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In-situ spectroscopic ellipsometry for studies of thin films and membranes

Wojciech Ogieglo

The properties of a thin polymer film can be significantly affected by the presence of a penetrant. It is also known that the behavior of ultra-thin polymer films (<100 nm) may deviate from the bulk behavior. This sole impact of film thickness reduction is often referred to as a nano-confinement effect. Superposition of the penetrant and the nano-confinement can have potential implications for many technological applications, such as protective and functional coatings, sensors, microelectronics, surface modification and membrane separations. In-situ ellipsometry is a powerful technique for the characterization a films in contact with penetrants, due to its high precision and non-invasive character. The technique is based on the analysis of the change in polarization state of light reflected from thin film samples.

This PhD thesis of Wojciech Ogieglo explores the applicability of in-situ ellipsometry to study fundamentals of various physical phenomena occurring in thin and ultra-thin polymer films in the presence of interacting penetrants. The work has been done within the Thin Films In Complex Fluids cluster of Nieck Benes.

The introductory part of the thesis reviews the work done with in-situ ellipsometry in the field of polymer films interacting with various penetrants. The review addresses a variety of topics, covering instrumental aspects of in-situ studies, approaches to data analysis and optical models, reported precision and repeatability, the polymer-penetrant systems that have been studied, the kind of information that has been extracted, and other in-situ techniques that have been combined with ellipsometry. Various examples are presented to illustrate different practical approaches, the consequences of the optical properties of the ambient, and the various ways that have been employed to bring polymer films in contact with a penetrant, ranging from simple ex situ like configurations (i.e. drying studies) to complex high pressure cells. The versatility of in-situ ellipsometry is demonstrated by examples of the distinctive phenomena studied, such as film dilation, penetrant diffusion mechanisms, film degradation, electrochemical processes, and the broad variety of polymer penetrant systems studied (glassy and rubbery polymers, multilayer stacks, etc.). An outlook is given on possible future trends.

Temperature-induced transition of the diffusion mechanism of n-hexane in ultra-thin polystyrene films, resolved by in-situ spectroscopic ellipsometry

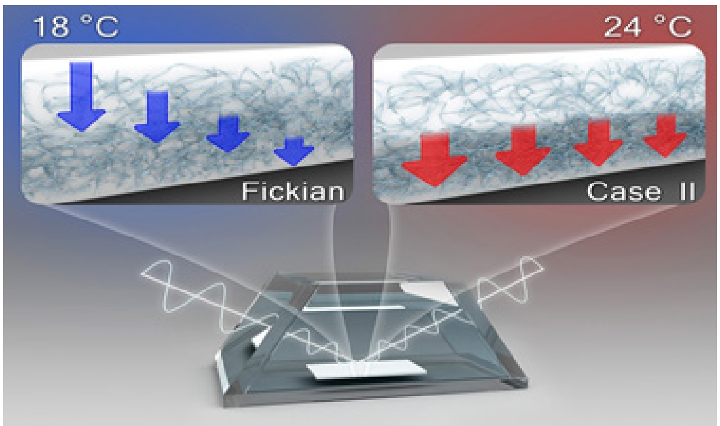

Figure 1: Transition in penetrant diffusion from smooth Fickian-like to a sharp front Case II process in a 150 nm polystyrene film.

The first experimental investigation included in the thesis describes a study on a transition in the diffusion mechanism of liquid n-hexane in thin PS films [1]. It is shown that in a very narrow temperature range around room temperature, from 16 - 28°C, the process changes characteristics from simultaneously occurring Fickian diffusion and polymer relaxation to purely relaxation limited Case II diffusion, Figure 1. The transition is shown to influence the kinetics dramatically with the timescales of the processes changing from several hours at 16°C to a few minutes at 28°C. Ellipsometry

Probing the surface swelling in ultra-thin supported polystyrene films during case II diffusion of n-hexane

The detailed optical modeling approach of the Case II diffusion, developed in the previous study, is applied to probe superimposed effects of nano-confinement and penetrant in ultra thin PS films [2]. It is shown that a region of about 14±3 nm exists in the outer surface of these glassy films that is swollen almost instantaneously upon contact with the penetrant, Figure 2. After this interfacial region is swollen, a much slower front diffusion follows. These findings may have significant implications for the areas where small molecule penetrants diffuse through ultra thin glassy polymer layers, i.e. membrane separations.

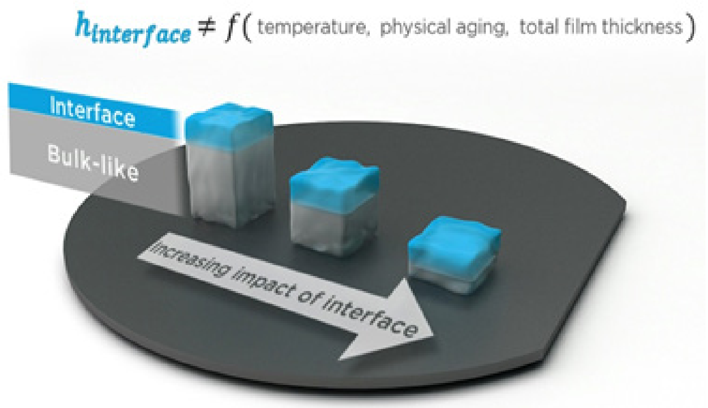

Figure 2: Increasing impact of the fast swelling interface with the reduction of total film thickness..

On the determination of penetrant volume fraction in swollen glassy polymers by means of effective medium approximation (EMA) in conjunction with optical reflection methods

The very high precision of in-situ spectroscopic ellipsometry is utilized to develop a procedure to accurately determine penetrant volume fraction in thin swollen glassy polymer films. The method is based on a Bruggeman Effective Medium Approximation and takes account for the relaxation of non-equilibrium Excess Fractional Free Volume (EFFV) of a glassy polymer upon sorption above glass transition temperature of the polymer – penetrant mixture, Figure 3. The newly developed method is compared to those not taking account for the EFFV relaxation but frequently applied in literature. The errors in penetrant volume fractions obtained when relaxation of EFFV is not accounted for are shown to be especially large for membrane-related high EFFV polymers, such as poly[1-(trimethylsilyl)-1-propyne] (PTMSP).

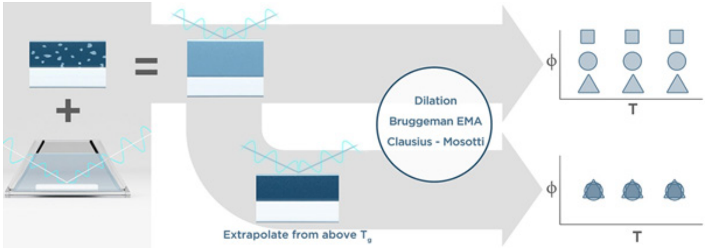

Figure 3: Schematics of a newly developed calculation approach to account for excess fractional free volume relaxation in swollen glassy films.

The subtle differences between temperature and penetrant induced glass transition in thin glassy films

This study focuses on the sorption and relaxation processes that occur in the vicinity of penetrant induced glass transition, Pg. It is shown for the first time, that although Pg is phenomenologically similar to thermally induced glass transition, Tg, significant differences in the dynamic behavior exist. These differences are related to the much more pronounced polymer matrix deformation by the sorbing penetrant around Pg that seems to activate complex long term chain relaxation processes. The dilation curvature alteration cannot always be straightforwardly treated as an indication of glass transition, as done in the case of the Tg. Such a slope change in the case of the Pg, is a complex consequence of mutually influencing sorption and relaxation phenomena, and is very much affected by the sample conditioning history. These findings are anticipated to contribute to better understanding of the complex plasticization phenomena in ultra-thin membranes.

Swelling dynamics of zwitterionic films in the presence electrolytes

The next two parts describe dynamic studies on thin films of zwitterionic polymers based on sulfobetaine methacrylate and n-butylacrylate. These materials represent an interesting class of polymers with a large potential in reduction of biofouling in ultrafiltration membranes. The first study, Figure 4, focuses on the characterization of the overshoot dynamic swelling response in the material upon exposure to 1 M NaCl solution [3]. Emerging and vanishing optical anisotropy within the polymer films is reported. The second study explores the effects of different salts and their concentration on the swelling the same polymer. The work provides meaningful insights on the behavior of zwitterionic copolymer films for applications such as membrane filtration with different salts and ionic strengths.

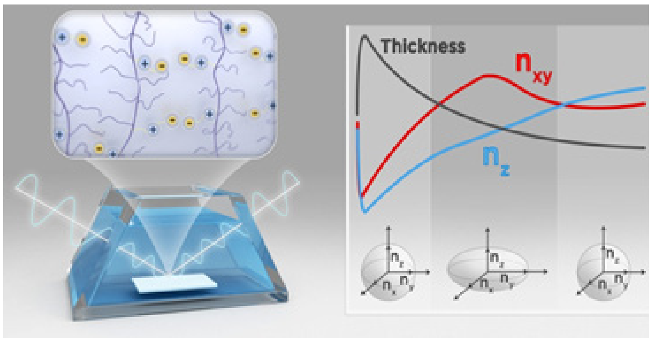

Figure 4: A dynamic study on emerging and vanishing optical anisotropy in swollen thin zwitterionic films.

Ellipsometry on composite membranes consisting of a thin selective layer and a porous substrate

Often in membrane technology composite membranes consisting of a porous substrate and a thin separating film are employed. Application of ellipsometry to such systems has been severely limited by the size of the substrate roughness and porosity. These surface features resulted in unwanted probing light scattering effects. In the Thesis appropriate optical models are developed that allow in-situ ellipsometry analysis of composite membranes, Figure 5. The models consider the surface roughness of the support as a distinct, graded density layer and are shown to be applicable to composite membranes with relatively thick, ~1 µm, separating layers [4]. The developed optical models are utilized for the non-equilibrium, high pressure permeation investigation of thin PDMS membranes [5]. This study utilizes the newly developed high pressure in-situ ellipsometry chamber which permits investigating the membrane behavior in conditions by far exceeding the ones found in nanofiltration Figure 6. It is found that the confinement of the films to the substrate implies the necessity of elastic deformation network correction. In the pressurized swollen film, the thickness and refractive index are found to be independent of pressure in the range of 1 – 100 bar suggesting that the molar volumes of the penetrant in the liquid and sorbed phases are not significantly different.

When a pressure difference over the membrane is applied and the solvent is allowed to permeate, a progressing reduction in thickness of the membrane is observed with increasing upstream pressure. The derived concentrations of n-hexane at the interface between thin film and support, at the permeate side, are in excellent agreement with values

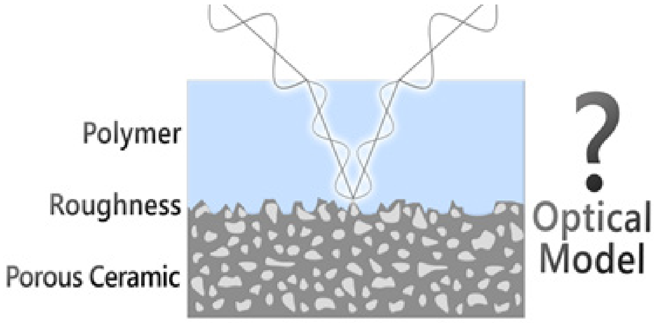

Figure 5: Schematics of ellipsometry analysis of a composite membrane, for which appropriate optical models have been developed.

calculated using the Solution-Diffusion model. This implies that in-situ spectroscopic ellipsometry allows quantification of the contribution of Solution-Diffusion to mixed mode transport through composite membranes.

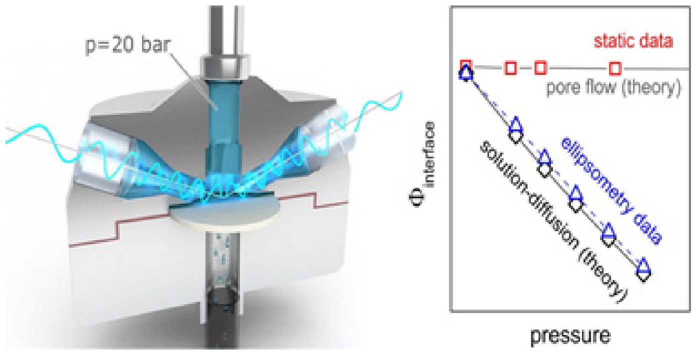

Figure 6: Schematics of a high pressure ellipsometry chamber allowing studying models describing transport through membranes.

Effects of time, temperature, and pressure in the vicinity of the glass transition of a swollen polymer

The last experimental study included in the Thesis extends the application of variable temperature and pressure ellipsometry to supported glassy films. In this work the effect of time, temperature, and pressure in the vicinity of the solvent induced glass transition are studied. Dynamic temperature scans reveal the pronounced changes in both equilibrium and kinetic properties of the system upon vitrification. The phenomenon of kinetically arrested swollen matrix is observed and explained in terms of the significant changes in the penetrant diffusion coefficient and the simultaneous emergence of the glass compression energetic barrier below the glass transition of the polymer – penetrant mixture. The PS – n-decane system shows no measurable compression, in a sense of the free volume reduction, when exposed to hydrostatic pressures up to 50 bar neither above or below its glass transition temperature. A small, but well resolvable, compression is shown to occur in dry polystyrene and is correlated to the partial relaxation of the excess fractional free volume. The results are of importance for membrane technology where swollen glassy selective layers are operated under high pressures to provide for molecular transport by solution-diffusion. At the end of the Thesis an outlook is provided of the remaining and interesting research questions that could be pursued in the future. The examples are divided into several categories, highlighting the entirely new directions, follow-up studies and attempts which couple in-situ ellipsometry with other techniques. Most of the content of the outlook is supported by a significant amount of preliminary results and observations.

For more information, please contact Dr. ir. Nieck E. Benes (n.e.benes@utwente.nl) or M.Sc. Wojciech Ogieglo (w.ogieglo@utwente.nl).

References

[1] Ogieglo, W., et al., Temperature-induced transition of the diffusion mechanism of n-hexane in ultra-thin polystyrene films, resolved by in-situ Spectroscopic Ellipsometry. Polymer, 2013. 54(1): p. 341-348.

[2] Ogieglo, W., et al., Probing the Surface Swelling in Ultra-Thin Supported Polystyrene Films During Case II Diffusion of n-Hexane. Macromolecular Chemistry and Physics, 2013. 214(21): p. 2480-2488.

[3] Ogieglo, W., et al., Relaxation induced optical anisotropy during dynamic overshoot swelling of zwitterionic polymer films. Thin Solid Films, 2013.

[4] Ogieglo, W., et al., Spectroscopic Ellipsometry Analysis of a Thin Film Composite Membrane Consisting of Polysulfone on a Porous α-Alumina Support. ACS Applied Materials & Interfaces, 2012. 4(2): p. 935-943.

[5] Ogieglo, W., et al., n-Hexane induced swelling of thin PDMS films under non-equilibrium nanofiltration permeation conditions, resolved by spectroscopic ellipsometry. Journal of Membrane Science, 2013. 437(0): p. 313-323

First graduation `European Master in Membrane Engineering'

At the end of the academic year 2012/2013, the first 18 EM3E students received their Master degree in Membrane Engineering. Within this European funded Erasmus Mundus educational program, the University of Twente collaborates with five other European universities, i.e. Universidade Nova de Lisboa (Portugal), Universidad de Zaragoza (Spain), Institute for Chemical Technology (Prague), Université Paul Sabatier (Toulouse, France) and Université Montpellier 2 (Montpellier, France). The EM3E Membrane Engineering program is a multiple degree Master program in Membrane Science and Technology at the interface between materials science and chemical Engineering. During the first semester of the first year, the students follow courses in France on materials science (Montpellier) or chemical engineering (Toulouse). During the second semester they continue their education in Prague. The second year they spend at the collaborating universities in Spain, Portugal or Twente, depending on the preferred application area. For the University of Twente the leading research theme is Water and Energy, while the Universidade Nova de Lisboa focuses on Biotechnology, Food and Health and the program at the Universidad de Zaragoza is dedicated towards Nanotechnology. Although many students apply for this program, only the top students are selected and receive a grant of the EU. The students get the opportunity to study and live in three different European countries, which is a very valuable experience. The students highly appreciate the program, its multidisciplinarity and the multicultural character.

Erasmus Mundus is an Excellence Program of the European Union. It aims at improving the quality of the European higher education, to promote it and to strengthen the collaboration between EU and non-EU countries.

Characterization of membranes for aqueous applications

Introduction

Pressure driven membrane processes are extensively applied for water purification and other aqueous filtrations. Well known pressure driven membrane processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). While MF and UF membranes separate on size differences between solute and pore diameter, NF and RO membrane are more dense and can be charged. This implies that NF and RO separation properties can also de determined by other interactions (charge, solution/diffusion).

To predict and understand the separation performance of pressure driven membranes, their characterization is essential. Two different types of characterization methods can be distinguished for porous membranes. The first type determines so called 'structure-related' characteristics of a membranes, which include pore size- and pore size distribution, (top layer) thickness and porosity of the membrane. 'Permeation-related' characteristics of a membrane provide information on the actual separation and involve flux measurements, molecular weight cut-off, and other retention measurements. Since pore size and -shape are not well defined, it is important to realize that it is very difficult to directly relate the structure-related parameters to permeation-related parameters.

At the Membrane Technology Group we have many characterization techniques available for membranes for aqueous applications. By choosing one or more of them, a better understanding of the performance and properties of porous membranes can be obtained. A few techniques are discussed in more detail below.

Capillary Flow Porometry

A well know characteristic of a microfiltration membrane is the bubble point. The method is based on measuring the gas flow across a liquid-filled membrane as a function of the applied gas pressure. The bubble point is defined as the pressure where the first gas bubble penetrates through the pore. Its value is given by the well known Laplace equation, which for circular pores and full wetting can be written as:

$$r_p = \frac{2\gamma}{\Delta P}$$

were r_p is the pore radius (m), γ the surface tension between the gas and the liquid (N/m) and ΔP the pressure difference (N/m^2). The bubble point method only gives the size of largest active pore in the membrane. To determine the pore size distribution of a microfiltration membrane, gas

Figure 1: Porolux™ 1000 capillary flow instrument.

pressure increase can be combined with a continuous measurement of the gas flow across the opened pores in the membrane. This technique is known as Coulter Porometry (named after a manufacturer of the equipment) or Capillary Flow Porometry. For this we use a Porolux™ 1000 (IB-FT GmbH) instrument (Figure 1). Although designed for flat sheet membranes, we adapted our equipment to be able to measure hollow fiber membranes.

This method starts with wetting an MF membrane with a pore filling liquid, usually a fluorinated hydrocarbon (Porofil™ or Galpore™). While increasing the gas pressure, starting at very low values, the gas flow across the membrane is measured continuously. At a certain minimum pressure the largest pore opens (the bubble point) and a gas flow can be detected. Further increase of the gas pressure will result in opening of smaller pores, and consequently a higher gas flow is measured. After all pores are opened ('wet curve'), the gas pressure is decreased to the starting value and the gas flow through all open pores is measured as a function of applied pressure ('dry curve'). From both curves (see Figure 2), the pore size distribution can be calculated using the Laplace equation and assuming circular pores. This includes also the minimum-, mean flow-, and maximum pore sizes. The mean flow pore size is defined as the pore size where the wet curve crosses the 'half-dry' curve (dotted green line in Figure 2). According to the manufacturer's information, the Porolux™ 1000 can be used for membranes with pore sizes between 13 nm and 500 μm. However, this depends very much on the pore filling liquid used, and the mechanical strength of the membrane. Especially for polymeric membranes, the material might not withstand the gas pressure necessary to open up small pores, e.g. when ultrafiltration membranes are tested. For ultrafiltration membranes, an in-house designed and built instrument can be used. This technique is called permporometry, is suitable for polymeric UF membranes (flat as well as hollow fiber shapes), and measures pores in the range 1.5-50 nm. Permporometry was described in detail in our Membrane News Twente edition Winter 2012.

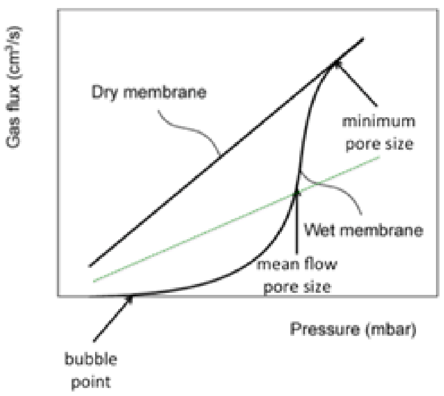

Figure 2: Schematic gas flow as a function of the applied pressure.

MWCO determination

The Molecular Weight Cut-Off (MWCO) value often is used by membrane manufacturers to characterize their porous ultrafiltration membranes. It is a typical permeation-related membrane characteristic. The value is defined as the molecular weight (MW) which is rejected for 90%. The rejection is defined as

$$R = \frac{c_F - c_P}{c_F} = 1 - \frac{c_P}{c_F}$$

where R is the rejection [-], c_F the feed concentration of a solute and c_P the permeate concentration of this solute. The rejection depends on many solute and process parameters like the type of solute, concentration, hydrodynamics, pressure, temperature and pH. MWCO measurements usually are carried out in separate experiments using different solutes, each with a certain MW. This results in a time consuming procedure for MWCO determination, in addition also neglecting differences in shape and flexibility of the solute and phenomena like concentration polarization and adsorption of the solute on the membrane.

At MTG we therefore do not use single solutes but a mixture of dextranes or polyethylene glycols (PEG) covering a broad molecular weight range around the expected MWCO. Tests are carried out in a standardized cell, where we carefully control pressure and cross flow velocity in order to create standard conditions for the measurements. After the permeation experiment is carried out, the MW distributions of feed and permeate are determined using Gel Permeation Chromatography (GPC). By calculating the rejection for each MW using the equation mentioned before, the rejection as a function of MW can be determined in a single permeation experiment. The molecular weight where the rejection is 90% now easily can be verified.

Scanning Electron Microscopy

One direct and powerful method to visualize pores in membranes makes use of Scanning Electron Microscopy (SEM). A SEM generates a small beam of primary electrons which are directed towards a membrane sample. Once these hit the membrane, they interact with electrons in the sample resulting in different signals. These signals create the final image. Secondary Electron Imaging (SEI) is the most often used signal. Secondary electrons are originating from the k-shell of the specimen atoms as a result of inelastic collisions with the beam electrons. SEI is used to visualize pore size (distribution) and -shape, membrane symmetry, cross sectional structure, toplayer thickness, and the presence of macrovoids. Backscattered Electron Imaging (BEI) is based on elastic collisions with the beam electrons. Larger atoms produce more backscattered electrons, and therefore result in a brighter image. BEI can be used to discriminate between regions with different chemical compositions. Finally, X-rays are generated in a SEM. These X-rays have energies typical for a certain element. Analyzing these energies gives information on the elements present in your sample. This technique is called Energy Diffraction Spectroscopy (EDS).

At MTG two SEMs are available. The JEOL JSM-6010LA is a brand new SEM capable of EDS analysis. It is a Low Vacuum SEM, capable of magnifications up to 50,000x, and high vacuum observations up to 300,000x (practically 50,000x at 5 kV). It has a SEI, a BEI and a Low Vacuum SEI detector. Besides these, the JSM-6010LA has an EDS detector which allows us to do record an EDS spectrum as well as to do EDS mapping. Elements from Boron upwards (with only a few exceptions) can be measured. This makes the 6010LA very suitable e.g. for investigation of membrane fouling.

The second SEM in our group is a JEOL JSM-6000F Field Emission SEM (FESEM). Instead of a Thermionic Emission Gun, the primary electron beam is generated using a Field Emission Gun. This results in a much smaller spot size at lower accelerating voltages, and consequently less damaging of the (polymeric) membrane sample. A much better resolution of max. 0.6 nm at 30 kV can be obtained (compared to 3.5 nm at 20 kV for a normal SEM). The JSM-6000F FESEM therefore is very suitable for higher magnifications (theoretically up to 950,000) and thus can even make pores of UF membrane visible. Figure 3 gives two examples FESEM images of an open UF membrane. t is important to realize the following drawbacks of SEM. Firstly, the sample needs to be

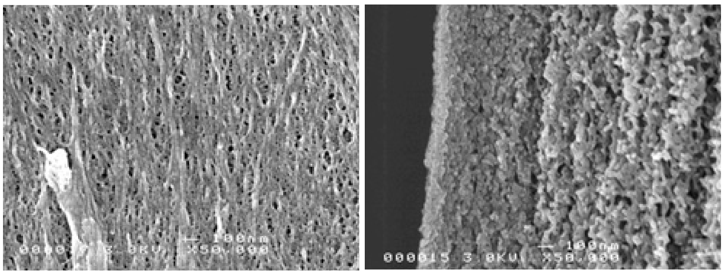

Figure 3: FESEM images of the surface and cross section of an open UF membrane (magnification 50,000x).

Idry before analysis, with the risks of pore collapse. Depending on the applied voltage and vacuum it requires a coating by e.g. gold or platinum to make the polymeric material conductive. In other words, the applied sample preparation technique might influence the porous structure on the images. At high magnifications or accelerating voltages the sample might be damaged. SEM usually does not give information on pore length and tortuosity. Finally, MF membranes often are depth filters implying a surface view will not show the right pore size.

If you want to know more on these and other characterization methods available at MST or you want your samples to be analyzed, please contact the EMI Twente:

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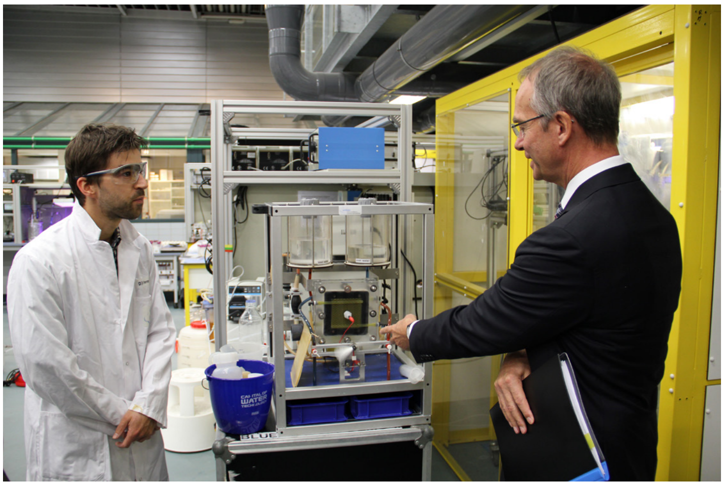
Blue Energy – Power from mixing seawater and river water

The Dutch minister of economic affairs Henk Kamp visited Wetsus, in Leeuwarden, at October 28. Because Wetsus contributes to the economic activity in Friesland, and is co-funded by this ministry, he was interested in the inventions and research developed at Wetsus and the related universities. Mr. Kamp was introduced among others in the research to reverse electrodialysis (Blue Energy), and was impressed by the potential of this pretty unknown renewable energy source. He listened with interest to the principle of this technology and the developments made at Wetsus and the Membrane Science & Technology group of the University of Twente.

Although Mr. Kamp was not aware of the technical principles, he did know about the technology from his colleague, Mrs. Schultz van Haegen, minister of Infrastructure & Environment, who opened a RED pilot plant facility at the Afsluitijk in The Netherlands four weeks earlier. This pilot plant facility of REDstack B.V. will test the power production from mixing seawater from the Wadden Sea and fresh water from the IJsselmeer. This facility has a capacity of 50 kW. Based on the MW can potentially be generated from mixing seawater and fresh water at this location.

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



Minster Henk Kamp (right) and David Vermaas (left) near a demonstration setup for reverse electrodialysis (RED).

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Membrane design for energy generation by reverse electrodialysis

Enver Guler

Reverse electrodialysis (RED) is a clean, sustainable, and thus a promising and potentially attractive technology for the generation of energy from the mixing of solutions with different salinity [1]. It utilizes the free energy of mixing these solutions (e.g. river water and seawater) to generate power. The principle of reverse electrodialysis is explained in Fig.1. 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 the transport of only anions towards an anode and cation exchange membranes allow only cations to pass through towards a cathode. At the electrodes a redox couple is used to provide the transfer of electrons through an external circuit, thus creating power. The ion exchange membranes are key elements in RED. However, up to now, limited research on the development of ion exchange membranes specially designed for RED has been done.

Research focus

Further improvement towards economically viable power production requires the development of ion exchange membranes especially designed and developed for RED. A large community of polymer chemists deals with the development of cation-exchange membranes, but the research on anion exchange membranes is limited. Although several routes are available for the preparation of cation exchange membranes, the possibilities for high-performance anion membranes (AEMs) are not broad. Therefore, development and preparation of AEMs is of special importance for a successful RED operation. This PhD research investigates the design and development of the RED process, with a special focus on fabrication, characterization and optimization of anion exchange membranes.

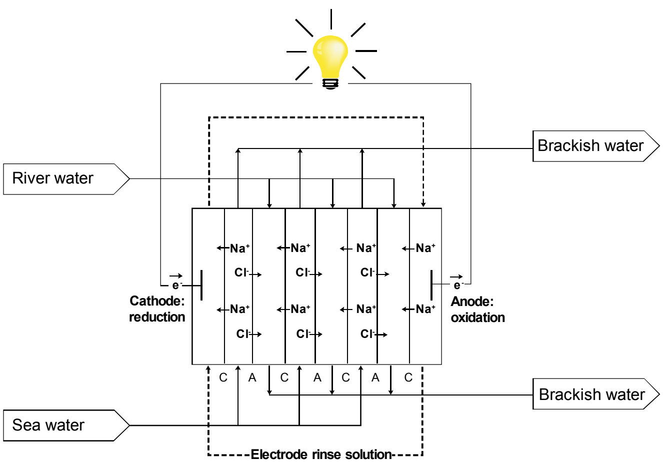


Figure 1: Schematic representation of a RED process.

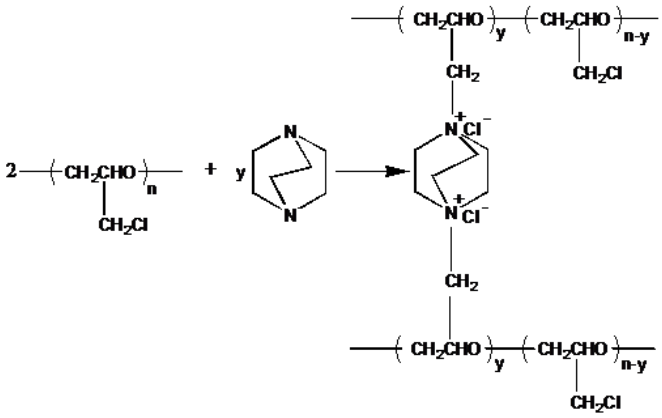


Figure 2: Reaction mechanism of amination-crosslinking of PECH polymers for anion exchange membrane preparation.

Fabrication of tailor-made anion exchange membranes

The conventional way to prepare AEMs usually requires many steps like polymerization, chloromethylation, amination and cross-linking. Among these, especially the chloromethylation reaction is not easy to handle, and requires the use of chloromethyl methyl ether, which is highly toxic and carcinogenic. In this study we have developed a method for the design and preparation of anion exchange membranes for application in RED. We adopted the elastomer polyepichlorohydrin (PECH), which has inherent chloromethyl groups, as polymer matrix (Figure 2), so that the chloromethylation reaction could be avoided [2].

We developed a membrane fabrication process for homogenous anion exchange membranes based on a single-step, environmentally-friendly method using a pre-halogenated polyether, polyepichlorohydrin (PECH). Such PECH membranes were prepared by blending PECH with polyacrylonitrile (PAN) to improve the mechanical stability. To the best of our knowledge, for the first time such tailor-made homogeneous anion exchange membranes were tested in a real RED stack (Fig. 3). Thinner membranes performed better as they had lower area resistances compared to that of relatively thick, commercially available membranes. Very thin anion exchange membranes with a thickness of 33 µm could be fabricated with a very low area resistance of 0.82 $\Omega \cdot cm^2$, resulting in the highest power density reported to date (1.27 W/m^2). To optimize the membrane properties such as area resistance and permselectivity, the blending ratio of active polymer PECH to supporting polymer PAN and the relative

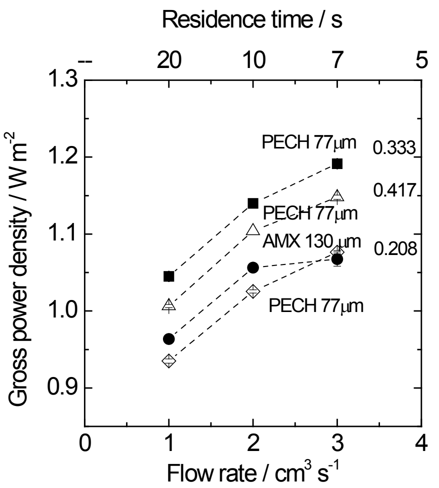


Figure 3: Practically obtained gross stack power density determined for tailor-made PECH membranes as a function of the flow rate for different blend ratios (■ CMX/PECH B-2; Δ CMX/PECH C; ● CMX/AMX; ◊ CMX/PECH A). Cation exchange membrane: CMX. The performance of the AMX membrane is shown for comparison.

amount of the aminating agent, DABCO, in the film forming solution (i.e. membrane casting solution) were varied. As the relative amount of PECH increased in the membrane casting solution, the area resistance exhibited a decreasing trend, as there are more functional groups available for amination thus increasing the ion-conducting properties. With increasing blend ratio, permselectivity decreased. This variation was attributed to the increased swelling degree with increasing blend ratio. When the amount of aminating agent was increased in the membrane casting solution, it was observed that, up to a certain amount, permselectivity improved and area resistance decreased due to simultaneous amination and crosslinking. At higher values of aminating agent, the variation of these parameters was almost independent. With increasing blend ratio, permselectivity decreased. This variation was attributed to the increasing degree of swelling with increasing blend ratio.

Performance-determining membrane properties

The electrochemical and physical properties of the membranes are RED performance-determining factors. Although several studies regarding the optimization and modeling of membrane properties for RED have been performed, conclusions based on real experimental data of the relationship between physicochemical membrane bulk properties and power density (power output per unit membrane area) were still lacking. In this work, bulk membrane properties of both a series of commercially available membranes and tailor made membranes and correlations of those to experimental RED performance data were investigated [3]. A RED stack completely built with tailor-made membranes, made of polyetheretherketone (SPEEK) as cation exchange membrane and polyepichlorohydrin (PECH) as anion exchange membrane was successfully constructed. The highest gross power density (1.3 W/m^2) was observed with the stack built with tailor-made membranes relative to the stacks built with commercially available membranes (Fig. 4).

For membrane designers, it is essential to know the governing membrane properties that are performance-determining in a RED process, as that defines the membrane fabrication routes and the ways how to optimize and improve the membranes. Thus, a, so-called `ANalysis Of VAriance`, ANOVA (sensitivity analysis), was performed. The results showed that a distinct correlation exists between the membrane resistance and the gross power density, rather than between the permselectivity and the gross power density.

Monovalent-ion-selective membranes

When natural seawater and river water are used as feed solutions in RED, the presence of multivalent ions is inevitable. Multivalent ions have a performance declining impact on the

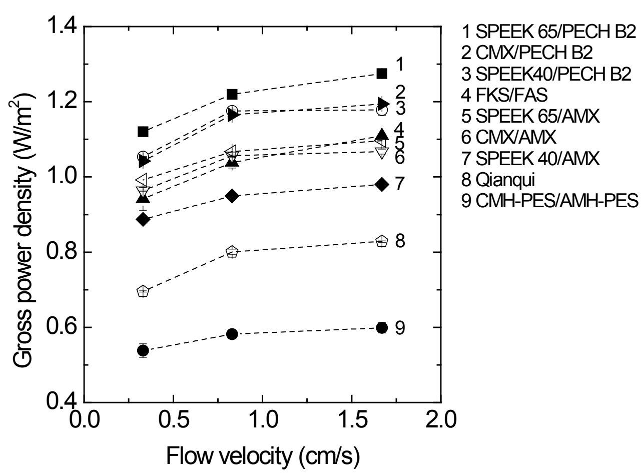


Figure 4: Experimental power density obtainable in RED for the different membrane couples investigated as a function of the flow rate (number of cells: 5; spacer thickness: 200 µm).

ion exchange membranes, i.e. these ions increase the electrical resistance and, in most cases, decrease the permselectivity. Since these membrane properties are the main performance determining factors in RED, the use of monovalent ion selective membranes that retain multivalent ions is proposed for the RED process (Fig. 5).

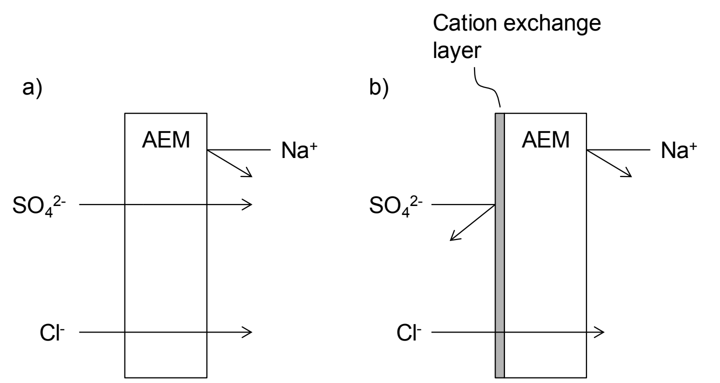


Figure 5: Mechanism of monovalent-ion selectivity by integration of a conventional ion exchange membrane (a) with a cation exchange layer (b).

Hence, the potential use of monovalent ion selective membranes in a RED system was investigated [4]. UV irradiation was used to coat anion exchange membranes (Fuji Film) with a negatively charged moiety (i.e. 2-acryloylamido-2-methylpropanesulfonic acid, AMPS, was used as active monomer). Thus, the negatively charged multivalent ions can be retained to some extent through electrical repulsion forces. After modification of the anion exchange membranes, 8% reduction of sulfate flux was achieved due to the coating layer. That corresponds to a monovalent ion selectivity that can be assumed as good as that of the commercially available Neosepta ACS membrane. Since the coating layer was negatively charged, it has also a capability to retain negatively charged matter, like organic foulants, e.g. sodium dodecylsulfate (SDS) and an slightly improved anti fouling potential was observed. SEM-EDX analyses showed that the thickness of the coating layer was about 1.5 µm only (Fig. 6) As the additional coating layer is rather thin, the area resistance of the obtained membranes did not increase significantly and standard permselectivity improved very slightly. This makes the use of such membranes advantageous over commercial monovalent ion selective anion exchange membranes (ACS and ASV), which have relatively high area resistances. However, the beneficial use of monovalent ion selective membranes was found to depend on the ionic composition of the river water. The results showed that it

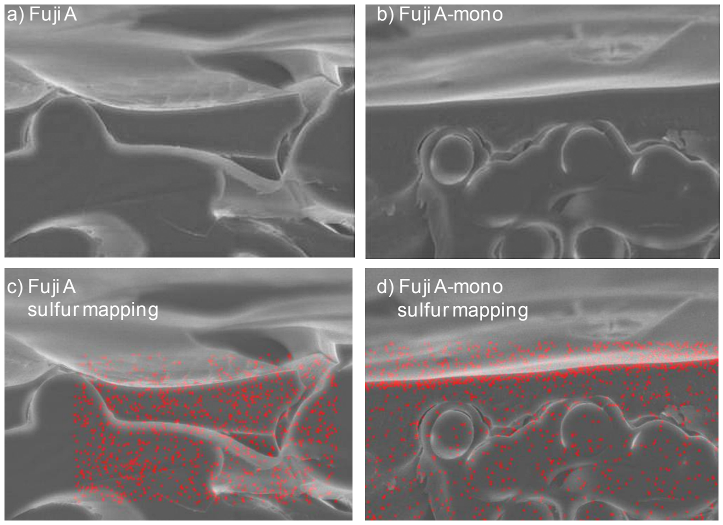


Figure 6: EDX sulfur mapping of cross-sections (magnification 2000x): (a) original Fuji A membrane (b) coated Fuji A membrane (= Fuji A-mono) (c) original Fuji A membrane with sulfur mapping (d) coated Fuji A membrane with sulfur mapping (red dots indicating sulfur-containing areas in membrane structure).

would be more beneficial to use such membranes in RED at relatively high content of multivalent ions in the river water.

Micro-structured anion exchange membranes

The use of non-conductive spacers to separate the membranes in the RED stack reduces the effective area for ionic transport thus reducing the RED performance. To eliminate this negative impact, structured anion exchange membranes with integrated flow channels were designed having different surface geometries [5]. This was done by casting the membrane forming solution on stainless steel microstructured molds followed by solvent evaporation, which creates perfect replicas of the molds. Straight ridge, wave and pillar-structured anion exchange membranes were prepared to investigate the RED performance (Fig. 7).

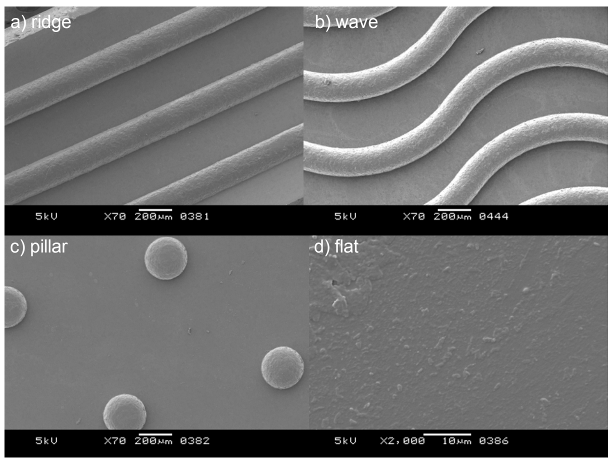


Figure 7: Surface morphology of tailor-made membranes: a) ridges b) waves c) pillars and d) flat membrane. Magnification a-c: 70x; Magnification d: 2000x.

This was the first time that homogeneous microstructured ion exchange membranes were tested in a RED stack. As homogeneous membranes usually have lower area resistances than their heterogeneous counterparts, the use of homogeneous membranes is more advantageous. Another crucial advantage of the use of micro-structured membranes in a RED stack is that the hydraulic friction (i.e. loss due to pumping) is significantly lower compared to that of the stack with flat membranes where the use of spacers is required. The knits of the filaments of the spacers behave as obstacles to fluid flow in the feed compartments thus increasing the hydraulic friction. High hydraulic frictions refer to high pumping costs that decrease the net power density obtainable in RED. For the pillar-structured membranes, next to a higher gross power density, also a 20% higher net power density was obtained when compared to their flat equivalents (Fig. 8).

Outlook

A pilot plant based on RED technology is currently being built at the Afsluitdijk (The Netherlands) using real feed waters from the Wadden sea and Lake IJssel.

The experience and know-how obtained from the present scientific research, will be transferred to this pilot scale facility to generate electricity on a large scale.

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

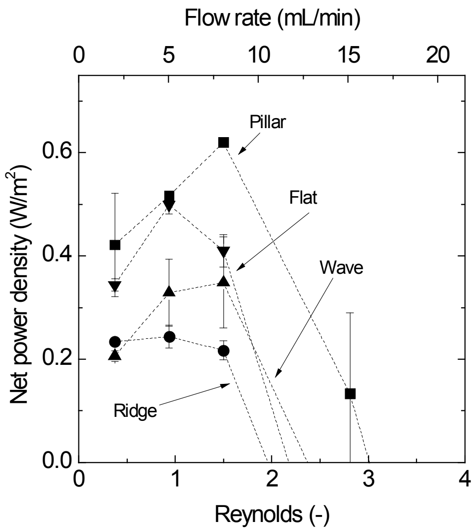


Figure 8: Net power density of the RED stacks using tailor-made anion exchange membranes.

References

[1] D.A. Vermaas, E. Guler, M. Saakes, K. Nijmeijer, Theoretical power density from salinity gradients using reverse electrodialysis, Energy Procedia, 20 (2012) 170-184.

[2] E. Guler, Y. Zhang, M. Saakes, K. Nijmeijer, Tailor-Made Anion-Exchange Membranes for Salinity Gradient Power Generation Using Reverse Electrodialysis, ChemSusChem, 5 (2012) 2262-2270.

[3] E. Güler, R. Elizen, D. Vermaas, M. Saakes, K. Nijmeijer, Performance-determining membrane properties in reverse electrodialysis, Journal of Membrane Science, 446 (2013) 266-276.

[4] E. Guler, W. van Baak, M. Saakes, K. Nijmeijer, Monovalent-ion-selective membranes for reverse electrodialysis, Submitted to Journal of Membrane Science, (2013).

[5] E. Guler, R. Elizen, M. Saakes, K. Nijmeijer, Micro-structured membranes for electricity generation by reverse electrodialysis, Submitted to Journal of Membrane Science, (2013).

In memoriam John Heeks (1948 – 2013)

John Heeks

On Friday October 11, 2013 our employee John Heeks passed away at the age of 64 years, two weeks after his retirement. John worked for 40 years at the University of Twente, initially employed at the University restaurant and since the early 80s as laboratory assistant at the faculty of Science and Technology, supporting our research group and the practical trainings of students. As a laboratory assistant, John was responsible for the construction of small equipment, safety and neatness in our labs and ordering of chemicals and office supply. But more than that, he was a 'jack-of-all-trades', taking care of many day-to-day things. During his employment at the University of Twente, John contributed to the education and development of many Bachelor, Master and PhD students to professional researchers and scientists. John was always willing to help others. And if he was not able to do so, he always knew someone that could help. His commitment was very much appreciated. With John's death, we lost a creative, inspiring personality and a wonderful colleague.

It all started in Twente

What is your name?
Bert Gebben

What are your date of birth and your place of birth?
January 6, 1960

What is your marital status and do you have children?
Married with children (2 boys)

Where are you currently employed and what is your position (please provide a short description of your current job)?
At Teijin Aramid Research as Group Head Wet-spinning, a large central research group including Twaron's spinning pilot-plant

Where is your company located and where do you live?
Arnhem, I live in Velp on bike-riding distance from my work

When did you start your PhD and when did you receive your PhD degree?
I started in 1984 and finished in 1988 on an IOP-project

On which topic did you do your PhD?
Chemically resistant and thermally stable polymer membranes

Do you still have contacts with your former PhD students from that time?
Yes, although I left the membrane-field directly after my PhD, I still have some contacts. For example with Erik Roesink, part-time professor at the group.

What was your first job after your PhD?
I became a research scientist at Akzo Nobel Corporate Research where my working field was polymer – bio-fluid interfaces for Akzo's Pharmaceutical Division. An extremely interesting working field, I co-developed an improved pregnancy test and a new fast aids-test. The first was commercialized, the second not.

How did your career develop?
After my Corporate Research time I became projectmanager Sympatex within Akzo's Fiber division (by the way Sympatex is a membrane, applied in textile applications). After my Sympatex-period I specialized in polyester, PET, especially for bottles. After that I became Department Head Polymerization with Akzo Nobels' Fiber Division, a large research group operating in Holland and Germany. With that my career shifted more towards management and away from science.

How do you relate your career to the experience you gained during your PhD?
Although Akzo has always regarded me as a polymer scientist (not as a membrane expert), my PhD in Twente certainly helped me getting a job at one of the largest industrial research groups at that time (Akzo Corporate research in Arnhem).
For my shift to Teijin my past experience with polymer membrane formation might have helped, but I am not sure about that

How did you experience your time in Twente?
Great! I look back to this period with much delight. But I notice that among many PhD's. Doing your PhD is mostly one of the best periods in your life. To be amongst peers, to fully focus on one thing, to have plenty of time to go into depths….Of course the Twente membrane group offered a very pleasant atmosphere at that time, with the late Marcel Mulder as an important exponent.

What important things did you learn during your PhD?
That professors are just like normal people :)
For me personally: freedom in actions, trust and a friendly

surrounding are the best requisites for top performance (I try to do use this in my leadership roles in industry as well, where I also see that this does not work for everybody)

What was the biggest challenge during your PhD?
(The questions are clearly getting more difficult….)
I found out that my biggest drive was the actual development of new products (something that by the way was of great use and advantage in my industrial career), but for your PhD you need especially high scientific quality. I think combining the latter with the first was my biggest challenge.

Do you maybe remember an anecdote or a specific moment of that time?
I remember the many marriages and PhD party's we had and the "performances" we organized to celebrate these events. Especially I remember the PhD of Hans Wijmans, shortly before he went to the USA, where we all were dressed as Muppets (I was Kermit the Frog) and professor Smolders and Bargeman were dressed as Waldorf and Stadler sitting on a huge cupboard criticizing all that was going on.

What was the best moment of your PhD (except the graduation)?
There are always only a very few moments in your life that you realize (or feel) something important has come to you, something that can change the course of things. For my PhD period this was the realization that reacting the aromatic polyhydrazides with aniline to form polytriazoles worked well. It was my own idea to try this out and immediately after the first polymerizations (even far before excessive testing and evaluations) there was the "feeling" that this was a success: it would lead to interesting membranes and with this I could finish my PhD. I remember this moment very vividly.

What would you have done differently if you could do your PhD again?
Looking back I tried to do things myself too much. Of course you earn a lot from this but it is not very efficient. Later on, in industrial research, I learned and appreciated the know-how of others.

Which advice do you have for the current generation PhD students?
ENJOY every moment!! (but now I sound like an old man)

What is your precious memory of the group?
Although the complete memory is precious, I still would like to recall Marcel Mulder. Perhaps it is because of his death, but to me he (or better the memory of him) personifies the group at that time.

What could be different in our research group?
This is very difficult for me to answer because unfortunately I do not know the group and the group's work at the moment very well. But generally, being many years in industry now, I am missing the build-up of fundamental know-how within the academic world. This is really something that the industry is in need of.

What did you miss while working in the group?
You mean in those days, 25 years ago? The first thing that comes to mind is women, but I will try to mention something different: At that time I was the only one working on polymer chemistry. Sometimes I missed in-depth discussions on polymer chemistry with other people in the group. As membrane technology is a multidisciplinary field, this phenomenon of being "alone" might be recognized by others too. When I started to work at Akzo Corporate research I was amongst many other polymer chemists.

Do you maybe want to add something else? Feel free.
Actually no! I am very happy to have fulfilled this questionnaire. It took more time than I anticipated. Especially finding some useful pictures (see above) took lots of time.

CapWa

New method of getting water from industrial "smoke"

The CapWa project aims to use water vapor from factory chimneys as a new source of water. With this techniques power plants are transformed into water producers instead of big water users. The results of field tests have shown that at least 40% of water present in a flue gas of an industrial power plant using membrane technology can be recovered. For a small scale 400 MW coal fired power plant this means that apart from being self-supporting water is produced for a community with 6000 inhabitants.

The membrane and module development team together with the membrane producer and pilot constructor.

Background

CapWa is an EU FP7-funded project, coordinated by DNV KEMA, revolving around the capture of evaporated water with novel membranes. Proofs of principle field tests have proven that this technology is ready for an industrial scale pilot. Therefore, in order to upscale the production of membrane modules, an international project consortium has been put together, consisting of eleven partners from Europe and three from Africa. The consortium consists out of energy companies, paper and board industry, a membrane producer, a drinking water company and several research institutes including the European Membrane Institute Twente.

The role of EMI in this consortium is to develop new membranes and coatings and to transfer the generated knowledge to the industrial partners esp. Membrana and CUT Membrane Technology to facilitate the up scaling and to support them in the characterization and performance testing.

Introduction:

High quality water is needed for most steam generating processes Characteristics of high quality (boiler) water are that it has a low conductivity and that it contains no organic components. In order to achieve these standards, raw water needs to be treated and demineralized. This treatment process can be very laborious and costly depending on the raw water source.

Water capturing

A 400 MW coal fired power plant needs 30m^3 water/h as boiler feed water. Due to coal firing it exhausts 150m^3 water as waste through the chimney. Therefore capturing 20% makes the power plant self-supporting. When 40% is captured, which is feasible with the CapWa membranes, the power plant also produces high quality water. In arid areas this is sufficient for a small city with 6000 inhabitants.

An example of a rather clean water source is the drinking-water supply. However, even in water rich countries like the Netherlands, authorities put limits on drinking-water use for industrial purposes. Therefore, industries turn to surface water as raw water source for their steam generation process, even though the investments needed to achieve the desired water quality are significant, both technically and economically. And all these restrictions being true for water rich countries, they are even more critical in arid regions, where there is a general shortage (or even absence) of fresh surface water. A promising solution for the high quality water supply is the capture of evaporated water with novel membranes in the flue gas stream(s).

The process

An example of a thermal process that produces a flue gas is the fossil fuels burning. This flue gas contains roughly 10% - 20% water, depending on the fuel used and the applied flue gas cleaning. This flue gas water vapor is rather clean compared to surface water. One way of capturing this water would be to cool down the flue gas stream. However, this process demands a large amount of energy. Moreover the condensate contains acidic compounds, which are harmful to steam generation systems. Thus, the most efficient way to collect the water would be to recover and clean the water in one step. The water vapor capture technology reflects this idea and uses a gas separation system based on water vapor selective membranes to capture the water in the vapor phase. In order to do so, membrane modules, built up out of hollow fiber membranes coated with water-selective material, are placed in the flue gas stream. A vacuum is applied to the inside of the fibers (the permeate side) to create a driving force. During the process, water molecules migrate through the membranes. Subsequent condensation of the water vapor yields a water quality that is close to that of demineralized water. Field tests have shown that up to 40% of the evaporated water can be captured in flue gas streams having temperatures up to 65°C.

Energy savings

Next to water savings the CapWa technology also makes the power production and paper drying processes more energy efficient. The reheater in the flue gas duct, necessary to avoid condensation and thereby corrosion of the chimney, is superfluous. Utilization of latent heat from the water vapor conden–sate further improves the energy process efficiency power stations as well paper mills.

Key benefits of the CapWa technology

o The raw water source -flue gas- is free of charge.

o Twenty percent water recovery has been proven in field tests. This makes a coal-fired power plant self-supporting from a demineralized water point of view.

o Forty percent water recovery is achievable. This makes a power plant also a water producer instead of a consumer.

o The technology is competitive with current water demineralized production processes.

o There is no need for reheating of flue gasses to prevent condensation in the stack when water is recovered. This means that energy can be saved.

o Corrosion attack is mitigated in the stack.

o The technology can be applied to any gas stream that contains water vapor.

o No waste water stream is formed.

o Little to no chemicals are used in the process.

More information about the CapWa project including a short illustrative video is available on http://www.watercapture.eu

The different stadia left upper corner and then clock wise: production of the support fiber; applying the selective coating (EMI, the Netherlands), construction of the pilot (Yodfat, Israel), shipment of the modules (CUT, Germany), pilot testing (IEC, Israel) and captured water.

The CapWa is nominated for two awards

- Sustainable, useful and beautiful are the keywords for the jury of Enlightenmentz 2013. The prize, awarded by Dutch knowledge platform Sustainable Products and Utilities magazine, focuses this year on shining examples of products and processes. The CapWa concept is nominated in the category products.
- Water innovator of year 2013, a Dutch award.

Further more you will find the CapWa project in the Best Project Award: Completed Projects competition from the EU Framework Programme 7 and earlier Framework Programmes in the field of Industrial Technologies.

For more information, please contact Dr. Zandrie Borneman (z.borneman@utwente.nl).

Awards

Charu Chawla

Charu Chawla (27) participated at the Engineering with Membrane (EWM) conference, presenting her research on “Bio-fouling in ultrafiltration membranes”. The conference took place from 4-7 September 2013 at Saint-Pierre d'Oléron, France and was sponsored by the European Membrane Society. Charu was awarded the ‘Best speaker’ award for her oral presentation on “Bio-fouling assessment in point of use (PoU) drinking water systems”, which included a cash prize of 500 euros.

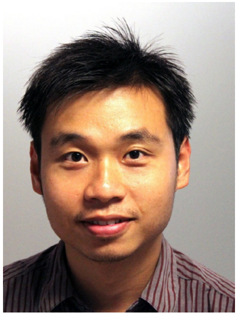
The fouling behavior of PoU systems is considerably different from large scale installations due to different operational conditions such as intermittent usage and the treatment capacity. In Charu’s PhD research, carried out at Wetsus in Leeuwarden, she intends to further understand the fouling behavior of PoU systems in order to improve the drinking water quality and quantity.

The United Nations outlines as one of its major targets the aim to reduce the number of people without access to safe drinking water by 50% (with 1990 as the base line). On a similar note, this research project is very close to her heart since she is confident that solving such problems would be helpful in eradicating some of the fundamental hurdles existing in the present day world.

So far she has established good agreement with the results obtained at EAWAG, Switzerland, who reported flux stabilization occurring at ultra-low pressure membrane filtration due to a very open biofouling layer. However, a huge potential lies ahead to further investigate the underlying biological and physical phenomenon resulting in such outcomes. This research is a part of Bio-fouling theme of Wetsus, Leeuwarden and the Membrane Science & Technology (MST) group of the faculty Science and Technology and the institute MESA+ of the University of Twente. More information on her project can be found at www.utwente.nl/tnw/mtg/people/phd/chawla/

New members

Nanofiltration for extreme conditions



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Kah Peng Lee graduated from University of Nottingham Malaysia Campus with a first class division MEng in Chemical Engineering degree in 2009. His research dissertation, titled 'Boron Removal from Ceramic Industry Wastewater by Adsorption-Flocculation Mechanism Using Palm Oil Mill Boiler Fly Ash and Polymer' was published in Water Research. His interest in water purification and separation processes led him to further pursuing his PhD study at the University of Bath, UK, under the sponsorship of the University Overseas Excellence Studentship. Under the supervision of Dr. Davide Mattia and Dr. Tom Arnot, he worked on his PhD thesis entitled 'Fabrication and Applications of Nanoporous Alumina Membranes'. The PhD work started with a fundamental and theoretical study of liquid flow in nanochannels, by using self-ordered anodic alumina membranes as the nanoporous media. This work, published in RSC Nanoscale, demonstrated experimentally for the first time the slippage of liquid flow on hydrophilic surface. Subsequently, a novel procedure was developed to prepare anodic alumina membranes in a tubular form, which subsequently were tested for practical applications, including protein separation and the formation of nanoemulsions. In addition, he also published a top 10 downloaded and cited review article in Journal of Membrane Science, on the material chemistry of reverse osmosis membranes. Upon the completion of the PhD study in August 2013, he moved to Enschede, the Netherlands, joining the Membrane Science and Technology Group at the University of Twente. He is working with Dr. Antoine Kemperman and Dr. Nieck Benes on the development of nanofiltration (NF) membranes for processes under extreme conditions. This project is executed within the Institute of Sustainable Process Technology (ISPT). At present almost all NF membranes are suitable for treatment of aqueous streams at pH levels between 2 and 10. However, many potential applications in the chemical industry require separation processes at more extreme conditions (lower or higher pH, and operation in environments with more aggressive organic chemicals). The objective of the project is to develop chemically robust NF membranes for bulk liquid separations in the chemical industry. NF membranes currently are predominantly prepared by interfacial polymerization on a support, which is often an ultrafiltration membrane. The approach of this project is to modify the chemistry of the conventional polymeric toplayer material. Interfacial polymerization is a very delicate and yet flexible process, the membrane properties can be altered by many process parameters: choice of reactants or solvents, concentration, reaction time, use of catalyst or phase transfer catalyst, etc. This project involves the understanding of the relationship between material stability and the polymer chemical structure, in addition to process optimization for ultrathin polymer film formation.

Polymeric membranes for virus disinfection, removal and de-activation from water

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My Name is Terica Raquel Sinclair, I am from the lovely island of Jamaica. I gained a Bachelor's degree in Chemical Engineering with a minor in Process and Environmental engineering from the University of Technology, Jamaica (UTECH) in 2009. My final project was entitled "Biodegradable polymers from local Cassava starch" where I developed polymer material suitable for a host of uses and after use would be beneficial to the environment as it was biodegradable. I then worked for two years as a Process engineer and Quality assurance manager at Salada foods Jamaica the country's number one choice in coffee until 2011. I was awarded the prestigious Erasmus mundus scholarship to pursue my master's in Membrane Engineering in a host of distinguished Universities across Europe (University of Montpellier II, France, Institute of Chemical Technology (ICT), Prague, Czech Republic and University of Zaragoza, Spain). In my master I specialized not only in membrane engineering and technology but I also focused on nano-science. I completed work on my final project "High- speed sterilization of water using cellulose grafted membrane with metallic nano-particles" after which I decided to move on academically and pursue a doctoral degree as I have a passion for research. I have an eclectic foundation having traveled and studied all over the world and I intend to build on that foundation during my four years of doctoral studies with the University of Twente and Wetsus where I will be working with the virus control team. As I embark on my project which aims to develop polymeric membranes for virus disinfection, removal and de-activation from water with great prospectus of being developed by our industrial partners who are very active in my project and are quite interested in my results and findings.

Fouling control in membranes using sacrificial layer approach

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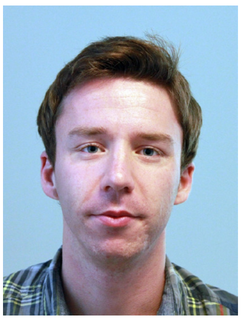
Shazia Ilyas performed her high school education with extended science education from F.G degree college, Lahore, Pakistan. After that she completed her BSc in Environmental Sciences from the College of Earth and Environmental Sciences (CEES), University of the Punjab Lahore Pakistan, in 2008. In September 2008, she joined the Institute of Environmental Sciences and Engineering, National University of Sciences and Technology (IESE-NUST), Islamabad, Pakistan and completed her Masters (MS) in Environmental Engineering in October 2010. In masters she selected the area of wastewater treatment and reuse and the topic for her masters research work was "Effects of COD/N ratios on treatment performance and fouling propensities in a membrane bioreactor (MBR) to treat domestic wastewater". The main emphasis of this research was on nutrient (nitrogen and phosphorus) removal and fouling control of an ultra-filtration membrane, using foam as an attached growth media. During her masters she also worked as a research assistant under the supervision of Prof Dr. Sher Jamal Khan for 1 year on a Higher Education Commission (HEC) funded project "Membrane Bioreactor Technology for Wastewater Treatment and Reuse". She completed her masters research work under the supervision of Dr. Sher Jamal Khan (internal supervisor) and Professor Dr. C. Visvanathan (external supervisor) from the Asian Institute of Technology (AIT) Thailand. Her masters research work was presented in 3rd and 5th International Conference on Challenges in Environmental Science and Engineering (CESE-2010) in Cairns, Australia and (CESE-2012), in Melbourne, Australia. Her work is also published in "Bioresource Technology" journal. After completing her masters, in January 2011 she joined her parent institute, the University of the Punjab. She served as university lecturer there in department College of Earth and Environmental Sciences (CEES), till November 2013. Starting October 2013, she continues her academic career as a PhD fellow under Erasmus Mundus Doctorate in Membrane Engineering (EUDIME) program at the Membrane Science and Technology Group within the University of Twente. She will be working under the coordination and supervision of Prof. Dr. Kitty Nijmeijer and Dr. Wiebe de Vos, in the project titled ``Fouling control in membranes using sacrificial layer approach``. In her part of the work, she will prepare polyelectrolyte multilayers based upon a layer by layer technique. Then effect of pH and salt concentration on sacrificial layers will be investigated. The main technique which will be used for this research is Reflectometry. Moreover the other properties of these polyelectrolyte multilayers will also be investigated, e.g., thickness, roughness, zeta potential, permeability, hydration and swellability etc. Her PhD involves two mobilities (1)University of Leuven (Belgium) for 6 months and (2) University of Montpellier 2 (France) for 6 months.

Blue Energy



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Timon Rijnaarts was born in Nijmegen on the 12th of april 1989. He studied at the high school of the Nijmeegse Scholengemeenschap Groenewoud from 2001 to 2007. Then he moved to Enschede to study Chemical Engineering at the University of Twente. He completed his Bachelor in 2010 with a thesis in the (at that time brand new) SFI group of Rob Lammertink on Porous Photocatalytic Membrane Microreactors under supervision of Can Aran. On this work a paper was published in the Journal of Photochemistry and Photobiology A.

After finishing his Bachelor he continued the Master Chemical Engineering with the specialization in Advanced Molecules and Materials. In this master he chose a broad array of subjects ranging from organic and inorganic chemistry down to nanotechnology courses, as his scientific interests are quite broad as well. In 2011 he performed an internship at the Istituto Italiano di Tecnologia in the group of

Liberato Manna on pH-responsive nanogels in Genua, Italy. He focused on tuning the pH-response by choosing new monomer starting materials for the free radical emulsion polymerization. Several characterization techniques were used to analyse the polymeric nanogels, such as NMR, (HR) TEM and DLS. Anti-cancer drug loading in these nanogels was achieved. With his fellow Chemical Engineering students he went to China for a study tour of three weeks. In this tour they visited high profile Universities and companies related to chemistry. Timon finished his Master of Science at the Molecular nanofabrication group of Jurriaan Huskens on nanoscale Metal-Organic frameworks. This project was started from scratch and involved an extensive literature study, development of several synthetic routes for these novel particles and numerous characterization techniques (i.e. XRD, SEM, EDX and XPS).

Apart from his scientific work, Timon also enjoyed teaching the next generation of students chemistry. After his graduation in Chemical Engineering in January 2013, he enrolled for the Science Education Master to obtain his teachers degree in Chemistry. He was a teacher on the Grundel high school in Hengelo (NL) for half a year teaching Chemistry to students ranging from 14 to 18 years old. In August 2013 he finished his Science Education degree with a research on Images of students on Chemists.

Sports also play a role in Timon's life. He has been quite active in sports since he was young, playing mostly football and judo during his early teen years. At the age of 17 he switched to fencing which he still enjoins today. Apart from sporting he was in the board of the Fencing association of the University of Twente for a year as Board Secretary responsible for communication, contact and planning.

In October 2013 he accepted a PhD position on Blue Energy in the group of Kitty Nijmeijer. The process involved is Reverse Electrodialysis (or RED in short). He will focus on membrane optimization through understanding of structure-property relationships. The major challenges in Ion-Exchange membranes he will evaluate are Fouling, Resistance and Monovalent-ion selectivity.

Vacancies

The Faculty of Science and Technology at the University of Twente represents a multidisciplinary environment for higher education and frontier research at the interfaces of applied physics, chemical technology and biomedical engineering. Key research topics include nanotechnology, sustainable energy, biomedical technology and technical medicine.

One of the important research themes of the faculty is Membrane Science & Technology. The group is the only academic polymer membrane group in The Netherlands and internationally leading in the field of membranes for Energy and Water Applications. Knowledge valorization occurs through the European Membrane Institute Twente (EMI Twente), which is a separate entity within the research group.

Within the research group Membrane Science and Technology of the University of Twente, we have a vacancy for a Ph.D. position.

Ph.D. position: "Understanding and controlling membrane fouling in produced water treatment" (location: TTIW Wetsus, Leeuwarden, NL)

Recent developments in oil production technologies emphasize the application of Improved Oil Recovery (IOR) and Enhanced Oil Recovery (EOR) technologies. These processes rely on the injection of large amounts of aqueous liquids into an oil reservoir, after which the crude oil is pumped back out along with dirty, so called produced water. This produced water then needs to be treated (cleaned) before disposal or re-injection of the water become a possibility.

Membrane technology is a very promising technology for produced water treatment, especially as it is one of the few technologies that can remove micron sized oil droplets. Still, membranes used in this process suffer from severe membrane fouling. In the complex mixture that is produced water, many components or combinations of components can foul the membrane leading to very substantial decreases in the flux of treated water. An added problem is that the fouling mechanism is poorly understood, making it difficult to design strategies to mitigate fouling.

In this project the focus is on first understanding and then controlling membrane fouling in produced water treatment. Using artificial produced water we will carefully study the interactions of the many components in produced water with membranes and model surfaces, to determine the exact fouling mechanisms. Based on this gained knowledge we will design ways to control membrane fouling, for example by functional membrane coatings or by feed additives.

The research will be conducted at Wetsus in Leeuwarden, NL (www.wetsus.nl) under the supervision of the Membrane Science and Technology group, faculty of Science and Technology of the University of Twente (www.utwente.nl/tnw/mst).

We are looking for highly motivated and enthusiastic researchers with an MSc degree in physical chemistry, colloid chemistry or a related topic, with 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, curriculum vitae (including references) and a list of BSc and MSc courses and grades to Dr. Ir. Wiebe M. de Vos (w.m.devos@utwente.nl; phone: +31 53 489 4495).

Within the research group Membrane Science and Technology of the University of Twente, we have a vacancy for a Ph.D. position.

Ph.D. position: "Membrane, module and process design for super critical CO_2 dehydration"
(location: TTIW Wetsus, Leeuwarden, NL)

There exists a strong interest in the drying of supercritical CO_2 gas streams with gas separation membranes. Current state of the art is the use of zeolite columns for the selective adsorption of water vapor. This process has several disadvantages, like large and heavy equipment and the discontinuity of the process (regeneration of the zeolite). The recirculation of compressed gas is very expensive and hard to defend economically as the removal of the water is done thermally. In this project the possibilities of membranes for dehydration of supercritical CO_2 will be explored. Such membranes transport water vapor preferably over CO_2 and offer an alternative route for the drying of such streams. The project involves membrane design, module construction and process and performance evaluation.

The research will be conducted at Wetsus in Leeuwarden, NL (www.wetsus.nl) under the supervision of the Membrane Science and Technology group, faculty of Science and Technology of the University of Twente (www.utwente.nl/tnw/mst).

We are looking for highly motivated and enthusiastic researchers with an MSc degree in chemical engineering or a related topic, with 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, curriculum vitae (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).

Wetsus, the research groups Environmental Technology of Wageningen University and the research group Membrane Science and Technology of the University of Twente have a vacancy for a PhD position.

Ph.D. position: "Dynamic gel-layer membranes for (waste) water filtration"
(location: TTIW Wetsus, Leeuwarden, NL)

Separation of particles is very important in (waste)water treatment. Particle separation by micro- and ultrafiltration (MF and UF) offers the advantage that 100% separation efficiency can be achieved. However, these membranes are expensive (typically 50-100 €/m2) and suffer from fouling. This proposal aims to develop an alternative by using a cheap supporting material for a dynamic gel-layer, which acts as the actual separation layer for small (colloid sized) particles (alternative for MF/UF membranes), and later on also for removal of specific dissolved substances (alternative for NF/RO membranes). The project involves membrane design and development, characterization and application. Due to (biological) degradation, fouling, compaction or other mechanisms, performance of the gel-layer will deteriorate in time. To address this aspect, also long term stability and removal and replacement mechanisms will be investigated. For more NF or even RO related applications it is possible to embed specific constituents in the gel layers that selectively remove e.g. organic micropollutants or specific ions. Additionally, to evaluate membrane performance under real conditions, larger scale experiments with realistic waste waters will be performed.

The research will be conducted at Wetsus in Leeuwarden (www.wetsus.nl), NL under the supervision of the research groups Environmental Technology of Wageningen University (http://www.wageningenur.nl/en/Expertise-Services/Chair-groups/Agrotechnology-and-Food-Sciences/Subdepartment-of-Environmental-Technology.htm) and the research group Membrane Science and Technology of the University of Twente (www.utwente.nl/tnw/mtg). Wetsus, centre of excellence for sustainable water technology, is a facilitating intermediary for frontier water research. The multidisciplinary collaboration between companies and universities from all over Europe in Wetsus results in innovations that contribute significantly to solutions for the global water problems. The sub-department of Environmental Technology of Wageningen University performs research in the field of Reusable Water, Renewable Energy and Recyclable Matter including soils and sediments. In cooperation with other research groups ETE addresses cleaner production issues and sustainable material chains. The Membrane Science & Technology group of the University of Twente is the only academic polymer membrane group in The Netherlands and internationally leading in the field of membranes for Energy and Water Applications. Research ranges from molecule to process and comprises the complete knowledge chain from membrane design and development, membrane characterization and application.

We are looking for highly motivated and enthusiastic researchers with an MSc degree in chemical engineering, bioengineering or a related topic, with excellent experimental and theoretical skills and an affinity for (micro)biological processes.

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, curriculum vitae (including references) and a list of BSc and MSc courses and grades to Dr. Hardy Temmink (hardy.temmink@wur.nl; phone: +31 317 484 805; Wageningen University) or Dr. Ir. Antoine Kemperman (a.j.b.kemperman@utwente.nl; phone: +31 53 489 2956; University of Twente).

PhD Defenses

Jeroen Ploegmakers

Membranes for ethylene/ethane separation

December 13, 2013, 16.45 h, University of Twente

David Vermaas

Energy generation from mixing salt water and fresh water - Smart flow strategies for reverse electrodialysis

January 17, 2014, 12.45 h, University of Twente

Enver Güler

Anion exchange membrane design for reverse electrodialysis.

January 31, 2014, 16.45 h, University of Twente

Wojciech Ogieglo

In-situ spectroscopic ellipsometry for studies of thin films and membranes

March 21, 2014, 16.45 h, University of Twente

Publications

- Erik van de Ven, Anisa Chairuna, Geraldine Merle, Sergio Pacheco Benito, Zandrie Borneman, Kitty Nijmeijer, Ionic liquid doped polybenzimidazole membranes for high temperature Proton Exchange Membrane fuel cell applications, Journal of Power Sources 222 (2013) 202-209, doi: 10.1016/j.jpowsour.2012.07.112
- Nico Wolthek, Klaasjan Raat, Jan Arie de Ruijter, Antoine Kemperman, Ate Oosterhof, Desalination of brackish groundwater and concentrate disposal by deep well injection, Desalination and Water Treatment 51 (2013) 1131-1136, doi: 10.1080/19443994.2012.694205
- Olga Kattan Readi, Miriam Girones, Wika Wiratha, Kitty Nijmeijer, On the isolation of single basic amino acids with electrodialysis for the production of biochemicals, Industrial & Engineering Chemistry Research 52-3 (2013) 1069-1078, doi: 10.1021/ie202634v
- W. Ogieglo, H. van der Werf, K. Tempelman, H. Wormeester, M. Wessling, A. Nijmeijer, N. Benes, n-Hexane induced swelling of thin PDMS films under non-equilibrium nanofiltration permeation conditions, resolved by spectroscopic ellipsometry, Journal of Membrane Science 431 (2013) 233-243, doi: 10.1016/j.memsci.2012.12.045
- E.J. Vriezekolk, A.J.B. Kemperman, M. Girones, W.M. de Vos, D.C. Nijmeijer, A solvent-shrinkage method for producing polymeric microsieves with sub-micron size pores, Journal of Membrane Science 446 (2013) 10-18, doi: 10.1016/j.memsci.2013.06.014
- E. Güler, R. Elizen, D. Vermaas, M. Saakes, D.C. Nijmeijer, Performance-determing membrane properties in reverse electrodialysis, Journal of Membrane Science 446 (2013) 226-276, doi: 10.1016/j.memsci.2013.06.045
- Jeroen Ploegmakers, Adriaan R.T. Jelsma, A.G.J. van der Ham, Kitty Nijmeijer, Economic evaluation of membrane potential for ethylene/ethane separation in a retrofitted hybrid membrane-distillation plant using unisim design, Industrial & Engineering Chemistry Research, 52-19 (2013) 6524-6539, doi: 10.1021/ie400737s
- Joao André, Zandrie Borneman, Matthias Wessling, Enzymatic conversion in ion-exchange mixed matrix hollow fiber membranes, Industrial & Engineering Chemistry Research, 52-26 (2013) 8635-8644, doi: 10.1021/ie3028608
- Géraldine Merle, Annisa Chairuna, Erik van de Ven, Kitty Nijmeijer, An easy method for the preparation of anion exchange membranes: Graft-polymerization of ionic liquids in porous supports, Journal of Applied Polymer Science, 129-3 (2013) 1143-1150, doi: 10.1002/app.38799
- Marlon S.L. Tijink, Maarten Wester, Griet Glorieux, Karin G.F. Gerritsen, Junfen Sun, Pieter C. Swart, Zandrie Borneman, Matthias Wessling, Raymond Vanholder, Jaap A. Joles, Dimitrios Stamatialis, Mixed matrix hollow fiber membranes for removal of protein-bound toxins from human plasma, Biomaterials, 34 (2013) 7819-7828, doi: 10.1016/j.biomaterials.2013.07.008
- Odne S. Burheim, Jon G. Pharoah, David Vermaas, Bruno B. Sales, Kitty Nijmeijer, Hubertus V.M. Hamelers, Reverse electrodialysis as an electric power plant, Chapter in Encyclopedia of Membrane Science and Technology, edited by Eric M.V. Hoek and Volodymyr V. Tarabara, Wiley and Sons, Inc., (2013) 1482-1500, ISBN 9781118522318, doi: 10.1002/978111522318
- O.M. Kattan Readi, E. Rolevink, K. Nijmeijer, Mixed matrix for process intensification in electrodialysis of amino acids, Journal of Chemical Technology & Biotechnology, (2013), doi: 10.1002/jctb.4135
- Wojciech Ogieglo, Joris de Grooth, Herbert Wormeester, Matthias Wessling, Kitty Nijmeijer, Nieck E. Benes, Relaxation induced optical anisotropy during dynamic overshoot swelling of zwitterionic polymer films, Thin Solid Films, 545 (2013) 320-326, doi: 10.1016/j.tsf.2013.07.077
- C. Kappel, K. Yasadi, H. Temmink, S.J. Metz, A.J.B. Kemperman, K. Nijmeijer, A. Zwijnenburg, G.-J. Witkamp, H.H.M. Rijnaarts, Electrochemical phosphate recovery from nanofiltration concentrates, Separation and Purification Technology, 120 (2013) 437-444, doi: 10.1016/j.seppur.2013.10.022
- David A. Vermaas, Joost Veerman, Ngai Yin Yip, Menachem Elimelech, Michel Saakes, Kitty Nijmeijer, High efficiency in energy generation from salinity gradients with reverse electrodialysis, ACS Sustainable Chemistry & Engineering, 1-10 (2013) 1295-1302, doi: 10.1021/sc400150w
- Alexandros Daniilidis, David A. Vermaas, Rien Herber, Kitty Nijmeijer, Experimentally obtainable energy from mixing river water, seawater or brines with reverse electrodialysis, Renewable Energy, 64 (2014) 123-131, doi: 10.1016/j.renene.2013.11.001

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.

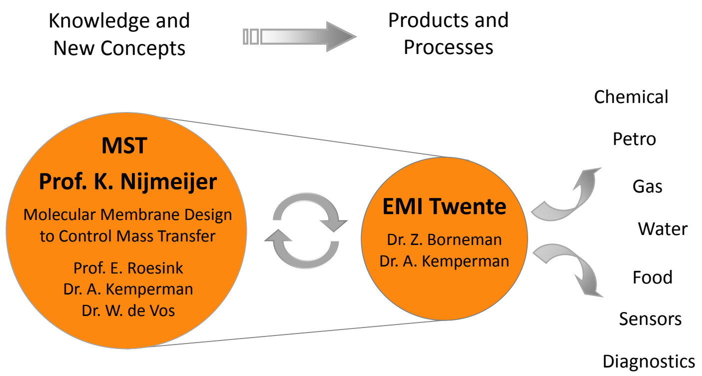

Figure 1: Organizational structure research group.

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.

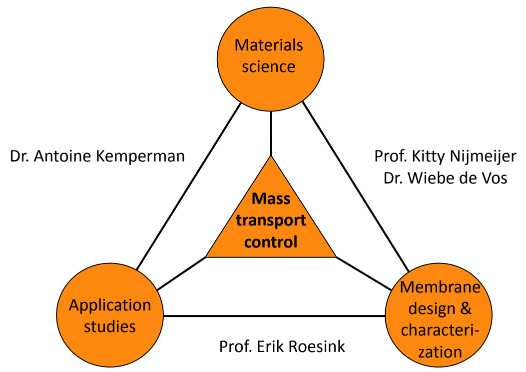

Figure 2 : Membrane Science & Technology.

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).

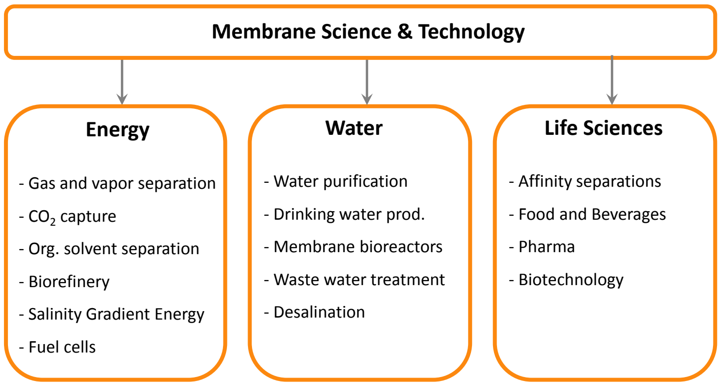

Figure 3 - Major application clusters Membrane Science & Technology.

Energy

The research cluster Energy is dedicated to the molecular design and synthesis of polymer membranes for e.g. gas and vapor separations (CO2 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 new and/or improved processes (e.g. faster processes, higher yields, less fouling). 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 longstanding 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. test cells for gas separation, UF and MF, casting knives, cloud point meters, hollow fiber spinning lines and spinnerets

More information

For more information, please contact:

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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 www.utwente.nl/tnw/mtg).

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