, the project focuses on delivering the proof-of-principle for membrane reactors in these applications.

The CARENA project investigates a wide range of different membranes and aspects. Materials include palladium alloys, proton conducting materials, zeolites, perovskites for oxygen conducting membranes, organic and hybrid membranes. But the focus is not limited to material development. Fundamental understanding of transport mechanisms, up-scaling of membrane fabrication, sensitivity to poisoning are important issues address in the project to obtain commercially viable membrane technology. The presentation will give an overview of the CARENA project goals and the membrane research. It will furthermore address the challenges in integrating reaction and separation in a membrane reactor.

L-28

Design and manufacturing of catalytic membrane reactors by developing new nano-architectured cata-lytic and selective membrane materials (DEMCAMER)

José Luis Viviente
Materials for Energy and Environment, Fundación Tecnalia Reseach & Innovation
Mikeletegi Pasealekua 2, E-20009, Spain
Email: joseluis.viviente@tecnalia.com
Keywords: multifunctional Catalytic Membrane Reactors, Autothermal reforming, Fischer Tropsch, Water Gas Shift, Oxidative Coupling of Methane

Process Intensification (PI), which is defined as "any chemical engineering development that leads to a substantial-ly smaller, cleaner, safer and more energy efficient technology", is likely to be the next revolution of the chemical in-dustry. The need for more efficient processes, including further flexible engineering designs and, at the same time, increasing the safety and environmental impact of these processes, is pushing the industry to novel research in this field. The chemistry and related sectors have already recognised the benefits of PI and estimate a potential for energy saving of about 1000 kilo tonnes of oil equivalent (toe) per year using these processes.

The technology of membrane reactor plays an important role in PI and is based on a device combining a membrane based separation and a catalytic chemical reaction in one unit. Every catalytic industrial process can potentially benefit from the introduction of catalytic membranes and membrane reactors instead of the conventional reactors. According to SusChem (European Technology Platform for Sustainable Chemistry, Strategic Research Agenda 2005) more than 80% of the processes in the chemical industry worth approximately €1,500 billion, depend on catalytic technologies, and one the shorter-term (5-10 years) objectives of this Platform is to "integrate reactor-catalyst-separation design: integration and intensification of processes requires the development of new catalytic concepts which break down the current barri-ers (for example, low flux in catalytic membranes)".

The DEMCAMER FP7 project (www.demcamer.org) proposes an answer to the paradigm met by the European Chemical Industry: increase the production rate while keeping the same products quality and reducing both production costs and environmental impacts. Through the implementation of a novel process intensification approach consisting on the combination of reaction and separation in a "Catalytic Membrane Reactor" single unit.

The aim of DEMCAMER project is to develop innovative multifunctional Catalytic Membrane Reactors (CMR) based on new nano-architectured catalysts and selective membranes materials to improve their performance, cost effec-tiveness (i.e.; reducing the number of steps) and sustainability (lower environmental impact and use of new raw materi-als) over four selected chemical processes ((Autothermal Reforming (ATR), Fischer-Tropsch (FTS), Water Gas Shift (WGS), and Oxidative Coupling of Methane (OCM)) for pure hydrogen, liquid hydrocarbons and ethylene production.

The DEMCAMER scheduled work plan will comprise activities related to the whole product chain: i.e. develop-ment of materials/components (membranes, supports, seals, catalyst,..) through integration/validation at lab-scale, until development/validation of four semi-industrial pilot scale CMRs prototypes.

Additionally, three research lines dealing with: 1) the collection of specifications and requirements, 2) modelling and simulation of the developed materials and processes, and 3) assessment of environmental, health & safety issues -in relation to the new intensified chemical pro-cesses- will be carried out.

For a maximum impact on the European industry this research, covering the complete value chain of catalytic membrane reactors, can only be carried out with a multidisciplinary and complementary team having the right expertise, including top level European Research Institutes and Universities (8 RES) working together with representative top industries (4 SME and 6 IND) in different sectors (from raw materials to petrochemical end-users).

Acknowledgements

The research under this project is receiving funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° NMP3-LA-2011-262840.

Disclosure

Then present document reflects only the author's views and the Union is not liable for any use that may be made of the information contained therein.

Advanced multi-fuel reformer for CHP-fuel cell systems (ReforCELL)

Keywords: Micro Combined Heat and Power, m-CHP, ATR, reformer, Fuel Cell, catalytic membrane reactor, BoP

Distributed power generation via Micro Combined Heat and Power (m-CHP) systems, has been proven to over-come disadvantages of centralized plant since it can give savings in terms of Primary Energy consumption and energy costs. The main advantage is that m-CHP systems are able to recover and use the heat that in centralized systems is often lost. Wide exploitation of these systems is still hindered by high costs and low reliability due to the complexity of the system.

ReforCELL(www.reforcell.eu) aims at developing a high efficient heat and power cogeneration system based on: i) design, construction and testing of an advanced reformer for pure hydrogen production with optimization of all the components of the reformer (catalyst, membranes, heat management etc) and ii) the design and optimization of all the components for the connection of the membrane reformer to the fuel cell stack.

The main idea of ReforCELL is to develop a novel more efficient and cheaper multi-fuel membrane reformer for pure hydrogen production in order to intensify the process of hydrogen production through the integration of reforming and purification in one single unit. To increase the efficiency and lifetime of the reformer, novel stable catalysts and high permeable and more stable membranes will be developed. Afterwards, suitable reactor designs for increasing the mass and heat transfer will be realized and tested at laboratory scale. The most suitable reactor design will be scaled up at prototype scale (5 Nm3/h of pure hydrogen) and tested in a CHP system.

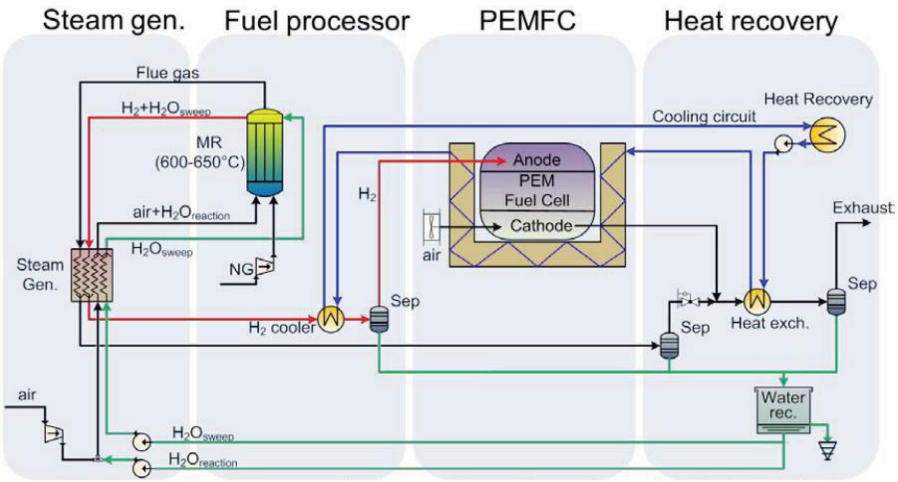


Fig. 1. Layout of PEM m-CHP unit using membrane reformer (MREF) for fuel processing

The connection of the novel reformer within the CHP will be optimized by designing heat exchangers and auxilia-ries required in order to decrease the energy losses in the system. The project aims to increase the electric efficiency of the system above 42% and the overall efficiency above 90%. Besides, a complete lifecycle analysis of the system will be carried out and cost analysis and business plan for reformer manufacturing and CHP system will be supplied.

Acknowledgements

This project is supported by the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement nº 278997.

Disclosure

The present publication reflects only the author's views and the FCH JU and the Union are not liable for any use that may be made of the information contained therein.

L-29

Metal Silica Membranes for Hydrogen Separation

J. C. Diniz da Costa
FIMLab – Films and Inorganic Membrane Laboratory
School of Chemical Engineering, The University of Queensland, Brisbane Qld 4072, Australia
Email: j.dacosta@eng.uq.edu.au

The sol-gel process is a versatile tool in pore size tailoring, particularly in the ultra micropore range (d_p<5Å). Lately, the embedding of metal oxides into silica films has opened a window of research opportunities for the preparation of high performance membranes. In this work, we discuss the role played by crystalline single and binary metal oxide particles assembly in amorphous silica films in terms of the formation of porous structures and silica functional groups. In addition, we report on the effect of surfactant functionalization in changing the oxidation state of metal oxides embedded in the silica matrix. This will be followed by new reports on the employment of pre-hydrolysed ES40 as a silica precursor instead of TEOS.

ES40 combined with metal oxides delivers a switchable gas permeation performance depending on the redox state of the membrane. This novel effect is attributed to a molecular gap created by the partial reduction and oxidation of metal oxides within the ES40 derived silica structure. Apart from separating H_2 from the other gases, these membranes can also separate CO_2 from N_2 which is quite rare in the case of silica membranes. In addition, ES40 is an ideal precursor for rapid thermal processing (RTP) scale up, where membrane tubes can be synthesised in a single day, instead of TEOS which generally takes up to 10 days for the processing of high quality membranes.

L-30

Non-oxide molecular sieve membranes for gas separation

M. Haacké, V. Rouessac, R. Coustel, M. Drobek, S. Roualdès, J. Durand, A. Julbe
Institut Européen des Membranes (ENSCM-UM2-CNRS UMR5635), Université Montpellier
(cc047) Place Eugène Bataillon, 34095 Montpellier cedex 5, France
Email: anne.julbe@univ-montp2.fr
Keywords: PECVD, thin film, silicon carbonitride

Non-oxide ceramic membranes based on silicon carbide and silicon carbonitride recently received significant attention in the membrane community, for both liquid and gas phase applications. The main advantages of silicon carbide include not only a combination of strength, thermal and chemical stability at high temperature, especially under hydrothermal conditions, but also functional properties such as semi-conductivity, photoluminescence and piezoresistivity. When considering these non-oxide materials as membranes for liquid phase separations, an impressive flux enhancement and low fouling resistance have been announced for macro- and mesoporous SiC-based membranes in comparison with classical oxides. In addition, SiC-based microporous membranes with molecular sieving properties were revealed to be attractive materials for hydrogen separation in the presence of steam.

Both Chemical Vapor Deposition (CVD) [1] and Polymer Derived Ceramic (PDC) [2] approaches have been considered in the literature for the preparation of molecular sieve SiC-based membranes. In our group a versatile strategy has been developed [3] which is based on Plasma Enhanced Chemical Vapour Deposition (PECVD). A typical FESEM observation of a thin amorphous silicon carbonitride membrane prepared by PECVD is shown in figure 1. Both hexamethyldisilazane (HMDSN) and ammonia have been used as precursors to control the deposition of a-SiCN:H thin molecular sieve layers on either flat or capillary ceramic supports with asymmetric pore structure. The plasma operating parameters, feed composition and post-treatments have been demonstrated to drastically impact the composition and microstructure of the membranes, their thickness, quality, oxidation degree, steam resistance and molecular sieving properties. A series of physico-chemical characterisation methods have been used to optimize the material microstructure and composition in relation with the plasma deposition parameters and with the gas permeation performance of the membranes up to 400°C. Helium permeance typically reached 5.10^{-7} $mol.s^{-1}.m^{-2}.Pa^{-1}$ at 300°C and 1 bar trans-membrane pressure; the associated He/N_2 and He/CO_2 permselectivities were 150 and 80, respectively. This presentation will point out the potential and limitations of the PECVD strategy for preparing efficient molecular sieve membranes for either H_2 or He separations.

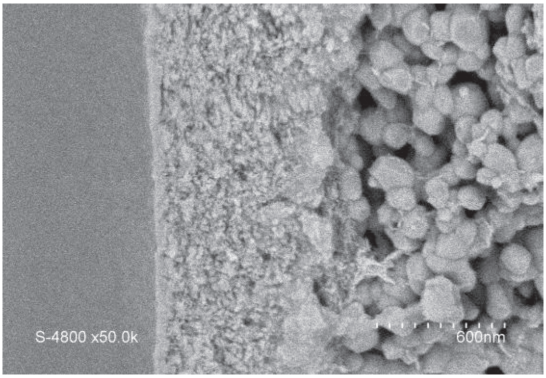


Fig. 4. FESEM observation of a silicon carbonitride molecular sieve membrane deposited by PECVD on a porous alumina support.

Acknowledgements

Part of this research work was funded by the French FUI, the region of Languedoc-Roussillon and OSEO Innovation (MISHY project).

References

[1] Ciora R.J., Fayyaz B., Liu P.K.T., Suwanmethanond V., Mallada R., Sahimi M., Tsotsis T.T., Chem. Eng. Sci. 59 (2004) 4957-4965.
[2] Elyassi B., Sahimi M., Tsotsis T.T., J. Membr. Sci. 316 (2008) 73-79.
[3] Kafrouni W., Rouessac V., Julbe A., Durand J., J. Membr. Sci. 329 (2009) 130-137.

L-31

Zeolite membranes for energy efficient separations in bio processes and power generation

Hannes Richter, Christiane Günther, Jan-Thomas Kühnert, Marcus Weyd, Ingolf Voigt
Fraunhofer Institute for Ceramic Technologies and Systems (IKTS), Department Nanoporous Membranes
Michael-Faraday-Straße 1, 07629 Hermsdorf, Germany
Email: hannes.richter@fraunhofer.ikts.de

Keywords: zeolite membranes, nanopores, vapour permeation, gas separation

Zeolites are crystalline tectosilicates with defined nanopores. Deposited as a thin layer on top of porous substrates membranes of high selectivity can be obtained.

With a pore size of 0.41 nm zeolite A membranes are perfect candidates for dewatering of organic solvents. A first industrial plant for the dewatering of ethanol was equipped with NaA membranes prepared by the Japanese company Mitsui Engineering and Shipbuilding Co. Ltd. (Mitsui). [1] In Europe inocermic GmbH (today Fraunhofer IKTS – Hermsdorf branch) equipped a first pilot plant for bio-ethanol dewatering by vapour permeation with zeolite membranes in 2007 and an industrial scale plant in 2009. [2]

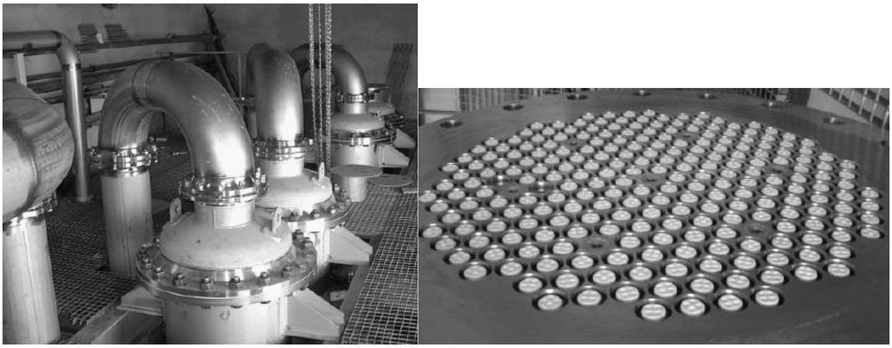


Fig. 1: Industrial pilot plant for dewatering of ethanol with NaA-membranes of Fraunhofer IKTS [2]

Besides the ethanol, several other organic solvents like methanol, propanol and higher alcohols as well as ketones and ethers can be dewatered with NaA-membranes. Today more than 2,000 m² zeolite A membranes are installed for industrial organic solvent dewatering.

With a pore size of 0.38 nm and 0.36 nm CHA and DD3R respectively are interesting candidates for CO_2/CH_4-separation. Very high CO_2/CH_4 mixed gas selectivities of > 100 should allows efficient upgrading of natural gas and bio gas. [3]

Sodalite (SOD) exhibits pore sizes in the range of the molecule diameter of hydrogen (0.29 nm) and water (0.26nm). Therefore SOD membranes are promising candidates for the H_2/CO_2-separation as well as for H_2O-seperation from different gas mixtures. The poore hydrothermal stability of hydroxo-SOD was improved by intercalation of sulfur into the crystal framework. This S-SOD exhibits excellent thermal and hydrothermal stability. Defect free membranes should allow the separation of H_2 from water gas shift reaction (WGS) or the water separation from fisher-tropsch synthesis (FTS).

But not only size exclusion, also preferred adsorption can by used for membrane separation with zeolites. Up-grading of bio-ethanol with silicalite or CO_2-seperation from WGS with ZSM-5 are promising examples. [4]

Acknowledgement

The research leading to these results has received funding from the European Union Seventh Framework Programme (*FP7/2007-2013*) under grant agreement n° 262840 (DEMCAMER). Also Helmholtz Alliance MEM-BRAIN is gratefully acknowledged.

References

[1] Y. Morigami, M. Kondo, J. Abe, H. Kita, K. Okamoto, Separation/Purification technology 25 (2001) 251-260

[2] M. Weyd, H. Richter, J.-Th. Kühnert, I. Voigt, E. Tusel, H. Brüschke, Chemie Ingenieur Technik 2010, 82, No.8, 1257-1260

[3] J. Van den Bergh et al., J. Membr. Sci. 316 (2008) 35

[4] M. Weyd, H. Richter, P. Puhlfürß, I. Voigt, Ch. Hamel, A. Seidel-Morgenstern, Journal of Membrane Science 307 (2008) 239-248

L-32

Tailor-made zeolites for gas separation processes

Miguel Palomino, Susana Valencia, Fernando Rey
Instituto de Tecnología Química, UPV-CSIC
Avda. de los naranjos s/n, 46022 Valencia, Spain
Email: migparo@gmail.com
Keywords: zeolites, adsorption, gas separation

The development of microporous materials with controlled pore openings and large adsorption capacities is of paramount importance for performing selective adsorptions and separations of gases, such as olefin separations, methane storage, CO_2 capture, etc., which are of industrial and/or environmental relevance. A number of selective adsorption or separation processes using these materials are based on selecting the pore aperture that is adequate to the kinetic diameters of the molecules that are attempted to be separated and/or adsorbed [1,2]. However, besides the pore topology other important variable for achieving effective separations is the composition of the adsorbent that is directly related to its polar character, being this is a key feature for each specific separation process. Indeed, in some cases it is required that non-charged materials such as pure silica zeolites are used, whereas in other cases highly polar frameworks are needed.

In this work, we have attempted the design of the most appropriated zeolite adsorbents for several industrially relevant gas separation processes, such as olefins/paraffins, linear/branched hydrocarbons and CO_2/CH_4, taking benefit of the large number of existing zeolite structures and the possibility of preparing them with different compositions.

Olefin–paraffin separations are of particular interest, since the separation of light olefins (ethene, propene and butenes) from light paraffins (ethane, propane and butanes) is currently performed by cryogenic distillation, which is a highly energy demanding process. Therefore, adsorption processes based on selective adsorbents such as zeolites that are able to discriminate between paraffins and olefins are of great interest. For this separation, the most preferred zeolites are those having no acidity to avoid olefin oligomerization that will lead to pore blocking after prolonged time. In particular, pure silica zeolites are the most appropriate as they do not contain acid sites and possess low defects content. We have studied the behavior of several small pore pure silica zeolites in the kinetic separation of propane and propene by measuring the kinetics of adsorption and determining the diffusion parameters. This has allowed us to conclude that these materials are able to perform this separation process, as it was the case of ITQ-32 (IHW) zeolite [3].

Separation of linear from branched hydrocarbons is also an industrially relevant process closely related to technologies for enhancing octane number in gasoline fuels. This separation can be performed by adsorption processes using molecular sieves such as zeolites NaA or CaA (LTA) with a Si/Al ratio of 1. However, if olefins are present in the streams the acidity of these materials will lead again to pore blocking due to oligomerization. Then, we have afforded the study of this process by using as adsorbent the pure silica analogue of LTA (ITQ-29 zeolite) [4] in the adsorption of 1-butene and isobutene. The results showed that pure silica ITQ-29 zeolite was able to adsorb the linear 1-butene, as the kinetic diameter (0.4 nm) is close to the pore aperture of the zeolite, whereas the branched isobutene is adsorbed in very small amount since its size is larger (0.5 nm) than the pore opening.

The CO_2/CH_4 separation process for natural gas upgrading is also a highly relevant topic since methane is seen as a strategic source of energy in a midterm time scale. For taking benefit of more natural gas deposits, the removal of several contaminants is required and one of those present in large amount is CO_2, which can be adsorbed in aluminium containing zeolites because the high electrostatic fields inside the pores results in a preferential adsorption of this molecule. It is generally accepted that the CO_2 adsorption capacity increases with increasing the Al content of the zeolite. However, this type of process that is based on the selective adsorption of one component (CO_2) at relatively high pressure and its release upon decreasing pressure, requires a good desorption of CO_2 and this can be difficult if the interaction with the polar zeolite is too strong. We studied the CO_2 and CH_4 adsorption properties of LTA zeolites exhibiting different polar character by varying the Si/Al ratios from 1 to ∞ and we were able to find an optimum for Si/Al ratios above 5 that maximizes the behavior of this zeolite as selective and regenerable adsorbent in CO_2/CH_4 separation [5].

We went a step forward in this separation and found that zeolite Rho was able to separate CO_2 from CH_4 with the highest selectivity ever observed for zeolites on the basis of its adequate polarity and its pore diameter that is in between that of CO_2 and CH_4. We observed that the enhanced CO_2 adsorption was due to structural changes in zeolite Rho [6].

References

[1] R.M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London, 1978.
[2] D.W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, John Wiley, New York, 1974.
[3] M. Palomino, A. Cantin, A. Corma, S. Leiva, F. Rey, S. Valencia, *Chem. Commun*. (2007) 1233.
[4] A. Corma, F. Rey, J. Rius, M. J. Sabater, S. Valencia, *Nature* **431** (2004) 287.
[5] M. Palomino, A. Corma, F. Rey, S. Valencia, *Langmuir* **26** (2010) 1910.
[6] M. Palomino, A. Corma, J.L. Jordá, F. Rey, S. Valencia, *Chem. Commun.* **48** (2012) 215.

L-33

Catalytic Membrane Reactors based on Mixed Conducting Oxide Membranes

J.M. Serra, S. Escolástico, J. Garcia-Fayos, M.P. Lobera, M. Balaguer
1Instituto de Tecnología Química (Universidad Politécnica de Valencia - Consejo Superior de Investigaciones Científicas). Av. de los Naranjos s/n.Valencia, Spain. 46022.
Email: jmserra@itq.upv.es

Keywords: Selective oxidation, Catalytic membrane reactor, OCM, ODHE, OTM membranes

This contribution focuses on the application of oxygen permeable membranes to the alkane activation at high temperatures. The employed membranes are based on mixed oxides with the perovskite crystalline structure and present mixed ionic-electronic conductivity. The synthesized and characterized membranes consist of ferrite-cobaltites with different alkali-earth and lanthanide metals. The oxygen separation from air was studied using argon and methane as sweep gas in the temperature range from 700 to 1000 ºC. It was possible to distinguish two different permeation regimes: (i) bulk diffusion limited at high temperatures; and (ii) surface exchange limited at lower temperatures. The membranes were used as catalytic membrane reactor for the conversion of alkanes and two different reactions were studied: (i) oxidative methane coupling and (ii) oxidative dehydrogenation of ethane.

Dense ionic oxygen conducting membrane reactors are highly attractive solutions for syngas production, oxidative dehydrogenation of ethane (ODHE) and oxidative coupling of methane (OCM), where both, separation and reaction are integrated in the same unit [1-5]. The membranes are typically tested as a function of the operating temperature, hydrocarbon % in feed, feed flow and oxygen % in the air "side". Reaction product and depleted air were analysed by gas chromatography.

For a BSFC membrane reactor, the ethane conversion increases with the temperature, and reaches a 97.5 % of ethane conversion at 875 ºC, while the selectivity of ethylene slightly decreases. Therefore, ethylene yield reaches a maximum value at 850 ºC. These results are in accordance with that obtained in others studies with a similar membrane reactor [6,7]. Oxygen permeation and catalytic reactions with ethane were studied on LnSFC and BSFC membranes active with several catalysts based of perovskite and fluorite oxides. The highest oxygen permeation is observed for BSFC membrane and the substitution of the Ln in the A-*site* had different effects on the oxygen permeation, activation energy and catalytic selectivity in the conversion of hydrocarbons into olefins and syngas.

References

[1] Plotkin, S. *Catal. Today*, 103 (2005) 10.
[2] Lopez Nieto, J.M. et al., Appl. Catal. A 157 (1997) 117.
[3] Coronas, J. et al. *Chem. Eng. Sci.* 49 (1994) 2015.
[4] Lu, Y. et al. Ma, *Chem. Eng. Sci.* 55 (2000) 4901.
[5] Lu, Y. et al. *J. Membr. Sci.* 170 (2000) 27.
[6] Serra, J.M. et al. *J. Electrochem. Soc.* 155(2) (2008) B207; Serra, J.M. et al., ChemSusChem 2 (2009) 957–961;
[7] Tessier, F. et al. *J. Solid State Chem.* 171 (2003) 143

L-34

Integration of Pd-membranes in catalytic micro reactors for hydrogen production: concepts & applications

Katja Haas-Santo
Institute for Micro Process Engineering, Karlsruhe Institute of Technology
Hermann von Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
Email: katja.haas-santo@kit.edu

Keywords: Microchannel, Membrane reactor, Membrane integration, Pd-membrane

The production of hydrogen in small scale received an increasing demand as on-site production is often favored against hydrogen delivers. The advantages of integrating hydrogen membrane separation with the heterogeneous catalytic reaction in microstructured devices will be described.

Several reactions as steam reforming of hydrocarbons, the water gas shift reaction and dehydrogenation of liquid organic hydrogen carriers (LOHC) are examples which can profit by the combination with direct separation of hydrogen out of the reactor. Membrane reformers benefit from the in-situ removal of hydrogen by the integrated purification and moreover by the shift of the reaction equilibrium [1]. Further benefits are lower costs for small scale production, compact design and high energy efficiency. As example steam reforming could profit by the shift of the thermodynamic equilibrium as lower reaction temperatures can be applied. For these applications dense metal membranes made of palladium and its alloys are well suited as they show high hydrogen flux and high selectivity at high temperatures (400-600°C). The combination with microchannel systems

The integration of the metallic membrane in the microstructured membrane module is a crucial factor for the construction of the membrane module for technical applications. The leak tight integration of the thin metallic foil is essential for the further design of multi-layer modules therefore sophisticated fabrication techniques are needed [2].

During the separation of hydrogen from a gas mixture the hydrogen flux through the membrane can be decreased by hydrogen depletion, competitive adsorption and concentration polarization. These effects are pronounced for thin membranes exhibiting a high H_2 flux as the governing mechanism of hydrogen permeation changes from bulk diffusion control to surface or gas phase diffusion control. By integrating microchannel structures in the membrane module high mass transfer rates and an increased hydrogen partial pressure on the membrane surface are anticipated.

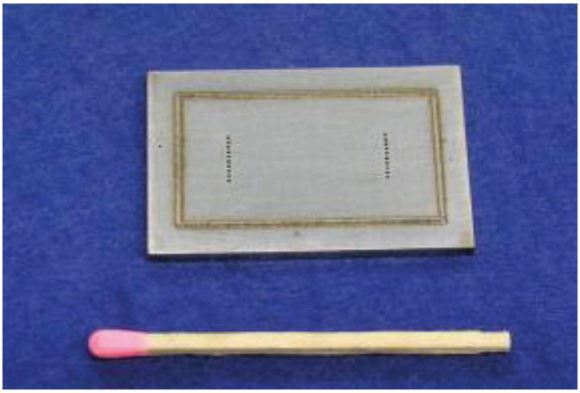


Fig. 5. Laser-welded microstructured membrane module [2].

References

[1] R. Dittmeyer et al., J. Mol. Cat. A **173** (2001) 135-184.
[2] T. Boeltken, M. Belimov, P. Pfeifer, T.A. Peters, R. Bredesen, R. Dittmeyer, Chem. Eng. Proc **67** (2012) 136-147.

L-35

OTM: market application

Isabel Moriña Díaz, Elisabet Esteban Portillo
Technology and Innovation Department, Inabensa, Ctra de la Esclusa s/n, 41.011, Sevilla, España
Email: isabel.morina@inabensa.abengoa.com

Keywords: Oxyfuel, cryogenic air distillation, OTM membranes

The use of the Oxygen Transport Membranes (OTM) is a promising alternative to traditional air separation method, ASU, to provide large amounts of O_2. ASU is an energy intensive process which increases the oxygen price. From the industrial point of view, obtaining oxygen by air separation membrane system is an essential component really attractive for oxyfuel technology development, because it involves dealing with one of its main gaps due to the main difference between the conventional and oxyfuel combustion resides in the combustor used that is practically pure oxygen instead of air.

As is world-wide known there is a problem concerning to CO_2 emissions, one of the major greenhouse gas. To combat this problem, the carbon capture technology arises, in which oxy-combustion technology has been located. The combustion with oxygen provides higher CO_2 concentrations in the flue gases which facilitates its separation, while achieving an increased efficiency of the plant. So it is considered the most promising technology to face the climate change.

The oxygen transport membrane technology requires a high degree of integration on an oxyfuel process since the membrane operating condition request a high temperature and a difference of pressure in both membrane sides to enhance the oxygen flux through it. Inabensa possess extensive knowledge and experience in the modeling integration of the oxygen membrane separation technology, and oxyfuel power plants have been studied taking into account the membrane and cryogenic method to provide oxygen. In this sense, the results obtained lead to a reduction in the efficiency losses versus current available oxygen separation technology (around 2 point less).

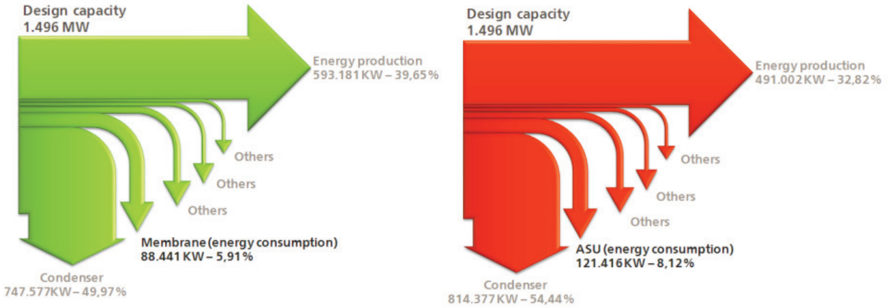


Fig. 6. Sankey diagram of an oxyfuel power plant

The application of oxy-fuel technology for power plants as CO_2 capture method presents a significant challenge to overcome, and it should be possible in a long term. Shortening the oxygen transport membrane implementation period, the application scope should be opened to a new market niches. In order to this, new immediately applications are identified such as it is the case of cement, ceramic, glass industry, etc. In these types of application the oxyfuel will improve the plant performance in terms of efficiency due to the fact that it is a process that operates at higher flames temperature and less fuel will be required.

L-36

CCS membrane development at CIUDEN´s technology development centre for CO_2 capture

P. Otero [a], J. A. Gutiérrez [a], I. Álvarez [a], F. Muñoz[a]
[a] Development Department and Scientific Department, CIUDEN
Av. Segunda nº2 (Poblado de Compostilla) 24404 Ponferrada, León, España/Spain
Email: ja.gutierrez@ciuden.es

Keywords: CCS, Coal, Pulverized Coal, CFB, oxycombustion.

CO_2 concentration to the atmosphere has risen faster than ever in the last century. This is highly due to fossil fuel combustion which is the major anthropogenic CO_2 source. The EU has adopted ambitious targets for reducing the emissions of greenhouse gases in the coming decades. The targets for 2020 are: *(1) to reduce greenhouse gas emissions by 20%, (2) to ensure 20% of renewable energy sources in the EU energy mix; (3) to reduce EU global primary energy use by 20% by 2020.* In particular, to reduce CO_2 emissions the EU members states will promote the commercial use of technologies for CO_2 capture, transport and storage through demonstration at industrial scale, including whole system efficiency and advanced research as included in the European Energy Roadmap 2050. Therefore, the EU plans are to set up a network of CCS demonstration plants on the short-term to test their viability, with the aim of commercial scale up of CCS (Carbon Capture and Storage) technologies on the mid-term.

Membrane technology is an important alternative for reliability, flexibility and economically competitiveness for two CCS process options: post-combustion and oxy-combustion. The use of membranes has applicability to CCS technologies mainly for CO_2 and O_2 separation, although most of the membrane studies for CO_2/O_2 production have been carried out at laboratory scale and will require a step further for commercial scale.

The application of membranes in fossil fuel power plants demands large superficial area membranes that can be maintained and repaired efficiently. Moreover, the membranes have to withstand pollution, fouling as well as temperature and pressure changes, conditions that cannot be endured by today's membrane technology. The development of cheaper and more robust membrane modules high permeability and selectivity is also foreseen. For example, the O_2 separation technology with membranes has been studied as an alternative way to produce O_2 to the cryogenics, VPSA, etc with promising results.

CIUDEN Technology Development Centre for CO_2 Capture (TDC es.CO_2) is a semi-industrial facility which aims to develop combustion capture and transport technologies feasibility to reach the industrial scale. TDC es.CO_2 is a flexible, modular and integrated installation ready to test and validate membrane technologies (either CO_2 or O_2) under a wide range of conditions in semi-industrial scale. It includes the following systems: Fuel Preparation System, Pulverized Coal Boiler 20 MW_{th}, Circulating Fluidized Bed Boiler 30 MW_{th}, Flue Gas Cleaning System, Recycled Gas Preparation System, CO_2 Compression and Purification Unit (CPU), CO_2 Transport

Experimental Rig, 3MW$_{th}$ Gasifier and a Fully Equipped Laboratory. Boilers are able to operate in both, air and oxy-mode.

This paper will present the capabilities of the TDC es.CO$_2$ for membrane testing at different conditions and purposes. From O$_2$ membrane production integration in the system and applied to the oxy-combustion facility mode to post-combustion technologies for membrane CO$_2$ separation, tested under real conditions. Furthermore, ancillary equipment is considered a key player on the development of this technology. Due to the high stresses that will suffer the materials and the special needs of the membranes (dust removal at high temperatures, cleaning system control, fouling control, etc), further study and development should be taken into account and the CIUDEN´s CCS facility can achieve important evaluations for the integration and testing of the system, both in materials performance and behaviour, and distributed control system of the process.

References

A. Leo, S. Liu, J. C.D.d. Costa, International Journal of Greenhouse Gas Control, 3 (2009)

M. Balaguer, C. Solis, J.M. Serra, Chemistry of Materials, 23 (2011)

S. Baumann, J.M. Serra, M.P. Lobera, S. Escolastico, F. Schulze-Kuppers, W.A. Meulenberg, Journal of Membrane Science, 377 (2011) 198-205.

M Lupion , B Navarrete, P Otero, V J Cortés, CIUDEN CCS Experimental Platform for oxycombustion technologies development in coal power generation (2009).

ZEP, Recommendations for research to support the deployment of CCS in Europe beyond 2020 (2013)

L-37

Membrane developments for hydrogen separation

Arian Nijmeijer, Peter Veenstra, John Saukaitis, Alan del Paggio
Shell Global Solutions International BV, Grasweg 31, 1031 HW Amsterdam
Email: arian.nijmeijer@shell.com

Keywords: hydrogen separation, palladium membrane, pre-combustion carbon capture, technology demonstration

Integration of Pd or Pd alloy membranes with reforming or WGS reactors, for pre-combustion fuel de-carbonization, is attractive for the reduction in CO_2 emissions. Recovery of CO_2 at high pressure and high purity (>90 mol%) as well as carbon conversions in excess of equilibrium limits may be achieved using various process schemes patented by Shell [1].

Successful evaluations of CRI/Criterion H_2 separation membranes in membrane steam reformers and as high temperature membrane separators have been performed by CRI/Criterion [2]. These membranes can be produced with a hydrogen permeance in the range of 50-70 [$Nm^3/m^2.h.bar^{0.5}$]. Both the hydrogen flux and the separation selectivity are stable at temperatures of 300-500°C and differential pressures of 4-65 bar. H_2 purity of >99% has been demonstrated for periods exceeding 10000 hrs in high temperature gas separations. A typical long term performance graph is provided in Figure 7.

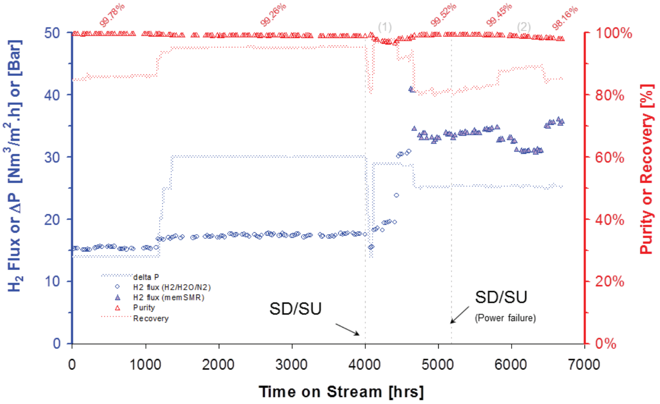


Figure 7: Long term performance of Pd membranes under changing conditions.

CRI is currently in the process of commercializing Pd and Pd alloy membranes on sintered porous metal supports. Successful evaluations of CRI H_2 separation membranes in membrane steam reformers and as high temperature membrane separators have been performed by CRI, and by third parties and the obvious next step would be a large scale demonstration of the technology in an industrial environment.

References

[1] Matzakos, A.N.; Wellington, S.L.; Mikus, T.; Ward, J.M.. U.S. Patent 6,821,501 B2, Nov. 23, 2004; Clomburg et al. U.S. Patent Application, US 2008/0179569 A1.
[2] Engwall, E.; Saukaitis, J.; Joshi, M.; Del Paggio, A. Pre-combustion fuel decarbonization with hydrogen separation membranes, AIChE National Meeting, November 2007.

L-38

R&D strategies for the reduction of CO_2 emissions from fossil fuel-fired high temperature processes

Prof. Dr.-Ing. Michael Modigell
Aachener Verfahrenstechnik, RWTH Aachen University, Aachen, Germany
GUtech, German University of Technology in Oman, Muscat, Oman
Email: Michael.Modigell@avt.rwth-aachen.de

It is expected, that due to a rising world energy demand, the total CO_2 emissions from fossil-fuel fired power plants will increase drastically within the next 40 years. Other increasing sources which significantly contribute to the problem are energy-intensive processes like iron and steel, cement and glass production. To mitigate the greenhouse effect caused by increasing CO_2 emissions, measures have to be taken to significantly reduce CO_2 emissions from fossil fuel powered processes. Besides short term measures like increasing the energy-efficiency of processes, mid- and long term strategies of carbon capture and storage (CCS) are pursued. The presentation will give an overview of the different strategies.

In the field of CCS there are three main technologies that realise removal of CO_2 from combustion and gasification processes: Post-combustion and Pre-combustion capture (ICCG) and the Oxyfuel combustion processes. While in post combustion CO_2 is separated from the flue gas, pre- and oxyfuel combustion are based on an air separation before the combustion process. In all of these technologies, membranes offer a big potential to reduce the specific power demand for the separation processes.

The presentation shows the principles and the requirements that membranes have to fulfil for the different CCS-technologies. Furthermore, other strategies for an efficient CO_2 reduction are shown in this presentation.

L-39

Integration of oxygen transport membrane in an oxyfuel circulating fluidized bed boiler coal plant

Paolo Chiesa, Matteo C. Romano, Fabio Furesi, Davide Tagliapietra, Luca Mancuso
Department of Energy, Politecnico di Milano, Via Lambruschini 4, 20156 Milan, ITALY
Email: paolo.chiesa@polimi.it

Keywords: Oxygen membranes, Oxyfuel, Circulating fluidized bed, Optimization

Concerns about rising concentration of greenhouse gases in the atmosphere have encouraged research into various ways of capturing and storing CO_2 before it is emitted. This technology is applied most naturally to large, point source emitters of CO_2 such as fossil fuel fired central-station electric power generators.

In principle, carbon sequestration can be accomplished according to three basic strategies:

- remove CO_2 from combustion gases, with no or minimal modifications to existing plants
- "decarbonize" the fuel, by re-allocating the heating value of the fuel on hydrogen while carbon is removed as CO_2.
- burning fuel with pure oxygen so that combustion products are essentially composed of CO_2 and H_2O, that can be easily removed by condensation.

The latter option, usually referred to as oxyfuel, requires massive O_2 production (typically carried out by means of cryogenic Air Separation Units, ASU) that brings about significant efficiency penalty and plant capital cost increase. Dense electrolytic high temperature Oxygen Transport Membranes (OTM), based on mixed ions-electrons conducting materials, are a promising alternative to cryogenic ASU, when integrated in power plants. The aim of this presentation is a techno-economic multivariable optimization of a power plant with carbon dioxide capture, based on oxy-fuel circulating fluidized bed boiler and membranes for oxygen production.

The results presented come from the activities carried out in the FP7 DEMOYS (Dense Membranes for Efficient Oxygen and Hydrogen Separation) project, co-financed by the European Commission and run by a consortium of 15 partners from 6 European countries [1]. The project essentially aims to further 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. In the frame of the activities of the DEMOYS project, Politecnico di Milano and Foster Wheeler are in charge of performance assessment and economic evaluation of large scale plants that adopt these membrane types for the production of electricity and hydrogen.

The core of the presentation is the techno-economic multivariable plant analysis assessing how the membrane design influences plant performance in term of conversion efficiency and cost of electricity. Optimization of the main design parameters, mostly involving the membrane operating conditions, aiming at the minimization of the cost of electricity produced will provide the general criteria for sizing the membrane modules.

References

[1] http://demoys.rse-web.it/

L-40

Membrane based CO_2 capture in coal fired integrated gasification combined cycles

Scherer V., Maas P., Franz J.
Energy Plant Technology, Ruhr-University Bochum
Universitätsstr. 150 , 44780 Bochum, Germany
Email: scherer@leat.rub.de

Keywords: Carbon Capture, Integrated Gasification Combined Cycle, Membranes

CO_2 capture based on Integrated Gasification Combined Cycle Power Plants (IGCC) is one of the major routes to an efficient carbon capture process for electricity generation. The synthesis gas after gasification and the following water gas shift (WGS) contains high concentration of CO_2 and H_2. Typical syngas pressures are between 20 and 40 bars. Both conditions, high concentrations and high pressure, are favorable for the use of membranes which can be either CO_2 or H_2 selective. On the other hand the raw synthesis gas contains major amounts of critical components for the life time of membranes like ash, Alkali or H_2S. This either requires careful gas cleaning or membranes which can withstand these harsh conditions.

The current contribution gives an introduction into IGCC power plants and their design principles. Compared with IGCC power plants without carbon capture, an IGCC with CO_2 capture needs a water gas shift reactor which converts the CO within the syngas to CO_2 by producing additional H_2 ($CO+H_2O$ -> CO_2 + H2). Because the water gas shift reaction has a major influence on the power plant performance, the possibilities to reduce the efficiency losses by WGS within an IGCC are discussed. The possible options to integrate H_2 or CO_2 selective membranes (polymeric, ceramic) into the process will be presented and the consequences on the power plant performance will be highlighted (Fig 1). A comparison of membrane based IGCC processes with "conventional" scrubbing processes for CO_2 capture will be given.

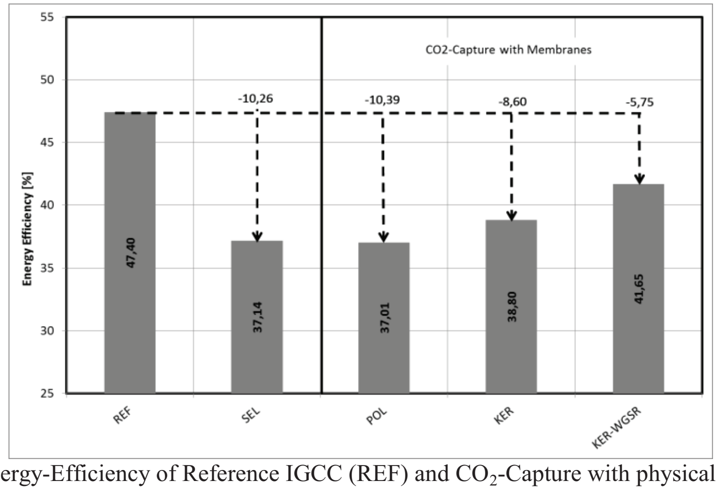


Fig. 8. Energy-Efficiency of Reference IGCC (REF) and CO_2-Capture with physical scrubbing process Selexol (SEL), with polymer (POL) and ceramic membranes (KER) and with a ceramic Water-Gas-Shift Membrane-Reactor (KER-WGSR).

References

[1] Franz J.: An evaluation of CO_2 and H_2 selective polymeric membranes for CO2 separation in IGCC processes, Journal of Membrane Science 359 (1-2), 173-183, 2010

[2] Scherer V. & Franz J.: CO_2 seperation via Pre-Combustion Capture Unitilizing membranes in Coal Power plants, in: Efficient Carbon Capture and Storage for Coal Power Plants, Stolten D. & Scherer V. (Eds.), Wiley-VCH, Weinheim, 431–468, ISBN: 978-3-527-33002-7, 2011.

POSTER COMUNICATIONS

P-1. Contribution of the surface exchange kinetics to the oxygen transport properties in ceria based composite membrane
Jong Hoon Joo, Geum Sook Park, Chung-Yul Yoo, Ji Haeng Yu

P-2. Electrical characterization and sintering properties of $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})_{1-y}\ XyO_{3-\delta}$(X = Y, Zr, y = 0.01…0.1)
Lana-Simone Unger, Christian Niedrig, Stefan F. Wagner, Wolfgang Menesklou, Ellen Ivers-Tiffée

P-3. Oxygen reduction activity of MIEC Brownmillerite – Ce doped $Ba_2In_2O_5$
C. P. Jijil, R. Nandini Devi

P-4. Electrical conductivity and oxygen permeability of Pr and Co doped $Gd_{0.9}Ce_{0.1}O_{1.95-\delta}$
Shiyang Cheng, Martin Søgaard, Andreas Kaiser and Peter Vang Hendriksen

P-5. Oxygen-Permeability through CO_2-Tolerant Fe_2NiO_4-$Ce_{0.8}Tb_{0.2}O_{2-\delta}$ dual phase composite membrane
María Balaguer, Julio García-Fayos, Cecilia Solís and José M. Serra

P-6. Oxygen production by means of catalytically activated asymmetric ceramic membranes based on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$
J. Garcia-Fayos, S. Escolástico, C. Solís, S. Baumann, W.A. Meulenberg and J. M. Serra

P-7. A mixed (protonic and electronic) conducting composite membrane for hydrogen separation
Ji Haeng Yu, Hwan Soo Kim, Chung-Yul Yoo, Jong Hoon Joo*

P-8. Water permeation studies on a BCY membrane reactor
Selgin Al, Evangelos Papaioannou and Ian Metcalfe

P-9. $BaCe_{1-x}Zr_xY_{0.15}O_{3-\delta}$ (x = 0.1, 0.2, 0.3, 0.4) proton conducting materials for hydrogen separation membrane applications
C. Mortalò, S. Fasolin, S. Boldrini, E. Mercadelli, A. Sanson, S. Barison, M. Fabrizio

P-10. $Ni\text{-}Al_2O_3$ composite membrane for hydrogen separation
Stefano Fasolin, Cecilia Mortalò, Monica Fabrizio and Simona Barison

P-11. Studies of the inhibition influence of other gases such as H_2O, CO, CO_2, N_2 on the H_2 permeation using a Pd-based membrane
M. M. Barreiro, M. Maroño, J. M. Sánchez

P-12. Hydrogen separation through doped $La_{5.5}WO_{11.25-\delta}$ based membranes
S. Escolástico, R. Zanón, C. Solís, J. Seeger, M. Ivanova, W. Meulenberg, J. M. Serra

P-13. Hydrogen surface exchange on proton conducting oxides studied by gas phase analysis with mass spectrometry
Ragnhild Hancke, Zuoan Li, Reidar Haugsrud

P-14. Conductivity relaxation study of La_6WO_{12}
C. Solís, S. Escolástico, R. Zanón, J.M. Serra

P-15. Conductivity relaxation experiments on oxide materials with large nonstoichiometry deviations
Andreas Falkenstein, David N. Mueller, Roger A. De Souza and Manfred Martin

P-16. Experimental surface characterization of oxygen ion transport membranes for flux model development under oxy-fuel combustion conditions
Anton Hunt, Giorgos Dimitrakopoulos, Prof. Patrick Kirchen and Prof. Ahmed Ghoniem

P-17. Influence of yttrium doping on the stability of the cubic $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ phase studied by electron microscopy
Matthias Meffert, Philipp Müller, Heike Störmer, Christian Niedrig, Stefan F. Wagner, Ellen Ivers-Tiffée and Dagmar Gerthsen

P-18. Thermo-mechanical characterization of $Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{1-x}Zr_xO_{3-\delta}$ and $La_{5.4}WO_{12-\delta}$ membrane materials for carbon capture processes
V. Stournari, J. Malzbender, T. Beck, L. Singheiser

P-19. Electrical conductivity relaxation on the $SrTi_xFe_{1-x}O_{3-\delta}$ system
Sebastiaan F.P. ten Donkelaar and Henny J.M. Bouwmeester

P-20. Electrical Conductivity Measuring Device Designed for Mixed Conducting Materials
M. Bernhardt, M. Esche, R. Kircheisen, R. Kriegel

P-21. Parametric study of the oxygen transport in a MIEC membrane by dynamic modeling
J.M. Gozálvez-Zafrilla, A. Santafé-Moros, S. Escolástico, J.M. Serra

P-22. Surface modification of $La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ hollow fiber membranes for oxygen separation
Marijke Jacobs, Bart Michielsen, Vesna Middelkoop and Frans Snijkers

P-23. Supported planar BSCF membranes for oxygen separation from air
P.Niehoff, F. Schulze-Küppers, S. Baumann, J.M. Serra, W. A. Meulenberg, R. Vaßen

P-24. Advanced processing of asymmetric oxygen transport ceramic membrane on porous metallic support
M. Scrignari, M.O. Jarligo, A. Comite and R. Vaßen

P-25. Characterization of high temperature hydrogen and oxygen transport membranes deposited by low pressure plasma spraying
F. Azzurri, A. Comite, .M. Gindrat , M O. Jarligo, R. Vaßen, J. Garcia-Fayos, S. Escolastico

P-26. Manufacturing of multi-layer membrane systems for hydrogen separation via tape-casting
Wendelin Deibert, J. Seeger, M. Ivanova, W.A. Meulenberg, R. Vaßen, H.P. Buchkremer

P-27. Formation and prevention of cracks in ultra-thin Silica membranes
Emiel J. Kappert, Denys Pavlenko, Arian Nijmeijer, Nieck E. Benes, P. Amy Tsai

P-28. Facile synthesis of Zirconia doped hybrid organic inorganic silica membranes
M. ten Hove, A. Nijmeijer and L. Winnubst

P-29. Water gas shift membrane reactor for applications in carbon capture technologies
D. van Holt, E. Forster, M. Müller, J.M. Serra, R. Vaßen, S. Baumann, W. A. Meulenberg

P-30. Deposition of thin, defect-free, alumina barrier layer for high temperature palladium membranes
F. Azzurri, A. Bottino, A. Comite, M. Scrignari, M. Broglia, F. Drago, P. Pinacci

P-31. Microporous silica membranes for CO_2 separation
J. Eiberger, M. Bram. K. Wilkner, T. Van Gestel, D. Stöver and H.P. Buchkremer

P-32. Inorganic porous hollow fibers for intensified fractionation and filtration
Patrick de Wit, Arian Nijmeijer, Nieck E. Benes

P-33. Partial oxidation of methane in catalytic reactors with MIEC membranes
A.A. Markov, M.V. Patrakeev, I.A. Leonidov, V.L. Kozhevnikov

P-34. Effect of the linking group and NiO underlayer to the conductivity of p-type DSSC
Luca D'Amario, Allison Brown, Travis White, Jonathan Freys, James Gardner, Anders Hagfeldt and Leif Hammarström

P-35. Potential of high temperature membrane-shift-reactors for pre-combustion CO2 capture in IGCC power plants
Philipp Meysel, Christian Kunze, Hartmut Spliethoff

P-36. Thermodynamic evaluation of the use of ITM for air separation in an anthracite coal oxy-fuel power plant
E. Portillo, F. Vega, I. Moriña and J. M. Serra

P-37. Syngas production at intermediate temperature through H_2O and CO_2 electrolysis with a Cu-based solid oxide electrolyzer
C. Gaudillere, L. Navarrete, J. M. Serra

P-38. Pilot module operation for efficient high temperature air separation
Nicolas Nauels, Michael Modigell

P-39. Tubular solid oxide electrolysers for CO_2 / H_2O reduction
L. Kleiminger, G.H. Kelsall

P- 1

Contribution of the surface exchange kinetics to the oxygen transport properties in ceria based composite membrane

Jong Hoon Joo[a], Geum Sook Park[b], Chung-Yul Yoo[a], Ji Haeng Yu[a*]
[a] Energy Materials and Convergence Research Department, Korea Institute of Energy Research, 152 Gajeongro, Yuseong-gu, Daejeon 305-343, Republic of Korea
[b] Graduate School of Green Energy Technology, Chungnam National University, Daejeon 305-764, Republic of Korea

Keywords: Oxygen transport membrane, dual-phase membrane, surface exchange kinetics, acceptor-doped ceria, ion conductivity

Mixed ionic and electronic conducting oxides (MIECs) are receiving considerable attention due to their potential applications involving high-purity oxygen production, partial oxidation of hydrocarbons, and sensors. A MIEC ceramic membrane with high oxygen permeability is a promising means to supply pure oxygen to power plants with carbon dioxide capture based on oxy-fuel combustion [1]. MIEC perovskite (ABO_3) materials containing rare and alkaline earth metals on the A-site and a transition metal on the B-site have been intensively studied owing to their high oxygen permeability. However, their chemical instability in reducing and CO_2-containing atmospheres limits their practical applications. In addition, their high thermal expansion coefficient can also cause problems such as cracking and delamination of membranes. Dual-phase membranes that consist of a fluorite structure for an oxygen ion conductor and a perovskite for an electronic conductor in a micro-scale are considered promising substitutes [2]. Dual-phase composites can benefit from the contribution of each component to overcome the limitations of single-phase perovskites. Since fluorite structured oxygen ion conductors have good phase stability under CO_2 and reducing atmospheres and relatively low thermal expansion coefficients, the addition of fluorite has the possibility of improving the chemical and structural stabilities of dense ceramic membranes. Although various material combinations for dual-phase membranes have been intensively researched, there have been relatively few systematic studies of each component’s contribution to the oxygen permeability in dual-phase membranes. In a previous work, based on a systematic study, we point out that the reported ionic conductivity of a dual-phase (fluorite/perovskite) membrane was underestimated due to neglecting the surface exchange kinetics in the case of a membrane with about 1 mm thickness [3]. In this study, in order to understand the contributions of the fluorite material to oxygen permeability in $Ce_{0.9}Gd_{0.1}O_{2-\delta}/La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (50:50 vol%) composites, the effects of the surface exchange on the oxygen transport have been investigated in terms of the surface coating. The characteristic thickness of the composite membrane was evaluated by using permeation data with a modified Wagner equation. Based on the results, the oxygen ion conductivity of GDC/LSCF composite has been reliably estimated.

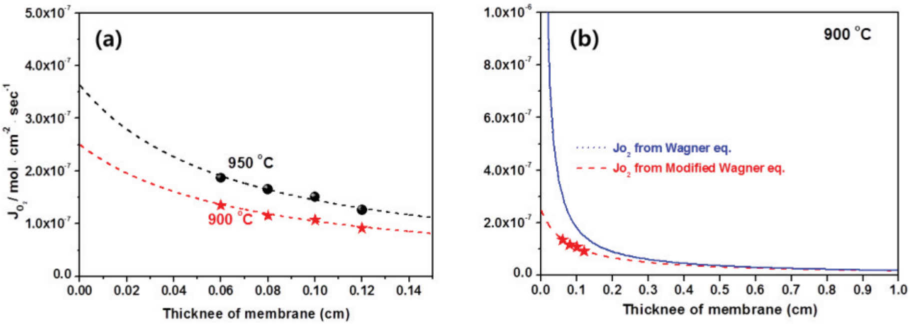


Fig. 1 (a) The oxygen permeation fluxes as a function of membrane thickness and temperature. The dotted lines are fitting lines for the LSC-coated composite membranes (GDC/LSCF) using the modified Wagner equation. (b) The oxygen permeation fluxes as a function of membrane thickness derived from the modified Wagner and Wagner equations.

References

[1] J. Sunarso, S. Liu, Y. S. Lin, J.C. Diniz da Costa, Energy Environ. Sci. **4** (2011) 2516.

[2] V.V. Kharton, A.V. Kovalevsky, A.P. Viskup, A.L. Shaula, F.M. Figueiredo, E.N. Naumovich, F.M.B. Marques, Solid State Ionics **160** (2003) 247.

[3] A.L. Shaula, V.V. Kharton, F.M.B. Marques, A.V. Kovalevsky, A.P. Viskup, E.N. Naumovich, J. Solid State Electrochem. **10** (2006) 28.

P- 2

Electrical characterization and sintering properties of $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})_{1-y}X_yO_{3-\delta}$ $(X = Y, Zr, y = 0.01\ldots0.1)$

Lana-Simone Unger, Christian Niedrig, Stefan F. Wagner, Wolfgang Menesklou, Ellen Ivers-Tiffée
Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruher Institut für Technologie (KIT),
Adenauerring 20b, 76131 Karlsruhe, Germany
Email: Lana.Unger@kit.edu

Keywords: Sintering behavior, microstructure, electrical properties, co-doped BSCF

Among the application-relevant materials class of mixed ionic-electronic conducting perovskite oxides (ABO3), $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) exhibits an outstanding oxygen permeation, resulting from its superior ionic and electronic transport properties. These qualities identify BSCF as a very promising candidate for high-temperature membranes to produce pure oxygen in a very efficient manner.

However, in the targeted temperature range for applications (between 700 °C and 900 °C) the cubic BSCF phase, which is responsible for the excellent oxygen permeation properties, is not long-term stable below 840 °C and undergoes a phase transformation to hexagonal phase. Previous studies in literature suggest the possibility of stabilizing the cubic phase of BSCF in the aforementioned temperature range by B-site co-doping (at levels of 1 to 10 mol-%) with Y or Zr, respectively.

This paper is focused on the influence of Y and Zr co-doping on the electrical performance of the BSCF matrix. To this end, single-phase co-doped BSCF powders prepared by mixed-oxide route were used to sinter ceramic bulk samples.

For electrical characterization the effect of co-doping on the sintering behavior was studied in order to reduce sample porosity to a minimum. In this way, very dense bulk samples could be obtained that were electrically contacted by sputtered Pt contacts in 4-wire technique. These optimized dense ceramic samples were electrically characterized at temperatures between 700…900 °C and oxygen partial pressures of 10-5…1 bar, enabling a direct comparison of electrical properties between the different compositions. Additionally, long-term electrical measurements at 800 °C in air shed light on the cubic phase stability of co-doped BSCF under operating conditions.

P- 3

Oxygen reduction activity of MIEC brownmillerite – Ce doped $Ba_2In_2O_5$

C. P. Jijil, R. Nandini Devi
Catalysis and Inorganic Chemistry Division
CSIR – National Chemical Laboratory, Pune - 411008, India
Email: cp.jijil@ncl.res.in

Keywords: Brownmillerite, Oxygen transport membrane, Oxygen reduction reaction, *In situ* high temperature XRD.

Fossil fuel will run out in another few decades". So the development of alternative power generating devices to fulfill our raising energy requirements has become the need of the hour [1]. Oxygen conducting materials with various potential applications are useful to attain this goal. These materials are used in various fields like energy sector as Oxygen Transport Membrane (OTM), energy and environmentally related catalytic reaction process such as effective utilization of natural gas, production of hydrogen and treatment of greenhouse gases. Dense ceramic membranes can be integrated into catalytic membrane reactors for carrying out different petro chemistry processes, where *in situ* separation of oxygen from air will make the whole process cost effective [2]. The main criterias for such materials to act as OTM are that it should possess high mixed ionic and electronic conductivity (MIEC) and should be stable under reaction conditions. The driving force for the oxygen separation is ascertained by the partial pressure gradient across the membrane [3]. Oxygen deficient materials such as Perovskite (ABO_3) and Brownmillerite ($A_2B_2O_5$) type of compounds are reported to exhibit high MIEC at elevated temperatures. Brownmillerites have an ideal stoichiometry of $A_2B_2O_5$ with layers of corner-shared BO_6 octahedra alternating with layers of corner-shared BO_4 tetrahedra. The structure can be considered as a cubic perovskite with a fixed concentration of oxygen ion vacancies that are ordered in two dimensional planes. $Ba_2In_2O_5$ has been reported to exhibit good MIEC at higher temperatures (>900 ºC). Appropriate doping in such systems will bring down the temperature at which high MIEC can be achieved. We propose room temperature electrochemical studies and oxygen reduction reaction (ORR) activity as a means to initial screening of potential candidates for further gas diffusion studies.

The present work reports the initial room temperature electrochemical studies of Ce doped $Ba_2In_2O_5$. $Ba_2InCeO_{5+\delta}$ was synthesized by solid state method and the compound was characterized by powder X-ray diffraction (XRD). Rietveld refinement using GSAS-EXPGUI was carried out to obtain the unit cell parameters (Fig. 1) [4]. The preliminary experiments using cyclic voltammetry and rotating disc electrode show that this compound exhibits good ORR activity and the activity is comparable with that of 40% Pt/C in alkaline medium (Fig. 2) [5]. Also the *in situ* high temperature XRD studies indicate that these materials are stable up to 900 ºC. So, with these properties it is anticipated that these materials should be good oxide ion conductors making them a potential OTM. The diffusion studies of oxide ions are under progress.

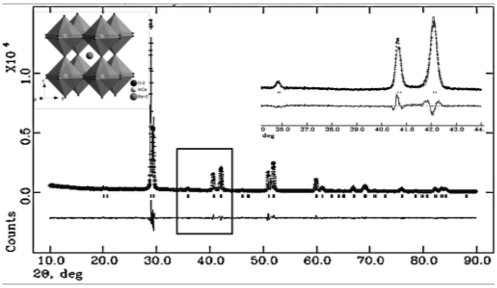


Fig. 9. Rietveld refinement of $Ba_2InCeO_{5+\delta}$ (star mark -experimental, bold line - calculated, bottom pattern - difference between experimental and calculated intensities); (left top) polyhedral representation of the highly disordered structure obtained after refinement

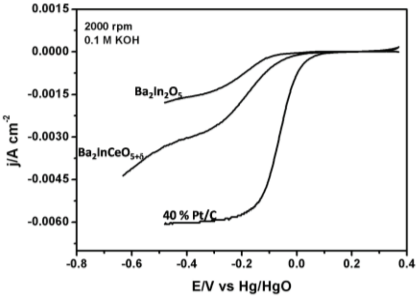


Fig. 2. Hydrodynamic voltammograms obtained at an electrode rotating speed of 2000 rpm with a rotating disk electrode. The experiments were performed in O_2-saturated 0.1 M KOH at a sweep rate of 5 mV s^{-1} using Hg / HgO as the reference electrode.

References

[1] Dresselhaus, M. S.; Thomas, I. L., *Nature*, **2001**, 414, 332.
[2] Dong, X.; Jin, W.; Xu, N.; Li, K., Chem. Commun., **2011**, 47, 10886.
[3] Liu, Y.; Tan, X.; Li, K., *Catal. Rev.*, **2006**, 48, 145.
[4] Toby B. H., *J. Appl. Crystallogr.*, **2001**, 34, 210.
[5] Jijil, C. P.; Sreekuttan, M.U.;, Sreekumar, K.; Nandini, Devi R., *Chem. Mater.*, **2012**, 24, 2823.

P- 4

Electrical conductivity and oxygen permeability of Pr and Co doped $Gd_{0.9}Ce_{0.1}O_{1.95-\delta}$

Shiyang Cheng, Martin Søgaard, Andreas Kaiser and Peter Vang Hendriksen
Department of Energy Conversion and Storage, Technical University of Denmark
Fredrikorgsvej 399, DK-4000, Roskilde, Denmark
Email: shic@dtu.dk

Keywords: Oxygen separation membrane, Gd-doped ceria, electronic conductivity

Dense ceramic oxygen separation membranes have received much attention in recent years. The membranes enable separation of oxygen from air at high temperatures and can be utilized in chemical reactors for the conversion of natural gas to syngas and for production of high purity oxygen. The oxygen permeation flux of a 27μm Gd-doped ceria membrane has been reported to be over 10Nmlcm^{-2}min^{-1} (H_2 at permeate side) at 1200K [1] due to the high electronic conductivity in the material under reducing conditions. However, a low *p*-type electronic conductivity of GCO in the vicinity of the feed side is a main factor limiting the total flux especially when the membrane is operated under not so harsh reducing conditions. According to the model work on a GCO10 membrane [2], the oxygen flux can be significantly improved if the *p*-type electronic conductivity can be enhanced. The *p*-type electronic conductivity of GCO10 can be enhanced by doping with Pr, leading to changes in the band structure [3]. The electronic conductivity can also be increased by addition of cobalt oxide into GCO because a Co-rich grain boundary serves as a *p*-type electronic conducting pathway [4]. In this work, Pr and Co are co-doped into GCO10, with the aim of obtaining enhanced *p*-type conductivity under oxidizing conditions.

The *p*-type conductivity of P5C5 ($Co_{0.05}Gd_{0.1}Pr_{0.05}Ce_{0.9}O_{2-\delta}$), P5($Gd_{0.1}Pr_{0.05}Ce_{0.9}O_{2-\delta}$), and P2C5($Co_{0.05}Gd_{0.1}Pr_{0.02}Ce_{0.9}O_{2-\delta}$) and GCO10 have been measured using Hebb-Wagner polarization method from 600°C to 900°C. Fig.1a) illustrates the *p*-type electronic conductivity of the four samples as a function of reciprocal temperature at a pO_2 of 1bar. P5C5, P2C5 and P5 all exhibits larger *p*-type conductivity and lower activation energy than GCO10, which is attributed to enhanced electronic conductivity in the bulk and grain boundaries. Fig 1b) shows the measured oxygen permeation flux of P2C5, P5C5 and a GCO10/LSCF dual phase composite membrane [5] (all membranes are approximately 1mm thick) measured under an oxygen pressure gradient of 0.21/1e-5atm. The calculated flux of GCO10 is also shown. The oxygen permeation flux of P2C5 and P5C5 is larger than GCO10 especially at low temperatures (600°C). Combining Fig 1a) and b), the enhancement of the flux is anticipated to be a result of the increased *p*-type conductivity in bulk and grain boundary.

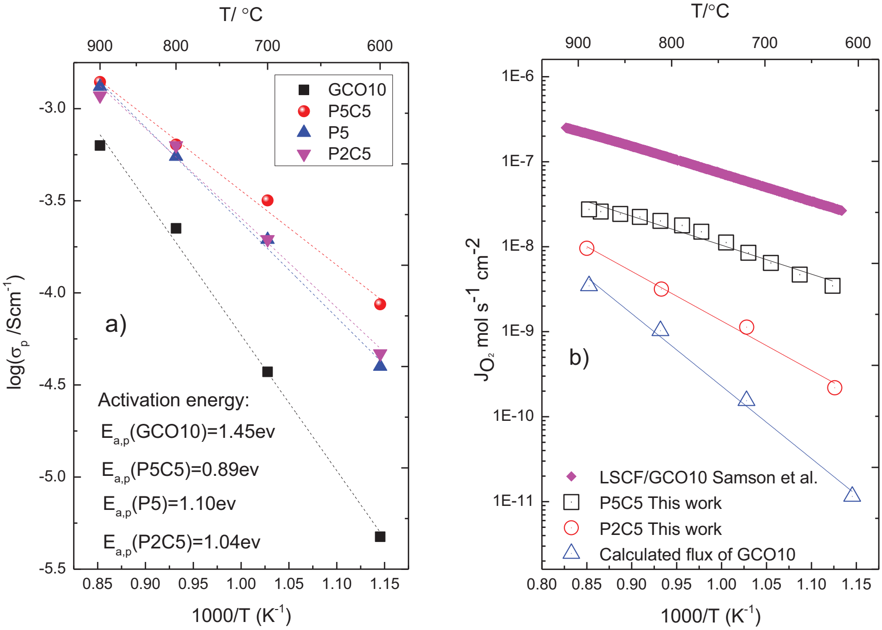


Fig.10. a) *p*-type conductivity vs. 1000/T b) Measured and calculated flux vs. 1000/T.

References

[1] M.S. C. Chatzichristodoulou, J. Glasscock, A. Kaiser, S. P. V. Foghmoes, and P. V. Hendriksen, J Electrochem Soc, 158 (2011) F73.

[2] C. Chatzichristodoulou, M. Søgaard, P.V. Hendriksen, Journal of the Electrochemical Society, 158 (2011) F61-F72.

[3] S. Lübke, H.D. Wiemhöfer, Solid State Ionics, 117 (1999) 229-243.

[4] K. Schmale, M. Grünebaum, M. Janssen, S. Baumann, F. Schulze-Küppers, H.-D. Wiemhöfer, Physica Status Solidi (B), 248 (2011) 314-322.

[5] A.Samson to be published.

P- 5

Oxygen-Permeability through CO_2-Tolerant Fe_2NiO_4-$Ce_{0.8}Tb_{0.2}O_{2-\delta}$ dual phase composite membrane

María Balaguer, Julio García-Fayos, Cecilia Solís and José M. Serra*
Instituto de Tecnología Química, UPV-CSIC, C/ Camino de Vera, s/n, Valencia 46022, Spain
Email: mabara@itq.upv.es; jmserra@itq.upv.es

Keywords: dual-phase, composite, oxygen permeation, oxyfuel

Dual phase composite membranes try to combine the best characteristics of their constituent materials to achieve large oxygen permeability and relatively good chemical and mechanical stability at elevated temperatures. Ceramic–ceramic (cercer) dual-phase membranes have been successfully prepared since early 2000´s decade. [1] They consist of a percolative oxygen ion-conducting oxide phase and a continuous electron-conducting oxide phase that, for its part, may be mixed ionic-electronic conductor (MIEC) to avoid blocking the ionic transport. Due to the influence of the grain boundary between different phases, large catalytic activity towards surface oxygen exchange is required as well. Following this composite strategy, several crystalline structures have been combined.[2] Perovskites are the MIEC materials with the highest electrical conductivities, but permeability is limited by low ionic conductivity. Doping strategies to increase the oxygen ion conductivity often affect the crystal and thermo-mechanical stability that increase vulnerability under a large oxygen concentration gradient and atmospheres containing CO_2, SO_2, H_2O or H_2S. Improved stability against these gradients and carbonation is expected by evading Co and alkaline-earth elements. Spinel structured materials are then used as electronic phase.[3] Fluorite materials such as yttria stabilized zirconia (YSZ) or $Ce_{1-x}B_xO_{2-\delta}$ (B=lanthanide) play the oxygen conductor role in composites since they are mainly ionic conductors and chemical stability is higher than that of perovskites. [4]

The present work reports a dual-phase membrane made of 60 vol% Fe_2NiO_4 (FNO) as electronic conductor and 40 vol% $Ce_{0.8}Tb_{0.2}O_{2-\delta}$ (CTO) for the ionic transport. CTO was reported to be MIEC even at high oxygen partial pressures due to the variable oxidation state of the Tb, [5] increasing surface reaction sites from triple points to the overall grain surface. Characterization of powders and membrane by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) showed that both phases are pure with no evidences of reaction between them up to the detection limits. DC conductivity ascertained the existence of a percolative electronic pathway. By decreasing the oxygen partial pressure (pO_2) the conductivity increases. The oxygen permeation has been tested in a planar disk with both sides covered with a catalytic layer. At 1000 ºC, Ar sweeping allow to obtain oxygen flux of 0.17 ml cm^{-2} s^{-1}, which increases up to 0.2 ml cm^{-2} s^{-1} when swept by CO_2. After 76 h in CO_2 the membrane remained stable and not influence in the oxygen permeation was observed, which represents a step forward towards its use in oxyfuel plants.

References:

[1] U. Nigge *et al. Solid State Ionics* 2002, 146, 163; [2] A.L.Shaula *et al. J Solid State Electrochem* 2006 10, 28; [3] H. Luo *et al*. *Angew. Chem. Int. Ed*. 2011, 50, 759; [4] J. Yi *et al. J. Memb. Sci.* 2006,280, 849; [5] M. Balaguer *et al. Chem. Mater.* 2011 23, 2333

P- 6

Oxygen production by means of catalytically activated asymmetric ceramic membranes based on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

J. Garcia-Fayos[1], S. Escolástico[1], C. Solís[1], S. Baumann[2], W.A. Meulenberg[2] and José M. Serra[1,*]
[1] Instituto de Tecnología Química, UPV-CSIC, C/ Camino de Vera, s/n, Valencia 46022, Spain
[2] Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research IEK-1, D-52425 Jülich, Germany
Email: jugarfa@itq.upv.es; jmserra@itq.upv.es

Keywords: LSCF, BSCF, oxygen transport membrane, asymmetric membrane, catalyst

Oxygen is currently produced principally by means of cryogenic separation of air. This technology requires the operation under very low temperatures and high pressures, and therefor very large energy demands, which makes this process only economically viable at large scale. A large number of industrial processes would benefit by the use of oxygen produced at reasonable costs, due to the improvement in the process efficiency and in environmental sustainability. The use of pure oxygen in combustion leads to a decrease in waste gas emissions (NOx, aerosols), a higher temperature in the flame and the possible implementation of CO_2 capture and storage strategies. Oxygen Transport Membranes (OTM) technology offers the potential to produce oxygen with lower energy demands, thanks to the operating principle and the very high (thermal) integration of OTM technology in different process in the energy and chemistry sector. OTM are materials consisting of metallic oxides presenting Mixed Ionic-Electronic Conducting (MIEC) properties, what makes them able to be used as oxygen permeation membranes at high temperatures (since oxygen can permeate through the oxide lattice in the ionic form O^{2-}). The most O_2-permeable MIEC membranes are typically based on perovskite oxides. This work focuses on the study of all-perovskite asymmetric membranes for oxygen separation with the formulae $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$.

Experiments: A 30-60 μm thin-film LSCF and BSCF membranes supported on porous substrates was characterized, studying O_2 permeation in dependence of temperature (1000-650 ºC), sweep gas flow (300-750 $ml \cdot min^{-1}$) and oxygen partial pressure in feed side (0.21-1 atm). Surface activation aiming to improve surface exchange is also considered. LSCF membranes also present good chemical and mechanical stability when exposed to CO_2-containig environments and under highly reducing atmospheres, being these features very interesting for applying this material in oxyfuel combustion and for conducting chemical reactions involving pure O_2 (e.g. partial oxidation of methane, etc.). Accordingly, LSCF membranes were tested varying CO_2 content in sweep stream (0-100%) at 1000-900 ºC, and under reducing conditions on sweep side by means the addition of 15% methane to the sweep stream.

Results and Discussion: BSCF and LSCF asymmetric membranes exhibited very high permeation fluxes, when surface activated and choosing the right operating conditions. For example, an oxygen flux of 13.2 $ml \cdot min^{-1} \cdot cm^{-2}$ was obtained through a LSCF membrane at 1000 ºC under O_2/Ar gradient. Furthermore, upon catalytic surface activation, oxygen fluxes at low temperature (600 ºC) improved up to 300%, confirming the direct effect of catalyst addition in the enhancement of surface exchange reactions. Additional tests under CO_2 and reducing environments have demonstrated LSCF good stability and performance, yielding at 1000 ºC an oxygen flux of 5.6 $ml\cdot min^{-1}\cdot cm^{-2}$ under full-CO_2 environment, using synthetic air as feed.

Conclusions: A complete permeation study over asymmetric thin-film BSCF and LSCF membrane was conducted. Several parameters were varied in order to understand oxygen permeation mechanism, i.e., variation of temperature, sweep gas flow, pO_2 in feed, and CO_2 % in sweep gas, and surface. LSCF membranes are very promising for oxygen separation, particularly for application in oxyfuel plants and catalytic membrane reactors.

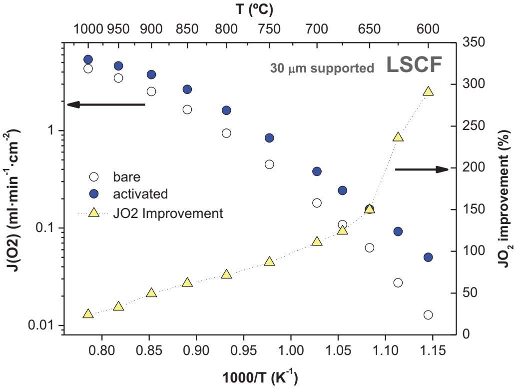


Fig. 11. Oxygen permeation through LSCF as a function of temperature and surface activation.

References: [1] S. Baumann, J.M. Serra, P. Lobera, S. Escolástico, F. Schulze-Küppers, W. A. Meulenberg, J. Memb. Sci. 377 (2011) 198-205; [2] J.M. Serra, J. Garcia-Fayos, F. Schulze-Küppers, S. Baumann, W. A. Meulenberg, J. Memb. Sci. (2013) doi

P- 7

A mixed (protonic and electronic) conducting composite membrane for hydrogen separation

Ji Haeng Yu*, Hwan Soo Kim, Chung-Yul Yoo, Jong Hoon Joo,
Energy Materials and Convergence Research Department, Korea Institute of Energy Research
152 Gajeongro, Yuseong-gu, Daejeon 305-343, Republic of Korea

Keywords: hydrogen separation membrane, composite, proton-conducting oxide

Proton conductors have attracted considerable attention for solid oxide fuel cell (SOFC), hydrogen pump, gas sensor, and membrane separators [1-3]. Doped $SrCeO_3$ exhibits appreciable proton conductivity in hydrogen-containing atmosphere at high temperature. However commercial realization has been hampered due to the reactivity of $SrCeO_3$ with CO_2. The chemical stability and proton conductivity are dependent on dopant type. The purpose of this work is to investigate chemical stability of $SrCe_{0.95}Gd_{0.05}O_{3-\alpha}$-$Ce_{0.9}Gd_{0.1}O_{2-\delta}$ composites in CO_2 and H_2 gases. $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ enhanced chemical stability of the cerate material in CO_2 and raised electronic conductivity in hydrogen atmosphere. Thermogravimetric analysis (TGA) was performed in gaseous CO_2 and electrical conductivity of the composites were also measured between 500 and 900°C in air and H_2 atmosphere. The hydrogen permeation of $SrCe_{0.95}Gd_{0.05}O_{3-\alpha}$-$Ce_{0.9}Gd_{0.1}O_{2-\beta}$ composite membranes was investigated as a function of volumetric content of $SrCe_{0.95}Gd_{0.05}O_{3-\alpha}$. The $SrCe_{0.95}Gd_{0.05}O_{3-\alpha}$-$Ce_{0.9}Gd_{0.1}O_{2-\beta}$ (6:4) membrane with a thickness of 1.0 mm showed the highest hydrogen permeability with the flux of 0.12 ml/min·cm^2 at 800°C in 100% H_2 as feed gas.

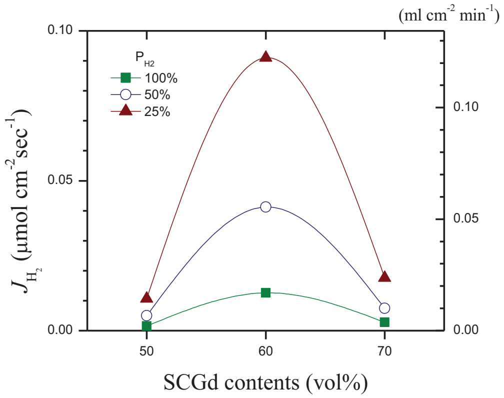


Fig. 1 Hydrogen permeation flux through mixed conducting composite membranes (thickness=1.0 mm) as a function of composition

References

[1] H. Matsumoto, S. Hamajima, T. Yajima, H. Iwahara, J. Electrochem. Soc. **148** (2001) D121.
[2] T. Schober, Solid State Ionic **163-163** (2003) 277.
[3] N. Taniguchi, E. Yasumoto, T. Gamo, J. Electrochem. Soc. **143** (1996) 1886

P- 8

Water permeation studies on a BCY membrane reactor

Selgin Al, Evangelos Papaioannou and Ian Metcalfe
Department of Chemical Engineering and Advanced Materials
Newcastle University, NE1 7RU, Newcastle upon Tyne, UK
Email: s.al @newcastle.ac.uk

Keywords: BCY, water permeation, perovskites, fuel cells

Yttria-doped barium cerate with different yttrium content exhibits both proton and oxygen ion conductivity at intermediate temperatures [1-3]. This type of perovskite ceramics can create protonic defects in water vapor rich environments according to the reversible reaction shown below.

$$H_2O\ (g) + V_O^{\bullet\bullet} + O_O \leftrightarrow 2OH_O^{\bullet} \quad (1)$$

These materials are suggested to be used as electrolytes for SOFCs whenever hydrocarbons are used as fuel due to steam permeation [4].Thus, internal reforming of fuel may be achieved. Internal reforming is more efficient but introduction of all of the water in the fuel cell inlet can lead to severe internal temperature gradients within the fuel cell as the reforming reaction is fast and endothermic. Steam permeable membranes such as yttrium-doped cerate can help to introduce water across the SOFC electrolyte while it is operational (see Fig 1). The distributed water introduction will result in controlled reforming and reduce fuel cell temperature gradients. However, the two defect species in Reaction 1 bring much complexity to the system. The mechanism of water disassociation and incorporation for SOFCs is not well understood. In this work, the effect of Platinum (Pt) electrode on permeation was investigated.

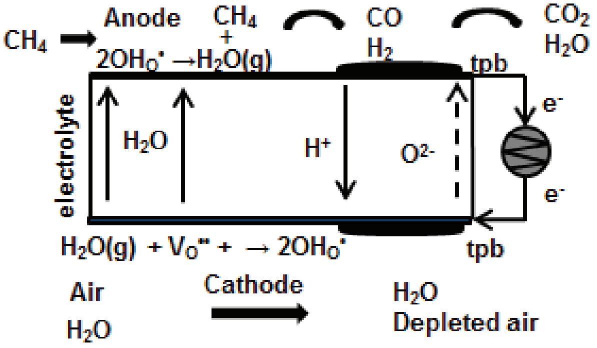


Fig. 1. The configuration of steam permeation dependence on tpb for SOFCs

Dense pellets of polycrystalline 20 mol% yttrium-doped barium cerate $BaCe_{0.8}Y_{0.2}O_{3-\alpha}$ (BCY20) was used for steam permeation studies. Dry helium in the permeate side and humidified nitrogen in the feed side was used to measure water permeation across the membrane under reference conditions. The three phase boundary (tpb)/ surface area ratio of the electrolyte was varied in order to investigate whether steam permeation happens at the tpb or over the exposed surface of the electrolyte. The results indicated that Pt on the feed side increases the water flux indicating the the feed side surface processes were limiting for the bare membrane. However, Pt on the permeate side appears to have a blocking role that results in a reduction of flux.

References

[1] Kreuer, K.D., T. Dippel, Y.M. Baikov, and J. Maier, Solid State Ionics, 1996. 86–88, Part 1(0) p. 613-620.
[2]Ricote, S., N. Bonanos, and G. Caboche, Solid State Ionics, 2009. 180(14-16): p. 990-997.
[3]Swartzlander, W.G.C.a.R., Proceedings of the 26th Risø International Symposium on Materials Science Solid State Electrochemistry, 2005(Sept): p. 185-196.
[4] Coors, W., *P.* Solid State Ionics, 2007. 178(7-10): p. 481-485.

P- 9

$BaCe_{1-x}Zr_xY_{0.15}O_{3-\delta}$ (x = 0.1, 0.2, 0.3, 0.4) proton conducting materials for hydrogen separation membrane applications

C. Mortalò [1], S. Fasolin [1], S. Boldrini, E. Mercadelli [2], A. Sanson [2], S. Barison [1], M. Fabrizio [1]
[1] CNR-IENI Corso Stati Uniti 4, 35127, Padova (Italy)
[2] CNR- ISTEC Via Granarolo, 64, 48018, Faenza (RA) (Italy)
Email: c.mortalo@ieni.cnr.it

Keywords: hydrogen separation, ceramic membrane, perovskite, mixed electronic-protonic conductor

Inorganic ceramic membranes based on mixed proton-electron conductors have received considerable attentions thanks to their possible applications such as hydrogen separation membranes, hydrogen pumps, hydrogen sensors and anodes for protonic ceramic fuel cells (PCFCs). Hydrogen separation from syngas at high temperatures (T > 500°C) is one of the most important hydrogen-producing technologies and has attracted extensive interest in last few decades [1].

In view of this, proton conducting electrolyte materials based on cerate-zirconate solid solutions are promising candidates for the development of hydrogen separation ceramic membranes. Among these, Y-doped $BaCe_{1-x}Zr_xO_{3-\delta}$ showed high proton conductivity and good chemical stability in CO_2- containing atmospheres, such as in case of syngas conditions [2].

In this work, with the final aim to fabricate asymmetric ceramic membranes for hydrogen separation, $BaCe_{1-x}Zr_xY_{0.15}O_{3-\delta}$ (x = 0.1, 0.2, 0.3 and 0.4, hereafter BCZY) proton conducting materials have been prepared by different synthetic procedures. In particular, for the powders preparation, various techniques such as sol-gel Pechini (SGP) method, microwave-assisted SGP method and solid state reaction have been developed. Morphology, structure, chemical stability and conductivity behaviour have been extensively investigated [3-4]. Moreover, die-pressing method and tape casting were explored to prepare porous cermets based on Ni-BCZY. On the other hand, aiming to prepare anode-supported PCFCs, a simple suspension spray process has been optimized for the deposition of dense BCZY films on porous Ni-BCZY substrates. In the same way, with the purpose to fabricate asymmetric ceramic membrane based on Ni-BCZY/Ni-BCZY porous-dense structure, a suspension spray method will be considered for the deposition of dense Ni-BCZY layers on Ni-BCZY porous cermets.

References

[1] T. Norby, R. Hausgrud, Nonporous Inorganic Membranes, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006
[2] K. D. Kreuer, Ann. Rev. Mater. Res. 33 (2003) 333.
[3] S. Barison, M.Battagliarin, T. Cavallin, L. Doubova, M. Fabrizio, C.Mortalo`, S.Boldrini, L.Malavasi, R.Gerbasi, J. Mater. Chem. 18 (2008) 5120.
[4] S. Barison, S., M. Fabrizio, M., S. Fasolin, F. Montagner, C. Mortalò, Mater. Res. Bull. 45 (2010) 1171.

P- 10

Ni-Al_2O_3 composite membrane for hydrogen separation

Stefano Fasolin, Cecilia Mortalò, Monica Fabrizio and Simona Barison
Institute for Energetics and Interphases, National Reasearch Council of Italy
Corso Stati uniti 4, 35127, Padova, Italy
Email: stefano.fasolin@ieni.cnr.it

Keywords: hydrogen, composite membrane, nickel, alumina

This work presents fabrication of Ni-Al_2O_3 composite membranes for hydrogen separation, by Solid State Reaction and an impregnation method. The role of Al_2O_3 precursor is also investigated. In fact, α-Al_2O_3 and γ-Al_2O_3 have been used as alumina source. Nickel source is $Ni(NO_3)_2 \cdot 6H_2O$. [1]

By Solid State Reaction procedure, mixtures containing α-Al_2O_3 or γ-Al_2O_3 and Ni 10 wt% are ball milled with a properly amount of ethanol in ZrO_2 jar. After 12 h of effective mixing, the mixtures are dried in air at 100 °C for 24 h. The so obtained powder are grounded and uniaxially pressed at 195 MPa in circular shape of about 1,3 cm. Different heat treatments at 900 °C, 1100 °C and 1300°C were tested to understand how this can affect the final phases and sintering behaviour.

With impregnation method, raw α-Al_2O_3 and γ-Al_2O_3 are ball milled with 5 wt% of Polyvinyl alcohol for 12 h in ZrO_2 jar. After 2 h at 85 °C, powders are grounded, uniaxially pressed at 195 MPa in circular shape of about 1,3 cm and heat treated (1000 °C and 1200 °C). After that, a $Ni(NO_3)_2 \cdot 6H_2O$ solution is introduced into sintered pellet in order to obtain final amount of Ni 10 wt%. The as obtained pellet were heat treated at 900°C to remove nitrate and water residuals.

After preparation, the membranes obtained by both methods were reduced at 1000 °C for 2 h in hydrogen atmosphere. Phases and morphologies were analyzed by means of XRD and SEM analyses respectively to compare the different membranes obtained.

References

[1] S. Vichaphund, D. Atong, Journal of Materials Science & Technology **26** (2010) 589.

P- 11

Studies of the inhibition influence of other gases such as H_2O, CO, CO_2, N_2 on the H_2 permeation using a Pd-based membrane

M. M. Barreiro[1], M. Maroño, J. M. Sánchez
[1]*CIEMAT, Combustion and Gasification Division, Avenida Complutense, 40, 28040 Madrid,*
Email: *mdelmar.barreiro@ciemat.es; josemaria.sanchez@ciemat.es*
Keywords: Palladium, hydrogen separation, membrane reactor, inhibition influence

The aim of the present study is investigate the inhibition influence of other gases from binary and ternary gas mixtures of H_2/N_2; H_2/CO_2, H_2/H_2O and $H_2/N_2/CO$ on hydrogen permeation. The effect on H_2 permeation with respect of the temperature in CO ternary mixtures and, as well as, the effect on H_2 permeation as a function of the feed gas flow rate and the pressure in binary and ternary mixtures are discussed.

The experiments were conducted with a semi-commercial supported Pd membrane (O.D. = 2.54 cm; L=15 cm) in a single membrane reactor from CRI Catalyst Co., U.S. The samples can be treated up to $2Nm^3/h$, 793K and 1700 KPa.

It is important to study the effect of CO on the H_2 permeation as a function of the temperature because it is well known that the CO can adsorb on the surface of the Pd membrane [1]. Due to this effect, the CO can create a competition with the H_2 to find the active sites of the Pd membrane and block the H_2 adsorption. The H_2 adsorption is the first step to permeate H_2 through the membrane. Experiments were run using N_2 to dilute the H_2/CO mixture to avoid to produce pinholes at the Pd membrane. Two mixtures of $H_2/N_2/CO$ (17.2/63.9/18.9) and (41.8/53.1/5.2) (% v/v) were analyzed. As well as, the same experiments were chosen using binary mixtures of H_2/N_2 (17.2/82.8) and (41.8/58.2) (% v/v) to make a comparison with the results of the ternary mixtures. The experiments started at 723 K during one hour and after that, the temperature was reduced to 653 K at a rate of 0.5 ºC per minute. The temperature was then kept constant for one hour. This procedure was repeated from 653 K to 623 K and from 623 K to 593 K. For all tests, the performance of the membrane was studied in absence of sweep gas and keeping the H_2 partial pressure at 150 kPa.

The result showed a high dependence of the H_2 permeation on the temperature. For ternary mixtures, it can be seen that from 653 K on, the H_2 flux was reduced strongly compared to the binary mixtures and this difference further increases. This result can suggest a change of the controlling step of the H_2 permeation through Pd membrane, that it is, from 723 K to 653 K, the controlling step is the diffusion of atomic H_2 in the metallic lattice and, from 653 K to 593 K, the controlling step can start to be the H_2 adsorption on the membrane surface.

In addition, the effect of the feed flow rate on pure H_2 and mixtures of H_2/N_2 (50/50) (% v/v), H_2/CO_2 (41.8/58.2) (% v/v) and $H_2/N_2/CO$ (41.8/83.1/5.2) (% v/v) on the H_2 permeation at 723, 653 and 593 K and at 150 kPa of H_2 partial pressure was studied. For all mixtures, a dependence of the H_2 flux on the feed flow rate was observed, showing an increase of the H_2 flux with respect to the feed flux until a stationary value was reached. Additionally, results showed that for all temperatures, the binary mixture of H_2/CO_2 had a stronger inhibition effect compared to the rest of the mixtures. It must be taken into account that the reverse water gas shift reaction

(CO_2+H_2 = CO+H_2O) is favored to occur at higher temperatures [2], resulting in a final quaternary mixture of H_2/CO_2/CO/H_2O.

Due to these results, an evaluation of the inhibition effect of the H_2O and the quaternary mixture with respect of H_2 permeation was evaluated. H_2 permeability tests were conducted using binary mixtures of H_2/N_2; H_2/CO_2 and H_2/H_2O at different driving force and at 723 K. The H_2 permeance was obtained as a mean of the linear fit. Contrary to previous studies using pure H_2 [3], the linear regression analysis showed a deviation from the Sievert´s Law. This result can denote that the gas film resistance, or the adsorption of the H_2 on the surface of the Pd membrane, probably can start to be the controlling step of the H_2 permeation through the Pd membrane. As well as, in agreement with K. Hou [4], results showed that the inhibition influence of other gases on the H_2 permeation followed this order: H_2O>CO_2>N_2.

Hydrogen permeation through the Pd membrane using a number of mixtures was evaluated at different temperatures, feed flow rate and pressures. Results show that the pressure, temperature and the feed flow rate have a strong influence on the H_2 permeation. As well as, the mixtures in presence of H_2O have a stronger inhibition of the H_2 permeation followed by the binary mixture of H_2/CO_2 and H_2/N_2/CO and H_2/N_2, respectively. Those results are useful to optimize the conditions to separate gas mixtures, and then it can be beneficial in order to enhance the conversion of equilibrium-limited reactions.

References

[1] J. Catalano et. al. Journal of Membrane Science 362 (2010) 221-233.
[2] M. M. Barreiro et. al. Proceeding of the Sixth International Conference on Clean coal Technologies (CCT 2013).
[3] F. Bustamante et. al. AIChE Journal 50 (2004) 1028–1041.
[4] K. Hou et. al. Journal of Membrane Science 206 (2002) 119-130.

P- 12

Hydrogen separation through doped $La_{5.5}WO_{11.25-\delta}$ based membranes

S. Escolástico[1], R. Zanón[1], C. Solís[1], J. Seeger[2], M. Ivanova[2], W. Meulenberg[2], J. M. Serra[1,*]
[1] Instituto de Tecnología Química, UPV-CSIC, Av. de los Naranjos s/n, 46022 Valencia, Spain
[2] Forschungszentrum Jülich GmbH IEK-1, 52425 Jülich (Germany)
Email: soesro@itq.upv.es; jmserra@itq.upv.es
Keywords: conducting materials, proton transport, tungstates

Ln_6WO_{12} compounds exhibit important mixed electronic–protonic conduction at high temperatures and under reducing conditions [1], furthermore they are also stable in CO_2-rich gas environments [2,3]. From this family of compounds, $La_{6-x}WO_y$ ($0.4<x<0.7$) presents the highest protonic conductivity reported to date. These compounds can be used as selective membranes for H_2 separation at very high temperatures (600-1000 ºC), and they offer the advantage that separation does not require the application of external currents. The separation of H_2 at high temperatures is a key component in pre-combustion strategies in power plants, typically integrated with water–gas shift or even with steam reforming catalytic converters. Another interesting use of H_2-permeable membranes is integration in new catalytic membrane reactors (CMRs), which can result in sustainable processes with less energy consumption and high reaction yields.

The present work focuses on the study of Mo and Re doping in $La_{5.5}WO_{11.25-d}$ to improve the electronic conductivity at low temperatures, and consequently, to increase the H_2 flow obtained at temperatures below 750ºC. Re and Mo present different oxidation states, which should result in increased electronic conductivity and generate additional oxygen vacancies, with a subsequent improvement in the overall ionic conductivity (both proton and oxygen-ion transport). Transport properties of the materials were studied by standard four-point DC conductivity measurements as a function of temperature for different environments. These measurements were focused on the study of the isotopic and hydration effect. Permeation measurements were performed on a double chamber quartz reactor and hydrogen was separated from a mixture of H_2-He (dry or saturated in water at 25 ºC) using argon as sweep gas. Membranes used consisted of a gastight thick disc with a diameter of 15 mm sintered at 1550 ºC. Both disk sides were coated by screen printing with a 20 μm layer of a Pt ink (Mateck, Germany) in order to improve the catalytic activity of the sample. The influence of three different parameters on the hydrogen separation was studied: operation temperature, hydrogen feed concentration and hydration degree of the membrane.After H_2 measurements, the sample integrity was checked by using XRD, SEM, and TEM. Stability in CO_2-rich atmospheres was evaluated by using thermogravimetric analysis (TGA), and the stability of the compounds under atmospheres containing COS, HCN, CO_2, CO, and H_2 was evaluated by using XRD.

References

[1] R. Haugsrud, Solid State Ionics 2007, 178, 555.
[2] S. Escolástico, C. Solís, J. M. Serra, Int. J. Hydrogen Energy 2011, 36,11946.
[3] S. Escolástico, C. Solís, T. Scherb, G. Schumacher, J. M. Serra, J. Membr. Sci. 2013, 444.
[4] S. Escolastico, J. Seeger, S. Roitsch, M. Ivanova, W. A. Meulenberg, J. M. Serra ChemSusChem in press (2013) (doi: 10.1002/cssc.201300091)

P- 13

Hydrogen surface exchange on proton conducting oxides studied by gas phase analysis with mass spectrometry

Ragnhild Hancke, Zuoan Li, Reidar Haugsrud
Department of Chemistry, Centre for Materials Science and Nanotechnology, University of Oslo
FASE, Gaustadalleen 21, NO-0349, Oslo, Norway
Email: ragnhild.hancke@smn.uio.no

Keywords: surface kinetics of HTPCs, H_2/D_2/HD isotope couples, surface exchange mechanism, critical thickness

In the search for mixed proton-electron conducting oxides with fast surface kinetics, a better understanding of the exchange mechanisms and role of surface defects therein is crucial. One approach, well known from heterogeneous catalysis, is to probe the distribution of different isotope specific gas species as a function of time over the solid sample surface. In the present study, we address the kinetics of H_2 dissociation and exchange on proton conducting oxides at elevated temperatures by H_2-D_2 isotope labeling in combination with mass spectrometry. Unsubstituted, Nd-substituted and Mo-substituted lanthanum tungstates (with general formula unit $La_{28-x}W_{4+x}O_{54+3x/2}v_{2-3x/2}$), as well as Y-doped barium cerate and Yb-doped strontium cerate are characterized with respect to differences in surface morphology and different conditions. These conditions include temperature, water vapor pressure and hydrogen pressure; the latter dependencies also subjected to a more detailed analysis based on point defect thermodynamics and chemical kinetics. The exchange rates are, moreover, related to the tracer surface exchange coefficients from H/D exchange and, finally, the critical thicknesses (L_C) of the different materials are estimated based on the respective surface exchange rates and ambipolar conductivities.

The temperature dependencies showed that the exchange rates of unsubstituted and Nd-substituted lanthanum tungstate have activation energies of 130 and 90 kJ mol^{-1}, respectively, whereas it is virtually non-activated for the Mo-substituted specimen. It is speculated whether this difference between the tungstates is related to the differences in the concentration of electronic charge carriers. The exchange rates of Y-doped barium cerate and Yb-doped strontium cerate have activation energies of 50 and 130 kJ mol^{-1}, respectively. The estimated critical thicknesses are displayed in Fig. 1. L_C is by far greatest for barium cerate, and for strontium cerate it is found to become as low as 0.02 μm in the temperature range relevant for hydrogen separation. For the lanthanum tungstates it is approximately 30 μm, and this suggests that for unsubstituted lanthanum tungstate, surface kinetic limitations must be overcome to reach a target flux of 1 mL min^{-1} cm^{-2} at 800 °C.

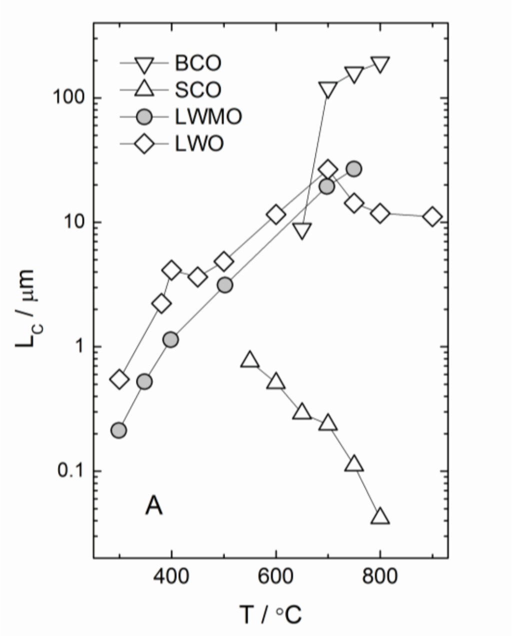


Fig. 12. Estimated critical thicknesses as a function of temperature for Y-doped barium cerate (BCO) Yb-doped strontium cerate (SCO), Mo-substituted and unsubstituted lanthanum tungstate (LWMO and LWO, respectively).

P- 14

Conductivity relaxation study of La_6WO_{12}

C. Solís, S. Escolastico, R. Zanón, J.M. Serra*
Instituto de Tecnología Química, UPV-CSIC, C/ Camino de Vera, s/n, Valencia 46022, Spain
Email: csolisd@itq.upv.es; jmserra@itq.upv.es

Keywords: La_6WO_{12}, conductivity relaxation, protonic conductor

La_6WO_{12} (LWO) based compounds present relatively high proton or ambipolar proton-electron conductivity together with chemical stability in CO_2 and H_2O rich atmospheres.

Oxidation and hydration kinetics has been studied by conductivity relaxation upon stepwise changes in the oxygen or water vapour activity [1-3]. The diffusivity of protonic defects involves proton transfer between neighbouring oxygen ions. Protons are incorporated in the oxide through the hydration process. It has been assumed [4] that in this material oxide ions in the oxygen sublattice exchange with available interstitial positions in the octahedron around W, getting anti-Frenkel (intrinsic) disorder and then, having the complete reaction: $H_2O + 2O_O^X + v_i^X \leftrightarrow 2OH_O^{\bullet} + O_i''$

Reported mass relaxation experiments [5] showed that the chemical diffusion of water in a (anhydrous) proton conductor is governed by ambipolar diffusion of protons and oxygen ions. More specifically, the relaxation behaviour depends on the participating charge carriers (O^{-2}, H^+, electrons or electron holes) and on the given water or oxygen activity stepwise change. Typically, proton diffusion in oxides is two orders of magnitude faster than oxygen diffusion [6]. In the present work, in order to investigate the hydration and oxidation kinetics of LWO, different conductivity relaxation measurements were performed on a single LWO sample by changing pO_2 and pH_2O/pD_2O under high pO_2 conditions. By assuming that the chemical diffusivity was constant across the pO_2 and pH_2O experimental window, the general solution for the spatial average concentration of species can be calculated employing established analytic solutions of Fick's second law.

Conductivity relaxation measurements of LWO at high temperature under high pO_2 have been studied: (1) by oxidation/reduction in dry and wet atmospheres; and (2) by hydration/dehydration in oxygen using H_2O and D_2O (as shown in Fig. 1). In this case, the hydration is governed by a unique water diffusion process, following a single-fold monotonic relaxation [3]. Surface exchange coefficients (*k*) and diffusion coefficients (*D*) are calculated from the fitting of the hydration-dehydration transients to the solution of Fick's second law. *D* values are in the range 10^{-5} - 10^{-6} cm^2/s from 913-1023 K, comparable to other proton conductors [3].

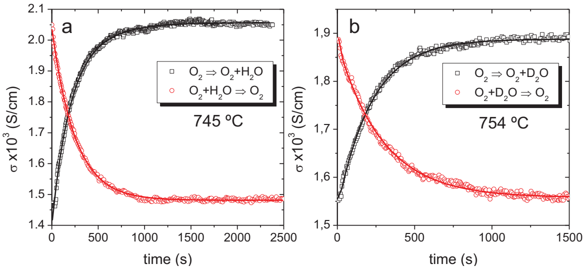


Fig. 1 Conductivity relaxation measurements at around 750 °C in O_2*-*O_2+H_2O *(a) and* O_2*-*O_2+D_2O *changes (b)*

D and *k* coefficients extracted from hydration/dehydration experiments are one order of magnitude lower than those obtained from oxidation/reduction experiments (not affected by the presence of protonic defects within the studied pH_2O, pO_2 and temperature range). This fact may be ascribed to the ambipolar diffusion of water, i.e., diffusion of protons and oxygen vacancies through the oxide [7,8]. The reason for the significantly smaller ambipolar water diffusion coefficient remains unanswered.

References

[1] HI Yoo *et al.*, *Phys. Chem. Chem. Phys.* 2008, 10 974.
[2] T. Kudo *et al.*, *Solid State Ionics*, 2009, 179, 541.
[3] HI Yoo and CE Lee, *J. Phys. Chem. Solids*, 2008, 69, 1758.
[4] R. Haugsrud, C. Kjølseth, *J. Phys. Chem. Solids,* 2008, 69, 1758
[5] D.K. Kreuer *et al.*, *Solid State Ionics*, 1994, 70-71, 278.
[6] T. Schober, WG. Coors, *Solid State Ionics* 2005, 176, 357
[7] K. D. Kreuer *et al.*, *Phys. Chem. Chem. Phys.* 1998, 103, 552.
[8] C. Solís, S. Escolástico, R. Haugsrud, J.M. Serra, *J. Phys. Chem. C*, 2011, 115, 11124

P- 15

Conductivity relaxation experiments on oxide materials with large nonstoichiometry deviations

Andreas Falkenstein, David N. Mueller, Roger A. De Souza and Manfred Martin
Institute of Physical Chemistry, RWTH Aachen University and JARA-FIT
Landoltweg 2, 52074 Aachen, Germany
E-mail: falkenstein@pc.rwth-aachen.de, desouza@pc.rwth-aachen.de
Keywords: conductivity relaxation, BSCF

The conductivity relaxation method is generally described as an easy to use method to obtain the oxygen transport parameters of mixed ionic and electronic conducting materials. Two important constraints when performing the experiment have been described in the literature: i) the change in oxygen activity in the surrounding gas phase should be very fast compared to the relaxation time of the sample (although it is possible to introduce a flush time correction if the change in oxygen activity is still faster than the relaxation [1]). ii) The change in oxygen activity is large enough to yield a significant change in the conductivity as a function of time, but it must be small enough to be within the linear regime [2,3,4].

Here we would like to draw attention to a third constraint: the amount of oxygen released or taken up by the sample should be negligible compared with the amount of oxygen flowing past the sample:

$$j_{\text{gas}} \cdot A_{\text{cell}} >> j_{\text{in/out}} \cdot A_{\text{sample}} \qquad (1),$$

where j_{gas} is the flux of oxygen in the reactor vessel, A_{cell} the reactor's cross-sectional area, $j_{\text{in/out}}$ the flux of oxygen through the sample's surface, and A_{sample} the sample's surface area.

When performing relaxation experiments on BSCF5582, the response of a potentiometric oxygen sensor situated behind the sample shows a huge deviation compared with the response when the same experimental setup is loaded with an inert sample of Al_2O_3 (see Fig. 1). If the oxygen that is released or taken up by the sample would be negligible, one would expect both curves in Fig. 1 to be identical. To optimise Equation (1) one can – amongst other possibilities – simply increase the flow rate to increase the left hand side of the equation. Fig. 2 shows the oxygen transport parameters D_{chem} and k_{chem} obtained as a function of the flow rate $\dot{V}$. Because the transport parameters in Fig. 2 are dependent on the flow rate the amount of oxygen released or taken up by the sample is not negligible [5].

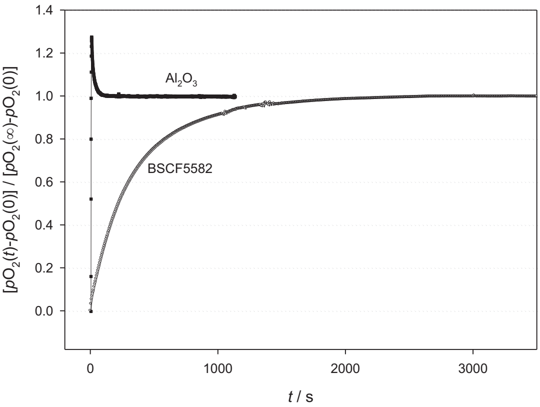


Fig 1. Normalised response of a potentiometric oxygen sensor situated behind the sample as a function of time.

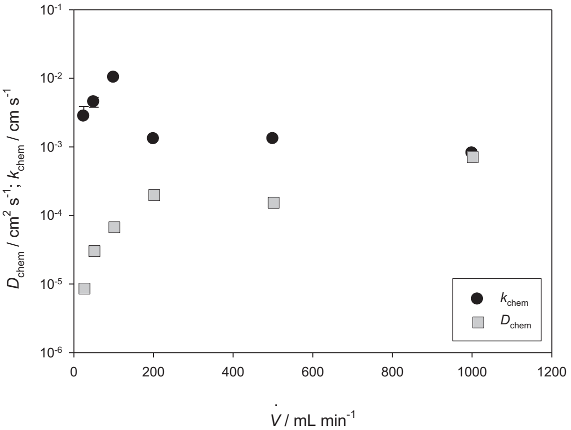


Fig. 2. Dependency of the oxygen transport parameters k_{chem} and D_{chem} on the flow rate

References

[1] M. W. den Otter, H. J. M. Bouwmeester, B. A. Boukamp, H. Verweij, *J. Electrochem. Soc.* **2001**, *146*, J1–J6
[2] S. Wang, A. Verma, Y.L. Yang, A.J. Jacobson, B. Abeles, *Solid State Ionics* **2001**, *140*, 125-133
[3] J. Maier, *J. Am. Ceram. Soc.* **1993**, *76*, 1212–1217
[4] M. Leonhardt, R. A. De Souza, J. Claus, J. Maier, *J. Electrochem. Soc.* **2002**, *149*, J19–J26
[5] A. Falkenstein, D. N. Mueller, R. A. De Souza, M. Martin, *in preparation*

P- 16

Experimental surface characterization of oxygen ion transport membranes for flux model development under oxy-fuel combustion conditions

Anton Hunt[1], Giorgos Dimitrakopoulos[1], Prof. Patrick Kirchen[2] and Prof. Ahmed Ghoniem[1]
[1]Massachusetts Institute of Technology, Dept. of Mechanical Engineering (*77 Massachusetts Avenue, Cambridge MA 02139, USA*)
[2]University of British Columbia, Dept. of Mechanical Engineering (*2054 Applied Science Lane, Vancouver BC, V6T 1Z4*)
Email: antonh@mit.edu

Keywords: ion transport membrane reactor, oxy-fuel combustion, oxygen flux, surface characterization

Oxy-fuel combustion is seen as an important facilitator in carbon sequestration; namely the production of a clean CO2 stream. Oxygen Ion Transport Membrane (ITM) technology for passively separating out pure oxygen from air is widely regarded as key in the development of low energy penalty oxy-fuel combustion processes. The coupling of an oxy-combustion reaction zone with the producing surface of an oxygen ITM is seen as beneficial as the fuel actively enhances oxygen flux. An order of magnitude rise in flux upon introduction of fuel have been observed through our experimental methods.

The oxygen flux mechanism, particularly in the presence of fuel is poorly defined however. As identified by [1] flux resistances are associated with the bulk ion transport through the membrane as well as the surface exchanges on both sides. Whilst the bulk ion diffusion is well understood through the Wagner equation [2], the surface exchange resistances require some experimental insight to determine what the critical rate-limiting reactions are. In conjunction with a detailed numerical model which simulates the conditions the membrane sees at the surfaces, a novel ITM reactor has been developed at MIT to employ in-situ surface characterization techniques.

Reactors used for oxygen ITM analysis under both inert and reactive operation have typically been small diameter (a few mm) tubular or button-cell discs housed in small heating chambers with through-flow and reverse stagnation flow configurations respectively. Traditionally gas composition measurements are taken at the well-mixed inlet and outlet streams far from the membrane surface allowing the measurement of overall performance metrics such as oxygen flux and fuel conversion. The coupling of these metrics to the surface reactions is not possible due to the lack of available measurements there.

The ITM reactor we present here is capable of these measurements. The reactor, shown in *Figure 1* and introduced in [3], consists of a large scale planar stagnation flow whereby the top air side and the bottom sweep or permeate side are separated by a 75x75mm membrane, of composition La0.9Ca0.1FeO3-d. The reactor is constructed from high temperature resistant metal alloy *Inconel 601*, with quartz/ceramic internal coverage for inert surfaces and has a dual heater system allowing operation of up to 1000°C. An in-situ quartz probe on the permeate side of the membrane (*Figure 2*) allows for spatial gas composition profiling near to and on the membrane surface.

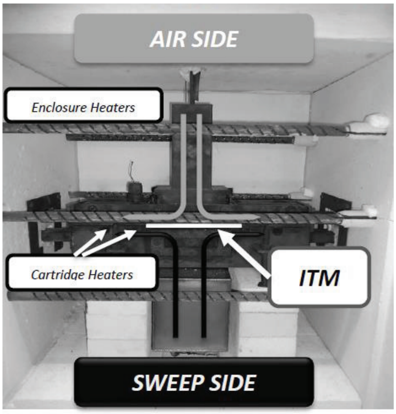


Figure 1: Novel ITM reactor in enclosure

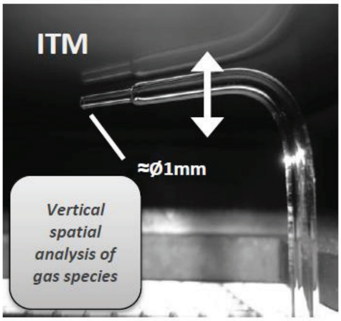


Figure 2: Quartz gas sampling probe for surface ITM measurements

Using a range of measurements of the overall oxygen flux and surface oxygen concentrations, an inert flux model (CO2 sweep gas) has been developed using a simplified 1-step surface reaction mechanism for the adsorption/incorporation of gas phase oxygen $(O2)$ with the oxygen vacancies $(VO\cdot\cdot)$ to form lattice oxygen ions (OOX); (*Equation 1*). A detailed numerical model has thus been developed in conjunction (*Refs.* [4-6]). The forward (kf) and reverse (kr) reaction rates as well as the lattice oxygen ion diffusion coefficient (DV) are fitted using a standard Arrhenius expression. Hereby we therefore present the first direct experimental characterization of the oxygen flux mechanism across ITMs, with future work to focus on adapting the mechanism to accommodate the presence of fuel on the sweep or permeate side. With a robust mechanism in place, optimization of industrial-scale membrane modules can proceed.

$$\frac{1}{2}O_2 + V_O^{\cdot\cdot} \overset{k_f/k_r}{\Longleftrightarrow} O_O^X + 2h^{\cdot} \qquad \textit{Equation 1}$$

References:

[1]: S.J. Xu, W.J. Thomson, Oxygen permeation rates through ion-conducting perovskite membranes, *Chem. Engineering Sci.* 54 (1999) 3839-3850.
[2]: Wagner, C. (1951). Diffusion and high temperature oxidation of metals. *Atom movements*, (pp. 153-173). Cleveland: ASM.
[3]: P. Kirchen, D.J. Apo, A. Hunt, A.F. Ghoniem, A novel ion transport membrane reactor for fundamental investigations of oxygen permeation and oxy-combustion under reactive flow conditions, *Proc. of the Comb. Inst.* 34 (2013) 3463-3470.
[4]: J. Hong, P. Kirchen, A.F. Ghoniem, Laminar oxyfuel diffusion flame supported by an oxygen permeable ion transport membrane, *Combustion and Flame*, 160 (2013) 704-717
[5]: J. Hong, P. Kirchen, A.F. Ghoniem, Interactions between oxygen permeation and homogeneous phase fuel conversion on the sweep side of an ion transport membrane, *J. of Memb. Sci.,* 428 (2013) 309-322
[6]: J. Hong, P. Kirchen, A.F. Ghoniem, Ion transport membrane heterogeneous catalysis, *J. of Memb. Sci.*, submitted, (2013)

P- 17

Influence of yttrium doping on the stability of the cubic $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ phase studied by electron microscopy

Matthias Meffert[1,2], Philipp Müller[1,2], Heike Störmer[1], Christian Niedrig[2], Stefan F. Wagner[2],
Ellen Ivers-Tiffée[2,3] and Dagmar Gerthsen[1,3]
[1] Karlsruher Institut für Technologie (KIT), Laboratorium für Elektronenmikroskopie,
Engesserstraße 7, 76131 Karlsruhe, Germany
[2] Karlsruher Institut für Technologie (KIT), Institut für Werkstoffe der Elektrotechnik,
Adenauerring 20b, 76131 Karlsruhe, Germany
[3] DFG-Center for Functional Nanostructures (CFN), Karlsruher Institut für Technologie (KIT),
76131 Karlsruhe, Germany
Email: matthias.meffert@kit.edu

Keywords: perovskite, oxygen separation membrane, yttrium, BSCF

Among several mixed-ionic and electronic conductors the cubic perovskite phase of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) possesses outstanding oxygen permeation properties due to its high oxygen non-stoichiometry. However, several studies reported a decrease of the oxygen conductivity in the intermediate temperature range which was attributed to the decomposition of the cubic perovskite phase into a hexagonal phase at temperatures below 840 °C [1-2]. One explanation for this behavior is the reduced oxygen vacancy concentration which leads to an increase of the Co-valence state and therefore to a reduction of the ionic radius accompanied by the formation of various secondary phases. Transmission electron microscopy (TEM) studies revealed additional secondary phases like CoO precipitates and plate-like precipitates consisting of hexagonal, cubic and barium cobaltate lamellae [3-5].

Since the decomposition of the cubic BSCF phase is mainly driven by the valence change of the B-site ions, doping with monovalent transition metals was investigated to improve the phase stability of the cubic phase without sacrificing the high oxygen permeability. Recent studies reported positive effects for dopants like Zr or Y [6-7].

In this study Y-doped BSCF bulk samples were prepared using the mixed-oxide route and annealed at temperatures between 700 °C and 900 °C in ambient air for 100 h. The Y-concentration was varied between 1 at% and 10 at%. Analysis of the phase composition was carried out by scanning electron microscopy and TEM in combination with energy dispersive X-ray spectroscopy (EDXS) and electron energy loss spectroscopy (EELS).

Y-doping fully suppresses CoO precipitates at even the lowest Y-concentration (1 at%). A higher Y-concentration ($\geq$3 at%) also suppresses plate-like precipitates. However, the hexagonal phase is still present at lower temperatures ($\leq$ 800 °C). The formation of the hexagonal BSCF phase requires nucleation centers like plate-like precipitates, CoO precipitates or grain boundaries. Therefore, the hexagonal phase in Y-doped BSCF only forms at grain boundaries which might improve the long-time stability due to the reduced number of degradation paths. At 800 °C annealing temperature the hexagonal phase can be observed at grain boundary triple points and increasingly decorates grain boundaries at lower temperatures as seen in fig 1(a). Chemical analysis of the hexagonal phase using EDXS reveals an increased Co-concentration and a lack of Fe and Y as shown in fig 1(b). This can be motivated by the larger ionic radii of Fe^{3+} and Y^{3+} compared to Co^{3+}. The increased Co-valence state in the hexagonal phase was confirmed using EELS.

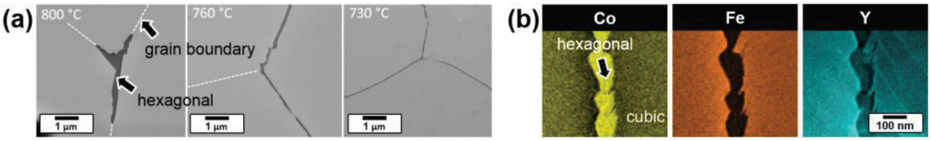


Fig 1. SEM images of samples annealed at 730 °C, 760 °C and 800 °C (a) and chemical mapping (EDXS) of grain boundary region (b) of 3 at% Y-doped BSCF

References

[1] S. Švarcová et al, SSI 178 (2008) p. 1787.
[2] C. Niedrig et al, SSI 197 (2011) p. 25.
[3] P. Müller et al, SSI 206 (2012) p. 57.
[4] P. Müller et al, Chem. Mater. 25 (2013) p. 564.
[5] K. Efimov et al, Chem. Mater. 22 (2010) p. 5866.
[6] S. Yakovlev et al, Appl. Phys. Lett. 96 (2010) p. 254 101.
[7] P. Haworth et al, Sep. Purif. Technol. 81 (2011) p. 88.
[8] This work has been performed within the project F.2 of the DFG Research Center for Functional Nanostructures (CFN). It has been further supported by a grant from the Ministry of Science, Research and the Arts of Baden-Württemberg (Az: 7713.14-300) and by the Helmholtz Association of German Research Centres through the portfolio topic MEM-BRAIN.

P- 18

Thermo-mechanical characterization of $Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{1-x}Zr_xO_{3-\delta}$ and $La_{5.4}WO_{12-\delta}$ membrane materials for carbon capture processes

V. Stournari, J. Malzbender, T. Beck, L. Singheiser
Forschungszentrum Jülich GmbH, IEK-2, 52425 Jülich, Germany

The investigation of the mechanical properties of membrane ceramic materials is critical in order to warrant the long term reliability of the entire separation system and thus a basis for the sustainability enhancement of the carbon capture membrane technology.

In the current work two groups of materials have been studied with respect to their mechanical properties with emphasis on the creep behavior. In particular, creep resistance is important for the membrane applications, since associated elevated temperature deformations would lead to change in dimensions, structural instability and eventually failure.

First, as basic component for the OXYFUEL process, a doped modification of the perovskite mixed ionic electronic conductor BSCF, that is known to have a high oxygen permeability, has been investigated. The material has been doped with Zr to overcome the elevated temperature structural instability of BSCF. Creep investigations have been carried out to examine the effect of dopant content variations on the mechanical properties for the series $Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{1-x}Zr_xO_{3-\delta}$ with Zr = 0.01, 0.03, 0.05 and 0.1. Complementary microstructural data are presented.

The second part of the work focuses on the initial investigations of mechanical behavior of $La_{5.4}WO_{12-\delta}$ (LWO54). This novel fluorite structured material shows ambipolar protonic-electronic conductivity, thus can be applied for the capture of CO_2 directly in the pre-combustion process. The effect of temperature and atmosphere on the creep behavior has been investigated. Furthermore data on elastic and fracture behavior are discussed along with microstructural studies.

P- 19

Electrical conductivity relaxation on the SrTi$_x$Fe$_{1-x}$O$_{3-\delta}$ system

<u>Sebastiaan F.P. ten Donkelaar</u>, Henny. J.M. Bouwmeester
University of Twente, Meander Building, ME212, 7500 AE Enschede, The Netherlands
Email: S.F.P.tendonkelaar@utwente.nl

Mixed ionic electronic conducting (MIEC) materials can be used as membrane materials for oxygen separation processes. Well known MIEC materials are perovskite materials containing cobalt. These perovskite materials have known stability problems, hence, ther need for alternative, cobalt-free, perovskite materials. In this study, iron doped strontium titanates (STF) are studied. STF with an iron content of more than 10 mol% iron seem to be good MIEC's at temperatures approaching 1000 °C [1]. STF forms a continuous solid solution between strontium ferrate and strontium titanate over the entire composition range. In the present paper, results of electrical conductivity relaxation (ECR) measurements will be presented for the STF system, in which different fractions of titanium doping were used (10, 30, 50 and 70 mol%). ECR measurements were done as a function of PO_2 in the range of 1 - 10^{-2} atm, but also as a function of temperature (900 - 700 °C). Below, typical results for STF70 are shown at a PO_2 step change of 0.21 to 0.105 atm. In which the average activation energy for the bulk diffusion is 134 kJ/mol and for the surface exchange is 319 kJ/mol. However, a typical abnormality seems to occur in al ECR measurements at around 800 °C. In the high temperature regime, D_{chem} and k_{chem} increase significantly as compared to the lower temperature regime. Whether this is due to a phase change is presently under investigation.

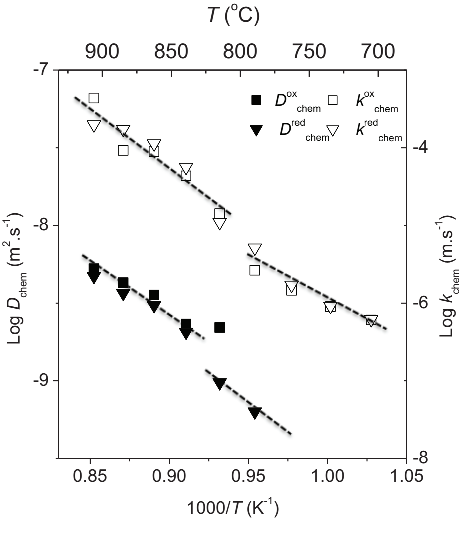


Fig. 1. D_{chem} and k_{chem} of STF70 as a function of temperature

References

[1] Jurado, K.R., et al., Solid State Ionics. 118 (1999)

P- 20

Electrical Conductivity Measuring Device Designed for Mixed Conducting Materials

M. Bernhardt, M. Esche, R. Kircheisen, R. Kriegel, Fraunhofer Institute for Ceramic Technology and Systems IKTS, Michael-Faraday-Str. 1, 07629 Hermsdorf,
Email: matthias.bernhardt@ikts.fraunhofer.de

Wagner's equation describes the oxygen permeation of MIEC membranes (Mixed Ionic Electronic Conductor) varying proportional with the ambipolar conductivity. The latter one is determined by the combination of ionic and electronic conductivity. Therefore, the characterization of the conductivity behavior depending on temperature and oxygen partial pressure enables an assessment of the influence of the operation conditions on the oxygen permeation. For that purpose, a special conductivity test rig was designed, built up and tested.

The test rig was especially designed for a quick material screening on dry pressed and sintered cylindrical samples with an outer diameter of appr. 15 mm. For the same reason, a special sample holder was constructed to measure the total conductivity according to the method described by van der Pauw [1, 2]. The electrical contacting was realized by Pt wires without application of additional con-tact layers. The oxygen partial pressure is controlled by YSZ sensors and can be varied between 10-6 bar and 1 bar for temperatures up to 1000 °C.

The conductivity behavior of BSCF5582 (Ba0.5Sr0.5Co0.5Fe0.2O3-□) was characterized at different temperatures and oxygen partial pressures. Corresponding to [3, 4, 5], the total conductivity decreases with the O2 partial pressure and the concentration of the defect electrons as expected for a p-type semiconductor. The activation energy was determined to 30 kJ/mol for temperatures below 500 °C in air. At higher temperatures, the conductivity in air decreases up to 750 °C and increases again slightly. This complex conductivity behavior at higher temperatures in air is caused by the competition of the rising charge carrier mobility and the decrease of the charge carrier concentration caused by the progressive loss of oxygen. A conversion to a simple thermal activated conductivity behavior of a typical semiconductor is observed for decreasing oxygen partial pressures.

References:

[1] L. J. van der Pauw, Philips Research Reports Vol.13, Eindhoven, 1958.
[2] L. J. van der Pauw, Philips Technical Review Vol. 30, Eindhoven, 1958.
[3] M. Burriel, C. Niedrig, W. Menesklou, S. F. Wagner, J. Santiso und E. Ivers-Tiffée, Solid State Ionice 181; S. 602-608,“ Elsevier, 2010.
[4] W. Zhou, R. Ran, Z. Shao, W. Zhuang, J. Jai, H. Gu, W. Jin und N. Xu, Acta Materialia 56; S. 2687-2698,“ Elsevier, 2008.
[5] Z. Chen, R. Ran, W. Zhou, Z. Shao und S. Liu, Electrochimica Acta 52 S.7343-7351,“ Elsevier, 2007.

P- 21

Parametric study of the oxygen transport in a MIEC membrane by dynamic modeling

J.M. Gozálvez-Zafrilla[1], A. Santafé-Moros[1], J. Garcia-Fayos, S. Escolástico[2], J.M. Serra[2,*]
1 Chemical and Nuclear Engineering Department, Universidad Politécnica de Valencia,
C/Camino de Vera s/n, 46022 Valencia, Spain
2 Instituto de Tecnología Química, UPV-CSIC, C/ Camino de Vera, s/n, Valencia 46022, Spain
Email: jmgz@iqn.upv.es; jmserra@itq.upv.es

Keywords: CFD, Oxygen transport membrane, Transport modeling

High purity oxygen production through ceramic membranes at high temperature [1] is an alternative to the cryogenic methods for several industrial applications. The use of membrane separation in fossil fuel power plants in the so called Oxyfuel process will make possible to minimize CO_2 emissions and reduce energy requirements and investment costs. Another important field of application of this kind of membranes is their implementation in high temperature catalytic membrane reactors while typically reactions are synthesis gas production from methane, oxidative coupling of methane to yield ethane and ethylene.

The most common oxygen ion conducting materials are based on the perovskite structure (ABO3) or related structures and comprise Fe/Co/Ni and mixtures of lanthanide and alkali earth metals in suitable proportions.

The present work is based on the modeling of oxygen transport in a lab scale experimental setup for permeation testing of oxygen transport membranes by means of computational fluid dynamics using COMSOL Multiphysics® [2]. The modeling considers gas hydrodynamics and oxygen diffusion in the gas phase and vacancy diffusion of oxygen in a perovskite disc shaped membrane at 1273 K.

In a first step, the model allows obtaining the coefficient diffusion of oxygen. The parametric study shows that the setup geometry and flow rate in the air compartment do not have major influence in the oxygen transport. However, very important polarization effects in the sweep gas (argon) compartment are identified.

The highest oxygen permeation flux and the lowest oxygen concentration on the membrane surface are obtained for the following conditions (in increasing order of importance): (1) a large gas inlet radius; (2) short gas inlet distance; and (3) a high gas flow rate. These results can be useful for the selection of the most suitable setup configuration and operating conditions and/or to prevent the use of inadequate operating conditions/setup geometries and to calculate the intrinsic material properties by considering the real fluid dynamics in both membrane chambers.

References

[1] J. Sunarso, S. Baumann, J.M. Serra, W.A. Meulenberg, S. Liu, Y.S. Lin, J.C. Diniz da Costa, J. Membr. Sci. 320 (2008) 13–41.
[2] J. M.Gozalvez-Zafrilla, A. Santafe-Moros; S. Escolástico, J.M. Serra, J. Membr. Sci., 378, 1-2 (2011) 290-300.

P- 22

Surface modification of $La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ hollow fiber membranes for oxygen separation

Marijke Jacobs, Bart Michielsen, Vesna Middelkoop and Frans Snijkers
Unit Sustainable Materials Management, Flemish Institute for Technological Research (VITO)
Boeretang 200, 2400 Mol, Belgium
Email: marijke.jacobs@vito.be

Keywords: Hollow fiber membrane, Mixed conductor, Oxygen permeation, Surface modification

Dense mixed ionic-electronic conducting hollow fiber membranes such as $La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ (LSCF) can be used for the oxygen separation from air at high temperatures with infinite selectivity. Possible applications of these membranes are the production of pure oxygen or they can be integrated in catalytic membrane reactors [1,2]. Since the hollow fiber membranes have a thickness of about 300 μm, the oxygen permeation flux through these membranes is limited by surface-oxygen exchange kinetics [3,4]. To improve this oxygen exchange, the membranes can be coated with a thin activation layer, which can be a porous layer of the membrane material itself to increase the surface area or a material layer with superior oxygen exchange properties such as $La_{0,8}Sr_{0,2}CoO_{3-\delta}$ (LSC).

In this study, hollow fiber LSCF membranes were prepared using dry-wet spinning. Then, these membranes were further functionalized by spray coating with both types of activation layers. These coating layers were analyzed by SEM and EDS to study the adhesion and porosity of the coatings. Furthermore, the effect of the coatings on the oxygen flux at temperatures between 800 and 1000°C was measured in an oxygen permeation measurement set-up. In addition, the effects of the thickness of the coating and the sintering temperature on the oxygen flux were investigated in order to optimize the coating layers. It was found that the activation layers have a positive influence on the oxygen flux, especially at temperatures above 850°C, which can be seen in Fig. 1. The highest increase of oxygen flux was obtained for a rather dense LSC activation layer on a dense LSCF hollow fiber membrane.

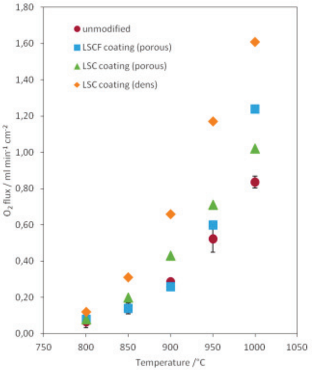


Fig. 13. The oxygen flux of a non-activated and three activated LSCF hollow fiber membranes in function of the temperature. The activation layers are a porous LSCF layer, a porous LSC and a dense LSC layer.

References

[1] A. Thursfield and I.S. Metcalfe, Journal of Membrane Science 288 (2007) 175

[2] J. Sunarso, S. Baumann, J.M. Serra, W.A. Meulenberg, S. Liu, Y.S. Lin and J.C. Diniz da Costa, Journal of Membrane Science 320 (2008) 13.

[3] X. Tan, Z. Wang, H. Liu and S. Liu, Journal of Membrane Science 324 (2008) 128.

[4] A. Kovalevsky, C. Buysse, F. Snijkers, A. Buekenhoudt, J. Luyten, J. Kretzschmar and S. Lenaerts, Journal of Membrane Science 368 (2011) 223.

P- 23

Supported planar BSCF membranes for oxygen separation from air

P.Niehoff[a*], F. Schulze-Küppers[a], S. Baumann[a], J.M. Serra[b], W. A. Meulenberg[a], R. Vaßen[a]
[a]Forschungszentrum Juelich, Institute of Energy and Climate Research, D-52425 Juelich, Germany
[b 2]Instituto de Tecnología Química, UPV-CSIC, C/ Camino de Vera, s/n, Valencia 46022, Spain
E-mail: p.niehoff@fz-juelich.de

Keywords: BSCF, oxygen transport membrane, transport limitations, oxygen flux

Over the last 20 years, membrane technologies register a growing attention, especially in the context of lowering the emissions of fossil fuelled power plants. Advanced concepts such as oxyfuel power plants, where the fossil fuel is combusted in an N_2-free, oxygen enriched gas stream are promising but have significant efficiency losses (8-10 %-points) associated with the oxygen generation, normally realized by cryogenic air separation. However estimates show, that the utilization of ceramic oxygen transport membranes (OTMs) result in much lower efficiency losses (5-6 %-points).

Such OTMs consist of gastight mixed ionic-electronic conductors (MIEC), which allow fast solid state oxygen diffusion via vacancies in the crystal lattice. One of the most promising materials is Ba0.5Sr0.5Co0.8Fe0.2O3-δ (BSCF), which shows the highest oxygen permeability.

The driving force of this oxygen transport is the chemical potential gradient across the the membrane thickness. Consequently, minimizing the membrane thickness increases the oxygen permeation until surface exchange kinetics become rate limiting. For very small thicknesses (<200µm) porous supports are necessary to ensure mechanical stability. These introduce additional permeation resistances such as concentration polarization which in turn can become rate limiting.

This work presents the manufacturing of supported thin film membranes made of BSCF via tape casting. The performance is discussed by systematically varying operation conditions such as temperature, feed/sweep flow and studying the influence on the oxygen permeation. Different transport limitations are identified and stepwise isolated/minimized by adjusting experimental conditions and sample structure, i.e. increasing the specific surface area with porous coatings.

The samples' microstructure especially regarding the porous support is analyzed using SEM/X-ray computer tomography. In this context, basic model approaches describing the complex permeation processes and transport mechanisms are presented. The development and manufacturing steps of a possible planar design for an industrial applicable modular membrane unit are introduced and discussed.

P- 24

Advanced processing of asymmetric oxygen transport ceramic membrane on porous metallic support

M. Scrignari[1,2], M.O. Jarligo[1], A. Comite[2] and R. Vaßen[1]
[1]Institut für Energie- und Klimaforschung (IEK-1), Forschungszentrum Jülich GmbH, 52428 Jülich, Germany
[2]Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, 16146 Genoa, Italy
Email: m.scrignari@fz-juelich.de

Keywords: oxygen transport membrane, $La_xSr_{1-x}Co_yFe_{1-y}O_{3-\square}$, Plasma Spray-Physical Vapor Deposition, metallic support

Asymmetric type of membranes with porous metallic supports has attracted research attention due to the advantage of good mechanical properties suitable for use at high temperatures and high permeation rates.[1] Recently, a new robust technique to deposit thin films known as plasma spray–physical vapor deposition (PS-PVD) was used to deposit $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) oxygen transport membrane on porous NiCoCrAlY supports.[2] The deposition technique combines the efficiency of thermal spray processes and characteristic features of thin PVD coatings. The measured gas tightness and the oxygen permeation rates at elevated temperatures for the assembly show promising results for the optimized membranes. To further improve the membrane assembly by increasing the contact surface area, a porous interlayer of LSCF was fabricated between the porous support and the dense membrane.

This paper reports on the advanced assembly of asymmetrical LSCF oxygen transport membrane on a porous metallic support and ceramic interlayer as shown in Fig. 1.

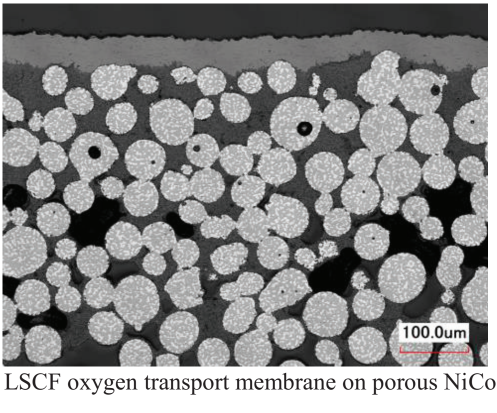


Fig. 14. Asymmetric LSCF oxygen transport membrane on porous NiCoCrAlY support.

References

[1] N. Zotov, S. Baumann, W.A. Meulenberg , R. Vaßen, Journal of Membrane Science 442(2013)119–123

[2] M.O. Jarligo, G. Mauer, M. Bram, S. Baumann, R. Vaßen, Thermal Spray 2013—Innovative Coating Solutions for the Global Economy, Proceedings of the International Thermal Spray Conference, May 13–15, 2013, Busan, Republic of Korea, Lima, R.S., Agarwal, A., Hyland, M.M., Lau, Y-C., Mauer, G., McDonald, A., Toma, F-L. editors, p 493-498

P- 25

Characterization of high temperature hydrogen and oxygen transport membranes deposited by low pressure plasma spraying

F. Azzurri[1], A. Comite[1], M. Gindrat [2],M O. Jarligo[3],R. Vaßen[3] J. Garcia-Fayos[4], S. Escolastico[4],
J. M. Serra[4]
[1]Department of Chemistry and Industrial Chemistry - University of Genoa Via Dodecaneso 31,
16146 Genoa, Italy
[2]Sulzer Innotec, PO Box 8404, Winterthur, Switzerland
[3] Institut für Energie- und Klimaforschung, Forschungszentrum Jülich GmbH, 52425 Jülich,
Germany
[4] Instituto de Tecnología Química, UPV-CSIC, C/ Camino de Vera, s/n, Valencia 46022, Spain
Email: azzurri@chimica.unige.it, www.chimica.unige.it/membrane.
Keywords: Hydrogen, oxygen, plasma spray, membrane characterization

Oxygen-and hydrogen-separation membranes based on mixed ionic electronic conducting oxides are expected to play a key role in the development of CO_2 emisson-free power plants.

In the framework of FP7 European project DEMOYS "Dense membranes for efficient oxygen and hydrogen separation", the "Plasma spray – physical vapour deposition (PS-PVD) process, has been adopted in order to prepare thin, dense, O_2 and H_2 high temperature transport membranes. Perovskites and ABO_3 related structures have been suitably synthesized and proper deposition parameters have been applied to achieve a thin and defects free coating layers. The full characterization of structural morphology and defects in the dense membranes allows for proper tuning the membrane preparation conditions as a function of both support and coating powder characteristics. In particular, FE-SEM coupled with EDX analyses and gas permeation tests (both at room and high temperature) could be easily applied to characterize the defectiveness of the coating layer.

In the present contribution some characterization results obtained from several samples by using single gas permeation and leakage tests, bubble pressure test and scanning electron microscopy observations are presented

As example, in Fig. 1a, the good level of coating reached by the plasma spray technique on porous metal supports is shown. No defectivities such as micro-cracks, residual porosity or pin-holes are present on the coating surface. The thickenss of the coating layer falls in the range of 40-60 µm (Fig. 1 b).

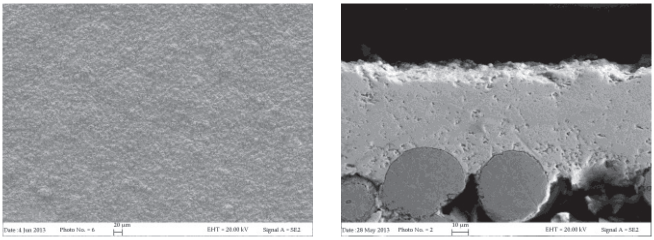


Fig.1:a) Surface morphology and b) Cross section for a High Temperature Hydrogen separation membrane

$La_{1-x}Sr_xFe_{1-y}Co_yO_3$ powder oxides (LSCF) coatings have been deposited by obtaining thickness varying from 35 to 60 µm. The presence of stratified microstructure, with a low degree of defectiveness and porosity, and the presence of some phase separations inside the dense layer (Sr- or Co-rich phases) are evident.

The single gas permeance measurements allowed to characterize the defectivities by quantifying their size. The examined samples, both for oxygen and hydrogen separation, exhibit very low room-temperature Helium and Nitrogen permeance values (about 10^{-8}-10^{-9} $mol*Pa^{-1}s^{-1}m^{-2}$ at about 7-9 bar). Regarding oxygen permeation, high fluxes have been reached at 1000 ºC, up to 3.1 $ml\cdot min^{-1}\cdot cm^{-2}$ in an Air/Argon gradient. In the low temperature range good permeation values have also been obtained, measuring 0.71 $ml\cdot min^{-1}\cdot cm^{-2}$ when feeding with pure oxygen at 750ºC. Oxygen permeation tests under rich-CO_2 and CH_4 containing environments were conducted in the range 750-600 ºC, obtaining good oxygen fluxes and demonstrating LSCF stability under such atmospheres.

P- 26

Manufacturing of multi-layer membrane systems for hydrogen separation via tape-casting

Wendelin Deibert, J. Seeger, M. Ivanova, W.A. Meulenberg, R. Vaßen, H.P. Buchkremer
Forschungszentrum Jülich GmbH, IEK.-1, Leo-Brandt-Straße, 52425 Jülich, Germany
Email: w.deibert@fz-juelich.de
Keywords: hydrogen, membrane, tape-casting, sintering

The reduction of CO_2-emissions is currently a major issue in German and European society. One approach in this direction is the development of new power plant concepts such as pre-combustion technology with carbon capture. Therefore, hydrogen has to be produced from fossil fuels e.g. via the water-gas-shift reaction. In order to obtain highly pure hydrogen, the use of dense proton conducting ceramic membranes for gas separation is very promising.

One of the materials which fulfills the desired properties is lanthanum tungstate ($La_{6-x}WO_{12-\delta}$). The conductivity and H_2-permeation of this material has already been investigated in bulk samples. The permeation rate can be further increased by producing a multilayered membrane structure, consisting of a thin dense membrane layer, a porous substrate and catalytic active layers to increase the incorporation of hydrogen into the membrane surface. The main function of the substrate layer is maintaining the mechanical stability of the system and additionally to guarantee sufficient gas transport to supply the membrane layer (sufficient porosity). The chosen manufacturing technology is the sequential tape-casting, a special type of the classical tape-casting process. Multilayered systems are produced by casting the different layers, starting with the membrane, on top of each other with co-firing the whole structure afterwards.

As starting powder a commercially available $La_{5.4}WO_{12-\delta}$ powder was chosen and widely characterized with different methods (XRD, SEM, optical dilatometry, particle size analysis, BET). The casting experiments were carried out with a micro tape-casting machine “KAROcast 300-7” by “KMS Automation GmbH” Schramberg, Germany. First attempts producing multilayer systems were started using the same powder for the membrane and substrate layer. The manufacturing started with casting the membrane layer, approximately 20 µm thick. The used slurry recipe was developed for dense layers. On top of it, the substrate was applied with a thickness of about 350 µm. To study the sintering behavior of the powder up to a temperature of 1500 °C, an optical dilatometer was used. It was also applied to perform in situ measurements of the bending of multilayer systems in order to better understand the sintering mechanisms. Finally, the membrane structure is fully characterized by He-leaktest, SEM and H_2-permeation.

P- 27

Formation and prevention of cracks in ultra-thin Silica membranes

Emiel J. Kappert[1], Denys Pavlenko[1], Arian Nijmeijer[1], Nieck E. Benes[1], P. Amy Tsai[2]
[1]Inorganic Membranes and [2]Soft Matter, Fluidics and Interfaces groups,
Faculty of Science and Technology and MESA+ Institute of Nanotechnology
University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
Email: e.j.kappert@utwente.nl

Keywords: hybrid silica, drying, cracking

Thin layers of silica and hybrid (inorganic-organic) silica are promising materials for membrane application in high-temperature gas separation. Introducing a covalently-bound organic bridging group into silica effectively increases hydrothermal stability of silica [1]. However, producing gas-selective membranes of high selectivity remains challenging. One possible origin for the limited gas-selectivity is the presence of defects and cracks formed during the drying of the coating.

Crack formation, if present, is normally observed during the first stage of drying. After drying, the amount of cracks in the coated layer can be measured by converting an optical microscopy image of the layer (Figure 1A) into an edge-outlined black-and-white image (Figure 1B). From these outlines, the crack density in the layer can be determined.

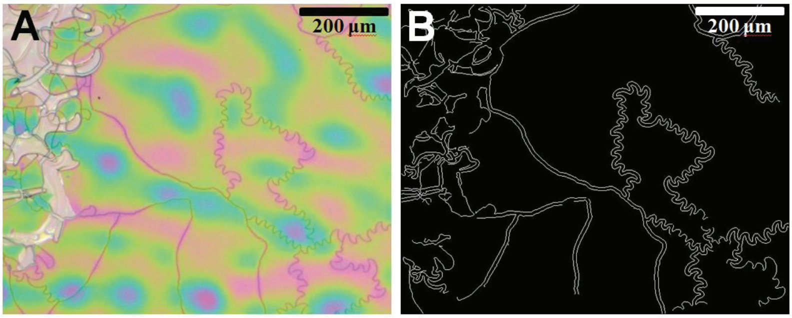


Figure 1: Optical microscopy image of cracked silica layer (A); detected cracks and outlines (B).

Crack densities were determined for films derived from TEOS, MTES, and BTESE sols, as a function of membrane parameters, such as coating thickness and number of coatings. As the thickness of the coating is increased, three different regions were observed: *region I*, where no cracks were recorded; *region II*, where crack formation is observed; and *region III*, where cracks cause the delamination of the layer from the substrate.

For gas separation membranes, even small cracks ruin membrane selectivity. Therefore, it is crucial to prevent cracks on the membranes. We experimentally measured the critical cracking thickness, which marks the transition from (non-cracking) region I and (crack-forming) regime II. Of all materials, silica shows the lowest critical cracking thickness, ~250 nm, whereas all the hybrid materials, the critical cracking thickness was found to be larger than 1 µm.

In general, thicknesses of several 100 nm are typically encountered in the production of selective (organo)silica membranes. The obtained data with ultra-thin coating layers provides insights into the formation of cracks during drying. Guidelines will be presented to avoid crack formation during production of (organo)silica membranes.

References

[1] Castricum HL, Sah A, Kreiter R, Blank DHA, Vente JF, Ten Elshof JE. Journal of Materials Chemistry 2008;18:2150.

P- 28

Facile synthesis of Zirconia doped hybrid organic inorganic silica membranes

M. ten Hove, A. Nijmeijer and L. Winnubst
Inorganic Membranes, Department of Science and Technology, MESA+ Institute for Nanotechnology
University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
Email: m.tenhove@utwente.nl

Keywords: microporous membrane, hybrid silica, hydrothermal stability, zirconia doping

The growing energy demand combined with increasing concerns about greenhouse gas emissions is driving the research towards the development of processes with integrated CO_2 capture. Therefore we propose a reactor concept in which inorganic membranes are utilized to provide the necessary separation. In this reactor concept, a membrane reactor for partial oxidation of methane (POM-MR) is followed by a water gas shift membrane reactor (WGS-MR).

A key factor for the development of a WGS-MR is the development of a hydrothermal stable, hydrogen selective micro-porous membrane. Silica based membranes show a high permselectivity towards hydrogen [1] but suffer from degradation in humid gas streams [2]. To increase the hydrothermal stability, hybrid organic-inorganic silica networks are utilized, which have proven to be stable for pervaporation purposes [2].

These hybrid silica networks have a lower H_2/CO_2 permselectivity as compared to pure silica. In this work, the incorporation of zirconia in the hybrid silica network is explored to enhance the molecular sieving properties. Zirconia doped BTESE was synthesized by sol-gel chemistry,. By using the proper sol reaction conditions (i.e. reaction time and temperature) a homogenous sol was obtained from which defect-free membranes could be made by tuning the concentration of the dip-coating solution. As seen in figure 1, the doped membranes showed a decrease in hydrogen premeance from $4.39\ 10^{-7}$ to $1.75\ 10^{-7}$ mol m^{-2} s^{-1} Pa^{-1}, but an increase in H_2/CO_2 selectivity from 3.9 to 12.3 and an increase in H_2/N_2 selectivity from 11.8 to 83, compared to undoped BTESE.

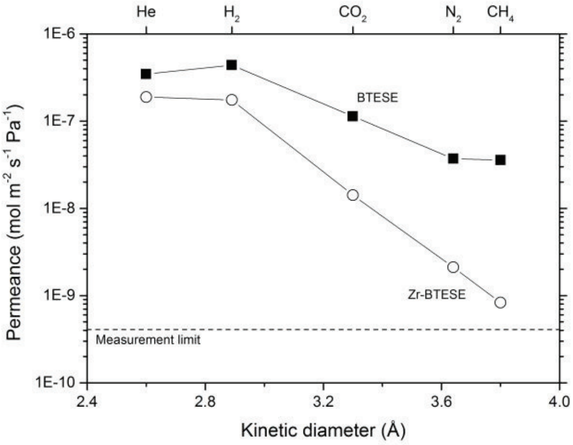


Figure 15: Gas permeation results for undoped and zirconia doped BTESE membranes

References

[1] R.M. de Vos, H. Verweij, High-Selectivity, High-Flux Silica Membranes for Gas Separation, Science, 279 (1998) 1710-1711.

[2] H.L. Castricum, A. Sah, R. Kreiter, D.H.A. Blank, J.F. Vente, J.E. ten Elshof, Hydrothermally stable molecular separation membranes from organically linked silica, Journal of Materials Chemistry, 18 (2008) 2150-2158.

P- 29

Water gas shift membrane reactor for applications in carbon capture technologies

D. van Holt[a*], E. Forster[a], M. Müller[a], J.M. Serra[b], R. Vaßen[a], S. Baumann[a], W. A. Meulenberg[a]
[a]Institute of Energy and Climate Research, Forschungszentrum Juelich, Leo Brandt Str., D-52425 Juelich, Germany
[2]Instituto de Tecnología Química, UPV-CSIC, C/ Camino de Vera, s/n, Valencia 46022, Spain
Email: d.van.holt@fz-juelich.de

Keywords: hydrogen permeable membranes, MIEC, pre-combustion, CO-Shift reaction

The concept of pre-combustion is an important and forward looking opportunity for advanced carbon capture in power plants. In the first step a fossil fuel is partially oxidized by pure oxygen resulting in synthesis gas mainly consisting of hydrogen and carbon monoxide. In the following water gas shift reaction steam is added to oxidize the carbon monoxide to carbon dioxide while steam is reduced to hydrogen. Subsequently, CO_2 is separated from hydrogen. However, the separation of carbon dioxide using conventional techniques like physical or chemical absorption leads to high efficiency losses up to 14 %-points. In contrast, a membrane reactor containing a catalyst provides the opportunity to a significant decrease in efficiency losses to 3.5 □ 6 %-points.

The high efficiency is realized because a catalytic membrane reactor combines the two process steps water gas shift reaction and gas separation, into a more efficient single step process. The gas separation is realized by hydrogen selective membranes. The continuous removal of hydrogen provides an additional advantage because it shifts the reaction equilibrium to the product side. The water gas shift reaction is exothermic and the equilibrium conversion is very limited at temperatures above 450°C but the reaction kinetics is strongly promoted in the high temperature range. As a consequence, integration of high-temperature highly-permeable hydrogen membranes into the WGS reactor will enable the operation at high space velocities, i.e. much smaller reactor units, and using inexpensive and stable catalysts if necessary.

This work deals with the development of such a membrane-catalyst system. The membranes investigated are microporous amorphous ceramics like silica based materials if temperatures from 200 – 450 °C are used. For the temperature range from 600 – 800 °C proton conducting ceramic membranes are determined. For the combination of the process steps water gas shift reaction and the following separation of hydrogen it is beneficial to apply the catalyst onto the membrane surface. Therefore, stability tests of membrane materials and catalysts under power plant oriented conditions are performed, particularly addressing hydrothermal stability, CO_2 and H_2S tolerance. Stable materials are then determined with regard to their compatibility with catalysts. In addition we have a close look to the catalytic activity of the membrane materials itself on the one hand and also the catalysts at temperatures up to 900 °C. Previous experiments carried out in this work show that barium zirconates like $BaCe_{0,x}Zr_{0,7}Y_{0,0y}X_{0,0z}O_{3-\delta}$ and also $La_{6-x}WO_{12-\delta}$ have promising properties under investigated parameters, particularly regarding the stability in sulphur and hydrocyanic containing atmospheres. Also stability tests up to 900 °C with NH_4Cl show a good stability for $BaCe_{0,x}Zr_{0,7}Y_{0,0y}X_{0,0z}O_{3-\delta}$.

P- 30

Deposition of thin, defect-free, alumina barrier layer for high temperature palladium membranes

F. Azzurri[1], A. Bottino[1], A. Comite[1], M. Scrignari[1], M. Broglia[2], F. Drago[2], P. Pinacci[2]
[1]Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, 16146 - Genoa, Italy
[2]R.S.E. S.p.A, Via Rubattino 54, 20154 Milan, Italy
Email: azzurri@chimica.unige.it

Keywords: barrier layer, alumina, sol-gel, palladium

Porous metal supports (PSS) are very promising materials for the development of H_2 selective membranes since the have numerous advantages in respect to the widely studied ceramic supports, but unfortunately their application is limited by the occurence of intermetallic diffusion phenomena at high temperatures. The intermetallic diffusion of elements from the support to the Pd layer can be prevented by deposition of a ceramic barrier layer between the support and the Pd layer. In addition, the ceramic layer improve the morphological characteristics of the support surface, by smoothing the starting roughness and partially occluding the large pores.

In particular, our study focuses on the deposition, by dip coating, of ceramic alumina barrier layers on porous stainless steel supports (PSS) having different level of roughness. PSS supports, as received or after 3,6, or 8 hours rubbing, have been deposited with suitably formulated alumina/organic additives sol-gel systems. After a careful support selection, by means of FESEM morphological analyses, bubble pressure tests and permeance tests, the composition of the alumina sol has been tuned as a function of surface roughness and defectivities. In Figure 1 surface of a not rubbed support, before (1a) and after (1b) the deposition of the properly formulated alumina sol-gel, is shown. In Figure 1b, the thin barrier layer uniformly covers the surface of the support following the surface profile.

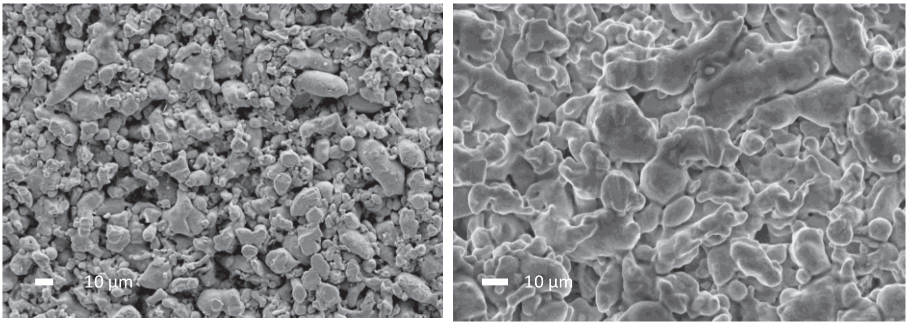


Fig. 16. Not rubbed PSS support a) before, b) after the deposition of the proper alumina barrier layer

The deposited alumina barrier layer was used as the substrate where a thin dense palladium layer can easily grow up. Indeed, the deposition of the alumina barrier is usually followed by the deposition of an “activation layer”starting from a laboratory made boehmite sol containing Pd seeds to activate the subsequent Pd growing by electroless plating. After each coating step the membrane quality is evaluated by He and

N_2 room temperature permeation tests. The permeation of not rubbed up support decreases after the deposition of the first alumina barrier coating up to a value of about 2 x 10^{-6} mol*$Pa^{-1}m^{-2}s^{-1}$ with a further 50% decrease after the deposition of the alumina-palladium based activation layer. The Palladium growth, carried out, The dense uniform palladium layer obtained on the PSS supports coated by the alumina barrier layer exhibits a Helium permeance of the order of about 10^{-9} mol*$Pa^{-1}m^{-2}s^{-1}$ at room temperature. Membranes has been tested for about 1500 hours up to 500°C with He and Hydrogen.

P- 31

Microporous silica membranes for CO_2 separation

J. Eiberger, M. Bram. K. Wilkner, T. Van Gestel, D. Stöver and H.P. Buchkremer
Institute of Energy and Climate Research IEK-1: Materials Synthesis and Processing,
Forschungszentrum Jülich GmbH
52425 Jülich, Germany
Email: j.eiberger@fz-juelich.de
Keywords: post-combustion carbon capture, silica membrane, amine modification

The combustion of fossil fuels leads to a flue gas that is, after several cleaning steps, released into the atmosphere. The main components of the flue gas are N_2, CO_2, O_2 and water vapor. As a means of reducing greenhouse gas emissions, it is desired to capture and store the CO_2. Moreover, increasing interest is drawn by a possible reuse of CO_2 instead of merely storing it. Membranes have a high potential to separate gases with low efficiency penalty and are comparatively easy to retrofit in existing power plants. The focus of this study is on the development of a CO_2/N_2 selective gas separation membrane.

This research investigates the possibility of CO_2 selective transport through a silica membrane. Liquid- and gas-phase deposition techniques are employed in post-synthesis grafting of aminofunctional alkoxysilanes on the pore walls of surfactant-templated silica membranes to enhance the CO_2 affinity. Stability tests of membranes under real flue gas conditions were conducted in a lignite- and a hard coal fired power plant.

The proposed gas separation mechanism works as shown in Figure 1: CO_2 shall adsorb reversible on functional amino groups. A partial pressure difference leads to a diffusion of CO_2 through the membrane. Reduced pore size blocks diffusion of N_2.

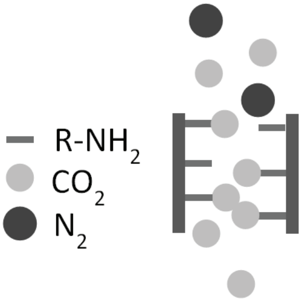


Fig. 1.Sketch of pore channel in functional silica layer

The developed standardized H_2/CO_2 selective system provides the groundwork. Necessary adjustments of functional layer for CO_2/N_2 selective system comprise the generation of small mesopores by surfactant-templating followed by post-synthesis grafting of aminofunctional alkoxysilanes on pore walls using liquid- and gas-phase deposition techniques.

Pore size tailoring is aspired by blending silica sol using cetrimonium bromide as the surfactant template molecule. The blended sol is applied on ceramic support disks using a dip-coating process. Thermal treatment will lead to the decomposition of template molecules. After thermal treatment the layer thickness is < 100 nm. Permporometry measurements show that the layers are defect free and have pores with Kelvin radii in the range 0.5 - 1.5 nm. Gas permeation is governed by Knudsen diffusion (He, H_2, CO_2, N_2). N_2-sorption measurements show that the material has a high porosity of about 50 % and a BET-surface of approx. 1000 m^2/g.

Amine modification takes place by refluxing specimens in a solution of 3-aminopropyltriethyxysilane in 1-propanol for several hours at elevated temperatures. The aminosilanes are supposed to react with the surface hydroxyl groups on the pore walls, generating CO_2 adsorption sites. This treatment leads to a significant change of the single gas permeation characteristics. CO_2/N_2 selectivities from 1 to 27 could be achieved at 75°C with CO_2 fluxes from $1x10^{-7}$ to $4x10^{-9}$ mol m^{-2} s^{-1} Pa^{-1}. Measurements using binary CO_2/N_2 mixtures are yet to be done.

Testing of ceramic membranes and membrane materials directly in the flue gas streams of a lignite fired plant at Niederaußem were conducted. Tested membranes show significant degeneration after exposure times of up to 41 days.

P- 32

Inorganic porous hollow fibers for intensified fractionation and filtration

Patrick de Wit, Arian Nijmeijer, Nieck E. Benes
Inorganic Membranes, Department of Science and Technology, Mesa$^+$ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
Email: p.dewit@utwente.nl

Keywords: Inorganic Porous Hollow Fibers, Flow Field Fractionation, Produced water treatment, Silicon Carbide

Recently, a new and facile method for the preparation of inexpensive inorganic porous hollow fibers (iPHF) with tunable small – down to ~250 µm – radial dimensions was published [1]. This current study exploits the excellent mechanical, chemical, and thermal stability of these fibers for two distinct bases: Non-Aqueous Flow Field Flow Fractionation (NAFFFF) and water/oil separation origination from oil and gas production. These two cases represent the versatility of these hollow fiber membranes; NAFFFF represents a small-scale analytic application; water/oil filtration represents a large-scale filtration application. Both cases require improvement of, for example, potting and fouling prevention.

In Flow Field Flow Fractionation (FFFF) a fluid flowing through a channel is exposed to an external force field, in order to generate separation. The external field can be induced by permeating a part of the liquid through the wall of the channel. This forces particles, macro molecules, or colloids towards the wall, which is opposed by diffusion from the wall towards the center of the channel, allowing separation based on differences in mobility [2]. Currently, only organic porous hollow fibers are used for hollow fiber flow field flow fractionation (HF5) . The limited chemical stability of these fibers hinders applications involving organic solvents. In the current project, we aim to develop inorganic porous hollow fibers that have appropriate properties for NAFFFF.

The second case focuses on a large-scale application. During the production of oil and gas vast amounts of water containing oil are co-produced. With the growing use of production chemicals, stable Oil in Produced Water (OiPW) emulsions are formed that are hard to treat using conventional techniques [3]. Preliminary studies show that membranes with appropriate surface chemistry are suitable for separation of the emulsified oil from the water. Silicon carbide is identified as a promising material, as it has shown to be less susceptible to fouling with oil as compared to other common materials. This study focusses on the interaction between the oil/water emulsion and the membrane surface and utilizes this knowledge to optimize iPHF properties.

Because no large membrane technology based on inorganic hollow fiber membranes exists, development of sealing and potting strategies and multi-fiber modules is required. In addition to silicon carbide, other inorganic materials can be considered. In particular, metals are of interest.

References

[1] Luiten-olieman, M. W. J., Raaijmakers, M. J. T., Winnubst, L., Bor, T. C., Wessling, M., Nijmeijer, A., & Benes, N. E. (2012). Journal of Membrane Science, 407-408, 155–163.
[2] Giddings, J., Yang, F., & Myers, M. (1976). Science, 193(4259), 1244–1245.
[3] Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., & Abidin, Z. Z. (2009). Journal of hazardous materials, 170(2-3), 530–51.

P- 33

Partial oxidation of methane in catalytic reactors with MIEC membranes

A.A. Markov, M.V. Patrakeev, I.A. Leonidov, V.L. Kozhevnikov
Institute of Solid State Chemistry, Ural Branch of Russian Academy of Sciences
Pervomayskaya Str., 91, Ekaterinburg 620990, Russia
Email: markov@ihim.uran.ru

Keywords: mixed conducting oxides, oxygen separating membranes, partial oxidation methane, synthesis gas

Oxygen separation from air and partial oxidation of methane can be combined in a single, self-sustaining process in a catalytic reactor with MIEC inorganic membranes. This approach is currently considered as one of the most promising methods for primary processing of natural gas. Laboratory tests of bench scale prototypes constitute an important step that may help to introduce this method to industry. The reactor scale and design features have considerable influence on heat balance, process parameters and reactor yield. In this work we focused on tubular POM reactors in order to study oxygen separation efficiency and performance of ferrous membranes.

In our earlier work we studied a number of ferrous materials and observed that solid solutions $(La,Sr)FeO_{3-\delta}$ exhibit quite promising properties' combination. The glycine-nitrate precursors were used in order to synthesize the desirable ferrites. Extrusion and firing procedures were utilized in order to obtain tubular ceramic membranes with the density of about 95%, and with the wall thickness and diameter of about 1 and 10 mm, respectively. POM catalysts were prepared by imbibing selected supports with appropriate metal nitrates followed by drying and calcination. The computerized experimental setup was equipped with gas flow controllers and temperature controllers that enabled mixing of gases and maintaining membrane temperature. The analysis of outlet gases was carried out with the help of a gas chromatograph.

We found that the functioning of the reactor with a single tubular membrane depended critically on the heating rate of the membrane and catalyst. This startup period of 20-100 h was necessary in order to provide appropriate oxygen activity gradient along and across the membrane, and also for activation of the catalyst and relaxation of mechanical stress in the membrane. The activity of the catalyst and the arrangement of the catalyst near the membrane were found to be important for fighting coke/soot formation, degradation of catalyst and membrane integrity. We achieved oxygen permittivity up to 8 $ml{\cdot}min^{-1}cm^{-2}$ at 950°C. The experimental results showed 90% selectivity for CO while oxygen permeation rate was in a very close correspondence with the values calculated from the conductivity data. However, the time of continuous operation did not exceed 300 h. The analysis of the reactor components revealed strong degradation of the membrane material. Substantial improvement of the reactor performance was achieved by decreasing the operation temperature to 850°C. The methane conversion exceeded 99%, the selectivity for CO was 90-92% while oxygen flux was near 3 $ml{\cdot}cm^{-2}$ during all the time of the run. Thus, the temperature decrease to just above the thermodynamic threshold for POM reaction (837°C) drastically favors long term stability of ferrous membranes. It should be noted that along with the demonstration of durability of the membrane the obtained results show also long term stability of the catalysts and sealants. Several attempts with other doped ferrous derivatives showed that though less permeable some ferrites can also be quite stable at 950°C. Though high yield and stability are mutually excluding properties their satisfactory match can be achieved by fine tuning of the membrane composition and operating regime. The continuous operation time of more than 7000 h was achieved.

The other POM reactor was equipped with several tubular membrane elements with the total effective area of about 156 cm^2. The maximal possible methane flow in this model achieved about 1200 $ml \cdot min^{-1}$. Larger flow resulted in soot formation while methane conversion dropped to 75% and selectivity hardly achieved 80%. The analysis of membranes after deactivation of the reactor showed different stages of degradation of membranes depending on their location. This observation suggests that membranes were exposed to different oxygen activity gradients. The non-uniform "chemical load" and ensuing local differences in the temperature of the membranes seem to be main reasons for oxygen separation efficiency smaller than in a single membrane reactor. Therefore special efforts are necessary in order to provide uniform distribution of temperature and oxygen activity gradient along and across the membranes.

This work was supported by the Russian Foundation for Basic Research (№13-08-96060 Ural) and the program of the Presidium of the Ural Branch of RAS (№12-3-2-002 Arktika).

P- 34

Effect of the linking group and NiO underlayer to the conductivity of p-type DSSC

Luca D'Amario, Allison Brown, Travis White, Jonathan Freys, James Gardner, Anders Hagfeldt
and Leif Hammarström
Dept. of Chemistry - Ångrström lab. Uppsala University
Room Ångström 70122 Sweden
Email: luca.damario@fotomol.uu.se

We investigate on chemical working mechanism of the p-type Dye-Sensitized-Solar-Cell (DSSC). On the basis of our previous work we examined the effects of changing the nature of the linking group of the dye. We found a strong dependence of the electrical conductivity of the cell with critical effects on the efficiency. The alterations of the property were attributed to the different anchoring groups. The proof of this was given by the electrochemical impedance spectroscopy (EIS) and the current-voltage (I-V) measurement using two different kinds of cells, the first one was prepared in the usual way and the second one was built with a NiO underlayer between the semiconductor film and the conductive glass (FTO).

P- 35

Potential of high temperature membrane-shift-reactors for pre-combustion CO_2 capture in IGCC power plants

Philipp Meysel, Christian Kunze, Hartmut Spliethoff
Institute for Energy Systems , Technische Universität München
Boltzmannstrasse 15, 85748 Garching, Germany
Email: p.meysel@tum.de

Keywords: IGCC, CO_2 capture, membrane reactor, water-gas shift reaction

Greenhouse gas emissions from conventional coal power plants are a growing concern. One promising concept to avoid CO_2 emissions and at the same time enable flexibility for power generation from coal is the Integrated Gasification Combined Cycle (IGCC). According to Kunze, integration of CO_2 sequestration in this process results in an efficiency drop of 11.4 %-points [2]. A major part can be attributed to exergy losses due to the requirement of gas cooling and excess water addition for high CO conversions of the water-gas shift reaction (WGSR) as well as the employment of conventional CO_2 scrubbing technique. The application of a water-gas shift membrane reactor (WGSMR) could enable the operation of the WGSR at higher temperatures and moreover separate the CO_2 in the same unit without additional energy demand. Within the framework of the joint research project HotVeGas I Aspen Plus calculations were conducted to identify the potential of future technologies and lead the way for further research [1][2].

Fig. 1 shows the advanced IGCC concept with integrated WGSMR that was part of the calculations. It was compared to a base case using conventional state of the art technologies. The main enhancements of the advanced concept can be attributed to a hot gas clean up, membrane enhanced CO conversion at high temperature and a direct CO_2 condensation.

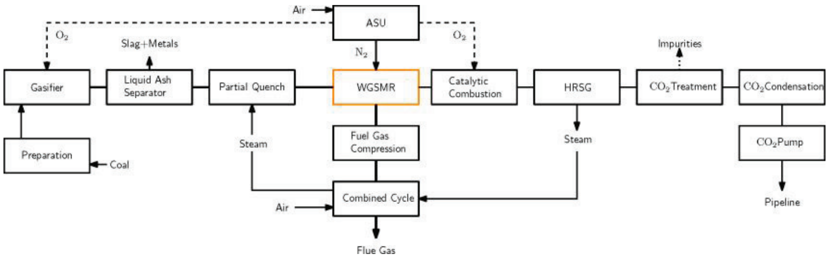


Fig. 17. Simplified process scheme of the IGCC-MR concept

As indicated in Fig. 2, depending on the assumed state of art, the integration of a membrane reactor could improve the overall efficiency compared to the base-case between 2.95 and 6.46 %-points.

The final configuration is based on the assumption of a sulfur resistant membrane reactor operating at temperatures of about 900 °C. So far, a membrane material that withstands such conditions has not been identified, yet. Nonetheless, the calculations show that further research in this field could pay off and lead the direction for long term goals.

In a first step of the second part of the HotVeGas project, different reactor models have been developed to allow more detailed studies of the WGSMR. In that context also experimental investigations are planned.

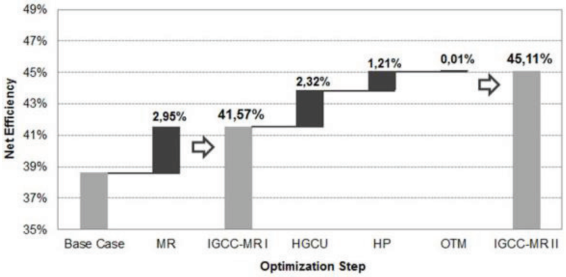


Fig. 18. Efficiency analysis of the IGCC-MR concept

References

[1] C. Kunze, H. Spliethoff: Comparison of IGCC concepts with oxy-fuel, pre- and post-combustion based carbon capture, 36th International Technical Conference on Clean Coal & Fuel Systems, Clearwater (USA), 2011

[2] C. Kunze, Simulation und Bewertung zukünftiger IGCC-Kraftwerkskonzepte mit CO_2-Abtrennung, Dissertation, Technische Universität München, 2012

P- 36

Thermodynamic evaluation of the use of ITM for air separation in an anthracite coal oxy-fuel power plant

E. Portillo[a], F. Vega[a], I. Moriña[b] and J. M. Serra[c]
[a]Department of Chemical and Environmental Engineering, ETS Ingeniería-University of Seville
C/ Camino de los Descubrimientos s/n, CP. 41092, Seville, Spain.
[b]Instalaciones Inabensa,S.A., Ctra de la Esclusa, CP. 41011, Seville, Spain
[c]Instituto de Tecnología Química, UPV-CSIC, C/ Camino de Vera, s/n, Valencia 46022, Spain
Email: eportillo@etsi.us.es

Keywords: ITM, thermodynamic evaluation, oxy-fuel combustion, coal-fired power plant

Currently, pulverized coal-fired power plants are one of the major sources of anthropogenic CO_2 emissions. In this sense, several CO_2 capture and storage (CCS) alternatives are being studied by many researchers. Oxy-fuel processes represent a promising technique for CCS in coal-fired power plants. This technology uses oxygen as oxidant for combustion. Now a day, cryogenic air separation (ASU) is the only mature technology to produce the high tonnage of oxygen required for a full-scale oxy-fuel power plant. However, the use of ASU systems involves an important energy penalty thereby reducing the net plant efficiency of. Ion transport membranes (ITM) are foreseen as good candidates for the replacement of ASU systems due to their potential to lower energy penalties. Basically, ITM can be operated in 4-end or 3-end modes in order to keep the differential oxygen partial pressure through the membrane that is necessary for the oxygen transport (see Figure 1). In the four-end mode, a previously heated stream of flue gas is recycled and used as sweep gas on the permeate side. In the three-end mode, the differential oxygen partial pressure through the membrane is given by a vacuum pump [1, 2].

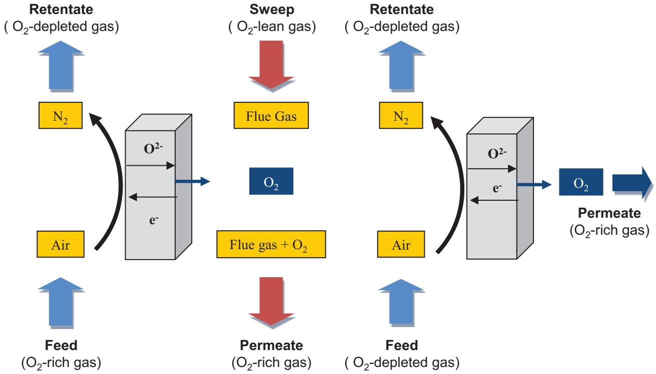


Fig. 19. Scheme of the ITM operation in 4-end mode (left) and 3-end mode (right). Adapted from [2].

In this work, Aspen Plus software was employed to the thermodynamic evaluation of the use of ITM as an alternative to ASU in an oxy-fuel power plant. Two operation modes, 4-end and 3-end, were considered for ITM. A 500 MW oxy-fuel power plant with ASU system was takes as reference case and Spanish anthracite coal was chosen as fuel. The results show that the net plant efficiency can be enhanced by using ITM instead of ASU: 3.4 % in 4-end mode and 0.3 % in 3-end mode (Fig. 2).

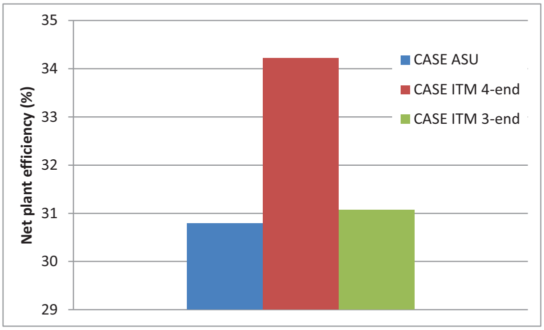


Fig. 2. Net plant efficiency

References

[1] R. Castillo, Journal of Energy Procedia. 4 (2011) 1026-1035.
[2] H. Stadler, Journal of Greenhouse Gas Control. 5 (2011) 7-15.

P- 37

Syngas production at intermediate temperature through H_2O and CO_2 electrolysis with a Cu-based solid oxide electrolyzer

C. Gaudillere, L. Navarrete, J. M. Serra
Instituto de Tecnología Química, UPV-CSIC, Av. de los Naranjos s/n, 46022 Valencia, Spain
Email: cgaudi@itq.upv.es; launaal@itq.upv.es; jmserra@itq.upv.es

Keywords: Solid Oxide Electrolysis Cell; Syngas; Carbon dioxide; Intermediate temperature

The growing interest of the scientific community towards the global warming and its consequences over environment lead to investigate new energy resources in order to decrease CO_2 rejection and dependence on fossil fuels. Hydrogen has been identified as a potential alternative fuel as well as an energy carrier for the future energy supply. An interesting opportunity for the clean production of hydrogen from water is the electrolysis at high temperature using oxygen-ion conducting ceramic materials. Indeed, Solid Oxide Electrolyzer Cells (SOEC), defined as the reverse of Solid Oxide Fuel Cells (SOFC), can promote water electrolysis to produce hydrogen thanks to external electricity. Due to the high operating temperature range (800ºC-1000ºC), noble metals can be discarded and reaction kinetics made easier.

Here we promote in the intermediate temperature range (600ºC-700ºC) H_2O electrolysis and CO_2 electrolysis using an oxygen-ion conducting solid electrolyzer cell constituted by a $Ce_{0.8}Gd_{0.2}O_{2-x}$ (GDC Gadolinium Doped Ceria) electrolyte, a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-x}$ (BSCF)-$Ce_{0.8}Gd_{0.2}O_{2-x}$ porous anode layer and a Cu-$Ce_{0.9}Gd_{0.1}O_{2-x}$ porous cermet cathode layer. Cu metal was preferred to conventional Ni since it is quite low cost and relatively inert towards coking reactions that could occur during CO_2 electrolysis. Electrical measurements coupled with gas monitoring by mass spectrometry are realized. Material stability is also evaluated by coking detection through Raman spectroscopy.

Electrochemical experiments have shown that syngas (H_2/CO) are produced without deactivation and thus confirmed that H_2O electrolysis and CO_2 electrolysis are feasible in the intermediate temperature range. H_2O electrolysis experiments revealed interesting hydrogen yields (for example 32% of the theoretical hydrogen production at -78 $mA.cm^{-2}$ and at 700ºC). Nevertheless, the catalytic or electrochemical process involving the production of carbon monoxide remains uncertain. DRIFT (Diffuse Reflectance Infrared Fourier Transform) experiments will be performed to identify the different adsorbed species and give an overview of the reaction mechanism. Moreover, the CO production remains especially low with a Faraday´s efficiency of 4% for a current density of -660 $mA.cm^{-2}$ at 700ºC. An interesting point is the absence of carbon deposit upon the Cu-GDC layer during the CO_2 electrolysis experiments. Indeed the carbon deposit could block the active site and cause the cell deactivation.

Further improvements concerning the cell manufacturing (thin films elaboration and microstructure optimization) and the electrocatalytic activity by the addition of a suitable catalyst (Pd, Pt) will be necessary to reach industrial targets.

P- 38

Pilot module operation for efficient high temperature air separation

Nicolas Nauels, Michael Modigell
RWTH Aachen University-Aachener Verfahrenstechnik Turmstraße 46, 52064 Aachen, Germany
Email: nicolas.nauels@avt.rwth-aachen.de

Keywords: Module, CFD, Pilot-Scale, BSCF

Mixed Ion Electron Conducting (MIEC) ceramic membranes offer a high potential for high purity oxygen production. Due to the high required operation temperature >700°C, the application of these membranes is of special interest in processes, where high temperatures are present. One possible field of application can be seen in the oxyfuel combustion for carbon capture and storage. Therefore fuel is combusted with a mixture of recirculated flue gas and pure oxygen. In the abscence of air nitrogen, the flue gas mainly consists of CO2 and water and can easily be prepared for sequestration. The required heat to operate an MIEC membrane can be taken from the combustion process and be integrated into the water steam cycle afterwards. Process calculations performed in the Oxycoal-AC research project indicate a power plant net efficiency loss of less than 6 %-points with an efficient integration of the membrane unit under elevated feed pressures (10-20 bar) and a moderate vacuum on the permeate side.

To demonstrate the membrane performance under the above-mentioned conditions, a membrane module with 14m² membrane area has been developed within the research project. To avoid sealing problems between the membrane and the module, a water cooled flange is used that encloses one end closed tubular membranes, consisting of $B_{0.5}S_{0.5}C_{0.8}F_{0.2}O_{3-\delta}$. The membranes are manufactured at RWTH Aachen University via cold isostatic pressing. With this area the module is designed to provide more than 0.5 t/d of oxygen under the targeted process conditions. The module was taken into operation in 2012.

Although providing high purity oxygen of >98%, a lower permeation rate in a dense packed module is observed compared to permeation rates obtained in experiments on single membrane tubes. To take a closer look at this fact, Computational Fluid Dynamics (CFD) investigations were performed. It was found out, that heat loss through the water cooled flange leads to local temperature differences that inhibit the permeation. Moreover, short-circuit flows occur so that the oxygen containing feed air is not lead to the membranes in a sufficient way, which decreases the effective driving force across the membrane. From the simulations, measures for constructive changes can be concluded. The poster will give an overview about the experimental module testing compared with the CFD simulations.

Fig. 20. Pilot membrane module

P- 39

Tubular solid oxide electrolysers for CO_2 / H_2O reduction

L. Kleiminger, G.H. Kelsall
Department of Chemical Engineering, Imperial College
South Kensington, London SW7 2AZ, UK
Email: l.kleiminger11@imperial.ac.uk

Keywords: CO_2 and steam electrolysis, tubular reactor, nickel cathode, YSZ solid oxide electrolyte

Increasing concern about the consequences of CO_2 emissions, especially from fossil-fuelled power plants, is driving the development of processes to reduce CO_2, with or without co-electrolysis of steam, Such processes enable energy storage in chemical bonds of syngas or hydrogen from steam electrolysis alone, but the large energy requirements necessitate use of renewable or surplus overnight energy for which costs can be negative.

This project aims to develop an energy-efficient electrochemical process to facilitate (co-)electrolysis of CO_2 and H_2O utilizing commercially available yttria-stabilized zirconia tubes (thickness ca. 800 μm) as oxide ion-conducting membrane at temperatures of ca. 750 °C):

Cathode:

$$CO_2 + 2e^- \longrightarrow CO + O^{2-} \qquad (1)$$

$$\nu_{H_2}\left(H_2O + 2e^- \longrightarrow H_2 + O^{2-}\right) \qquad (2)$$

Electrolyte:

$$\left(1+\nu_{H_2}\right)\left(O^{2-}\left(\text{cathode}\right) \xrightarrow{\text{electrolyte}} O^{2-}\left(\text{anode}\right)\right) \qquad (3)$$

Anode:

$$\left(1+\nu_{H_2}\right)/2\left(O_2 + 4e^- \longleftarrow 2O^{2-}\right) \qquad (4)$$

Overall:

$$CO_2 + \nu_{H_2}H_2O \longrightarrow CO + \nu_{H_2}H_2 + \left(1+\nu_{H_2}\right)/2\,O_2 \qquad (5)$$

Results (such as Fig. 1) will be reported primarily for nickel-YSZ composite cathodes, as nickel has been identified previously as a suitable choice for CO_2 reduction [1]. However, the effect of infiltrating electrocatalysts (e.g. copper) into the nickel cathode will be discussed. The system could be run reversibly in fuel cell and electrolyser mode.

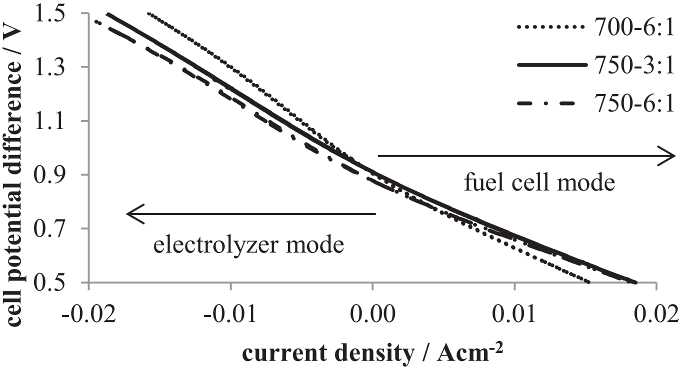


Fig. 1. Effect of current density on cell potential difference for 6:1 and 3:1 CO_2:H_2 feed ratios at 700-750°C for Ni-YSZ|YSZ|LSM-YSZ|LSM solid oxide electrolysis/fuel cell.

Electrolysis off-gases were analysed using mass spectrometry to determine charge yields and CO_2 conversions. CO_2 electrolysis and co-electrolysis modes were investigated at different gas compositions. Co-electrolysis was superior to CO_2 electrolysis in terms of overall performance and stability. Adsorption modelling indicated steam adsorption was favoured over CO_2 adsorption; i.e. steam electrolysis is the main electrochemical process, whereas CO_2 to CO conversion is predominantly via reverse water gas shift (RWGS) reaction:

RWGS-reaction: $$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad (6)$$

Future work will focus on decreasing the electrolyte thickness by shifting from electrolyte-supported to electrode-supported systems, as has been employed for fuel cells [2].

Reference

[1] Kim-Lohsoontorn, P.; Bae, J. Journal of Power Sources, **196** (2011), 7161.

[2] Droushiotis, N.; Doraswami, U.; Kelsall, G.H.; Li, K. Journal of Applied Electrochemistry, **41** (2011), 1005.

AUTHOR INDEX

ISBN 978-84-9048-111-0

SUMMER SCHOOL

Inorganic Membranes for Green Chemical Production and Clean Power Generation

HELMHOLTZ GEMEINSCHAFT

NoE-ALLIANCE MEM-BRAIN

EERA
European Energy Research Alliance

demOys

SEVENTH FRAMEWORK PROGRAMME

HETMOC

CARENA

NASA-OTM PROJECT

VLC/CAMPUS
VALENCIA INTERNATIONAL CAMPUS OF EXCELLENCE

mci Sostenibilidad energética

INSTITUTO DE TECNOLOGÍA QUÍMICA

CSIC
Consejo Superior de Investigaciones Científicas

UNIVERSITAT POLITÈCNICA DE VALÈNCIA