

2014  
winter

# Membrane News Twente



Membrane Science & Technology

News magazine of the Membrane Science and Technology Group

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

## Welcome

This is already the 10th year that we make this newsletter to provide you with all developments on membranes in our group.

About nine years ago, our group in very close collaboration with Wetsus, started to work on Blue Energy, the generation of power from the mixing of river water and seawater using ion exchange membranes. Very recently, on November 26, his Majesty King Willem-Alexander of The Netherlands officially opened the first large scale Blue Energy installation worldwide on the Afsluitdijk in the Netherlands. An exciting achievement considering the few square centimeters of membrane area that we started with. You will find some impressions in this newsletter.

In this edition you will also find a summary of the work of two PhD researchers who will defend their thesis early 2015. Joris de Grooth addresses the topic of Layer-by-Layer deposition to tailor membrane properties towards the rejection of micro pollutants. The versatility of the LbL approach easy control of the layer properties and as such the membrane properties. Salman Shahid discusses the development of MOF-mixed matrix membranes for low and high pressure CO<sub>2</sub>/CH<sub>4</sub> separations. It especially investigates the effect of the MOF type on the performance of the membranes, and the effect of the presence of MOFs on the plasticization resistance of the membranes. Especially for the work on MOF-mixed matrix

membrane development, access to Scanning Electron Microscopy (SEM) is essential to visualize membrane structures. In this edition you will find an extensive description of the technical possibilities and features of our SEM equipment. Equipment of our group is available for academic research, but also for contract research projects through the European Membrane Institute.

As in every newsletter, you will also find an update of our membrane publications, new people, awards, etc. and we invited one of our former employees to reflect on the time in Twente. This time in the category "It all started in Twente", Jean-Marc Duval, who started his PhD in 1989, will share his memories with you.

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 the Membrane Science and Technology group of the University of Twente, I would like to wish you pleasant Christmas holidays and a prosperous and happy 2015!



## Follow MST on Facebook!



Interested in the latest news of our Membrane Science and Technology group? Follow us and like us on Facebook ([www.facebook.com/membranetechnology](http://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 group. Enjoy!

# Polymer-Metal Organic Framework (MOF) mixed matrix membranes for gas separation applications



Salman Shahid

Membrane technology is an attractive approach for gas separation applications and, more specifically, for CO<sub>2</sub> capture because of its advantages (low footprint, energy efficiency, cost effectiveness) over conventional separation processes such as pressure swing adsorption, cryogenic distillation or absorption [1]. However, performance of polymeric membranes is often limited by a trade-off between membrane permeability and selectivity, the so-called Robeson upper bound [2]. Additionally, in high pressure CO<sub>2</sub> capture applications, excessive swelling of the polymer membrane often leads to plasticization resulting in decreased separation performances.

Inorganic membrane materials on the other hand offer excellent separation performances combined with high chemical and thermal stability, but have high costs and lack easy processability [3]. Mixed matrix membranes (MMMs) offer the opportunity to combine the benefits of low cost and the easy processability of polymeric materials with the excellent transport performance of inorganic fillers. However, MMMs often do not possess their predicted separation performance behavior, as MMMs frequently suffer from insufficient adhesion between the polymer matrix and the filler particles leading to non-selective voids, resulting in high fluxes but low selectivities.

## Scope of the project

The main goal of this work was to develop high-performance MMMs based on metal organic frameworks (MOFs) for low and high pressure gas separation applications. Approaches to understand and overcome the rather complex behavior of plasticization in MOF-MMMs and the aspect of poor MOF-polymer interfacial compatibility were developed in this work.

## Performance and plasticization of MOF-MMMs

MOFs have been reported to enhance the permeability and selectivity of polymer based membranes at relatively low pressures. While the plasticization behavior of pure polymer membranes is well studied in literature [4], there are only very few studies on the plasticization behavior of MOF-MMMs. In this part of the research, different MOF

materials (Fe(BTC) (mesoporous), MIL-53(Al) (breathing MOF), ZIF-8 (flexible MOF) and Cu<sub>3</sub>(BTC)<sub>2</sub> (rigid)), were incorporated in a polymeric polyimide (PI) matrix and the performance of the resulting MMMs in terms of gas separation enhancement was evaluated [5, 6]. In addition, the CO<sub>2</sub> induced plasticization resistance of the MOF-MMMs was investigated.

Cross-sectional SEM images of the 30 wt.% MOF-MMMs are shown in Figure 1. A mixture of different casting solvents (dioxane/NMP - 20/80) and an improved priming protocol was developed for membrane preparation. This resulted in a good dispersion and embedding of the MOF particles in the PI matrix.

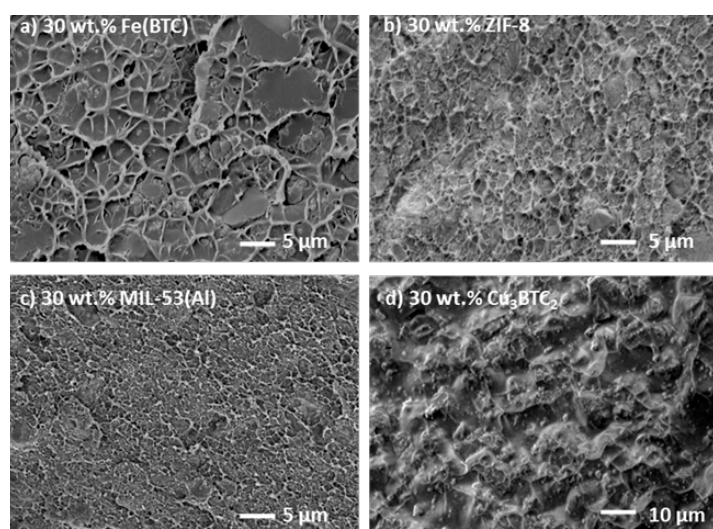


Figure 1: SEM images of polyimide MMMs with 30 wt.% (a) Fe(BTC), (b) ZIF-8, (c) MIL-53(Al) and (d) Cu<sub>3</sub>BTC<sub>2</sub>.

Fe(BTC), ZIF-8 and MIL-53 MMMs showed the crater like morphology typical for MOF-polymer MMMs and the eye of each crater is formed by a MOF particle. The Cu<sub>3</sub>BTC<sub>2</sub> MMMs show a different morphology attributed to the larger crystal size of Cu<sub>3</sub>BTC<sub>2</sub>. The large Cu<sub>3</sub>BTC<sub>2</sub> particles are completely wrapped by the polymer matrix and fracturing under liquid N<sub>2</sub> causes the polymer layer to break by brittle fracture without plastic deformation, giving a more smooth cross-section compared to the crater-like morphology obtained for the other (nano-sized) particles (Figure 1a-c). The increased density, glass transition temperature and improved degradation behavior of the

membranes also confirmed a good MOF-polymer interfacial contact. Among these MOF-MMMs, membranes based on ZIF-8 showed the highest permeability while  $\text{Cu}_3\text{BTC}_2$  based membranes showed the highest selectivity (Figure 2 and 3).

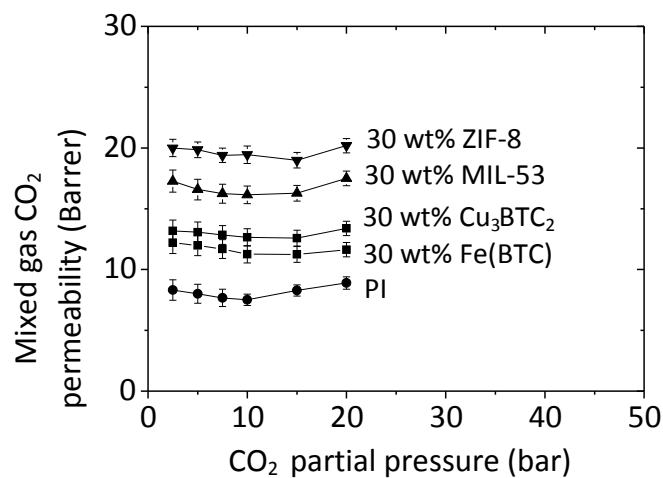


Figure 2: Mixed gas  $\text{CO}_2$  permeability of MMMs with different MOF loadings.

The respective increase in performance of the MMMs is very much dependent on the MOF crystal structure and its interactions with  $\text{CO}_2$ . Although moderate improvements were shown for the MOF-MMMs over native PI membranes at low pressures, the benefits of MOF incorporation (i.e. high  $\text{CO}_2$  permeability and  $\text{CO}_2/\text{CH}_4$  selectivity) became more significant at higher pressures. All MOF-MMMs showed a comparable delay in plasticization pressure irrespective of the MOF structure. As a consequence, membrane selectivity of the MMMs remained sufficiently high, also at higher pressures. This in contrast to the selectivity of native PI that significantly decreased at higher pressures (Figure 2).

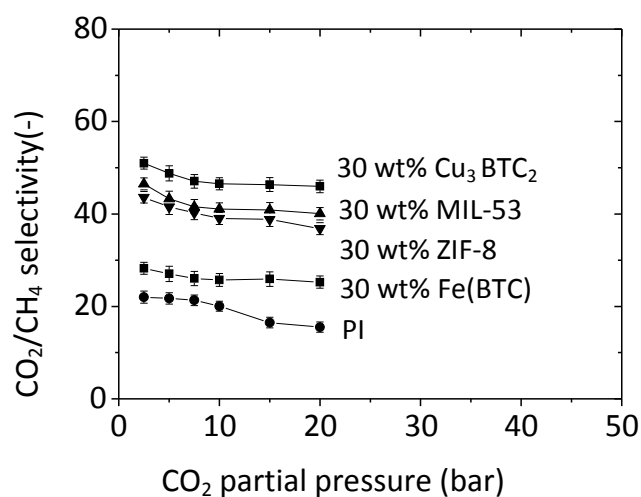


Figure 3: Mixed gas selectivity of MMMs with different MOF loadings.

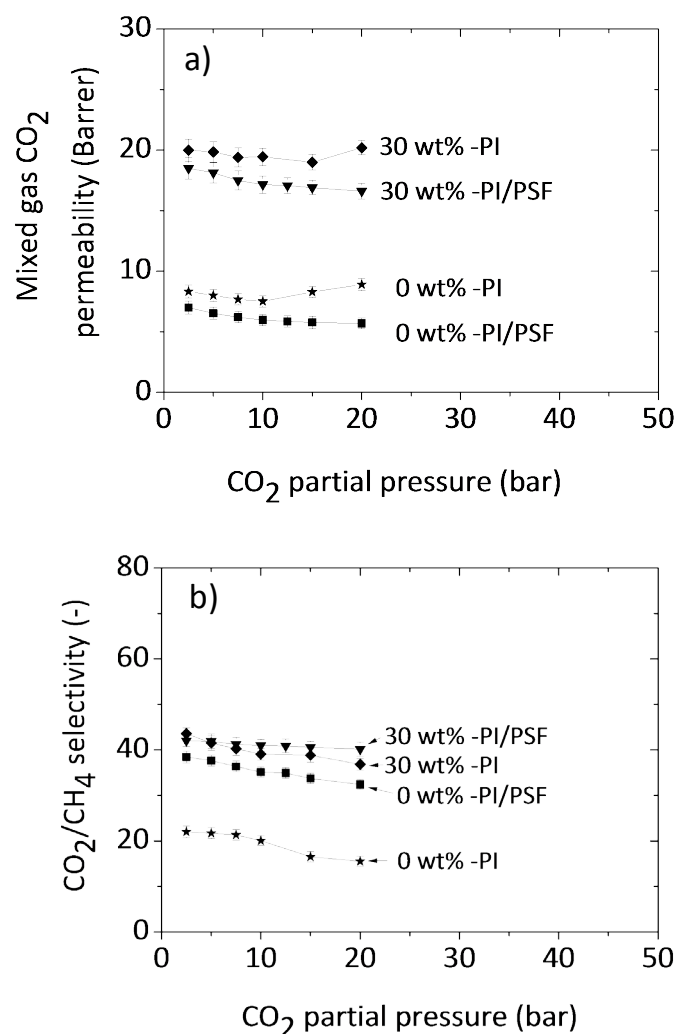


Figure 4: Mixed gas (a)  $\text{CO}_2$  permeability and (b)  $\text{CH}_4/\text{CO}_2$  selectivity of PI and PI/PSF MMMs as a function of pressure for different ZIF-8 loadings at  $35^\circ\text{C}$ .

### ZIF-8 based PI/PSF MMMs

Earlier research showed that PI blended with polysulfone (PSF) improved the  $\text{CO}_2$  plasticization resistance of PI but suffered from low  $\text{CO}_2$  permeability. Considering their enhanced stability, PI/PSF blends were used as a matrix for MMMs with ZIF-8 [7]. An optimized PI/PSF blend ratio (3:1) was used and performance and stability of PI/PSF MMMs filled with different concentrations of ZIF-8 were investigated. PI and PSF were miscible and provided good compatibility with the ZIF-8 particles, even at high loadings. TGA results showed higher thermal stability of the MMMs compared to the pure PI/PSF blend. As predicted, experimental results showed that the permeability of both  $\text{CO}_2$  and  $\text{CH}_4$  increased with ZIF-8 loading due to moderate increase in sorption capacity and faster diffusion through the ZIF-8 particles. In pure gas measurements, the PI/PSF blend showed a plasticization pressure of  $\sim 18$  bar, while the ZIF-8 MMMs showed a slightly higher plasticization pressures  $\sim 25$  bar attributed to the increased restriction in polymer chain mobility in the MMMs due to the presence of the ZIF-8 particles.

Figure 4 shows the mixed gas  $\text{CO}_2$  and the  $\text{CH}_4/\text{CO}_2$  selectivity of PI and PI/PSF MMMs as a function of the pressure for different ZIF-8 loadings at 35 °C.

In mixed gas separation measurements, PI/PSF membranes and ZIF-8 MMMs both showed suppression of plasticization, compared to PI based MMMs [5]. This was confirmed by a constant mixed gas  $\text{CH}_4$  permeability and nearly constant selectivity with pressure (up to 20 bar  $\text{CO}_2$  partial pressure). The effect was clearly stronger with higher ZIF-8 loadings. This work revealed that the enhanced stability of PI by blending it with PSF and the higher  $\text{CO}_2$  permeabilities due to the incorporation of the ZIF-8 particles increase the commercial viability of PI and broadens its applicability, especially for high pressure  $\text{CO}_2$  gas separations.

### Novel method for preparing MMMs

As stated above, for successful implementation of MMMs in industrial separations, several challenges need to be overcome. These challenges especially include a homogeneous dispersion of particles in the polymer matrix and a defect-free polymer-filler interface. In the last part of this work a novel route for the preparation of defect free MMMs via a particle fusion approach was developed. This approach improved the MOF-polymer interaction and eliminated MOF incompatibility, agglomeration and particle distribution problems, even at high loadings of MOF. Additionally, surface modification of the matrix polymer PI with 1-(3-aminopropyl)-imidazole further improved the interactions between polymer and MOF and led to an excellent ZIF-8/PI interfacial compatibility. The particulate morphology of a mixture of the modified polymer particles and the filler particles was transformed into a dense membrane structure

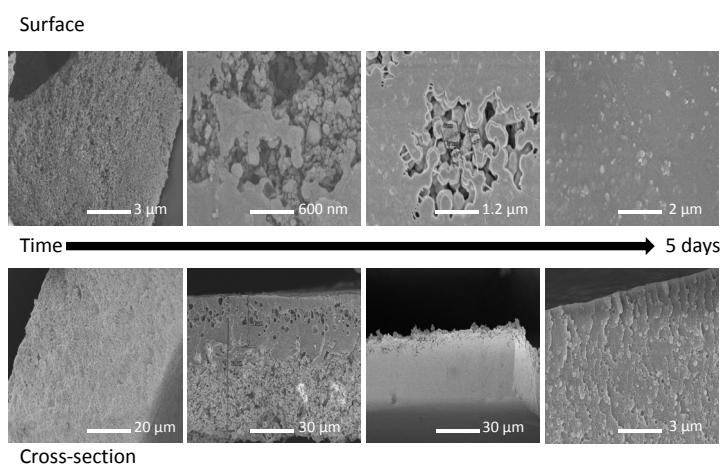


Figure 5: Surface and cross-sectional transformation from a particulate morphology to a dense MMM morphology over a period of 5 days in a controlled vapor atmosphere.

by keeping the film in a controlled vapor environment, which induced film formation (Fig. 5).

With this method, we showed it was possible to successfully prepare MMMs with MOF loadings as high as 30 wt.% without any non-selective defects. Upon increasing the ZIF-8 loading, MMMs showed significantly better performance in the separation of  $\text{CO}_2/\text{CH}_4$  mixtures as compared to both the native polymer and the MMM prepared by simple polymer blending and solution casting. The  $\text{CO}_2$  permeability increased up to 200 % combined with a 65 % increase in  $\text{CO}_2/\text{CH}_4$  selectivity, compared to native PI (Figure 6). Gas sorption studies further confirmed that selective ( $\text{CO}_2/\text{CH}_4$ ) gas transport is mainly governed by the increase in diffusivity selectivity, which in all cases increased more than the solubility selectivity.

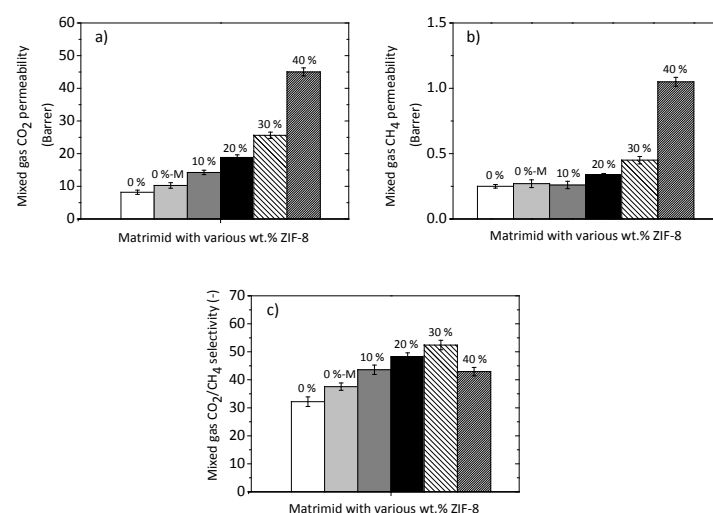


Figure 6: Mixed gas (a)  $\text{CO}_2$  permeability, (b)  $\text{CH}_4$  permeability and (c)  $\text{CO}_2/\text{CH}_4$  selectivity of prepared membranes for different ZIF-8 loadings at 5 bar and 35 °C (0 wt. %: pure PI; 0 wt. %-M: modified PI; 10, 20, 30 and 40 wt. %: MMM with respective ZIF-8 loadings).

The ZIF-8 MMMs prepared by this particle fusion technique showed a significant improvement in  $\text{CO}_2$  permeability and selectivity compared to solution cast blend ZIF-8 MMMs, as investigated in our previous study [6]. This study showed that it is possible to increase the gas separation performance of MMMs when challenges associated with the preparation and the formation of defect free MMMs can be overcome. The presented approach provides a simple method to eliminate these challenges. In addition, particle fusion is a very versatile MMM preparation route, not only for this specific ZIF and polymer, but for numerous combinations of polymers and MOFs.

## Overall performance and conclusions

An overall comparison of the gas separation performance of MOF-MMMs prepared during this project and the Robeson upper bound (2008) as a benchmark, is presented in Figure 7. The comparison only includes data obtained for MOF-MMMs with 30 wt.% MOF loading at a pressure of 5 bar and 35°C. Table 1 presents the details and operating conditions of the data presented in Figure 7.

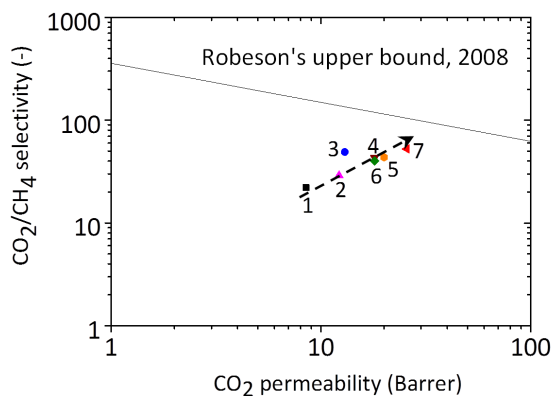


Figure 7: Summary of gas separation results of MOF-MMMs (30 wt.% MOF loading) prepared during this PhD and measured at 5 bar and 35°C under mixed gas conditions. See Table 1 for details of different membranes and specific experimental conditions.

Significant improvement was achieved for different MOF-MMMs compared to pure PI membranes. Irrespective of the preparation method, incorporation of MOFs in a PI matrix resulted in enhanced  $\text{CO}_2$  permeability and selectivity. Fe(BTC) based MMMs showed a relatively lower increase in permeability and selectivity compared to other MOF-MMMs attributed to polymer chain rigidification around the Fe(BTC) particles.

Among ZIF-8, MIL-53(Al) and  $\text{Cu}_3\text{BTC}_2$ , membranes based on ZIF-8 and MIL-53(Al) showed enhanced  $\text{CO}_2$  permeability with moderate increase in selectivity, while  $\text{Cu}_3\text{BTC}_2$ -MMM showed higher selectivity. Comparing the membrane preparation method, membranes prepared by the particle fusion approach showed better gas separation performance than the membranes prepared via solution casting. This can be attributed to

Table 1. Experimental details of the data presented in Fig. 7. All membranes measured at 5 bar and 35 °C under mixed gas conditions.

Codes	Membrane	Preparation method
1	PI*	Solution casting
2	PI-Fe(BTC)	Solution casting
3	PI- $\text{Cu}_3\text{BTC}_2$	Solution casting
4	PI-MIL-53(Al)	Solution casting
5	PI-ZIF-8	Solution casting
6	PI/PSF-ZIF-8	Solution casting
7	PI-ZIF-8	Particle fusion

\*PI: Matrimid® 5218

a better MOF dispersion and improved compatibility at the MOF-polymer interface. This overall evaluation of our results shows that MMMs with MOF particles can provide new opportunities for enhanced permeability and selectivity. Especially proper selection of MOF, polymer and fabrication method shows potential to reach membrane performances beyond the Robeson upper bound.

The public defense of this work is expected to take place on February 5, 2015. For more information, please contact Prof. dr. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl; phone: +31 (0)53 489 4185).

## References

- [1] A. Brunetti, F. Scura, G. Barbieri, E. Drioli, Membrane technologies for  $\text{CO}_2$  separation, *J. Membr. Sci.*, 359 (2010) 115-125.
- [2] L.M. Robeson, The upper bound revisited, *J. Membr. Sci.*, 320 (2008) 390-400.
- [3] N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura, *Advanced Membrane Technology and Applications*, Wiley, Hoboken, NJ, 2008.
- [4] A. Bos, I.G.M. Pünt, M. Wessling, H. Strathmann, Plasticization-resistant glassy polyimide membranes for  $\text{CO}_2/\text{CO}_4$  separations, *Sep. Purif. Technol.*, 14 (1998) 27-39.
- [5] S. Shahid, K. Nijmeijer, High pressure gas separation performance of mixed-matrix polymer membranes containing mesoporous Fe(BTC), *J. Membr. Sci.*, 459 (2014) 33-44.
- [6] S. Shahid, K. Nijmeijer, Performance and plasticization behavior of polymer-MOF membranes for gas separation at elevated pressures, *J. Membr. Sci.*, 470 (2014) 166-177.
- [7] S. Shahid, K. Nijmeijer, Matrimid®/polysulfone blend mixed matrix membranes containing ZIF-8 nanoparticles for high pressure natural gas separation, Submitted to *Journal of Membrane Science* (2014).

## Follow MST on Twitter!



The Membrane Science and Technology group has its own Twitter account!  
Follow @MST\_UTwente for the latest news of the MST group in a nutshell!

# First Blue Energy power plant worldwide

On November 26, 2014, his Majesty King Willem-Alexander of The Netherlands officially opened the first Blue Energy power plant in the world. In this test plant at the Afsluitdijk (NL) the mixing of sweet river water from lake IJssel and salt seawater from the Wadden Sea is used to generate sustainable energy. The use of smart ion exchange membranes makes it possible to capture this energy of mixing and to transform it into electricity. The membranes and the technology are developed by researchers from the Membrane Science and Technology group of the University of Twente in very close collaboration with Wetsus, Centre of Excellence for Sustainable Water Technology and Fujifilm.

When this demonstration shows that the approach is successful, it will be possible to generate five to ten percent of the total electricity consumption worldwide with Blue Energy. With its large rivers such as the Rhine and the Meuse, The Netherlands has great potential in this area. The company REDstack BV now takes 'Blue Energy' to market in The Netherlands. The University of Twente makes an important contribution to the research and the further development of the plant, which involves intensive collaboration with the research institute Wetsus, REDstack BV, Fujifilm and other organizations.

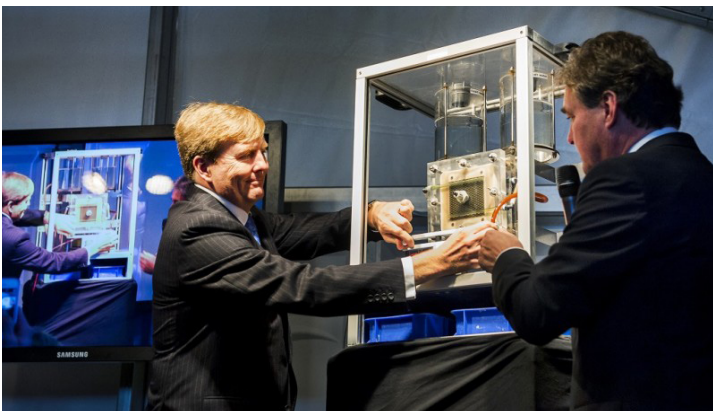


Figure 1: Official opening of the Blue Energy plant by his Majesty King Willem Alexander of the Netherlands (left) and Rik Siebers, Director REDstack BV (right)

The expectation is that Blue Energy will succeed in generating energy for 8 cents per kilowatt-hour (without subsidies), which is comparable to solar and wind energy. In addition, Blue Energy can be generated continuously, contrary to solar and wind energy, which are both dependent on their availability and the weather. The total quantity of electricity that could be generated on the Afsluitdijk is equal to 1200 billion AA batteries a year, or, in other words, sufficient for

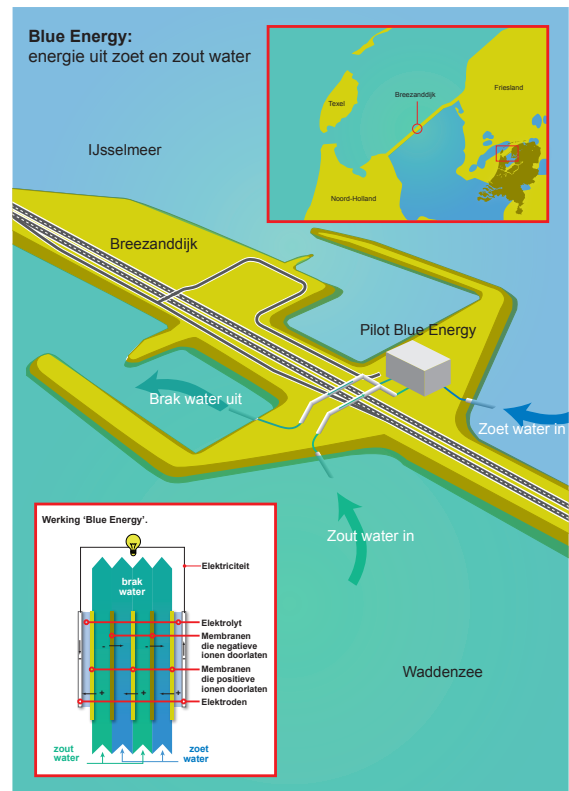


Figure 2: Site map of Blue Energy plant at the Afsluitdijk, The Netherlands

the energy requirements of 800.000 inhabitants. Salinity gradient energy can be captured in reverse electro dialysis (RED), in which ion exchange membranes are used for selective charge transport. The ions from the concentrated stream (e.g. seawater) are transported to the diluted stream (e.g. river water). The cations can only pass the cation exchange membranes (CEMs), while the anions can only pass the anion exchange membranes (AEMs). This selective transport creates a voltage drop over each membrane, as defined by the Nernst equation. Several membranes can be stacked to cumulate the voltage, with alternately seawater and river water in the compartments between these membranes. At the end of the membrane stack, the ionic current is converted into an electrical current at the electrodes (e.g. using a redox reaction), which can be used as a power source.

The installation at the Afsluitdijk currently contains four hundred square meters of membranes, and is able to process 220,000 liters of salt water and 220,000 liters of fresh water every hour. This figure will be increased to 100,000 square meters during the next few years. In order to save space, different membranes are placed immediately adjacent to one another, at a distance of only 0.3 to 0.5

millimeters. A commercial installation will eventually need millions of square meters of membranes. This seems much, but practically speaking this is certainly feasible. The total investment costs for the current installation at the Afsluitdijk and the costs to operate the plant for the next 5 years are in the order of 9 billion euros. When successful, further scale-



Figure 3: The Blue Energy plant of RED stack, with partners A.Hak, Magneto Fujifilm and Wetsus. It is co-financed by SNN, The Ministry of Economics Affairs and Provincie Friesland.

up and commercialization is expected in six to eight years. Research on this topic at the University of Twente started about 8 years ago when Piotr Długołęcki showed during his PhD research the huge potential of the technology and developed a system with ion conductive spacers. After that David Vermaas investigated the hydrodynamics and pollution of the membranes. He optimized the way in which water passes through the membranes and came up with a number of ways on how to reduce pollution of the membranes. At the same time Enver Güler occupied himself with the membrane development. He developed a membrane that yields the highest energy to date. Recently two new PhD candidates, Timon Rijnaarts and Jordi Moreno continued this research work on the development of membranes with improved ion exchange properties and better fouling mitigation in the real application, respectively.

For more information or literature about this work, please contact Prof. Dr. Ir. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl; phone: +31 (0)53 489 4185).

## Award

### Charu Chawla wins the OSPT Lecture Award at NPS14

At the recently held NPS14 (the 14th Netherlands Process Technology Symposium) meeting in De Fabrique in Maarsse (Utrecht, The Netherlands, 3-5 November 2014), Charu Chawla was awarded 'the OSPT Lecture Award for the best scientific lecture'. The price consisted of €2500, to be spent on the attendance of a scientific conference. The NPS is the biggest symposium in The Netherlands for engineers and scientists active in process engineering. It is already the second oral presentation award Charu Chawla wins, the first one was at the EMS Engineering With Membranes 2013 conference in Saint-Pierre d'Oléron, France.

The presentation of Charu Chawla was entitled 'Biofouling in low pressure point of use systems'. Charu is PhD student of the MST Group at Wetsus, Leeuwarden (Biofouling theme). Her PhD project focuses on the fouling behavior of membranes for drinking water treatment in decentralized point of use (PoU) systems. Biofouling has been a major barrier to the performance of membranes, thereby lowering the efficiency of the treatment systems. However, for intermittently used filtration systems it has been observed recently that biofilms actually can be beneficial to the filtration processes. Due to the inherent activity



Charu Chawla



of microorganisms such as the growth and decay in the biofilm structures, these tiny creatures lead to the stabilization of flux and keep the process in operation for extended durations. The goal is to investigate how the physiology and permeate quality would be affected in PoU drinking water systems, especially for water quality available in developing nations. Charu has shown that even in the absence of biofouling, fluxes in PoU systems are stabilized.

For more information, please contact Dr. Antoine Kemperman (a.j.b.kemperman@utwente.nl; phone: +31 53 489 2956).

# Scanning Electron Microscopy facilities at MST



Herman Teunis

## Introduction

Scanning electron microscopy (SEM) is a method for high-resolution imaging of surfaces. The SEM uses electrons for imaging, much as a light microscope uses visible light. The advantages of SEM over light microscopy include much higher magnification (>300,000X) and greater depth of field up to 100 times that of light microscopy. While light microscopy is used to observe details up to 0.25  $\mu\text{m}$ , SEM can reveal details up to 0.4 nm. The principle of SEM is based on the interactions between the specimen and a focused beam of electrons.

At the interface of the sample, various signals are generated containing information about the surface's topography and composition. Typical types of signals are: secondary electrons (SE), backscattered electrons (BE), characteristic X-rays, light (cathode luminescence), specimen current and transmitted electrons. Most commonly used detectors, also available within the Membrane Technology Group in Twente, are the secondary electron (SEI) detector, backscattered electron (BEI) detector and Energy Dispersive X-ray Spectrometry (EDS) detector.

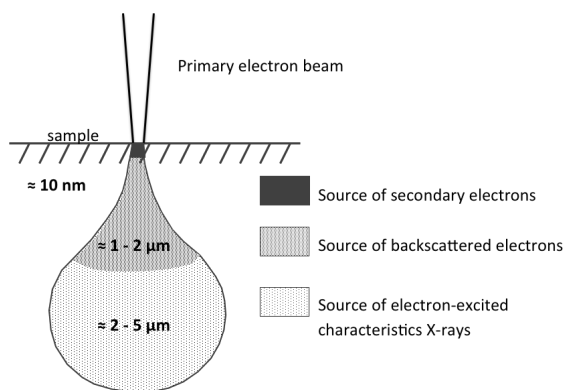


Figure 1: Depth profile of electrons responsible for the different type of SEM images

The incident electrons cause electrons to be emitted from the sample due to elastic and inelastic scattering events within the sample's surface and near-surface material. The energy of backscattered electrons will be comparable to that of the incident electrons. The BEI detector elucidates the surface structure with a depth profile of 2 – 5 micron. The energy of the backscattered electrons is 50 eV up to the energy of the interacting primary beam. Emitted lower-energy electrons resulting from inelastic

scattering are called secondary electrons. Secondary electrons can be formed by collisions with the nucleus where substantial energy loss occurs or by the ejection of loosely bound electrons from the sample atoms. In comparison with the BEI detector the image that is created by the SEI detector originates from the top surface since the penetration depth of the SEI is only 5 to 50 nm. The energy of secondary electrons is typically 50 eV or less.

EDS detection makes use of the X-ray spectrum emitted electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle. Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. The detection limit of EDS analysis in the SEM depends on the composition of the sample being analyzed, but is in the range 0.1-0.5 wt%. It is an effective technique for major and minor element analysis, but lacks the sensitivity for trace-element analysis.

SEM's are roughly divided into two categories. The first type uses a thermionic emission gun to generate the electron beam and uses either a tungsten filament or a LaB6 cathode filament. The maximum resolution is about 3 nm at a magnification of 300,000 X. The second type is the Field Emission SEM (FESEM). This type uses a sharpened, tungsten, metallic tip and a conducting fluorescent screen enclosed in ultrahigh vacuum. Here the sample is held at a large negative potential relative to the fluorescent screen resulting in a strong electrostatic field, which generates the electron beam. The maximum resolution is 0.4 nm at a magnification up to 1,000,000 times.

## SEM's at the Membrane Technology Group Twente

The Membrane Technology Group has both types of SEM available in their infrastructure. One is a normal tungsten SEM, the JEOL JSM-6010LA. The other is a FESEM, the JEOL JSM6000F. For the users the main difference between the two machines is the resolution and the energy necessary to visualise the microscopic structure. The JSM-6010LA has a resolution of 4 nm at 20 kV. The JSM6000F has a resolution of 0.6 nm at 30 kV. For comparison the specification of the SEM's are listed in table 1.



**Table 1: Specifications and of the SEM's available within the Membrane Science and Technology Group.**

	JSM-6010LA	JSM6000F
Max. resolution (High vac)	4 nm (at 20 kV)	0.6 nm (at 30 kV)
Max. resolution (Low vac)	5 nm (at 20kV)	n.a.
Acc. Voltage range	0.5 – 20 kV	0.5 -30 kV
Magnification range	5 – 300,000 X	10 – 950,000 X
Detectors	SEI, BEI, LVSE, EDS	SEI, BEI
Max. specimen size (mm)	150 (diameter)	23 x 6
Max. specimen height (mm)	48	2
Specimen chamber vacuum (Pa)	0.1 (HV) 1-100 (LV)	10 <sup>-5</sup>
EDS resolution	133 eV or better at @ MnK $\alpha$	n.a.

Table 1 demonstrates that the SEM JSM-6010LA offers more different approaches to reveal the microstructures. One important extra option is the ability to investigate samples in the low vacuum mode, which does not require additional sample preparation. Normally, a SEM sample is first dried thoroughly and subsequently coated with a thin conductive layer. This layer is needed to protect the sample for beam damaging and charging. When a microscope is equipped with a low vacuum option, it has the possibility to investigate non-conductive samples without applying the conductive coating, even when the samples are not dried.

The second extra option of the JSM-6010LA is the possibility to do elemental analysis (EDS) of the specimen. The EDS has two operational modes:

### Spectrum

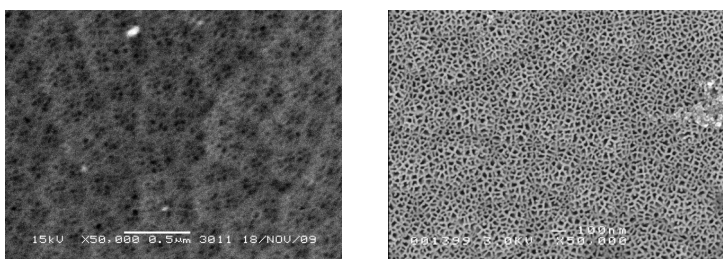
A plot of X-ray detected versus their energies. The characteristics X-rays allow the elements present in the sample to be identified.

### Mapping

An image showing how the distribution of elements is divided over the sample surface. In a mapping image every element has its own specific color.

### Examples

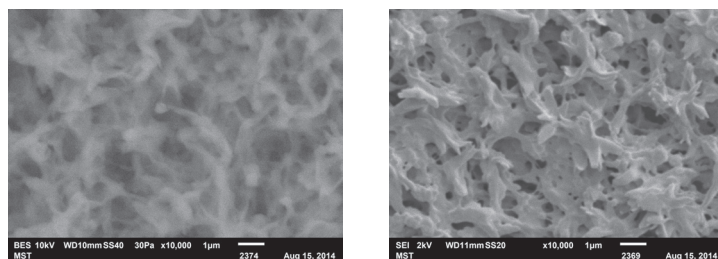
To illustrate the most striking difference between the two microscopes, images were recorded of an identical sample.



**Figure 2: SEM and FESEM images of the surface of an Anodisc® ceramic membrane, both magnification 50,000 times.**

On the left side, the image recorded by the JSM-6010LA is shown. On the right side, the image recorded by the JSM6000F is shown. Notice the difference in detail and the difference in

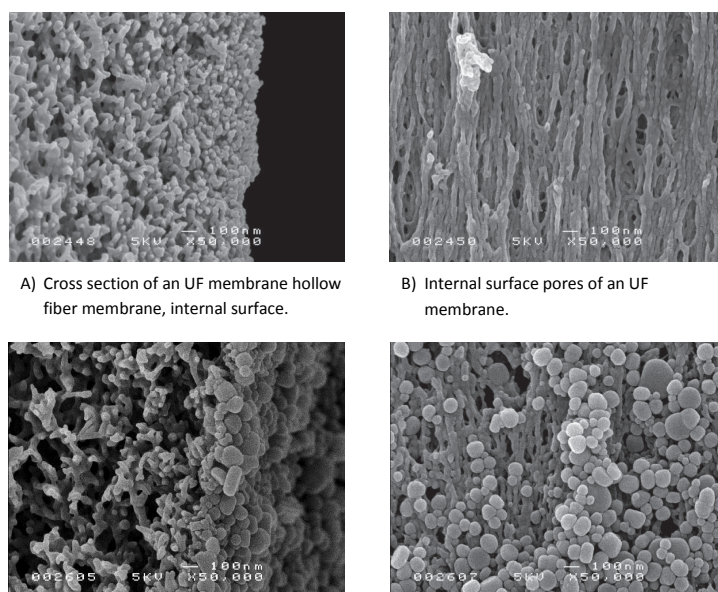
accelerating voltage 15 kV versus 3.0 kV. At a much lower accelerating voltage, the JSM6000F outperforms the JSM-6010LA with respect to image detail. Another advance of FESEM is the reduced beam damage using sensitive materials because of the lower energy input.



**Figure 3: Low vacuum versus high vacuum mode (JSM-6010LA) using a 0.45 µm PVDF membrane.**

In figure 3, a specimen is first observed in LV-mode (JSM-6010LA) without a conductive coating, resulting in the image on the left side. After recording this image, the specimen was coated with a thin layer of Platinum, resulting in the image on the right side. The main difference between the two images is the low vacuum in the specimen chamber (30 Pa) and the application of the BEI detector. The application of the BEI detector at low vacuum is necessary because the SEI detector cannot operate in the low vacuum mode without destroying it.

In figure 4 examples of high resolution images are shown using the JSM6000F FESEM. Images A-D show cross sections and surfaces of ultrafiltration membranes. A and B are pristine membranes. C-D are nanoparticles fouled membranes.



**Figure 4: High-resolution images of UF membranes, magnification for images A-D 50,000 X.**

SEM and FESEM samples need in the high vacuum mode a protective coating (2 till 5 nm) to promote heat conduction otherwise the energy originating from the electron beam melts/burns down and charges the specimen. At lower magnifications often a gold sputter coated layer is applied. A gold sputter coating is relatively easy to apply and is very useful for low and moderate magnifications. The drawback of a gold coating is that the layer is relatively thick before a smooth layer is obtained. At low magnifications an extreme

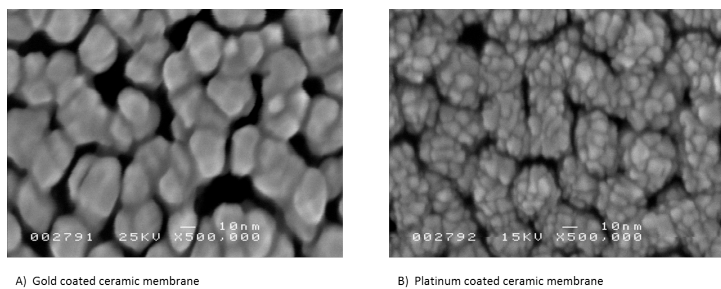


Figure 5: Grain sizes of gold A) and platinum B) coatings that are applied in electron microscopic research to protect the samples for melting/burning and charging.

thin coating layer can be applied. The drawback of a thin coating layer however is a more uneven distribution of the protecting layer which may result in charging, image drift and beam damage of the membrane. On the other hand a thick coating layer obscures details by covering, bridging or clogging nano gaps and pores. Especially at higher magnification the relative big grains of the gold particle are fading morphological details. For this reason a thin surface coating with smaller sized platinum grains is preferred when

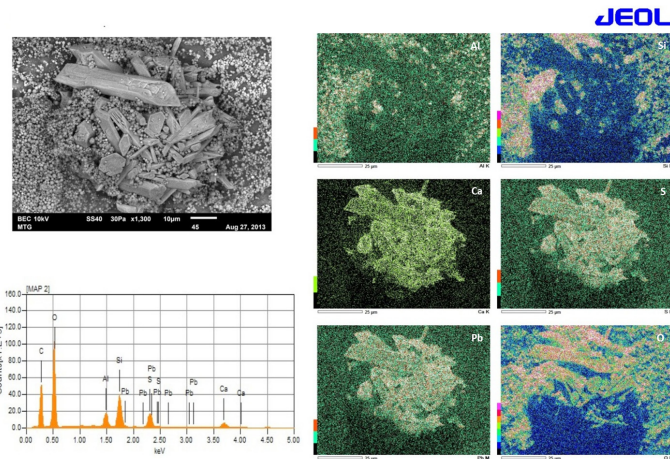


Figure 6: EDS analysis. Image left top BSE image; left bottom EDS spectrum, images right six element mappings.

high magnifications, as is common in FESEM imaging, are needed to reveal surface details. Figure 5 shows the effect of the different coatings at a magnification of 500,000 times. Figure 6 shows the EDS analysis results including mapping. Figure 6 is divided into three sections. On the upper left side the original SEM image is displayed recorded using the BEI detector since EDS requires uncoated samples. On the lower left graph the EDS spectrum is displayed, showing peaks of the identified elements. On the right side, six mapping images are displayed. Each image shows the distribution of a specific element and its actual location on the specimen. The combination of the peaks in the spectrum provides information about the chemical composition of the investigated specimen

## Awards

### Best Poster prize

During the traditional Poster Day of the Dutch Membrane Society (NMG) and its Flemish and German sister societies, Sinem Tas, PhD student of the Membrane Science and Technology group of the University of Twente, was awarded a poster prize for the best scientific poster. The Poster Day is organized every two years, consecutively in The Netherlands, Belgium or Germany. This year's event was organized by RWTH Aachen by the group of Prof. Matthias Wessling.

Sinem works on the development of ion selective membranes by using crown ether polymers based on host-guest interactions. She aims at the direct incorporation of crown ether moieties into a polymer chain as repeating unit. This in contrast to the frequently applied blending of crown ethers with polymers or post functionalization of linear polymers. With the in-chain crown ether approach, the synthesized such crown ether polymers exhibit excellent stability (no leaching out of the crown ether), while at the same time such structures show unique membrane functions, for example, the selective binding of a specific ion to a very high degree of ion specificity. For more information, please contact Prof. Kitty Nijmeijer (e-mail: d.c.nijmeijer@utwente.nl; phone: +31 53 489 4185).



---

## Best PhD paper of the year award of the Twente Water Centre

During the 2014 Twente Water Week 2014 Enver Güler is awarded for his paper 'Micro-structured membranes for electricity generation by reverse electrodialysis' in the Journal of Membrane Science. A jury of the Twente Water Centre (TWC) chose the winning paper among five nominated papers.



Enver Güler

Reverse electrodialysis (RED) is a clean, sustainable, potentially attractive technology for the generation of energy from the mixing of solutions with different salinity. It utilizes the free energy of mixing these solutions (e.g. river water and seawater) to generate power. In RED, a concentrated salt solution and a less concentrated salt solution are brought into contact through ion selective membranes (anion exchange membranes, AEMs, and cation exchange membranes, CEMs) that are alternately patterned in a stack. Anion exchange membranes allow only anions to pass through towards an anode and cation exchange membranes allow only cations to pass through towards a cathode.

In the awarded paper, Enver Güler describes a simple, versatile method to prepare so called microstructured membranes: membranes with various structures (ridges, pillars, waves) of the surface. These structures mitigate the water and induce mixing, consequently increasing mass transport. Traditionally, standard, non-conductive spacers are used to separate the membranes in the stack. This induces a high resistance due to the non-conductive character of the spacers. The structures on the membranes developed by Enver Güler are made of the same ion exchange materials as the membrane. Consequently, their resistance is much lower than when standard non-conductive spacers are applied, resulting in increased power outputs. Especially the pillar-structured membranes exhibited a more uniform flow distribution compared to the other types. 21% lower ohmic resistance was obtained resulting in 38% higher gross power density and 20% higher net power density for the pillared structures compared to the flat membranes with spacers.

Enver was a former PhD candidate of MST and graduated in January 2014. He is now working in Wetsus (Leeuwarden, NL) as post-doctoral researcher.

The Twente Water Centre (TWC) of the University of Twente is a centre of expertise in the area of water systems and governance. The Centre is unique in bringing together and balancing the natural and social sciences. The Twente Water Centre offers an interdisciplinary platform to researchers, students and society. The aim is to span the boundaries of individual expertise of scholars and their disciplinary research departments. Among the research themes are the understanding of the physical processes in water systems, human interference, uncertainty, risks, governance of water challenges and water resource management. Next to research on urgent water challenges, the Twente Water Centre also denotes water curricula and facilitates valorization activities.

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

---

**We wish you Merry Christmas  
and Happy 2015!**

**Membrane Science and Technology Group  
University of Twente  
The Netherlands**

# Polyelectrolyte Multilayer Nanofiltration Membranes



Joris de Grooth

Accessibility to safe drinking water is and will always be essential to human life. When not readily available, several techniques already exist to increase the water quality to a more potable standard at an acceptable price. Depending on the type of water to be treated, these techniques are designed to remove harmful bacteria and viruses or to desalinate brackish or seawater. However, with the increase in our population and the subsequent intensification of our water (re)use, different contaminants are appearing. These are small, unwanted, organic molecules, e.g., hormones, medicines, pesticides, some of which can, even at low concentrations, disrupt the endocrine system. As current (waste) water treatment methods are not specifically designed for these emerging contaminants, the need for a treatment method capable of the removal of these low molecular weight contaminants is foreseen. Besides, most water treatment plants currently are large, centralized facilities that require substantial capital and personal investments, resulting in additional geographical and/or economic barriers. This means that nowadays in developing countries there are plenty of people still deprived of fresh drinking water. Decentralizing the water treatment based on a low cost and simple process, keeping the emerging contaminants in mind, is the next step in increasing the accessibility of potable water throughout the globe.

In this PhD project, the development of selective membranes for water treatment facilities to cope with the aforementioned issues was covered. By using hollow fiber membranes, the water purification process can be simplified compared to using spiral wound membranes, a significant advantage for decentralized water treatment plants. The selectivity of ultrafiltration membranes is improved by coating a dense separation layer on the membrane. For this, the simple and versatile “layer-by-layer” (LbL) technique is used. By exposing a negative substrate to a polycation in an aqueous solution, a thin layer of that polycation is adsorbed on the surface. With the modified substrate, now positively charged, the same process can be done with an aqueous solution of a polyanion. This process can be repeated over and over again, steadily building a polyelectrolyte multilayer on top of the substrate that acts as a selective layer in water purification

(see Figure 1). The versatility of the LbL technique allows for an easy control over layer properties, such as thickness, density and charge, by varying the coating conditions, the type of polyelectrolytes and the amount of layers. This versatility makes the LbL system for the design of dense filtration layers, as is shown during this project.

A key property of all membranes for water treatment

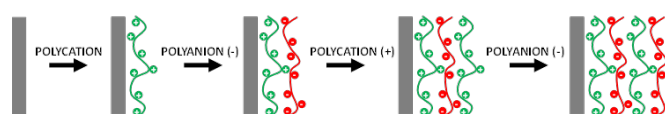


Figure 1: Simplified representation of the layer-by-layer technique.

purposes is the life time of the membrane. We showed that an adequate membrane life time can indeed be obtained for polyelectrolyte multilayers modified membranes, if certain criteria are met. First of all, the presence of ionic charges on the membrane support significantly enhances the adherences of the multilayer on the membrane when high shear forces and reversed flow are applied. Second, the capability to withstand chemical degradation by hypochlorite is superior when quaternary ammonium polycations are used in the layer (Figure 2). We show that when both criteria are met, backwashable hollow fiber nanofiltration membranes can be made that have a life time comparable to commercial ultrafiltration membranes.

Since the obtained multilayers can be as thin as a couple of nanometers, typical membrane characterization

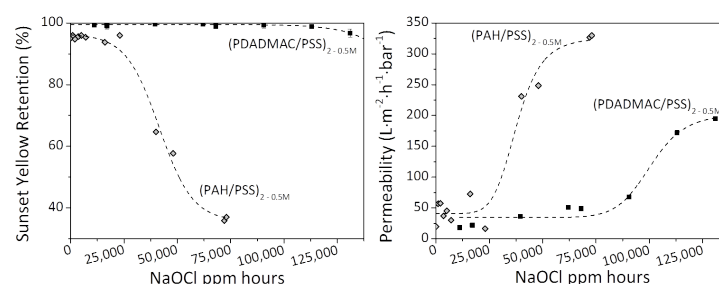


Figure 2: Evolution of retention (left) and permeability (right) in sodium hypochlorite at pH 8 of membranes coated with (PAH/PSS)<sub>2</sub> or (PDADMAC/PSS)<sub>2</sub> at 0.5 M NaCl. 1,000 ppm hours represents and exposure to 1,000 ppm NaOCl for 1 hour. The lines are added to guide the eye.

techniques (e.g., scanning electron microscopy) are not sensitive enough to visualize the layer on the membrane. Therefore, throughout this thesis, the buildup of multilayers on a model surface is initially monitored via reflectometry and subsequently correlated to changes in membrane performance when similar layers are adsorbed onto the fiber. This topic was already described in more detail in the Membrane News Twente in the summer of 2014. By carefully assessing the differences in the membrane performance between a polycation or a polyanion terminated layer (the so-called odd-even effect), we identified that the multilayer can either be coated inside or on top of the pores of an ultrafiltration membrane. When coating porous membranes with a relative large pore size, a transition is observed from coating in the pores to coating on top of the pores. By opting for a membrane with smaller pores, coating only on top of the pores is ensured.

The strength of the LbL technique is that a variety of polyelectrolytes and coating conditions can be used, all contributing the final properties of the ultrathin multilayer. Increasing the ionic strength results in thicker layers per coating step, both on model surfaces and on the hollow fiber. On the membrane this leads to an increase in resistance per coating step, due to enhanced coverage of the membrane pores. However, these thicker layers are also more open, resulting in a loss of ion/water selectivity (Figure 3). This means that when designing PEM modified membranes, it is essential that both the amount of layers and the ionic strength during coating are regarded in optimizing and controlling the PEM modified membrane properties.

Next to the classical polycations and polyanions,

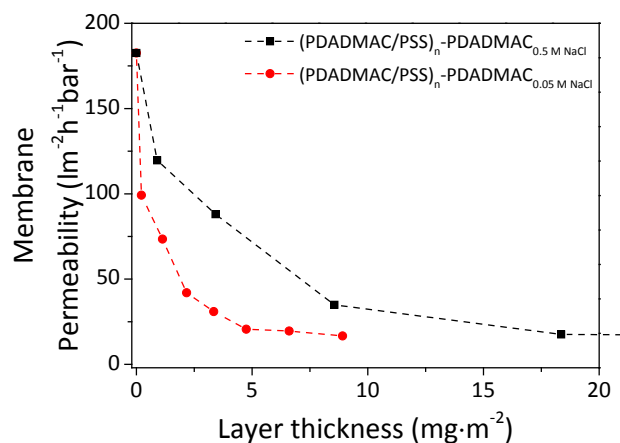


Figure 3: Comparison of PEM mass and membrane permeability for layers coated from different NaCl concentrations: 0.05 M (red circles) and 0.5 M (black squares). To exclude any odd/even effects only PDADMAC terminated layers are regarded.

polyzwitterions for membrane filtration purposes have also been investigated for this project. Polyzwitterions are charged polymers that have both a positive and a negative charge on the same pendant group. The most notable properties of the polymers is tendency to reduce fouling and their response to electrolyte solutions. Unlike polyelectrolytes, the solubility of polyzwitterions is increased at higher salt concentration, the so-called “anti-polyelectrolyte effect”. For a water insoluble zwitterionic copolymer it is shown that thin polymer film swelling in an aqueous solutions significantly increases with the amount of zwitterionic groups and that extent of the swelling is a function of the salt concentration and type of electrolytes.

A water soluble polymer containing only zwitterionic pendant

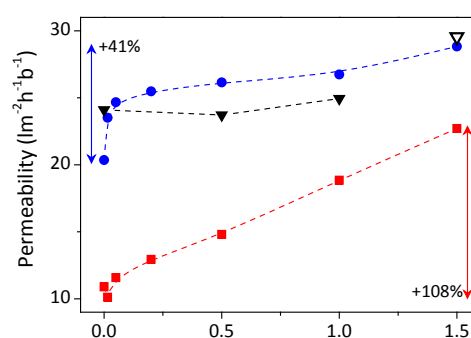


Figure 4: Ionic strength responsive behavior of (PDADMAC/PSS)<sub>2</sub> (▼, ▽), (PDADMAC/PSS)<sub>2</sub>-(PDADMAC/PSBMA)<sub>1</sub> ■ and (PDADMAC/PSBMA)<sub>5</sub> (●) modified HFS membranes.

groups is successfully incorporated into a multilayer with a polycation. In the layer buildup, the anti-polyelectrolyte effect is manifested by the response to the ionic strength during the coating solutions. In contrast to classical polycation/polyanion multilayers, for the polycation/polyzwitterion layers the layer thickness is decreased when coating at higher ionic strengths. The permeability of the obtained membranes is shown to be stimuli responsive to the ionic strength during filtration, with an increase in permeability of >100% when switching from pure water to a 1.5 M NaCl filtration solution (Figure 4). Again, this is attributed to the anti-polyelectrolyte effect. In cases that this responsiveness is not wanted, we show that crosslinking a zwitterionic multilayer negates this effect. The crosslinking yields membranes that have a stable, non-responsive, permeability when filtering solutions with an ionic strength of up to 1.5 M NaCl. The polyzwitterion is also incorporated into a multilayer bearing both a polycation and a polyanion (Figure 5). The presence of the polyzwitterion remarkably changes the selectivity of the three layer coated membrane for both inorganic electrolytes and low

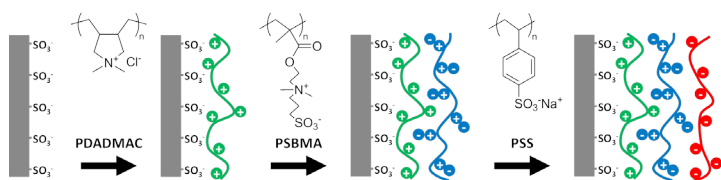


Figure 5: Schematic representation of the coating of a charged hollow fiber membrane with a trilayer of PDADMAC (+), PSBMA (z) and PSS (-) on a charged hollow fiber membrane.

molecular weight organic micropollutants. Incorporating the polyzwitterion into the films leads to PEM membranes that are suited for removal of both positive and negative charged micropollutants (Figure 6).

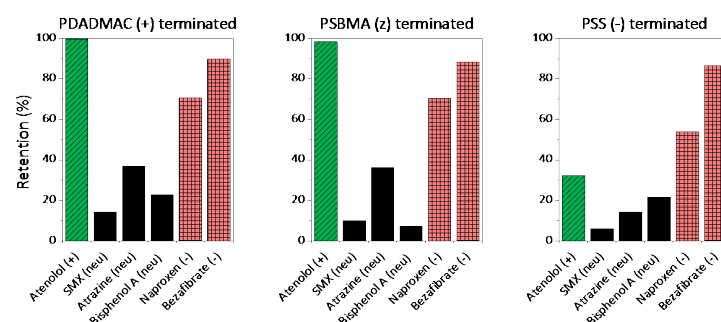


Figure 6: Retention of different micropollutants at pH 5.8 by HFS membranes coated with (PDADMAC/PSBMA/PSS)<sub>2</sub>/PDADMAC (+), (PDADMAC/PSBMA/PSS)<sub>2</sub>/PDADMAC/PSBMA (z), and (PDADMAC/PSBMA/PSS)<sub>3</sub> (-). Filtration experiments were performed under turbulent conditions ( $Re=3,500$ ) and at a trans-membrane pressure of 1.75 bar.

Colors represent micropollutant charge: green for positive, black for neutral, and red for negative micropollutants.

This PhD project has highlighted the possibilities of PEM modified membranes for water purification, by being able to tune the final membrane properties not only by changing the coating conditions but also by selecting different charged polymers. With a good understanding of the nature and buildup of the multilayer, the combination of the LbL technique with hollow fiber membranes can be the next step in ensuring safe drinking water throughout the globe.

For more information about this work, please contact Dr. Wiebe de Vos (w.m.devos@utwente.nl; phone: +31 (0)53 489 4495).

## References

- [1] G. Decher, J. D. Hong, J. Schmitt, Buildup of Ultrathin Multilayer Films by a Self-Assembly Process: III. Consecutively Alternating Adsorption of Anionic and Cationic Polyelectrolytes on Charged Surfaces, *Thin Solid Films.*, 210–211 Part 2 (1992) 831-35.
- [2] Joris de Groot, Radek Oborný, Jens Potreck, Kitty Nijmeijer, Wiebe M. de Vos, The Role of Ionic Strength and Odd–Even Effects on the Properties of Polyelectrolyte Multilayer Nanofiltration Membranes, *J. Membr. Sci.*, 475 (2015) 311-319.
- [3] Joris de Groot, Wojciech Ogieglo, Wiebe M. de Vos, Miriam Gironès, Kitty Nijmeijer, Nieck E. Benes, Swelling Dynamics of Zwitterionic Copolymers: The Effects of Concentration and Type of Anion and Cation, *Eur. Polym. J.*, 55 (2014) 57-65.
- [4] Joris de Groot, M. Dong, Wiebe M. de Vos, Kitty Nijmeijer, Building Polyzwitterion-Based Multilayers for Responsive Membranes, *Langmuir*, 30 (2014) 5152-61.
- [5] Joris de Groot, Dennis M. Reurink, Jeroen Ploegmakers, Wiebe M. de Vos, Kitty Nijmeijer, Charged Micropollutant Removal with Hollow Fiber Nanofiltration Membranes Based on Polycation/Polyzwitterion/Polyanion Multilayers, *ACS Appl. Mater. Interfaces.*, 6 (2014) 17009-17017.

## New people

### Membrane, module and process design for super critical CO<sub>2</sub> dehydration

Andrew Shamu moved in 2009 to Muenster to study Chemical Engineering at the University of Applied Science Muenster, after gaining his chemical technician and university-entrance diploma. In 2012 he performed his bachelor internship at BASF Coatings, where he had to generate an auxiliary and operating materials cadastre for a car coating plant at the factory premises in Muenster. During his internship he could detect saving potentials and established a priority characterization technique to determine further saving potentials.

After Andrews's bachelor degree, he resumed his studies at the University Muenster and focused on Chemical Processing. During this he got acquainted with membrane technology, and he decided to do his master thesis at the Membrane Science and Technology Group at the University of Twente. There he examined the fouling behavior of nanoparticles on membrane surfaces, and created a mechanistic model based on particle-particle interactions that could predict the particle deposition behavior at different process conditions.

In October 2014 he joined the Membrane Science and Technology Group as a PhD candidate. His project is a collaboration between Wetsus and the University of Twente. It investigates the potential of membranes to remove water from supercritical CO<sub>2</sub>.

Name: Andrew Shamu

Origin: Germany

Contact

+31 (0)58 2843184

a.shamu@utwente.nl



# It all started in Twente

## What is your name?

Jean-Marc DUVAL

## What are your date of birth and your place of birth?

Born on 16 November 1967

## What is your marital status and do you have children?

Married, 3 children: 2 boys (12 & 16), 1 girl (14)



## Where are you currently employed and what is your position (please provide a short description of your current job)?

I am currently employed by the Michelin Tire Company in Clermont-Ferrand, France. My current position is head of Industrial Methods for the 2 wheels tires division. It consists of making the link between tire R&D and Industry, by designing proper manufacturing processes and work methods to achieve good products for the end user.

## Where is your company located and where do you live?

Michelin Tire is an international company. For the moment, I am employed in Clermont-Ferrand, France. This town is the historic headquarter of the company and is located in the center of France in a volcanic region.

## When did you start your PhD and when did you receive your PhD degree?

I started in Oct. 1989 and received my PhD degree in March 1993.

## On which topic did you do your PhD?

The title of my PhD was: Adsorbent filled polymeric membranes. The idea was to investigate the effect of adsorbents (zeolites, carbon molecular sieves...) on the gas

and liquid separation properties of polymer materials. For this research I was sponsored by a French petrochemical company.

## Do you still have contacts with your former PhD students from that time?

Yes with a couple of them, but unfortunately geographical distance makes it quite difficult to meet. I am also happy to receive the news through the MST News letter.

## What was your first job after your PhD?

I joined the Michelin tire company in Clermont-Ferrand in April 1993 as a R&D engineer in the field of synthetic elastomers. One year later I moved to Bordeaux in a synthetic rubber production facility.

## How did your career develop?

After 1 year and a half in Clermont-Ferrand, I moved to Bordeaux to work as Process department manager in a Michelin synthetic rubber production facility. In 1999 I took the technical management responsibility for the synthetic elastomer division, covering 2 plants and relations with the R&D department. In 2004, I came back to Clermont-Ferrand and after 9 months in the Human Resources department, I joined the Michelin tire world, which meant first learning what a tire is and how to design it. I was then involved in tire design within the Earthmover product line for 2.5 years (tires for mining, quarries and construction sites). I then changed to worldwide industrial project management for the same product line, working on projects in France, Spain, USA, Brazil and India. In 2012 I Joined the 2 wheels tire division (bicycle

and motorbike) in my current position.

### **How do you relate your career to the experience you gained during your PhD?**

Although I was not directly involved in the membrane field during my career, my PhD experience helped me a lot when I was in the synthetic elastomer business: technically thanks to the knowledge acquired and also because I could better understand and compare R&D processes and practices. The international experience in Twente, result of the diverse origins of PhD students, was also an asset when I later had to work with teams from various foreign countries. Since then I always advised young students to go abroad to live such an experience.

### **How did you experience your time in Twente?**

It was a great experience first because of the nice and rich relationships within the membrane research group. Other students came from various countries e.g, Germany, China, Australia, Slovenia, Korea, Russia, Brazil and the Netherlands of course. It made cultural exchange a day to day activity. Although I did miss my home country from time to time, I enjoyed the student life in Twente. Also the scientific discussions were enriching and helped me for my research.



### **What important things did you learn during your PhD?**

First of all it helped me open my mind to different scientific approaches and cultures. The frequent scientific discussions were challenging and enriching and allowed to make real progress in my research field.

This was really important for my first steps in the company I joined after my graduation.

### **What was the biggest challenge during your PhD?**

My biggest challenge was to adapt to a new way of life in

a foreign country. I first started to use English on a day to day basis but I quickly found out that the best way to integrate myself to the group would be to learn Dutch. That's what I tried using my basic German language knowledge and some private lessons. After a year or two, I could use Dutch on a day to day basis, although not perfectly. This helped me a lot to feel part of the Group.



### **Do you maybe remember an anecdote or a specific moment of that time?**

There are many moment I like to remember. First we had funny moments with Betty and Zandrie when they taught typical Dutch idioms: my pronunciation could lead to misleading situations. I also enjoyed playing volleyball or soccer with the group members, as well as playing Klaverjassen during lunch time. These were key moments to share with all members of the team.

### **What was the best moment of your PhD (except the graduation)?**

I really enjoyed moments when the group could gather besides research work, such as week-ends that were organized to sail across the IJsselmeer or study tours in other countries. We were acting as a team during these events and could use this experience to move forward together in our research fields

### **What would you have done differently if you could do your PhD again ?**

Most probably I would take more time to regularly move one step back in order to be more efficient in my experimental plans.

### **Which advice do you have for the current generation PhD students?**

They should take this opportunity to build a multi-cultural experience that will be an asset for their future career and be open for challenging discussions about the various scientific topics that are covered within the group. For foreign students, do not hesitate to learn Dutch to better enjoy your time in Twente.



### **What is your precious memory of the group?**

I cannot forget Marcel Mulder and Kees Smolders for their warm welcome within the group. They really helped me to feel confident and move forward even in difficult situations. Furthermore I could rely on Betty and Antoine's assistance in my research, as well as support from Astrid Bulte, Jeroen Boom, Erik Meuleman, Matthias Wessling, Heiner Strathman and many others through challenging scientific discussions.

### **What could be different in our research group?**

It is difficult for me to answer as my time in the Group was more than 20 years ago and I do not know the present Group very much. Maybe more connection to the industrial world

would improve the knowledge of membrane applications. This could be done through more visits to Industry and / or lectures given by industrial fellows.

### **What did you miss while working in the group?**

Not much actually. At the beginning, I did miss my country from time to time but it did not last very long.

### **Do you maybe want to add something else? Feel free.**

I would like to thank all those that contributed to my research and helped me to feel at home in Twente during 3.5 years. I know that I owe them part of who I am today.

## **Vacancies**

### **Ph.D. position: "Membrane development for fuel feedstock production by a combined approach of controlled plasma conversion and membrane separation" (location: University of Twente, The Netherlands)**

Production of CO<sub>2</sub> neutral fuels produced from sustainable energy provide a method to store energy. An innovative route to produce CO<sub>2</sub> neutral fuels is production of CO from CO<sub>2</sub> by plasma-assisted conversion, followed by a separation step and further chemical processing of CO to produce a fuel. The plasma conversion step uses a novel concept for the reduction of CO<sub>2</sub> into CO and O<sub>2</sub>. The subsequent separation of the reaction products will be done using membrane technology based on Polymer-Molecular Organic Framework (MOF) mixed matrix membranes. The separated reaction products can then be transformed into fuels using a combination of Water Gas Shift (WGS) and methanation. The goal of this proposal is to control and enhance the plasma and separation step and integrate them into the fuel production chain.

As a PhD student at the University of Twente you will work on the design and synthesis of such MOF-polymer membranes and characterize these. You will also investigate the application of the developed membranes for the separation of gas mixtures both at low and high pressure and in the presence of CO after the plasma conversion. This project will be conducted in close collaboration with a second PhD that will work on a project dedicated to the design of the plasma conversion step.

### **Ph.D. position: "Gel membranes for (waste) water filtration" (location: Wetsus, Leeuwarden, NL)**

In this project you will develop an exciting alternative technology for preparing microfiltration membranes. These membranes have a large potential for wastewater treatment because they can achieve a 100% particle separation efficiency, but are expensive and suffer from fouling. To develop a cheaper alternative, you will produce biopolymers from wastewater and use these polymers to deposit a gel layer on a porous carrier material. This gel layer will achieve the actual particle separation. You will investigate how to make such a gel layer, characterize its chemical, mechanical and structural properties, and relate this to short- and long-term filtration performance for synthetic as well as real wastewaters.

The research will be conducted at Wetsus in Leeuwarden, NL ([www.wetsus.nl](http://www.wetsus.nl)) under the supervision of the research groups Environmental Technology of Wageningen University and the Membrane Science and Technology of the University of Twente.

As a PhD student you can demonstrate a strong affinity with (bio-)polymers, methods to characterise polymers and gels. We are looking for highly motivated and enthusiastic researchers with MSc degree in chemical engineering, bio-engineering, food-engineering or related topic. Candidates should have excellent experimental and theoretical skills.

We prefer candidates with a good team spirit, who like to work in an internationally oriented environment. Fluency in English is a requirement. An interview and a scientific presentation will be part of the selection procedure.

We offer you a PhD position for 4 years. Your starting salary will be € 2083, - gross per month in the first year and up to € 2664, - gross per month in the last year.

Interested candidates are invited to send, by email, a motivation letter, CV (including references) and a list of BSc and MSc courses and grades to Prof. Dr. Ir. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl; phone: +31 53 489 4185), for the project Membrane development for fuel feedstock production and to Dr. Ir. Antoine Kemperman (a.j.b.kemperman@utwente.nl; phone: +31 53 489 2956; University of Twente), for the project Gel membranes for (waste) water filtration.

## Ph.D. Defenses

### Joris de Grooth

A tale of two charges: zwitterionic polyelectrolyte multilayer membranes

February 4, 2015, 14.45h, University of Twente

### Salman Shahid

Polymer-metal organic frameworks (MOFs) mixed matrix membranes for gas separation applications.

February 5, 2015, 14.45h, University of Twente

## Publications

- Enver Güler, Willem van Baak, Michel Saakes, Kitty Nijmeijer, Monovalent Ion Selective Membranes for Reverse Electrodialysis, *Journal of Membrane Science* 455 (2014) 254-270.
- Salman Shahid, Kitty Nijmeijer, Performance and Plasticization Behavior of Polymer–MOF Membranes for Gas Separation at Elevated Pressures, *Journal of Membrane Science* 470 (2014) 166-177.
- Vic H. A. van Dijk, Gideon Simmelink, Guido Mul, The Influence of Water Vapour on the Photocatalytic Oxidation of Cyclohexane in an Internally Illuminated Monolith Reactor, *Applied Catalysis A: General* 470 (2014) 63-71.
- Stephen B. Abbott, Wiebe M. de Vos, Laura L. E. Mears, Robert Barker, Robert M. Richardson, Stuart W. Prescott, Hydration of Odd–Even Terminated Polyelectrolyte Multilayers under Mechanical Confinement, *Macromolecules* 47 (2014) 3263-3273.
- Shirin Alexander, Terence Cosgrove, Wiebe M. de Vos, Thomas C. Castle, Stuart W. Prescott, Aggregation Behavior of Polyisoprene–Pluronic Graft Copolymers in Selective Solvents, *Langmuir* 30 (2014) 5747-5754.
- Joris de Grooth, Mo Dong, Wiebe M. de Vos, Kitty Nijmeijer, Building Polyzwitterion-Based Multilayers for Responsive Membranes, *Langmuir* 30 (2014) 5152-5161.
- Joris de Grooth, Wojciech Ogieglo, Wiebe M. de Vos, Miriam Gironès, Kitty Nijmeijer, Nieck E. Benes, Swelling Dynamics of Zwitterionic Copolymers: The Effects of Concentration and Type of Anion and Cation, *European Polymer Journal* 55 (2014) 57-65.
- Ivonne Escalona, Joris de Grooth, Josep Font, Kitty Nijmeijer, Removal of BPA by Enzyme Polymerization Using NF Membranes, *Journal of Membrane Science* 468 (2014) 192-201.
- L. Faust, H. Temmink, A. Zwijnenburg, A. J. B. Kemperman, H. H. M. Rijnaarts, Effect of Dissolved Oxygen Concentration on the Biofloculation Process in High Loaded MBRs, *Water Research* 66 (2014) 199-207.
- L. Faust, H. Temmink, A. Zwijnenburg, A. J. B. Kemperman, H. H. M. Rijnaarts, High Loaded MBRs for Organic Matter Recovery From sewage: Effect of Solids Retention Time on Biofloculation and on the Role of Extracellular Polymers, *Water Research* 56 (2014) 258-266.
- A. H. Galama, D. A. Vermaas, J. Veerman, M. Saakes, H. H. M. Rijnaarts, J. W. Post, K. Nijmeijer, Membrane Resistance: The Effect of Salinity Gradients over a Cation Exchange Membrane, *Journal of Membrane Science* 467 (2014) 279-291.
- Harro Mengers, Nieck E. Benes, Kitty Nijmeijer, Multi-Component Mass Transfer Behavior in Catalytic Membrane Reactors, *Chemical Engineering Science* 117 (2014) 45-54.
- John R. Varcoe, Plamen Atanassov, Dario R. Dekel, Andrew M. Herring, Michael A. Hickner, Paul A. Kohl, Anthony R. Kucernak, William E. Mustain, Kitty Nijmeijer, Keith Scott, Tongwen Xu, Lin Zhuang, Anion-Exchange Membranes in Electrochemical Energy Systems, *Energy & Environmental Science* 7 (2014) 3135-3191.

# Membrane Science and Technology

## Vision

The research group Membrane Science and Technology of the University of Twente, headed by Prof. Kitty Nijmeijer, focuses on the multidisciplinary topic of polymer membranes to control mass transfer through interfaces.

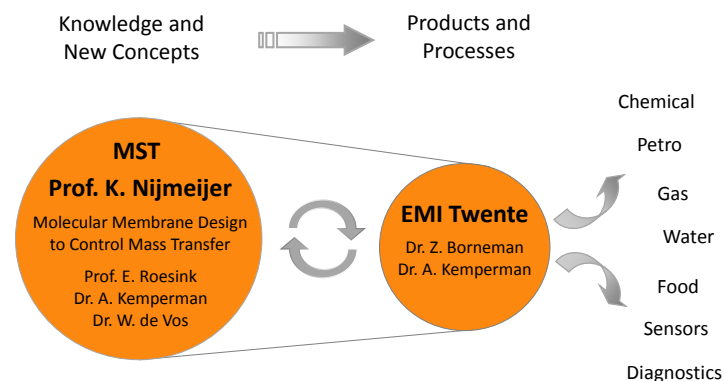


Figure 1: Organizational structure research group.

The group consists of two separate entities (Figure 1): the academic research group Membrane Science and Technology (MST) and the European Membrane Institute Twente (EMI), which performs confidential research directly with the industry.

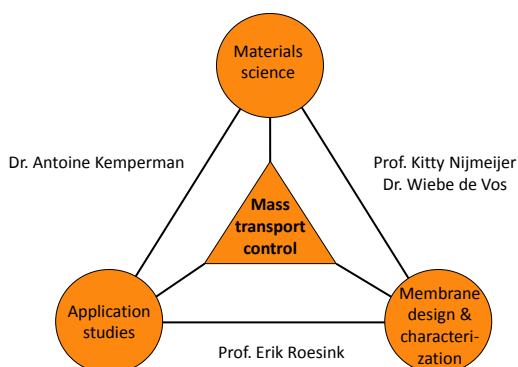


Figure 2: Membrane Science & Technology.

Research within the group is dedicated to the design, development, characterization and application of polymer membranes for Energy, Water and Life Sciences. We aim at tailoring membrane design, morphology and characteristics on a molecular level to control mass transport in applications (Figure 2). More specifically, our research focuses on the separation of molecular mixtures and achieving selective mass transport. We consider our expertise as a multidisciplinary knowledge chain ranging from molecular design towards process applications.

Most of our research is dedicated towards specific applications. We distinguish three main application clusters, i.e. Energy, Water and Life Sciences (Figure 3).

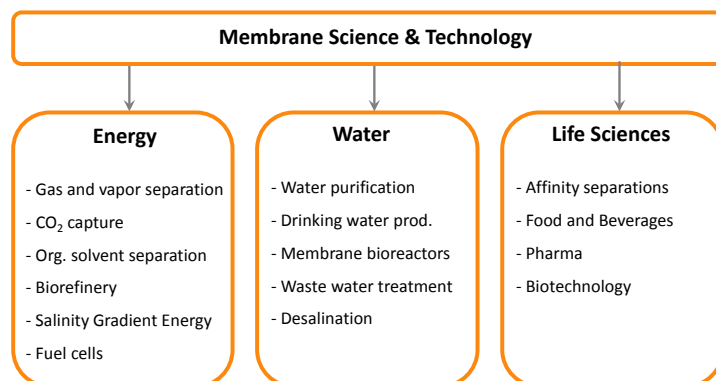


Figure 3: Major application clusters Membrane Science & Technology.

## Energy

The research cluster Energy is dedicated to the molecular design and synthesis of polymer membranes for e.g. gas and vapor separations (CO<sub>2</sub> capture, olefin/paraffin separation,



water vapor removal), biorefinery applications, fuel cells and the generation of energy from the mixing of salt and fresh water ('salinity gradient energy' or Blue

Energy). Relevant research aspects are control of structure-properties relationships, ultimate selectivity, molecular recognition, and separation of complex, multi-component mixtures.

## Water

Within the application cluster Water, research addresses the development of membranes and the application of membrane technology for water treatment, e.g. water purification, desalination, membrane bioreactors and waste water treatment. In particular it investigates the relation between membrane design, morphology and membrane properties in relation to performance, selectivity and causes, consequences and control of fouling.

## Life sciences

The cluster Life Sciences focuses on the design of porous membranes to separate complex multicomponent mixtures in pharmaceutical, food, beverage and biotech applications. Important subjects are the tuning of the material properties and structure (e.g. pore morphology and porosity), the

development of functional materials (e.g. affinity separations of biomolecules) and the creation of improved processes. In addition, aspects related to process design and industrial implementation, such as scale-up of novel membrane fabrication methods, are investigated. The research group consists of 30-35 people among which approximately 15-20 Ph.D. students, three permanent researchers, five B.Sc. and M.Sc. students and five academic staff members. Next to the head of the group, Prof. Kitty Nijmeijer, the staff consists of Prof. Erik Roesink, Dr. Wiebe de Vos, Dr. Antoine Kemperman and Dr. Zandrie Borneman, who is responsible for the EMI Twente. Next to extensive, general knowledge on polymer membrane science and technology, each of the staff members has his/her own specific field of dedicated expertise (Table 1).

Table 1: Specific expertise of the staff members of MST.

Name	Specific expertise
Prof. Kitty Nijmeijer	Membrane design and characterization, molecular selectivity, molecular recognition, dense membranes, Energy and Water
Prof. Erik Roesink	Membrane formation, porous systems, phase inversion, solvent-free membranes, biomimetic membranes, Water and Life Sciences
Dr. Antoine Kemperman	Causes, consequences, cleaning and control of membrane fouling, interactions at the interface, Water European Membrane Institute (EMI) Twente: Confidential contract research directly with the industry
Dr. Wiebe de Vos	Membrane surface science, surface modification, multilayers, polymer brushes, Water and Energy.
Dr. Zandrie Borneman	European Membrane Institute (EMI) Twente: Confidential contract research directly with the industry

## Knowledge valorization

Our group has decided to establish a significant effort in the valorization of its knowledge. The European Membrane Institute Twente (EMI Twente) was established in 1995 and performs confidential contract research directly with the

industry and public organizations. Research is governed by questions from stakeholders. To guarantee confidentially, we work with highly skilled researchers with long standing experience in membrane technology

in our group. Students are not involved. EMI Twente creates, transfers and translates (fundamental) scientific knowledge into products, processes and applications. Projects can last from only a few days up to three years and can involve membrane development and synthesis, membrane characterization, and/or membrane application studies. The EMI Twente acts as the interface between the academic research and the industrial needs.

## Services

The EMI Twente provides the following services:

- Membrane development
- Membrane characterization
- Membrane application studies
- Desktop studies
- Consultancy
- Selling of equipment (e.g. cells for gas separation, UF and MF, casting knives, cloud point meters, hollow fiber spinning lines, spinnerets)



For more information, please contact:

Prof. Dr. Kitty Nijmeijer

d.c.nijmeijer@utwente.nl

www.utwente.nl/tnw/mtg

Dr. Zandrie Borneman (EMI Twente)

z.borneman@utwente.nl

www.utwente.nl/tnw/emi

## MNT- Information

Membrane News Twente is published two times per year and aims to inform the membrane community about the activities of the Membrane Technology Group of the University of Twente ([membrane@utwente.nl](mailto:membrane@utwente.nl) [www.utwente.nl/tnw/mtg](http://www.utwente.nl/tnw/mtg)).

### Editors

Kitty Nijmeijer

Shazia Ilyas