

Membrane News Twente

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News magazine of the Membrane Technology Group

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"Membranes on the move"

April this year the Membrane Technology Group moved to a new building: Meander. After more than 30 years in the old and dark building of Chemical Technology, we left it and moved to a new, light and open building. The moving went very smoothly and efficient thanks to the help of many people in and outside the group and we are extremely satisfied with our new 'home'.

The name of the building, Meander, is chosen because the new building meanders around the trees in that area. The building is located in the vicinity of the old Chemical Technology building and it is connected to the Horst tower, which is the location were all teaching activities of the faculty of Science & Technology are concentrated. The Meander hosts many other research groups. Most of these groups belong to the research institute Impact, which focuses on process tech-

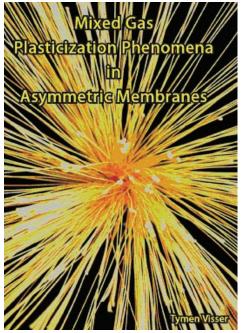


nology and more specific on Sustainable Energy and Smart Devices & Materials. The official opening of the Meander is planned on November 23, 2007 (more information will follow later), but of course you are welcome to visit us whenever it is convenient to you. To get an impression of the moving and our new building, please have a look at the pictures on this page.



Mixed gas plasticization phenomena in asymmetric membranes

Ph.D. thesis Tymen Visser (publicly defended on November 24, 2006)



In the past two decades glassy polymer membranes have been successfully employed in several industrial gas separation processes. The majority of these applications concern 'easy and straightforward' applications like the separation of air. When a feed stream contains plasticizing components, the separation is more complex because glassy polymer membranes generally lose their separation performance in that case. The number of membrane applications in the field of gas separation is rather constant, mainly due to membrane stability issues, although there exists a large market potential for polymeric membranes in this area. To boost the number of applications in this market, polymer membranes with improved stability need to be developed and fundamental knowledge on the complex behavior of plasticization is a key issue in this development.

There exists a tremendous amount of literature concerning the transport of gases through glassy polymer membranes. Despite industrial reality, scientific data on mixed gas plasticization phenomena in asymmetric polymer membranes are surprisingly scarce. This Ph.D work systematically investigates the influence of feed gas composition and pressure on the separation performance of asymmetric hollow fiber membranes of different polymer materials.

One of the most important findings is the existence of a subtle balance between competitive sorption and plasticization effects in CO_2 -separations [1]. For asymmetric membranes this balance is highly dependent on the membrane material used (e.g. polyimide-based materials, cellulose acetate, polyphenylenoxide) [2]. Asymmetric hollow fiber membranes based on homogeneous Matrimid-based blends have very good gas separation properties in CO_2 -separations compared to other materials, despite the occurence of plasticization effects (Figure 1). The effect of plasticization combined with competitive sorption may even improve the separation performance at elevated CO_2 -feed gas pressures. On the other hand, asymmetric membranes of a P84/Matrimidblend are susceptible to C_3 -hydrocarbon plasticization in the separation of feed gas mixtures of C_3H_6 and C_3H_8 [3], which are much stronger plasticizers than CO_2 . Surprisingly, in contrast to CO_2 -separations, the presence of competitively absorbing CH_4 as ternary component does not seem to counteract C_3 -plasticization [3]. Overall the obtained results show that Matrimid-based asymmetric hollow fiber membranes are potentially very interesting for industrial gas separation processes, especially in CO_2 -

Kinetic sorption experiments with six different gases $(CO_2, C_3H_8, C_3H_6, Xe, Kr and Ar)$ in films of the glassy polyimide Matrimid demonstrated that any gas – even noble gases – shows non-Fickian diffusion and may induce irreversible sorption relaxations upon reaching a critical amount of volume dilation [5].

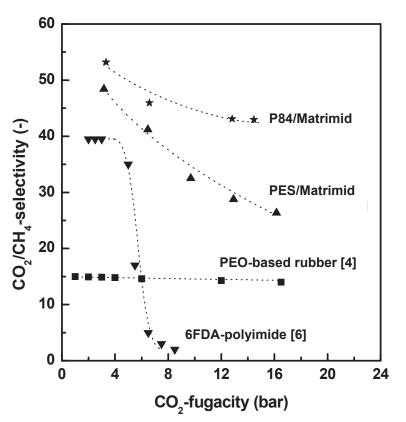


Figure 1: Mixed gas CO_2/CH_4 -selectivity as a function of the CO_2 -fugacity for two Matrimid-based glassy polymer membranes using a80/20 vol.% CO_2/CH_4 -feed gas mixture and a PEO-based rubberymembrane [4]....continues on next page2

Above this critical amount of volume dilation, kinetic sorption behavior becomes non-Fickian (Figure 2). For all gases studied, this critical volume dilation is unique and is dependent on the partial molar volume of the gas and its solubility in the polymer matrix.

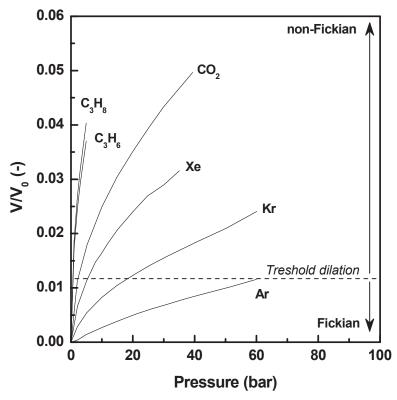


Figure 2: Estimated dilation isotherms in Matrimid polyimide for six different gases. The dashed lines indicate a threshold amount of dilation required to induce non-Fickian sorption kinetics.

 Visser, T., G.H. Koops, and M. Wessling, On the subtle balance between competitive sorption and plasticization effects in asymmetric hollow fiber gas separation membranes. Journal of Membrane Science, 2005. 252(1-2): p. 265-277.
Visser, T. and M. Wessling, Materials dependency of mixed

gas plasticization behavior of asymmetric membranes. submitted to Journal of Membrane Science.

3.Visser, T. and M. Wessling, Propylene/propane separation with Matrimid based hollow fiber membranes. submitted to Journal of Membrane Science.

4.Lin, H., et al., High-performance polymer membranes for natural-gas sweetening. Advanced Materials, 2006. 18(1): p. 39-44.

5.Visser, T. and M. Wessling, When do sorption-induced relaxations in glassy polymers set in? Macromolecules,2007. 40: p. 4992-5000.

6. Staudt-Bickel, C. and Koros, W.J., Improvement of CO_2/CH_4 separation characteristics of polyimides by chemical crosslinking. Journal of Membrane Science, 1999. 155: p. 145-154.

More information Matthias Wessling m.wessling@utwente.nl +31 (0)53 489 2950

The Membrane Technology Group participates in a large European project entitled NanoGLOWA (nano membranes against global warming, contract number: NMP3-CT-2007-026735) to develop membranes for the removal of CO₂ from fossil fuel fired power plants.

 CO_2 is one of the main contributors to the greenhouse effect, and its concentration has increased significantly during the last decades. One of the main anthropogenic sources of CO_2 are fossil fuel fired power plants. To limit the emission of CO_2 , capture (and subsequent use or storage) of this CO_2 is necessary. Current technologies for CO_2 capture e.g. technologies based on absorption in chemical

Membranes for CO₂ capture

Literature

or physical solvents, are not very cost and energy efficient.

NanoGLOWA brings together universities, power plant operators, industries

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and SMEs and 26 organizations from 14 European countries join their forces in this project. The ultimate goal of Nano-GLOWA is to develop, manufacture and install membranes and processes for the separation of CO_2 from flue gases. Both post and pre combustion and oxy fuel will be considered. Five different membrane tracks will be investigated in parallel: Three tracks focusing on polymeric membranes, one on carbon membranes and one on ceramic membranes. The work of the Membrane Technology Group is dedicated towards the development and characterization of functionalized polymeric membranes.

For more information, please contact Kitty Nymeijer (d.c.nijmeijer@utwente.nl), Jens Potreck (j.potreck@utwente.nl) or Sander Reijerkerk (s.r.reijerkerk@utwente.nl) or have a look at the NanoGLOWA website (www. nanoglowa.com).

Membrane Runners participate in Batavieren Race

As a recurring annual event, the Membrane Technology Group participated also this year in the Batavieren Race, which was organized on April 28 and 29, 2007. The group was registered as the "Membrane Runners", and 26 people ran with an extreme effort to demonstrate that membrane scientists are not only tenacious in their field of research, but also in various other activities.

The Batavieren Race is a large, annual runners event from Nijmegen to Enschede. The first Batavieren Race was organized in 1972 by a group of students from the University of Nijmegen. The name of the race refers to the route that Batavians took in 50 B.C. The first race followed the original route. However, for infrastructural reasons, the route was changed for the second edition and has remained basically the same for the next competitions. The race with a total distance of 185 km is divided into 25 stages ranging from 3.4 to 11.9 km. Membrane participants ran in turns from Nijmegen to Enschede for 16 hours showing a great group spirit. Among the 320 teams that took part in the race, the Membrane Runners were ranked on the 210th place, which was better than last year performance.

At the end of the day the efforts of the runners were rewarded with a social get-together. Each year after the race, a barbecue is arranged for all group members followed by the biggest student party in Europe in the campus of the University of Twente. This year the Membrane Technology Group gathered together at Rob's place in Hengelo to celebrate the success of our runners in the Batavieren Race!!!



This event would not have been possible without the aid of our sponsors. The Membrane Runners would like to express their gratitude to Sybrand Metz from Wetsus (Research Institute for Sustainable Water Technology), Bernd Krause from Gambro Dialysatoren GmbH, and Zandrie Borneman and Antoine Kemperman from the European Membrane Institute Twente for their financial support.



wetsus

GAMBRO.



Since the 1st of February, Arian Nijmeijer is the new part-time professor of Inorganic Membranes at the University of Twente. His background is a MSc and PhD in Inorganic Materials Science, both obtained at the University of Twente. In his PhD work he studied the use of inorganic silica membranes for hydrogen removal in membrane steam reformers. After obtaining his PhD, he joined Shell Global Solutions International BV in the year 2000. He became active in the Innovation and Research department of Shell Global Solutions, where he was involved in the creation of a membrane technology group, which was established late 2004. The focus of this membrane group is to deploy membrane technology in refineries, chemical plants and exploration and production operations.

In his one day a week assignment at the UT, Arian will focus on the development of ceramic membrane materials for

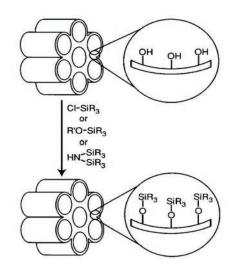


Figure 1. Grafting ceramic membranes

New part-time professor Inorganic Membranes

applications ranging from nanofiltration and pervaporation to gas separation. The group will build on strengths from the past, which involve highly defined mesoporous ceramic membranes for (non-) aqueous nanofiltration. Materials under investigation include zirconia, titania and silica membranes. Some of these membranes will be grafted with polymers to introduce specific affinity for certain organic molecules and/or to reduce the pore size of these membranes to a molecular weight cut-off in the order of 250 g/mol.

These well-defined mesoporous ceramic membranes can also act as supports for highly selective pervaporation and gas separation membranes. State-of-the-art ceramic membranes for pervaporation and gas separation (notably hydrogen separation) are microporous silica membranes. These membranes have shown not to be fully stable under steam containing conditions. Therefore the development of more stable membranes was started and in the mean time microporous titania membranes have been further developed.

A last important research track is the development of dense mixed ionic/ electronic conducting membranes for oxygen separation. These membranes

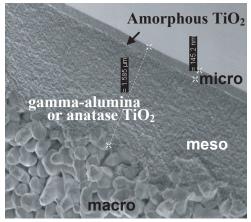


Figure 2. Microporous TiO₂ membrane

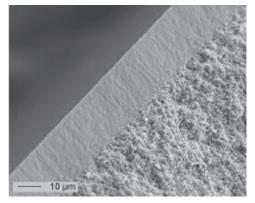


Figure 3. Dense ceramic membrane for oxygen separation.

basically consist of a dense ceramic structure that exhibits oxygen vacancies. Oxygen can selectively be built into these vacancies and in this way pure oxygen can be obtained at the permeate side of the membrane. These membranes typically work at high temperatures (>700 degrees Celcius) and various materials issues currently hinder the further development of these membranes into an economically viable option for oxygen production. It is the aim of the inorganic membrane group to study these materials to enhance oxygen permeability and to investigate and mitigate degradation/ageing phenomena in these membranes. These membranes can also be used for synthesis gas production by partial oxidation of methane. However, as the reaction conditions for partial oxidation of methane involve highly reductive atmospheres, one can understand that the materials issues under these severe reaction conditions become even worse than in the case of pure oxygen production. The understanding and mitigation of these issues will be part of the research program of Inorganic Membranes in the coming years.

For more information, please visit our website (http://mtg.tnw.utwente.nl) or contact Prof. Dr. Ir. Arian Nijmeijer (a.nijmeijer@utwente.nl).

Introducing...

Ceramic hollow fiber membranes for nanofiltration

Name Izabela Struzynska Origin Poland Contact



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Izabela Struzynska is a PhD student from Poland. She finished her Bachelor and Master studies at the Nicolaus Copernicus University in Torun, Poland. In February 2007, she started her PhD in the Inorganic Membrane Group. Her research is dedicated to the production of ceramic hollow fibre membranes for nanofiltration.

Porous metallic and ceramic microreactors

Name

Jigar Jani Origin India Contact +31 53 489



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Jigar is a 26-year-old PhD student from India. He finished his Bachelors in Chemical Engineering in Sardar Patel University, India in 2001 and worked for 1.5 years as a process engineer in a chemical consultancy in India. He received his MSc degree in Process System Engineering from the University of Dortmund, Germany in January, 2007. He started his PhD in Membrane Technology Group on June 1, 2007. His focus area of research is to explore new concepts for gas-liquid reactions inside microreactors using fluid dynamic simulations to aid in the design. The study of catalytic systems that are of interest for the porous microreactors will also be analyzed.

Microporous hybrid silica membranes with enhanced hydrothermal property in gas separation

Name Hong Qi Origin China Contact www.membrane.nl +31 53 489 4581 h.gi@utwente.nl



Hong joined the membrane technology group as a visiting scholar on March 3, 2007. He was born in Xinjiang, China on October 24, 1974. He studied at Nanjing University of Technology, where he obtained his BSc degree and completed his PhD in 2001. The focus of his Ph.D work was on preparation and characterization of macroporous ceramic support for microfiltration. He was working in the Membrane Science & Technology Research Center, Nanjing University of Technology before he arrived at UT. The topic of his one-year project at UT is "Preparation of microporous hybrid silica membranes with enhanced hydrothermal property in gas separation".

Behavior of gas bubbles in spacer filled flat channels

Name Paul Willems Origin The Netherlands Contact www.membrane.nl +31 53 489 3674 p.willems@utwente.nl

Paul is a 28-year old postdoc from The Netherlands. After completing his PhD on Gas Assisted Mechanical Expression of Oilseeds in the Separation Technology group at the University of Twente, he started his postdoc on June 15, 2007. He will be studying the behavior of gas bubbles in spacer filled flat channels.

Porous metallic and ceramic microreactors

Name David Salamon Origin Chech Republic Contact www.membrane.nl +31 53 489 3674 d.salamon@utwente.nl



David is a 30-year-old post-doc coming from the Czech Republic. He received his PhD in inorganic technology and materials after his study at the Institute of Inorganic Chemistry of the Slovak Academy of Sciences, Slovakia. His PhD project was dedicated to the preparation of alpha-sialon ceramic with defined microstructure. After that he went to work with Prof. Shen at the Stockholm University on ceramic-based nanomaterials. Aim of the project was to use spark plasma sintering method for the preparation of new materials. He started his post-doc project at the Membrane Technology Group in March, 2007. The project focuses on the preparation of shaped inorganic membranes suitable for microreactor application.

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.

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> > **Layout** Zeynep Çulfaz

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Introducing...

Membranes for electrodialysis

Name

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Contact



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Nilesh is 27 years old. He obtained his Bachelors of Engineering (B.E.) in Chemical Engineering from the Dr. Babasaheb Ambedkar Marathwada University (India). Last year he obtained his Master of Science (M.Sc.) degree from the Fachhochschule Muenster (Germany). On March 15, 2007 he joined the European Membrane Institute Twente as a researcher to work on membranes for electrodialysis.

Development of new redox flow fuel cells

Name Seyed Schwan Hosseiny Origin Germany Contact www.membrane.nl +31 53 489 2869 s.s.hosseiny@utwente.nl



Schwan is a 27-year-old PhD student. He finished his Master studies at the University of Applied Sciences in Muenster (Germany). He started his PhD in the Membrane Technology Group on April 1, 2007 and he will work on the development of a new redox flow battery which can replace the expensive vanadium-vanadium redox battery.

Picture of the Month Competition The picture of the month is chosen from all the pictures that were taken in the MTG group during the last month(s). The winner receives free drinks for one night and gets to pick the winner from next month's contributions. All the winners can be found on the website

http://mtg.tnw.utwente.nl

Separation of oil from strongly saline emulsions using membrane technology

Name Mehrdad Hesampour Origin Iran Contact www.membrane.nl

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Mehrdad is a 30-year-old Ph.D student. He studied Chemical Engineering and got his Bachelor degree from the Ferdowsi University and his MSc degree from the Sharif University of Technology, Iran. He joined the membrane group in Lappeenranta (Finland) at 2005 and started his thesis last year. He joined the membrane technology group of the University of Twente as an exchange student for a period of six months and will be working on the separation of oil from strongly saline emulsions.

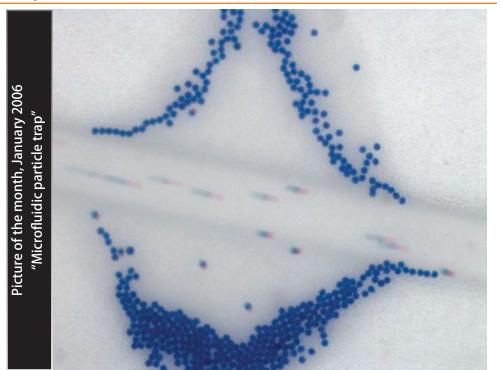


Porous metallic and ceramic microreactors

Name Halil Can Aran Origin Turkey Contact www.membrane.nl +31 53 489 2957 h.c.aran@utwente.nl



Can is a 25-year-old PhD Student from Turkey. He finished his Bachelor studies at the Istanbul Technical University and obtained his MSc degree in Chemical Engineering at RWTH Aachen University in Germany. He finished his master thesis at Degussa AG in Germany and joined the Membrane Technology Group in May 2007. The aim of his research is to explore new concepts for multiphase reactions inside microreactors and economically fabricate new metallic and ceramic microreactors.



The image shows a close-up of a polymeric film with a microfluidic channel network, prepared by phase separation micromolding. A silicon mold has been used in a second step to emboss shallow diamond structures inside this film, partly overlapping with the channels. When fluid is introduced into the channels, the diamond structures are filled due to capillary forces. Since the connection between neigbouring diamonds is very small, particles can be trapped inside, as is demonstrated for 6 micron latex particles. This principle may be used to e.g. capture cells from blood. Picture by Jorrit de Jong

Papers, patents and graduations

Membranes and microfluidics: a review. Jong, J. de, Lammertink, R.G.H. & Wessling, M., Lab Chip 6, 2006, 1125-1139.

Fullerene-Modified Poly(2,6-dimethyl-1,4-phenylene oxide) Gas Separation Membranes: Why Binding Is Better than Dispersing. Sterescu, D.M., Stamatialis, D.F., Mendes, E., Wübbenhorst, M.& Wessling, M., Macromolecules 39, 2006, 9234-9242.

Membraantechnologie 11 over de voortgang van het membraanonderzoek in Nederland en België. Kemperman, A.J.B., Posterdag NMG 2005 (uitgegeven: maart 2006), Uitgave van het Nederlands Membranen Genootschap (NMG).

Micro Reactor Technology. Lammertink, R.G.H., Young Chemist Workshop 16-18 March 2006 University of Twente, Enschede, Netherlands

Salinity-gradient power: Evaluation of pressure-retarded osmosis and reverse electrodialysis. Post, J.W., Veerman, J., Hamelers, H.V.M., Euverink, G.J.W., Metz, S.J., Nymeijer, K. Buisman, C.J.N., J. Membrane Sci. 288 (2007) 218-230.

Tailoring surface properties for controlling droplet information at microsieve membranes. Geerken, M.J., Lammertink, R.G.H. & Wessling, M., Colloids and Surfaces A: Physicochem. Eng. Aspects 292, 2007, 224-235.

One-step fabrication of porous micropatterned scaffolds to control cell behavior. Papenburg, B.J., Vogelaar, L., Bolhuis-Versteeg, L.A.M., Lammertink, R.G.H., Stamatialis, D. & Wessling, M., Biomaterials 28, 2007, 1998-2009.

Nanofluidics - Silicon for the perfect membrane. Berg, A. van den & Wessling, M., Nature 445, 2007, 726-726.

Porous Microfluidics Devices – Fabrication and Applications. Jong, J. de, Geerken, M.J., Lammertink, R.G.H. & Wessling, M., Chemical Engineering and Technology 30 No. 3, 2007, 309-315.

Morphology and Microtopology of Cation-Exchange Polymers and the Origin of the Overlimiting Current. Balster, J., Yildirim, M.H., Stamatialis, D.F., Ibanez, R., Lammertink, R.G.H., Jordan, V. & Wessling, M., Journal Phys. Chem. B. 111, 2007, 2152-2165.

Dana Sterescu (September 24, 2007) Synthesis and preparation of a new generation gas separation membranes

Ellen van Voorthuizen (December 6, 2007) Membrane processes for nutrient recovery from black water

Ph.D.

Publications

Arian Nijmeijer (December 13, 2007) Part time professor Inorganic Membranes

The Membrane Technology Group

Multidisciplinary approach in membrane science and technology

The Membrane Technology Group focuses on the multi-disciplinary topic of membrane science and technology. We consider our expertise as a multidisciplinary knowledge chain ranging from

molecule to process. The knowledge chain comprises the following elements:

- Colloid and interface science
- Macroscopic mass transport characterization and model-

ing

- Material Science
- Material Processing
- Module and system design
- Process technology

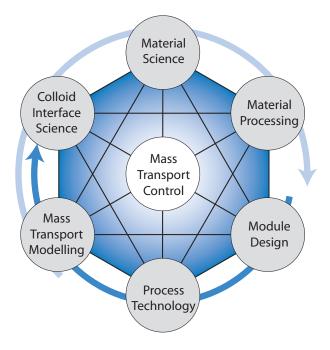
The research team is assembled such that permanent staff members cover one or more of the disciplines involved.

The majority of the research deals with separation of molecular mixtures and selective mass transport. Our research program distinguishes four application clusters:

- Sustainable Membrane Processes
- Water
- Biomedical and Life Science
- Micro Systems Technology

The research clusters are embedded in three research institutes, IMPACT (process technology), BMT (biomedical) and MESA+ (nanotechnology).

Knowledge transfer and utilization



Total mass transport control by a multidisciplinary approach. The membrane & Interface science group together with the Membrane Process Technology and the Inorganic Membranes groups cover the full spectrum of mass transfer phenomena in membrane separation. From the very small scale to module and process design the combined knowledge of the groups can handle any membrane related problem.

Over the past years, our group has focused especially on knowledge utilization and transfer. We experienced that the time scales for research progress are extremely different in industry and academia. Even within industry a significant difference exists in time-scales between small and medium enterprises and multi-national cooperations. We have adjusted our organization structure such that we can distinguish between long-term scientific activities and short-term technology transfer. We have established the European Membrane Institute (EMI) Twente for this purpose.

The EMI performs research and development work on new membrane products and processes. The work often focuses on the production of a tangible deliverable.

