2016 summer
Membrane News Twente
News magazine of the Membrane Science and Technology Cluster
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Membrane Science & Technology

Welcome

A warm welcome to the new Membrane Science and Technology Cluster! Where in the past Membrane Science and Technology was a research group, solely dedicated to research on polymeric membranes, recent changes have led to a new and much stronger and broader positioning of Membrane Science and Technology (MST) within the University of Twente. Together with the Inorganic Membrane group (Prof. Arian Nijmeijer) and the Soft Matter, Fluidics and Interfaces group (Prof. Rob Lammertink) a large cluster was formed dedicated to research on membranes. The MST cluster allows for easy cooperation and sharing of knowledge and infrastructure.

Within this new cluster we now have 10 staff members, 9 technicians and over 30 PhD students working on membrane materials and membrane processes using inorganic, organic and hybrid membranes. Moreover we study membrane applications ranging from drinking water production, waste water treatment, solvent resistant nanofiltration, gas separation and electrochemical membrane applications. In this newsletter we detail the new structure of MST, presenting our full range of expertise.

But more changes are coming. We are very happy to announce that on 1 September Tymen Visser will start as the new director of the European Membrane Institute (EMI). Under his guidance, the EMI will keep offering high quality and confidential contract based research, but in the new structure the EMI will be able to offer an even broader array of membrane and material based expertise.

We also welcome a new part-time professor within MST: Prof. Dr. W. A. Meulenberg, head of Gas Separation Membranes at the IEK-1 of Forschungszentrum Jülich, was recently appointed as professor in the field of ion conducting membranes within the Membrane Science and Technology Cluster.

In this newsletter you will further find an overview of promotion ceremonies and a more in depth scientific insight into the expertise of Prof. Arian Nijmeijer and Prof. Louis Winnubst of Inorganic Membranes.

We invite you to read this newsletter and hope you will enjoy it. In case you have additional questions or you would like to receive further information or publications, please feel free to contact us at MSTtnw@utwente.nl or +31 53 489 2950.

On behalf of all members of Membrane Science and Technology at the University of Twente, we would like to wish you pleasant holidays!

The MST cluster during the yearly cycling tour.

Follow MST on Facebook!

Interested in the latest news of our Membrane Science and Technology Cluster? Follow us and like us on Facebook (www.facebook.com/membranetechnology). There you will find all our most recent publications, PhD defenses, and MSC colloquia, as well as the more social aspects of our cluster. Enjoy!

New structure of Membrane Science and Technology

Membranes in Twente just got bigger. Within a new organizational structure, principal investigators (PIs) that are active within membrane research are joining forces. The cluster on Membrane Science and Technology provides the basis for facility sharing, expertise exchange, and collaboration. As such, we aim to continue the long history of membrane research at the University of Twente.

The cluster comprises over 50 researchers, staff, and technicians, all working in research related to polymeric, inorganic, and hybrid based membranes for many key applications and the exploring of new ones. Joint lectures have recently been initiated, where colleagues share and discuss their findings. With this clustering, the width of expertise has significantly broadened, and research facilities are shared.

Currently, within the cluster we have the following PIs and their corresponding expertise:

Prof.dr.ir. Nieck Benes. Films in Fluids: Thin film synthesis and characterization, and inorganic hollow fibers.

Prof.dr. Henny Bouwmeester. Electrochemistry Research Group: Electrochemical research with emphasis on ionic-electronic transport in condensed phases.

Prof.dr.ir. Rob Lammertink. Soft matter, Fluidics and Interfaces: Transport phenomena near interfaces.

Prof.dr.ir. Arian Nijmeijer. Inorganic Membranes: Ceramic membranes for gas separation, organic solvent nanofiltration and oil & gas produced water treatment.

Prof.dr.ir. Erik Roesink. Advanced Membranes for Aqueous Applications: Polymeric membrane development for water treatment.

Dr.ir. Wiebe de Vos. Membrane Surface Science: Surface modification and characterization of polymeric membranes.

Prof.dr. Louis Winnubst. Porous Ceramic Membranes: Chemically modified ceramic membranes and its gas/solvent transport behaviour.

The European Membrane Institute (EMI) also gains from this clustering, by expansion of materials and process knowledge. The new EMI director, dr.ir. Tymen Visser, will build on his extensive industrial experience, including membrane gas separation. Valorization activities and contract research within the field of inorganic membranes will further complement the portfolio of the EMI that was until now based on polymeric membranes. The new EMI establishes direct connections to industry, which is increasingly important within the research landscape of membrane science and technology.

New structure of Membrane Science and Technology.

Membrane research at Inorganic Membranes

The main research direction within this theme is on the development of porous ceramic membranes and the study of transport behaviour for application in molecular separations under demanding conditions. Focus is on:

1. Sol-gel derived ceramic membranes for gas separation
2. Polymer-functionalized ceramic membranes for solvent nanofiltration
3. New avenues for the fabrication of zeolite membranes for gas separation

A summary of some recent developments in these projects will be given.

1. Sol-gel derived hybrid silica membranes for gas separation

Within the Inorganic Membranes (IM) group there is a long-term experience in fabrication of ceramic membranes by means of sol-gel methods. Generally, asymmetric membranes are used, consisting of a macoporous α-alumina support (pore size 80 nm) topped with a 3 μm thick mesoporous γ-alumina intermediate layer (pore size 5 nm) on which a microporous (pore size << 1nm) separation layer is applied. A typical SEM picture of such a membrane is given in Fig. 1.

Amorphous silica is an attractive material for the application as a microporous inorganic membrane to be used for separation of gases by means of molecular sieving. These membrane separation layers are made by acid-catalyzed sol-gel processing using e.g. tetraethylorthosilicate (TEOS) as precursor. However, these pure silica structures show a very low stability in water vapour, especially at high temperatures, which limits its application in many industrial processes that involve hydrothermal conditions.

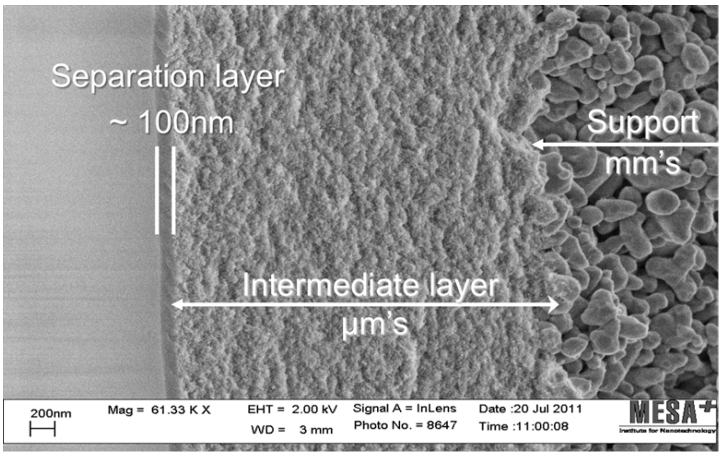

Fig. 1: SEM picture of a typical microstructure of a multi-layer ceramic membrane.

An effective way to obtain hydrothermal stable silica-derived membranes is by using alkoxide precursors that contain a hydrolytically stable organic bridging group between two silicon atoms, such as 1,2-bis(triethoxysilyl)ethane (BTESE) (see Fig. 2). These BTESE-derived, or 'hybrid silica', membranes show good performances in pervaporation for dewatering of several alcohols and remain stable in an aqueous environment for several years under industrially relevant conditions. For the use of these hybrid silica membranes in gas separation, however, up to now these membranes lack the separation performance required to separate e.g. hydrogen from carbon dioxide.

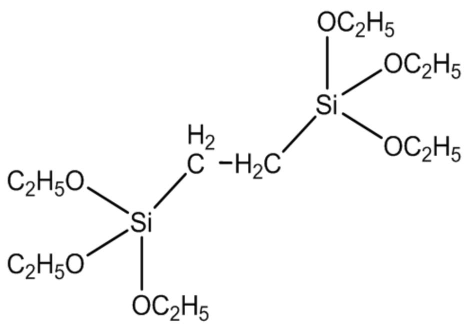

Fig. 2: 1,2-bis(triethoxysilyl)ethane (BTESE) used as a precursor for sol-gel synthesis of the hybrid silica membranes.

At IM the process parameters of the hybrid silica sol synthesis, like precursor concentration, acid concentration and hydrolysis ratio, were tuned to obtain a mono-modal particle size distribution. The resulting membrane, obtained by a single sol-coating/calcining step, was found defect-free (impermeable for big gases like SF_6), however the selectivity for gas separation of smaller gases was found not to be sufficient [1].

In recent work the sol-gel process is studied in more detail [2]. Here, not only the acid concentration during sol synthesis is varied, but also the influence of the humidity of the support during coating/dipping of the sol is studied. Using a 'dry' or a 'wet' support strongly influences the gelation behaviour and the resulting membrane pore morphology. A more dense pore structure is obtained by limiting the acid content in the dipped sol and using a dry support. In this way high gas (perm) selectivities are achieved, resulting in the highest H_2/N_2 and CO_2/CH_4 permselectivities found to date for pure hybrid silica membranes (Fig. 3).

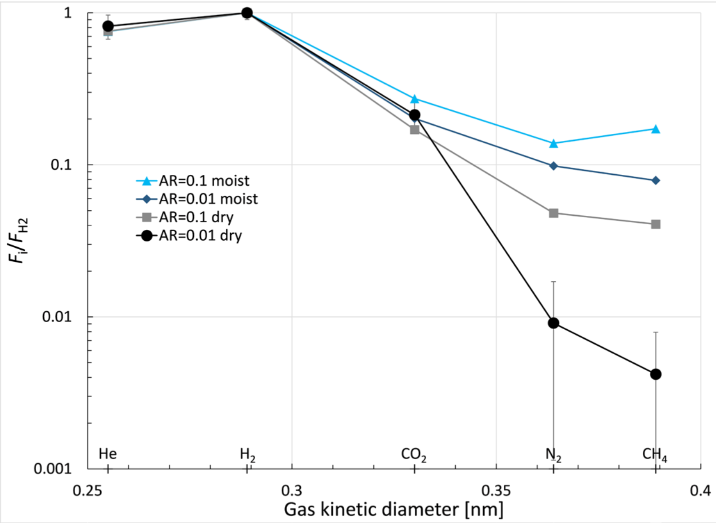

Fig. 3: Single-gas permeances, normalized to the permeation of H_2 (F_i/F_{H2}) of BTESE-based membranes. Membranes are fabricated from sols with a high (AR = 0.1) or low Acid Ratio (AR = 0.01) (AR = [H+]/[Si]). Sols were coated onto support systems pretreated at relative humidity (RH) < 0.5 % ('dry') or RH = 90 % ('moist') [2].

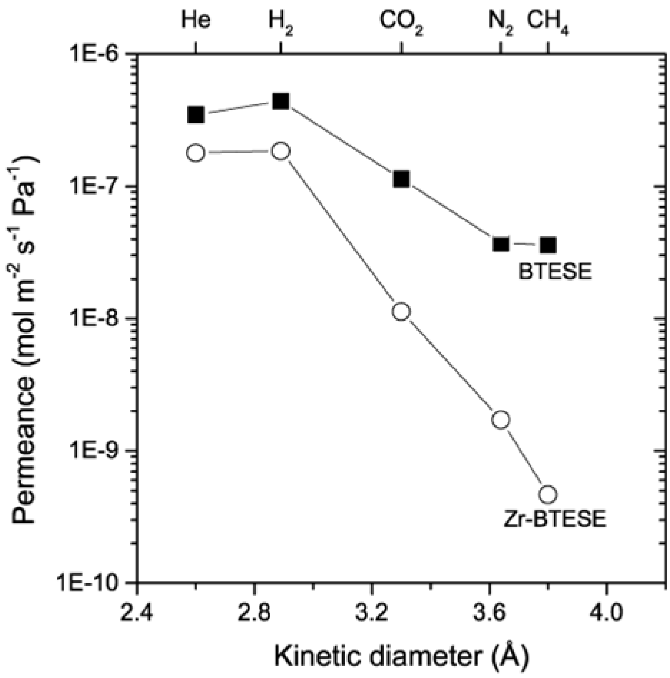

Fig. 4: Gas permeances versus gas kinetic diameter for pure BTESE hybrid silica membranes and Zr-doped BTESE membranes [3].

In another study a simple sol-gel method is developed to incorporate zirconia in the hybrid matrix (Zr-BTESE) [3]. The Zr-doped BTESE membranes show a slight decrease in hydrogen permeance as compared to an undoped BTESE membrane, but a large increase in H_2/CO_2 (from 4 to 16) and H_2/N_2 (from 12 to 100) permselectivity is achieved by using these metal-doped hybrid silica membranes (Fig. 4).

2. Polymeric-functionalized ceramic membranes for solvent nanofiltration.

The separation of organic compounds on a molecular level is one of the growing areas in membrane technology. This approach makes numerous industrial processes more environmental friendly. State-of-the art polymeric or ceramic membranes do not always meet stability and/or selectivity demands at process-relevant conditions like separation/purification of harsh organic solvents and operations at high temperatures or pressures.

In order to fulfil these operational requirements a concept is developed, based on mesoporous (pore size 5 - 10 nm) ceramic membranes, as a non-swelling and non-compactable, rigid material, acting as a support, on which polymer materials are immobilized; i.e. covalently or electrostatically bonded. In this way the pore size and surface chemistry of membranes can be adjusted for any specific separation application by varying the composition/structure of the polymer.

A first series organically-modified ceramic membranes concerns the reaction of polydimethylsiloxane (PDMS) with γ-alumina membrane layers having a pore size of 5 nm. For covalent bonding of PDMS polymers to the surface –OH groups of the ceramic surface, a linker/coupling agent is required. Silanes can be used as coupling agents acting as a bridge between the inorganic surface and the polymer to be grafted. An example of such a grafting reaction is schematically given in Fig. 5 [4]. Several PDMS-modified hydrophobic nanofiltration membranes are synthesized and fully characterized [5, 6]. Analysis techniques like FTIR and TGA confirmed that both linker and polymer were successfully grafted and that the ceramic pore walls were modified, while rendering a hydrophobic membrane (Fig. 6). Solvent permeation showed that these hydrophobic nanofiltration membranes could reproducible be fabricated, while having a stable and high solvent flux.

The most drastic way to show chemical stability was the exposure of PDMS-grafted membranes for more than 100 days in several solvents (like hexane, toluene, isopropanol) at room temperature and in isopropanol at 75 °C or in toluene at 80 °C (Fig. 7). After these harsh treatments the membranes remained hydrophobic and the organic solvent permeance behaviour of these membrane did not change, while the molecular weight cut-off (MWCO) remained constant as well (~ 500 Da) [6].

The solvent permeation of these PDMS-grafted ceramic

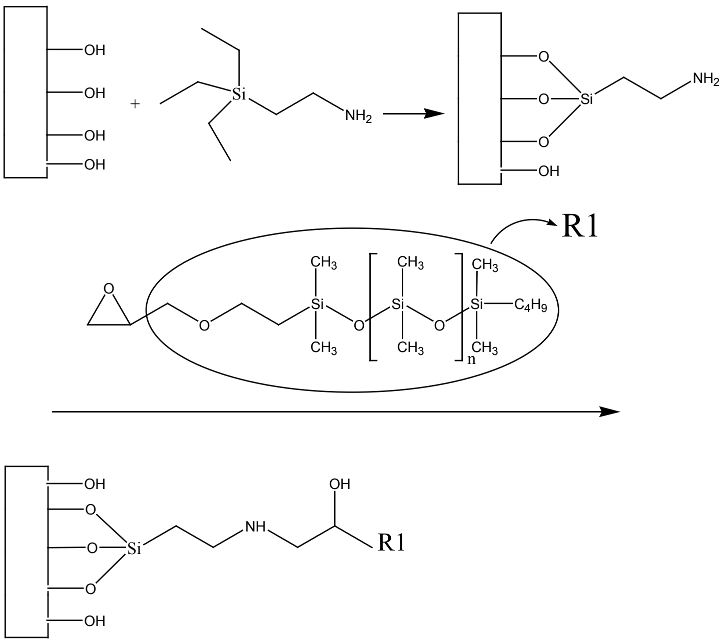

Fig. 5: Reaction of 3 aminopropyltriethoxysilane (APTES) as 'linker' with a γ-alumina membrane surface and subsequent reaction of a mono(2,3-epoxy) polyether-terminated polydimethylsiloxane (PDMS) [4].

membranes was found to be mainly governed by Darcy's and Hagen–Poiseuille pore-flow model, but with taking into account swelling of the grafted moiety. If compared with full polymeric membranes, swelling is low and can better be controlled. It is suggested that the permeable volume of the membrane reduces by swelling of the grafted organic moiety by the solvent used. This model provides a way to predict the performance of grafted porous ceramic membranes for solvent filtration [7].

In the fall of 2015 a new project in this field has started: 'Modular Functionalized Ceramic Nanofiltration Membranes'. This is a joint project with the Organic Materials and Interfaces group of Ernst Sudhölter at TU Delft. This work is part of the research programme performed within the framework of the Institute for Sustainable Process Technology (ISPT) and is jointly financed by the Netherlands Organization for Scientific Research (NWO) and ISPT, within the call 'Process Technology Fundamentals: New principles for sustainable separations'. In this project versatile synthesis methods will be developed for the fabrication of a new family of organic solvent-resistant nanofiltration membranes. Besides, the transport behaviour of a broad range of organic solvents will be studied as well in order to gain a more fundamental understanding of the interactions between membrane and solvents/solutes, used for nanofiltration. The research on transport and modelling will be the main part of the work of our new IM PhD student Renaud Merlet.

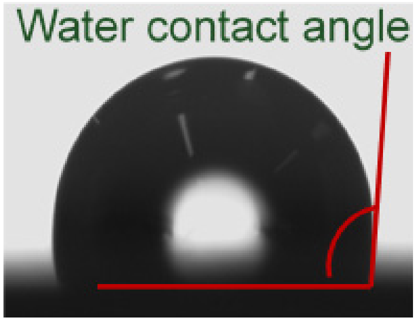

Fig. 6: Water droplet on a hydrophobic, PDMS-grafted, ceramic membrane.

3. New avenues for the fabrication of zeolite membranes for gas separation

This project, sponsored by STW, started in October 2015 (http://www.stw.nl/nl/content/new-avenues-fabrication-zeolite-membranes). It is a joint project with the Catalysis Engineering group of Freek Kapteijn and Jorge Gascon at TU Delft. In both groups a PhD student is working on this subject. Here, reproducible and easy to scale-up approaches will be developed for the production of defect-free and low-cost zeolite membranes to be used for gas separation. The solution is sought by integrating low cost, highly-engineered supports in the synthesis of zeolitic membranes and by acquiring a more fundamental insight in the several steps during the membrane fabrication process. Pelin Karakiliç is the PhD student working in Twente on this project.

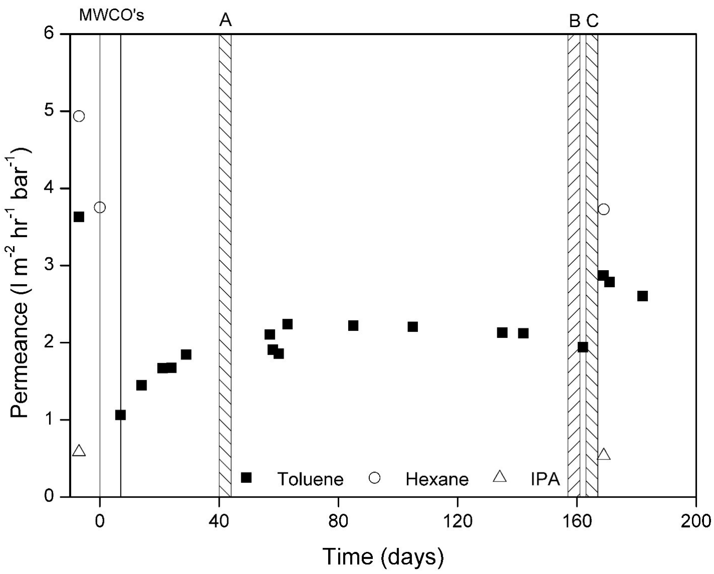

Fig. 7. Toluene permeability as function of time of a PDMS-grafted ceramic membrane. In period A the solvent was changed to hexane and after 4 days back to toluene. In period B the membrane was treated in toluene at 80 °C for 4 days and in period C in isopropylalcohol (IPA) at 75 °C for 5 days. The permeability data at time < 0 days represent initial experiments (MWCO's = molecular weight cut off measurements were performed in these periods) [5].

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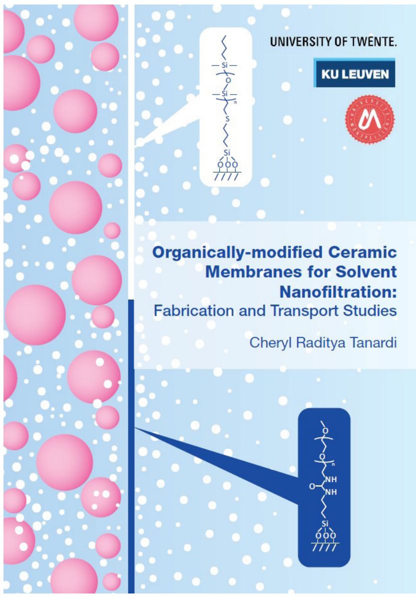
1+2+3=6 Promotions

In the past months, 6 PhD students of the Membrane Science and Technology cluster defended their thesis. Even more special was that some of our students decided to have their defenses on the same day. Here we give a small overview of these graduations.

1. On Thursday November 12, 2015 Cheryl Tanardi defended her PhD thesis entitled "Organically-modified Ceramic Membranes for Solvent Nanofiltration: Fabrication and Transport Studies". Cheryl was supervised by Prof. Dr. Louis Winnubst and Prof. Dr. Ir. Arian Nijmeijer.

Solvent Resistant Nanofiltration (SRNF) is a potential technology to recover organic solvents in chemical processes. For this application, a chemically stable membrane that can endure continuous exposure towards organic solvents is required. The thesis of Cheryl Tanardi deals with the preparation of chemically stable nanofiltration membranes through grafting of porous ceramic substrates with organic molecules and the study of their solvent and solute transport properties. This research was in the framework of Erasmus Mundus Doctorate in Membrane Engineering (EUDIME) together with Prof. Dr. Ivo F.J. Vankelecom (Leuven) and Prof. Dr. André Ayral (IEM Montpellier).

The full thesis of Dr. Cheryl Tanardi can be found under:
http://doc.utwente.nl/97941/



The thesis of Dr. Cheryl Tanardi.

2. On the 5th of February, 2016 Erik Vriezekolk and Krzysztof Trzaskuś defended their PhD theses. These PhD candidates both performed their work in the Clean Water theme of the NanoNextNL program. Erik and Krzysztof started on the same day, finished on the same day and even acted as each other's paranymph during their respective ceremonies.

Erik Vriezekolk defended his thesis "All the same: Isoporous Membranes for Water Purification" and was supervised by Dr. Ir. Wiebe M. de Vos and Prof. Dr. Ir. Kitty Nijmeijer. In his work Dr. Vriezekolk studied three different approaches to create isoporous membranes, with a special emphasis on the use of diblock-copolymer self-assembly to create ordered and uniform pores in the range of 10-50 nm. Finally, Erik Vriezekolk also established the tuning parameters to control the obtained pore sizes, for example by addition of a small amount of homopolymer.

The full thesis of Dr. ir. Erik Vriezekolk can be found under:
http://doc.utwente.nl/99173/

Later that day, Krzysztof Trzaskuś defended his thesis entitled "Filtration of Engineered Nanoparticles Using Porous Membranes". This work was supervised by Dr. Ir. Antoine Kemperman and Prof. Dr. Ir. Kitty Nijmeijer and focused one of the new foulants, engineered nanoparticles. Such nanoparticles are increasingly used for a wide variety of applications, but tend to end up in the surface water. Krzysztof showed that filtration, even with pores much larger than the size of the nanoparticles, is still a suitable way to remove those nanoparticles.
The full thesis of Dr. Krzysztof Trzaskuś can be found under:
http://doc.utwente.nl/99174/

Dr. Krzysztof Trzaskuś (left) and Dr. Erik Vriezekolk on the day of their defense.

3. On the 11th of March 2016, a total of three PhD students defended on the same day: Damon Rafieian, Yali Zhang and Sinem Tas (see photo).
Damon Rafieian defended his thesis on "Catalytic Water Cleaning: Materials and Transport Aspects" and was supervised by Prof. Dr. Ir. Rob Lammertink. His work focused on the design and use of a photocatalytic micro reactor to remove small organic molecules (micro-pollutants) by oxidizing them. The enhanced mass and photon transfer in micro-reactors leads to very fast photocatalytic reactions and thus degradation of small organic pollutants.
The full thesis of Dr. Damon Rafieian can be downloaded via:
http://doc.utwente.nl/99733/

Yali Zhang defended her thesis "Interfacial Transport and Reactions in a Multiphase Microfluidic System", research that was supervised by Prof. Rob Lammertink. In her microfluidic system, Yali was able to very accurately locate and control fluid interfaces to study aspects such as fluid dynamics, mass transport and reaction kinetics. This included a study on a microfluidic pervaporation system and a study on interfacial polymerization performed within a highly controlled two phase system inside a microfluidic device.
The full thesis of Dr. Yali Zhang can be found under:
http://doc.utwente.nl/99735/

Dr. Sinem Tas, Dr. Yali Zhang and Dr. Damon Rafieian (from left to right) with their thesis.

And finally, Sinem Tas defended her thesis on "Bio-inspired ion selective crown-ether polymer membranes" and was supervised by Prof. Dr. Ir. Kitty Nijmeijer. The work of Sinem demonstrated how crown ethers could be incorporated in PAEK and SPAEK polymers that were in turn incorporated in polymeric membranes. Such membranes then showed ion-selective properties due to the very selective interaction between ions and crown ethers.
The full thesis of Dr. Sinem Tas can be found under:
http://doc.utwente.nl/99734/

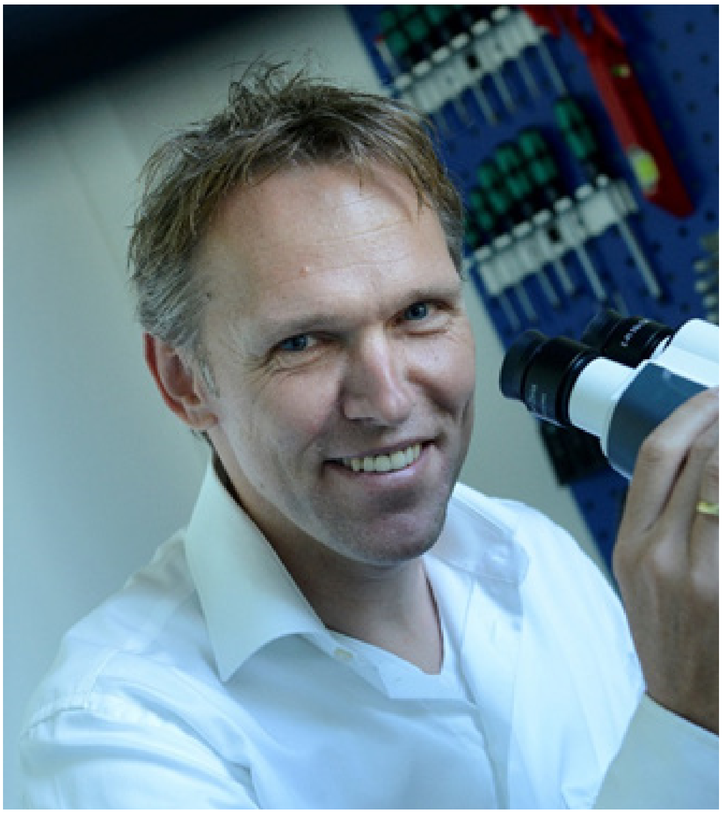
(VENI), VIDI, VICI!

The VENI, VIDI, VICI grant scheme of the Dutch Science Foundation is generally recognized as the most prestigious grant scheme in the Netherlands. Each of the three grants caters towards a specific position in an academic's career, with the VENI intended for starting academics (3 years after PhD), the VIDI for starting group leaders (8 years after PhD) and the VICI for established group leaders (15 years after PhD). The grant scheme is very competitive, with a successful application rate of just 15%, and is intended for the pursuit of groundbreaking new ideas.

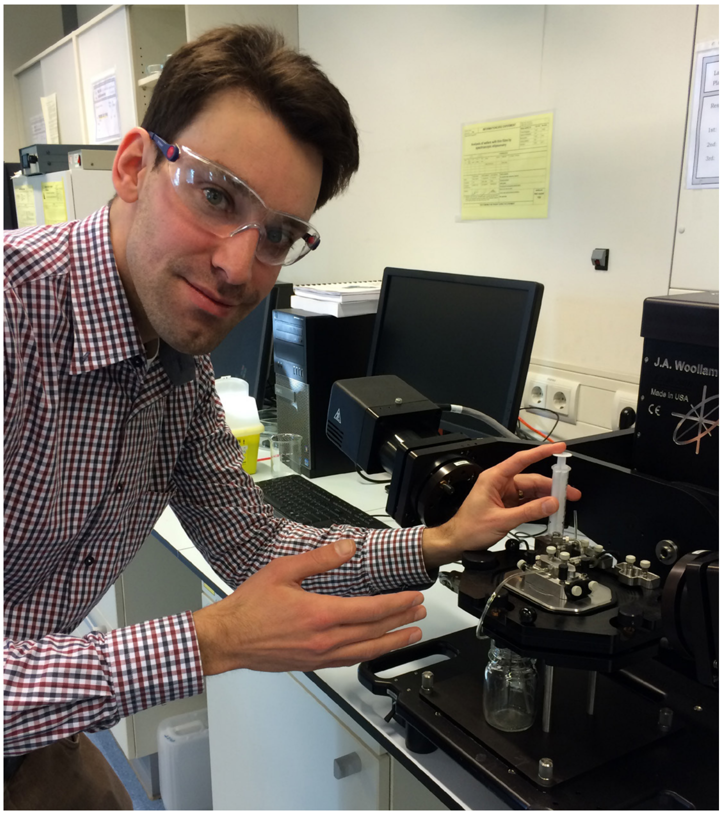
Within Membrane Science and Technology, we are very happy to have received two of these prestigious grants in the past months.

Prof. Rob Lammertink, who already received a VIDI grant in 2006, was in 2016 awarded a VICI grant with a value of 1.5M€ for his project "Mixing at the boundary". This research will focus on the phenomena that occur in liquids on walls. Due to the specific properties of the wall, a liquid can be set in motion. This motion can subsequently be used to increase the transport of substances, which has enormous consequences for membrane based separation processes and catalytic processes.

Dr. Wiebe M. de Vos, a recipient of the VENI award in 2012, was awarded a VIDI grant in 2016 for his project "Advanced and sustainable membranes, completely produced in water". Dr. de Vos will use the grant of 800k€ to develop a much more sustainable method to produce polymeric membranes, a method that does not require the use of toxic and environmentally unfriendly solvents such as NMP. A natural benefit of the proposed method is that it allows a very direct route towards advanced membranes with for example: anti-fouling, responsive, catalytic or ion-selective properties.



Prof. Rob Lammertink



Dr. Wiebe M. de Vos

Follow MST on Twitter!

The Membrane Science and Technology Cluster has its own Twitter account!
Follow @MST_UTwente for the latest news of the MST cluster in a nutshell!

New staff members

New director of European Membrane Institute (EMI)

Dr. Tymen Visser

As of 1st of September 2016 Tymen Visser will be the new Director EMI Twente. Tymen earned his doctoral degree at the University of Twente in 2006 with his thesis on mixed gas plasticization phenomena in asymmetric glassy polymer membranes after studying Chemical Engineering at the same University. After working one and a half year as post-doctoral researcher for the EMI Twente he joined the start-up company Vaperma in Quebec (Canada) in January 2008, where he started as a senior researcher and became head R&D soon after. In this role he was responsible for the R&D team and was leading all development projects concerning hollow fiber membranes based on advanced membrane materials for gas and vapor separation. In 2011 he moved back to Europe and joined Evonik Fibres GmbH in Austria, a subsidiary of Evonik Industries AG, where he was responsible for the development, scale up and implementation of new polyimide hollow fiber based membrane products (SEPURAN®) for the gas separation market, and made crucial contributions to the technological establishment of the membrane business. Most recently he moved to the head office located in Marl, Germany to take up a role as business development manager within the SEPURAN® team. We are very happy Tymen will join our team and are sure he will be successful in expanding the activities of the EMI Twente!

Part-time Professor Ion Conducting Membranes

Prof. Dr. W. A. Meulenberg

Prof. Dr. W. A. Meulenberg, head of Gas Separation Membranes in the Institute of Energy and Climate Research – Materials Synthesis and Processing (IEK-1) of Forschungszentrum Jülich, was appointed professor in the field of ion conducting membranes within the Membrane Science and Technology Cluster, on 1 April 2016. The appointment of Prof. Dr. Meulenberg will intensify the long-standing collaboration and strategic partnership between Jülich and Twente in this area, particularly with Prof. Dr. H.J.M. Bouwmeester, Prof. Dr. A.J.A. Winnubst, and Prof. Dr. Ir. A. Nijmeijer. In addition, Prof. Meulenberg will also contribute to the educational programme of the university in the field of chemical engineering. Ceramic ion conductors are used for efficient gas separation, for example for the gas supply in membrane reactors or for the production of fuels and chemicals, as well as in solid oxide fuel cells.

MNT- Information

Membrane News Twente is published two times per year and aims to inform the membrane community about the activities of the Membrane Science and Technology cluster of the University of Twente (membrane@utwente.nl www.utwente.nl/tnw/mtg).

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