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Membrane News Twente

News magazine of the Membrane Technology Group

MNT, p/a University of Twente - TNW/MTO
postbox 217 , NL-7500 AE Enschede, Netherlands
membrane@utwente.nl - http://mtg.tnw.utwente.nl
Telephone: +31 (0) 53 489 2950 - Fax: +31 (0) 53 489 4611

Membranes for Energy and Sustainable Processes

The research cluster Membranes for Energy and Sustainable Processes (or in full Membrane Materials Science and Technology for Energy and Sustainable Process Applications) focuses on the preparation, development and application of membranes for the production of energy and for the replacement of traditional energy consuming processes (Figure 1). Research focuses both on

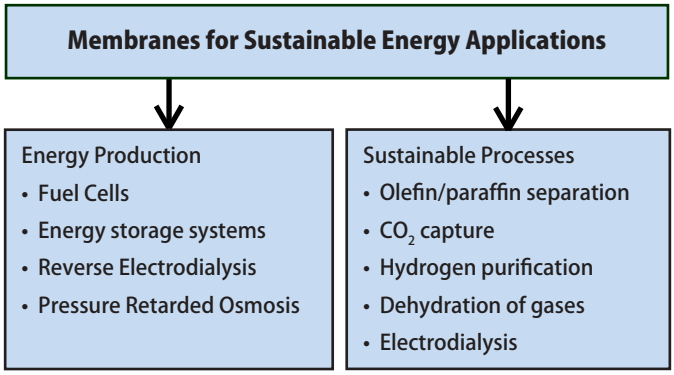

Figure 1: Research cluster Membrane Materials Science and Process Technology for Sustainable Energy Applications.

the fundamental understanding of mass transport through polymer membranes to identify structure-properties relations and on the application of membrane technology in the specific application areas.

Sustainable energy production

Research on energy production focuses on the generation and storage of sustainable energy. A major part is dedicated to fuel cells and energy storage systems (e.g. direct methanol fuel cell, Figure 2). Energy storage systems use the same principle and configuration as a fuel cell, with this distinction that the redox reactions at the anode and the cathode side proceed in both directions, depending on whether the cell is charged (energy storage) or discharges (power production). Crucial is the transport of ionic species (e.g. protons, hydroxyl ions) through the membrane. It is governed by a complex, nanometer scale morphological organization in the membrane (e.g. formation of channels for proton transport) and by the interactions between the ionic species and the specific groups in the membrane. Integration of the membrane with the electrodes is of major importance as well.

Transport of ions also plays an important role in the research on Reverse Electro Dialysis (RED, salinity gradient power, Figure 3). In RED, a concentrated salt solution (e.g. sea

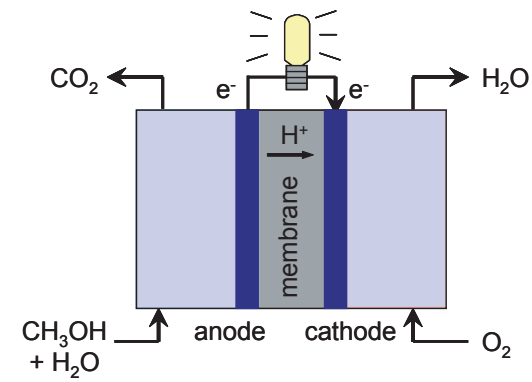

Figure 2: Principle of a direct methanol fuel cell.

(PES beads synthesized by phase separating an emulsion)

water) and a less concentrated salt solution (e.g. river water) are brought into contact through an alternating series of anion exchange membranes (AEM) and cation exchange membranes (CEM) to produce sustainable energy. The membranes are the key elements in RED and research focuses on analysis, control and optimization of the transport of ions through these membranes.

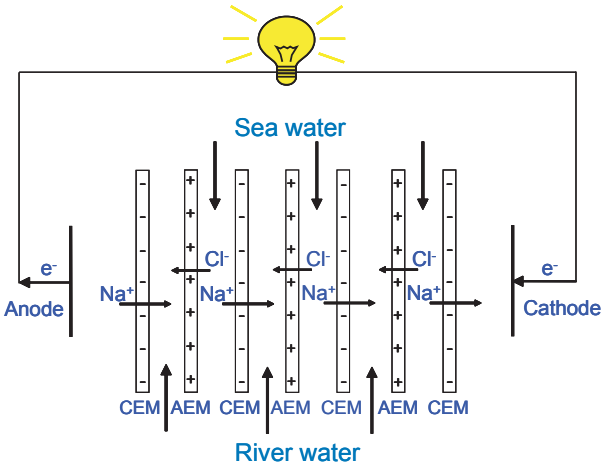

Figure 3: Principle of Reverse Electrodialysis (RED).

Sustainable processes

The research cluster Sustainable Process Applications is dedicated to the replacement of traditionally energy consuming processes by more sustainable and energy efficient membrane based alternatives. Two major directions can be currently distinguished: 1) Gas and vapor separations and 2) Electrodialysis and molecular imprinted membranes.

Figure 4: Coal fired power plant (Borssele, The Netherlands).

Gas and vapor separations

Membranes are an attractive alternative for energy consuming separations such as e.g. the capture of CO_2 (Figure 4) or the separation of olefins and paraffins. Research focuses both on the fundamental understanding of gas and vapor transport (solution, diffusion and permeation) through polymer membranes to identify structure-properties relations and on the application of membrane technology for the design of energy efficient gas and vapor separation processes. An alternative process for gas separation is the use of a membrane contactor to perform gas-liquid contacting processes in a controlled way. More information on this topic can be found on page 4 of this newsletter.

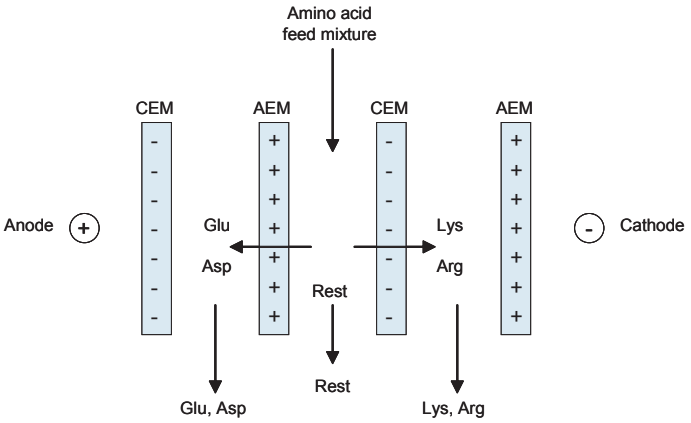

Figure 5: Principle of electrodialysis for the fractionation of amino acids.

Electro dialysis (ED) and Molecular Imprinted Membranes (MIMs)

Electro dialysis is a cost and energy efficient separation technology for the separation of charged feed mixtures, e.g the fractionation of amino acids for the production of building blocks for the chemical industry (Figure 5). Charged components migrate and are separated under the influence of an electrical potential gradient. ED makes use of alternating series of anion (AEM) and cation (CEM) exchange membranes as well. Research not only includes membrane development and ion transport characterization, but also module and process design and improvement of the hydrodynamics.

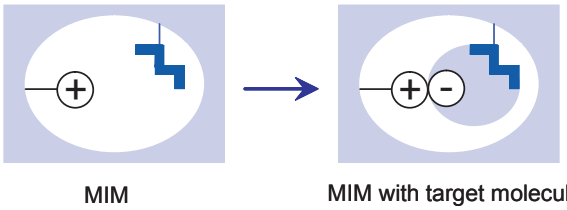

Figure 6: Molecular Imprinted Membrane with recognition function for target molecule.

A new concept is the use of molecular imprinted membranes (MIMs, Figure 6). MIMs are membranes with recognition functionality for the target molecule(s). Such 'smart' membranes have a molecular selectivity due to the use of templates to create well-defined and selective trans-membrane transport pathways. The concept is flexible and offers the possibility to easily adjust the geometry, adsorption capacity as well as the functionality of the structure towards the specific separation. To enhance mass transport, this concept can be integrated with ED.

For more information please contact Dr. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl; phone: + 31 (0)53 489 4185).

Mixed Matrix Membranes

A new platform for enzymatic reactions

Ph.D. thesis, João de Sousa André

João de Sousa André

Enzymes have been used for centuries in their native form in applications ranging from early food processes to modern applications in pharmaceutical and chemical industries. The interest in enzymatic reactions arises from the higher specificities and yields obtained, as well as in the reduced waste and energy consumption.

Enzymes started being immobilized in order to perform enzymatic reactions using specific enzymes, as well as to increase their long-term stability. Enzymes can be immobilized in a variety of supports, ranging from particles to membranes. Membranes are of particular interest, since they permit the reaction to take place in dynamic mode using controlled conditions.

In recent years, a new membrane platform consisting of the synergistic combination of chromatographic particles and membranes has been developed. These membranes, termed mixed matrix membranes (MMM), consist of a macro porous polymeric support in which small chromatographic particles are embedded (Figure 1). This concept combines the flow characteristics of membranes, a low pressure drop along the bed and a high trans membrane flux, with the high selectivity and capacity of chromatographic beads. An additional benefit of the MMM platform is the flexibility of design, which allows for the preparation of different geometries, such as flat-sheet or fiber membranes.

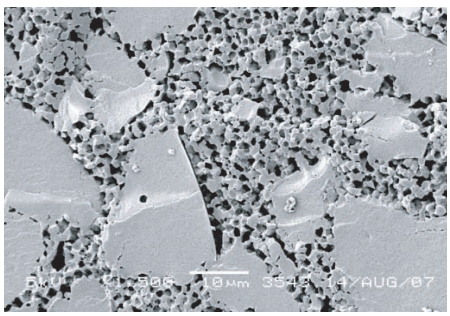

Figure 1: Chromatographic particles are embedded in the macro porous wall of the polymeric hollow fiber.

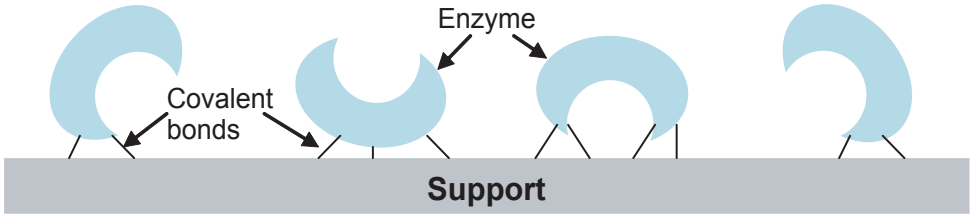

Figure 2: Schematic representation of enzyme immobilization using covalent bonds.

In his Ph.D. project João de Sousa André prepared mixed matrix membranes with different geometries in conjugation with different chromatographic beads to evaluate their performance in enzymatic reactions. In his research he proved three different membrane concepts:

1)Flat-sheet mixed matrix membranes prepared with Eupergit particles embedded in an ethylene vinyl alcohol (EVAL) polymeric support. Enzymatic activity was established by covalently coupling trypsin to the oxirane groups from the Eupergit particles (Figure 2). The performance of this system was evaluated by the enzymatic conversion of L- benzoyl-arginine-ethylester. The enzymatic activity was found to be higher than when using the Eupergit particles in a packed bed mode. The enzymatic activity of immobilized trypsin could be further enhanced by chemically modifying the Eupergit particles before the Trypsin coupling.

2)The same enzymatic conversion reaction was also studied using mixed matrix hollow-fibers. The developed hollow-fiber showed an enhanced enzymatic activity when compared to the flat-sheet MMM.

3)Finally a polyether sulfone (PES) based mixed matrix hollow fiber was developed for the immobilization of glucose oxidase (GOx). In this hollow fiber strong cation-exchange resins (Lewatit SP112) were

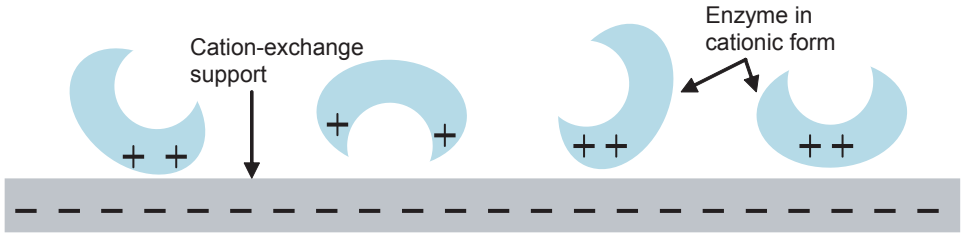

Figure 3: Schematic representation of enzyme immobilization in a cation-exchange support.

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embedded to electrostatically couple the GOx (Figure 3). The performance of this concept was compared with the enzymatic activities obtained with a covalently coupled GOx system using the EVAL/Eupergit hollow-fibers. The conversion with electrostatically coupled enzymes was more than doubled compared to the covalently coupled GOx.

The research performed by João de Sousa André proves that Mixed Matrix Membranes are well suited as a support for enzymatic reactions. The activity of immobilized enzymes mainly depends on flow hydrodynamics where the use of the newly developed catalytic mixed matrix membranes are superior over packed bed systems.

For more information please contact Dr. Zandrie Borneman (z.borneman@utwente.nl; phone: + 31 (0)53 489 2965).

João de Sousa André will defend his thesis on February 6, 2009. He currently works as Application & Development Engineer at fluXXion B.V., where he is involved in the development of state of the art microsieves. He can be reached at joao.sousa.andre@fluxxion.com.

Kitty Nijmeijer elected as member of the EMS council

Kitty Nijmeijer, assistant professor in the Membrane Technology Group, has been elected as new member of the Council of the European Membrane Society (EMS) for the period 2009-2012.

The major aim of the EMS is to promote contacts and the exchange of knowledge and ideas, both fundamental and applied in nature, on membrane science and technology between universities, institutes and industries. It also promotes the use of membranes and membrane processes. Ways to do so include e.g. the organization of summer schools, poster prizes and lecture awards for young researchers, best paper award, support of conferences (e.g. Euromembrane), etc.

Half of the Council is renewed every 2 years, by postal ballot, for a term of 2 years. Council members are elected for a period of 4 years. The Council meets two to three times a year, but has almost daily electronic contact. More information can be found at www.emsoc.eu/site/home/index.php.

Poster award for Katja Fischbein

Katja Fischbein, Ph.D. student at the Membrane Technology Group, has been rewarded with the poster price at the 12th Dutch-Flemish Symposium and Poster Day Membrane Technology. The event, which was organized by the Belgian Membrane Group (BMG) and the Dutch Membrane Society (NMG), combines the presentation of a large number of posters with a selected, limited number of presentations. It is a platform for exchange of a wide variety of aspects on fundamental and applied membrane science and technology, with participants from universities, institutes and industries.

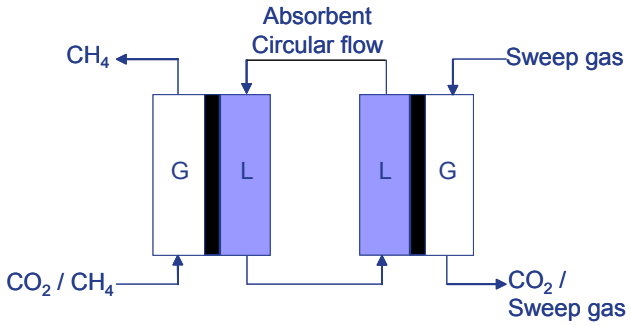

Figure: Schematic representation of a gas-liquid membrane contactor of CO_2/CH_4 separation.

Katja Fischbein presented her work on 'gas-liquid membrane contactors for CO_2/CH_4 separation'. The traditional method for CO_2 capture is amine based absorption technology, which is energy and cost intensive, has significant liquid losses due to evaporation and has a limited operational flexibility. In a membrane contactor (see Figure), a gaseous feed (CO_2/CH_4) and an absorption liquid are brought into contact through a membrane and one of the feed components (CO_2) is selectively removed through the membrane and by the absorption liquid. Both the absorption liquid and the membrane thus contribute to the overall process performance. One of the major advantages of a membrane contactor is that the gas and the liquid flow can be controlled independently and that the evaporation of absorption liquid can be (partly) prevented by the use of a suitable membrane. In her work, Katja Fischbein investigates the potential and the operational flexibility of such a membrane contactor for the separation of CO_2/CH_4.

For more information, please contact Katja Fischbein (k.fischbein@utwente.nl; phone: + 31 (0)53 489 2962) or Dr. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl; phone: + 31 (0)53 489 4185).

A new home for Inorganic Membranes

On December 1st of 2008 the Inorganic Membrane Group moved to the building where their colleagues of Membrane Science and Technology already reside since April 2007: The Meander.

Diligence of the group members and others, combined with months of thorough preparation resulted in a very fast move to the new location. In only two days all equipment and group possessions were moved from the old, dark, leaky and dirty Langezijds building to the new, light and clean labs and offices on the second and third floor of the Meander.

The pictures on this page give an impression of the moving. Of course, you are more than welcome to visit us for a full tour.

Introducing...

Modification of porous ceramic membranes for CO_2/CH_4 separation

Name
Venkata Giri Prasad Sripathi

Origin
India

Contact
http://mtg.tnw.utwente.nl
0031 (0) 53 489 2961
v.g.p.sripathi@utwente.nl

Giri was born in Andhra Pradesh, India on 1st August 1980 completed his MSc in Chemistry at Umea University, Sweden. He did his MSc theses on the topic titled “Synthesis of gold nanorods with high aspect ratio”.
After his MSc, he gained research experience by working on a project for 2 years which focused on the synthesis of silica coated gold nanoparticles in order to prepare metal enhanced fluorescence ultra-sensitive diagnostic systems (point of care diagnostics).
In October 2008 he started a DSTI PhD project in the Membrane Technology group. This project focuses on the modification of porous ceramic membranes for CO_2/CH_4 separation.

Introducing...

Molecular imprinted membranes for the removal of trace components

Name
Anne Corine IJzer

Origin
Netherlands

Contact
http://mtg.tnw.utwente.nl
0031 (0) 53 489 3474
a.c.ijzer@utwente.nl

Anne Corine IJzer studied Chemical Technology at the University of Twente and performed her Master assignment in the Membrane Technology Group. She studied the structure-property relationship of block-copolymers for use in gas separation. After graduating she became a PhD student in the Membrane Technology Group on the subject of: "Molecular imprinted membranes for the removal of trace components". This project is part of a larger DSTI project which is realized by a project team in which, apart from University of Twente, 2 universities, one GTI and 6 main chemical industries participate.

Surface oxygen exchange kinetics of perovskite oxides

Name
Chung-Yul Yoo

Origin
South Korea

Contact
http://mtg.tnw.utwente.nl
0031 (0) 53 489 2998
c.yoo@utwente.nl

Chung-Yul was born on February 10, 1982 in South Korea. He finished his Bachelor and Master degree at Ajou University in Suwon, South Korea and joined the Inorganic Membranes Group as a PhD student in October 2008. The main focus of his research is to study the surface oxygen exchange kinetics of perovskite oxides, which show promise for use as membrane or electro catalysts in solid oxide fuel cells. Fundamental studies of the surface oxygen exchange kinetics on perovskite oxides will be carried out using oxygen isotope exchange and conductivity relaxation as main techniques.

Alkaline fuel cell

Name
Geraldine Merle

Origin
France

Contact
http://mtg.tnw.utwente.nl
0031 (0) 53 489 2961
g.merle@utwente.nl

Geraldine Merle is a 28-year-old Post-Doc from France. She finished her MSc in Chemical Science at the Montpellier University. In October 2005, she started her PhD at the European Membrane Institute, in Montpellier, France. The goal of her project was the conception of enzymatic electrodes to build a glucose/dioxygen biofuel cell and a hydrogen biofuel cell. Recently, she started as a Post-Doc in the Membrane Technology Group. Her project focuses on alkaline fuel cells and includes synthesis and characterization of anion exchange membranes and the integration with the electrodes.

Electrodialysis for the separation of amino acids

Name
Olga Kattan

Origin
El Salvador

Contact
http://mtg.tnw.utwente.nl
0031 (0) 53 489 2107
o.m.kattanreadi@utwente.nl

Olga Kattan was born in San Salvador, El Salvador. Before finishing her studies in Chemical Engineering at the Central American University Jose Simeon Canas in El Salvador, she moved to Hamburg, Germany, to perform her Bachelor Thesis as an exchange student at the Technical University of Hamburg. Two years later she obtained her MSc in Biotechnology from the same university. During the last year of her MSc, she performed a scientific training at BASF AG, in Ludwigshafen, Germany. Basically, she worked on the investigation and characterization of emulsions for the formulation of oil based pesticides. In October 2008, she joined the Membrane Technology Group as a PhD student. Her project explores the application of electrodialysis for the separation of amino acids. The aim is the development of an energy efficient process for the production of building blocks for the chemical industry based on the use of cheap feedstocks (e.g. cheap protein/amino acid sources).

Membranes for flue gas treatment

Transport behavior of water and gas in hydrophilic polymer membranes

Ph.D. thesis, Jens Potreck

The removal of water vapor from gas streams is an important industrial operation and many applications can be found in e.g. the dehydration of flue gas, natural gas dew pointing, the drying of compressed air and the storage of fruits and vegetables under protective atmosphere. Membrane technology using polymeric membranes is a promising and attractive technology for dehydration purposes because of its high energy efficiency, inherent simplicity and small footprint.

Permeation of gases and vapors through dense polymer membranes is determined by the solubility and diffusivity of these components in the polymer. This thesis analyzes the sorption, diffusion and permeation behavior of two different types of highly water permeable, hydrophilic polymer membranes (the glassy polymer sulfonated poly (ether ether ketone, SPEEK) and a rubbery PEO based block copolymer (PEBAX® 1074)) for the removal of water vapor from gas streams.

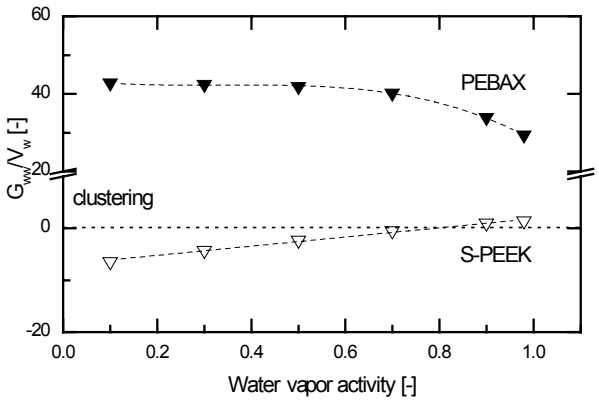

Figure 1: Cluster integral as a function of the water vapor activity for S-PEEK with a sulfonation degree of 59% and PEBAX® 1074 at 20 °C. Above the line Gww/Vw = 0, clustering of individual water molecules into larger water clusters can occur.

The highly hydrophilic nature of the polymers results in extremely high amounts of absorbed water. Thermodynamic analysis of water vapor sorption in the two polymers reveals the Gibbs energy of sorption is negative and that in all cases water sorption is exothermic and by the enthalpy. Water sorption is entropically unfavorable. The results suggest that in PEBAX® additional sorbed water molecules experience a water-like environment, whereas in S-PEEK the polymer-water interactions prevail. This observation is supported with results from cluster analysis (Figure 1).

Jens Potreck

The results proof the occurrence of both Fickian sorption behavior (MF) and relaxational phenomena (MR1 + MR2) in SPEEK, already at very low water concentrations in the polymer. The Fickian diffusion coefficient of water vapor in the glassy polymer SPEEK changes over three orders of magnitude. The corresponding values in the rubbery polymer PEBAX® are a factor 10 to 100 higher and vary over two orders of magnitude.

Gas permeation measurements with binary mixtures of H_2O/N_2 and H_2O/CO_2 reveal that extremely high water vapor permeabilities can be obtained with both membranes. The water vapor permeability strongly increases with increasing water vapor activity. In PEBAX® 1074 the nitrogen permeability slightly decreases with increasing water vapor activity. We hypothesize this is due to the presence of water in the polymer which changes the gas solubility. In combination with the increase in water vapor permeability, this leads to a strong increase in water vapor over nitrogen selectivity with increasing water concentration in the polymer (Figure 2).

Measurements with ternary gas mixtures ($H_2O/N_2/CO_2$) show that the presence of only 10% CO_2 induces a severe increase in N_2 permeability in SPEEK, leading to a three

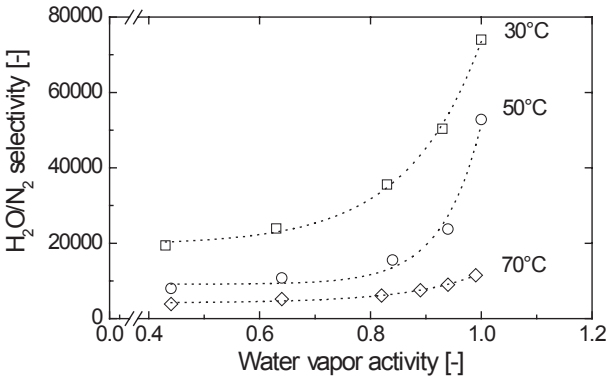

Figure 2: Water vapor over nitrogen selectivity as a function of the water vapor activity for PEBAX® 1074 at 30, 50 and 70°C.

fold decrease in selectivity with ternary mixtures compared to the ideal, hypothetical value obtained from binary mixtures with either H_2O/N_2 or H_2O/CO_2 (Table 1). Nevertheless high CO_2/N_2 selectivities with reasonable CO_2 permeabilities could be obtained. Permeability and selectivity values in PEBAX® 1074 are almost unaffected by the presence of CO_2 as third component.

Table 1: Nitrogen and carbon dioxide permeability, and carbon dioxide over nitrogen selectivity for S-PEEK measured using a binary (N_2/H_2O, CO_2/H_2O) mixture and a ternary (CO_2 (10 vol.%)/N_2 (90 vol.%)/H_2O) mixture (T = 50°, p = 2.5 bar, a = 0.9).

		Binary mixture	Ternary mixture
Permeability (Barrer)	N_2	0.04	0.21
	CO_2	11.49	11.99
Selectivity (-)	CO_2/N_2	287	57

The results not only show the high potential of these polymers for dehydration purposes, they also show that these polymers offer attractive routes to the integration of dehydration and CO_2 capture using membrane technology.

For more information please contact Dr. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl; phone: + 31 (0)53 489 4185).

Jens Potreck will defend his thesis on January 30, 2009. A digital copy of his thesis can be obtained by sending an email to info@membrane.nl. Jens is employed at the Research and Development department of Norit/X-Flow. He can be contacted at potreck@xflow.nl.

The authors would like to thank Rob Heijboer from KEMA (consultant in the field of the production, transportation, distribution and end use of electricity, www.kema.com) for the fruitful and inspiring discussions. This research was financially supported with a grant of the Dutch Program EET (Economy, Ecology, Technology), and by the European Union (IP NanoGLOWA (NMP3-CT-2007-026735)).

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Most-cited paper award author for Henny J.M. Bouwmeester

For the second year in a row, Henny J.M. Bouwmeester has been honored with the Elsevier most-cited paper award for his paper "Dense ceramic membranes for methane conversion" (published in Catalysis Today 82 (2003) 141-150). The paper is recognized in the "Top-50 most cited articles" as published in Elsevier's Catalysis journals 2002-2006 & 2003 – 2007.

The paper discusses the performance characteristics of mixed oxygen-ionic and electronic conducting membranes. These enable separation of oxygen from air at elevated temperatures (>700 °C) with infinite selectivity (see figure). Integration of the membranes in a catalytic membrane reactor for the catalytic partial oxidation of methane to syngas provides a method to significantly reduce the capital costs of the conversion of natural gas to liquid added-value products.

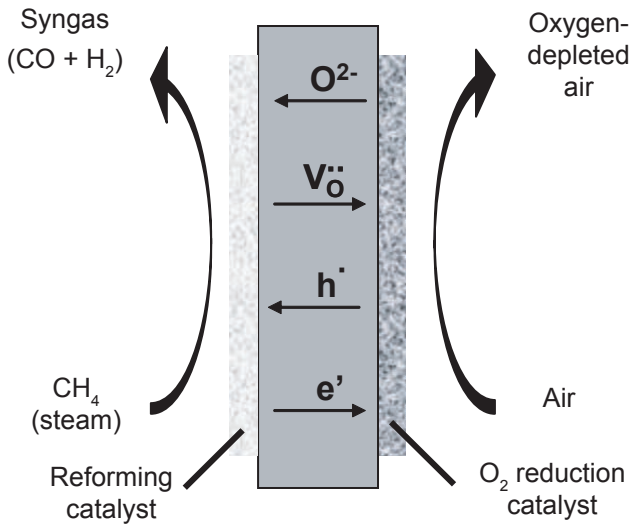

Figure : Operating principle of a ceramic membrane reactor with an oxygen selective membrane for the partial oxidation of methane to syngas.

University of Twente hosts ICOM 2011

In 2011 the ICOM (International Conference on Membranes and Membrane Processes) will be hosted by the Membrane Technology Group of the University of Twente. ICOM is the largest international conference for the exchange of fundamental and applied knowledge and research on membrane science and technology. The event will be take place in Amsterdam from July 23 till July 29, 2011.

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Theses

Alisia Peters
January 9, 2009
Micro-patterned interfaces affecting transport through and along membranes

Jens Potreck
January 30, 2009
Membranes for flue gas treatment
Transport behavior of water and gas in hydrophilic polymer membranes

Joao de Sousa Andre
February 6, 2009
Mixed Matrix Membranes: a new platform for enzymatic reactions

Hakan Yildirim
March 20, 2009
Development of new membrane materials for direct methanol fuel cells

Bernke Papenburg
June 19, 2009
Design Strategies for Tissue Engineering Scaffolds

MNT- Information

Membrane News Twente is published two times per year. The aim is to inform the membrane community about the activities of the Membrane Technology Group.

Editors
Matthias Wessling
Kitty Nijmeijer
Zeynep Çulfaz

Layout
Zeynep Çulfaz

Email
membrane@utwente.nl

Internet & MNT archive
http://mtg.tnw.utwente.nl

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