Water Phenomena in PEM

Sorption, Swelling and Breakthrough Processes

International Workshop
NTNU, Trondheim, Norway, 3 - 4 October 2013

FINAL PROGRAM

Chairperson
Peter Berg, NTNU, Norway

Co-Chairperson
Michael Eikerling, SFU, Canada

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Conference website: www.ntnu.edu/physics/pem2013

Financial support provided by NTNU and SIU (www.siu.no).

Program Schedule

Thursday, 03 October 2013

Room: D5-175, 5th floor, Science Building (Realfagbygget), NTNU – Gløshaugen Campus

08:30-08:45	Peter Berg, NTNU	*Welcome*
08:45-09:20	Tom Zawodzinski, Univ. Tennessee-Knoxville & Oak Ridge National Lab.	*'Thermodynamics' of water/solution-PEM interactions: New targets, methods, data and analysis*
09:20-09:55	Gérard Gebel, CEA-LITEN-DEHT LCPEM	*From water sorption to water management: X-ray and neutron scattering studies*
09:55-10:30	Michael Hickner, Penn. State University	*Water binding interactions in super-acid proton exchange membranes*
10:30-10:50	**Coffee Break**	
10:50-11:25	Steven Holdcroft, Simon Fraser University	*Water transport through PFSA and hydrocarbon ionomer membranes*
11:25-12:00	Jay Benziger, Princeton University	*What makes Nafion special?* *How do water and protons move through ionomers?*
12:00-13:30	**Lunch**	Location: Kjelhuset, NTNU campus
13:30-14:05	Keith Promislow, Michigan State University	*Continuum models of network formation in ionomer membranes*
14:05-14:40	Jürgen Fuhrmann, WIAS Berlin	*Numerical strategies for electrolyte simulations*
14:40-15:00	**Coffee Break**	
15:00-15:35	Adam Weber, Lawrence Berkeley National Lab.	*The role of the interface in controlling transport phenomena in PFSAs*
15:35-16:10	Renate Hiesgen, University of Applied Sciences Esslingen	*Atomic force microscopy studies of structure and conductivity of polymer electrolyte membranes*
18:00-	**Workshop Dinner**	Grenaderen Restaurant, Trondheim

Friday, 04 October 2013

Room: H2 (129), Main Building (Hovedbygningen), NTNU – Gløshaugen Campus

08:45-09:20	Michael Schuster, FuMA-Tech GmbH	*Polymer electrolyte membranes (PEM) as key component of batteries and fuel cells: Recent developments*
09:20-09:55	Yu Morimoto, Toyota Central R&D Labs.	*Perfluoro-sulfonimide ionomer for PEFCs*
09:55-10:30	Atsushi Ohma, Nissan Research Center	*Ionomer in catalyst layers and its influence on the transport properties*
10:30-10:50	**Coffee Break**	
10:50-11:25	Viatcheslav Freger, Technion - IIT	*Hydration and relaxation in Nafion*
11:25-12:00	Armand Soldera, Université de Sherbrooke	*Multiscale simulation to explore the effects of water in Nafion*
12:00-13:30	**Lunch**	Location: Science Building cafeteria
13:30-14:05	Signe Kjelstrup, NTNU	*Thermal osmosis and thermoelectric potentials in polymer electrolyte fuel cell membrane materials*
14:05-14:40	Sandrine Lyonnard, CEA Grenoble	*Structure/transport interplay in perfluorinated membranes and model surfactants systems probed by scattering techniques*
14:40-15:00	Michael Eikerling, SFU	*Concluding Remarks*

Local Transportation

All locations (workshop, workshop dinner, restaurants, etc.) are within walking distance. Walking from the hotel to the campus takes about 25 minutes. Other destinations are closer. If you prefer not to walk, we recommend taxis.

Getting from the airport to the hotel and back to the airport:
Coaches run essentially every 10 minutes and cost about $40 USD return.
Taxis are about $100 USD each way. The train is perhaps not the best option.

There are two bus companies:

1) **Flybussen** (http://www.nettbuss.no/rutetilbud/flybuss/flybussen-i-trondheim) runs every 10 min. and stops in the city center.
2) **Værnes – Ekspressen** (http://vaerneseksprессen.no/index.php/rutetider/avganger#) runs less frequently (15 – 45 min. intervals) but it stops almost in front of the hotel. The closest stop is the Bakkegata stop near the hotel.

The coaches leave right in front of the airport exit doors. When you arrive at international arrivals, you need to proceed to the main airport hall. Please ask for directions, if necessary.
Also, the drivers are usually more than happy to point out the right stop near the hotel.

Hotel (see map below)

Rica Bakklandet Hotel, Trondheim city center, Nedre Bakklandet 60
Phone: (+47) 72 90 20 00 (https://www.rica-hotels.com/hotels/trondheim/rica-bakklandet-hotel/).
The single rooms will include breakfast and free wifi.
Rate: NOK 945 per person/night.

Workshop/Lunch Location (see map below)

The workshop, including the lunches, will be held at the NTNU Gløshaugen campus. On the first day, the workshop will be held in room D5-175 (5th floor) in the Science Building (Realfagbygget). On the second day, it will be held in H2 (129), Main Building (Hovedbygningen).

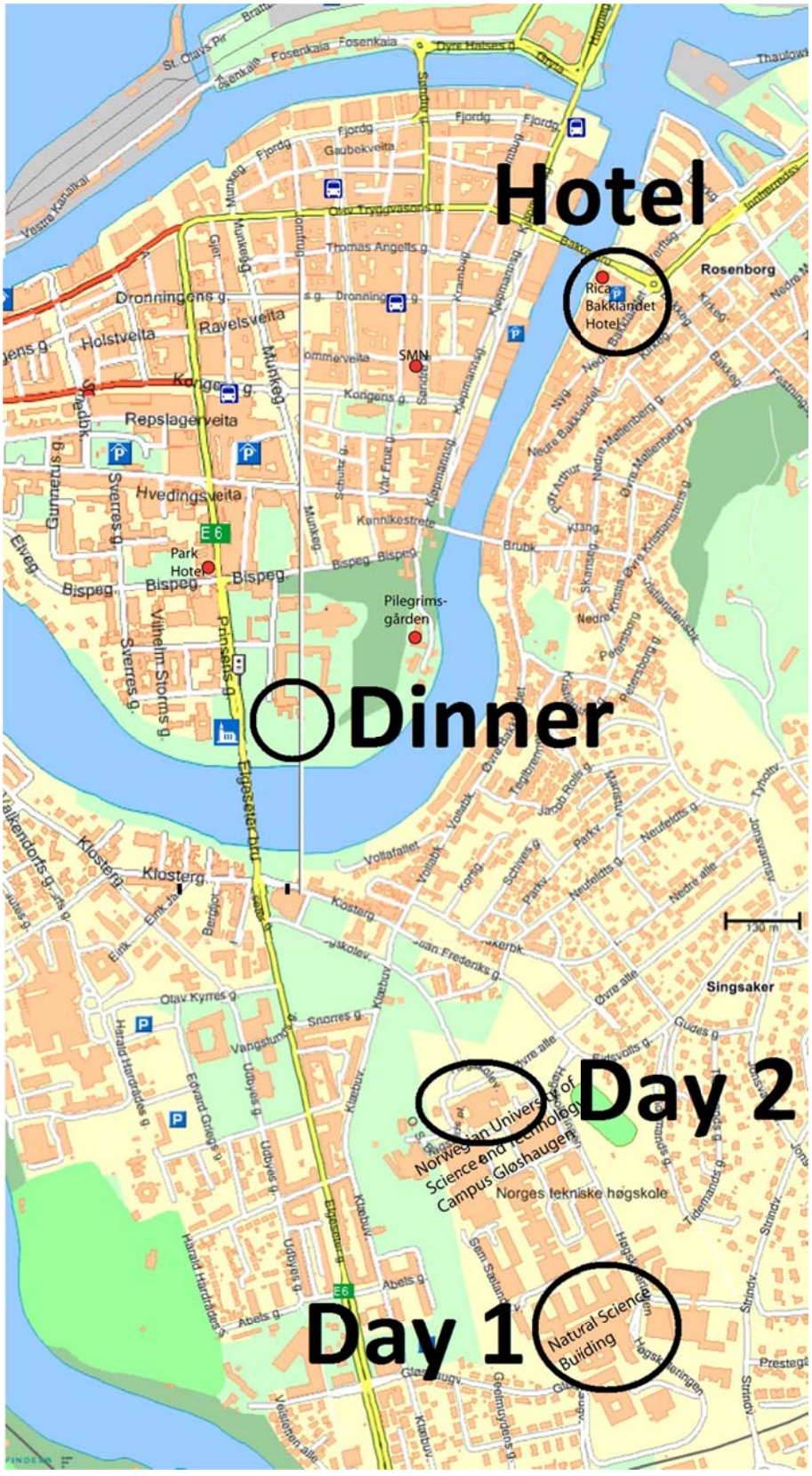
Workshop Dinner (see map below)

The workshop dinner will be held at the Vertshuset Grenaderen (http://www.grenaderen.no/), Kongsgårdsgt. 1, 7013 Trondheim, Phone: (+47) 73 51 66 80. The three-course dinner includes one non-alcoholic beverage for each guest. Additional beverages need to be purchased by the guests.

Fees

The workshop dinner costs 500 NOK. In addition, the workshop fee for non-speakers is 1000 NOK. Students do not need to pay a workshop fee. Invoices will be sent to participants if applicable.

Map


Hotel
Dinner
Day 2
Day 1
Natural Science Building
Norges teknisk-naturvitenskapelige universitet
Norges tekniske høgskole
Rica Bakklandet Hotel
Park Hotel
Pilegrims-gården
SMN
Rosenborg
Singsaker
Dronningens g.
Kongens g.
Munkeg.
Bispeg.
Prinsens g.
Elgeseter bru
Klosterg.
Thomas Angells g.
Nedre Bakklandet
Nedre Elvehavn
Øvre alle
Nedre alle
Gløshaugen
Campus Gløshaugen

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Abstracts

(in alphabetical order)

What makes Nafion special? How do water and protons move through ionomers?

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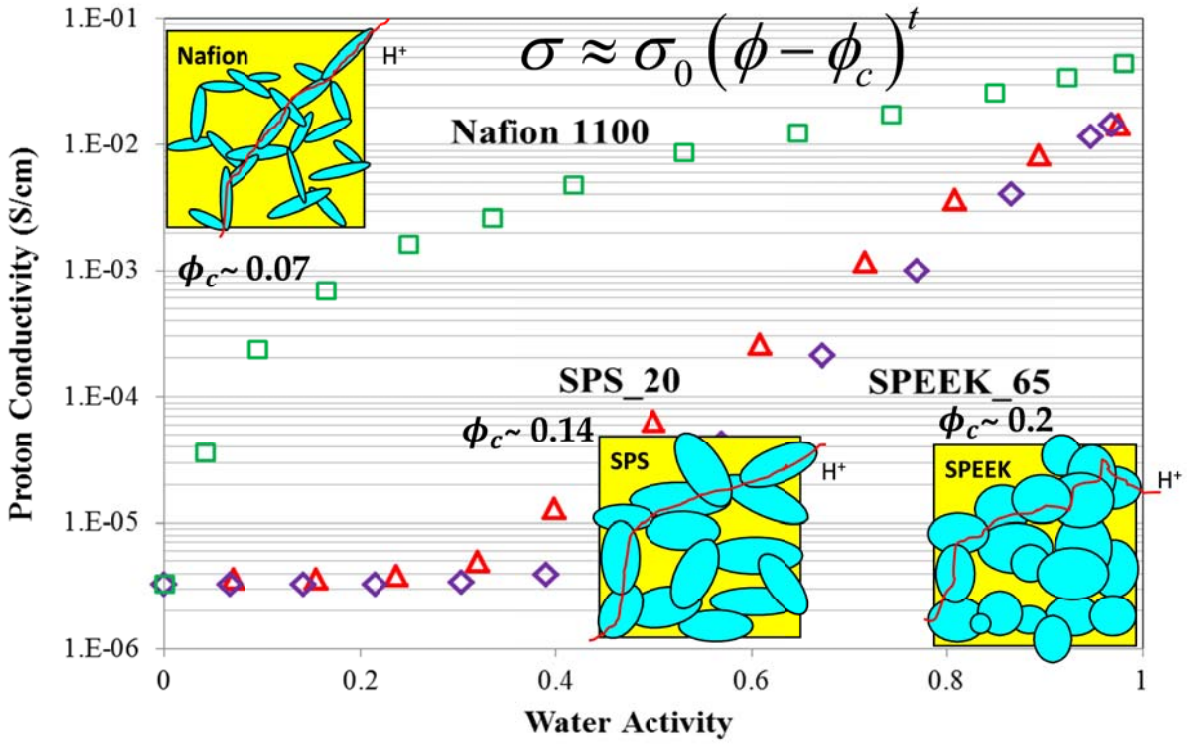
Abstract

Ionomer membranes are the heart of Polymer Electrolyte Membrane Fuel Cells. Proton and water transport are strong functions of water activity in ionomers. Proton conductivity increases by six orders of magnitude as water activity increases from 0 (0% humidity) to 1 (100% humidity) [1]. Other ionomers have high proton conductivity when submerged in liquid water, but these ionomers never perform as well as Nafion in Fuel Cells. Why does Nafion perform so well?

The transport properties of Nafion, sulfonated polyether etherketone (SPEEK) and sulfonated polystyrene (SPS) have been measured as functions of degree of sulfonation, temperature and water activity [2,3]. Water and protons are transported through hydrophilic domains. The volume fraction of the hydrophilic domains increases with water activity. Proton and water transport have a percolation threshold of 0.07 vol fraction in Nafion; above the percolation threshold water diffusion and proton mobility increase quadratically with water volume fraction. The percolation thresholds for SPEEK and SPS were 0.20 and 0.14 respectively, indicating different shapes of hydrophilic domains for different ionomer [4]s. The percolation thresholds were independent on the degree of sulfonation, but the intrinsic conductivity did increase with sulfonation. We will show how the shape and percolation of hydrophilic domains depends on molecular structure.

Water transport in PEMs involves the coupling of interfacial mass transport, diffusion and polymer swelling. Interfacial transport resistance at the vapor/membrane interface may be the limiting transport resistance. We show that the interfacial transport resistance is a key reason why Nafion is such a good PEM for fuel cells; the interfacial resistance retains water inside the polymer membrane giving rise to high proton conductivity. The internal diffusional resistance and external interfacial transport resistances are coupled in ionomers, which affects the water distribution and coupled water and proton transport of electro-osmotic and electrophoretic drag[5].

[1] C. Yang, S. Srinivasan, A.B. Bocarsly, S. Tulyani, J.B. Benziger, *J. Membrane Sci*. **237**, 145-161 (2004)
[2] P.W. Majstzrik, M.B. Satterfield, A.B. Bocarsly, J. Benziger, *J. Membrane Sci*. **301**, 93-106 (2007)
[3] Q.A. Zhao, P. Majsztrik, J. Benziger, *J. Phys. Chem. B* **115**, 2717-2727 (2011)
[4] X.M. Wu, X.W. Wang, G.H. He, J. Benziger, *J. Polymer Sci. Part B-Polymer Physics* **49**, 1437-1445 (2011)
[5] M.J. Cheah, I.G. Kevrekidis, J. Benziger, *J. Physical Chemistry B* **115**, 10239-10250 (2011)


$\sigma \approx \sigma_0 (\phi - \phi_c)^t$
Nafion
H+
Nafion 1100
ϕ_c~ 0.07
SPS_20
ϕ_c~ 0.14
SPS
H+
SPEEK_65
ϕ_c~ 0.2
SPEEK
H+
Proton Conductivity (S/cm)
1.E-01
1.E-02
1.E-03
1.E-04
1.E-05
1.E-06
0
0.2
0.4
0.6
0.8
1
Water Activity

Hydration and relaxation in Nafion

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Abstract

Nafion is a perflourinated ionomer that has been the benchmark ion-selective membrane material in fuel cells and other electrochemical applications for nearly 4 decades. Quantitative understanding of hydration and water transport in Nafion has been complicated by the fact that the material apparently tends to remain trapped in quasi-equilibrium that may strongly depart from the true equilibrium state in given conditions. This postulation combined with simple theoretical picture of mirophase separation in Nafion may rationally explain the controversial phenomenon known for a century as Schroeder's paradox, whereby different hydration levels are measured in contact with liquid water and its vapor at identical chemical potential of water. This non-thermodynamic behavior apparently results from the an elastic-interfacial analogue of Laplace pressure that is exerted on the aqueous microphase within the polymer. Even though such "Laplace" pressure should vanish in pure water or saturated vapor, since Nafion should dissolve and form a stable solution, a slow relaxation effectively prevents dissolution and keeps the "Laplace" pressure finite leading to a paradox behavior. This explanation suggests that (a) the perflourinated matrix of Nafion may relax extremely slowly at ambient temperature and (b) the surface may present a special, faster relaxing region that may undergo structural transitions depending on the phase sate of the environment. Evidence of both (a) and (b) has been obtained recently, supporting the proposed model and pointing to the fact that hydration of Nafion involves several relaxation modes drastically different in their relaxation times. The most puzzling is the enormously large value of the longest relaxation time. We discuss possible reasons for such slow relaxation that is ultimately responsible for keeping Nafion in water in its unique highly conducting solid state.

Numerical strategies for electrolyte simulations

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Abstract

Recent developments in electrochemical modeling have lead to an increased interest in numerical simulations of electrolytic systems which are able to resolve the polarization boundary layer. Classically, the problem is formulated based on the Nernst-Planck-Poisson system for ion transport in a self-consistent electrical field. Various model improvements are currently discussed in order to take into account the volume constraint for solute concentrations, see e.g. [1,2]. Furthermore, coupling to the (Navier-) Stokes equations of fluid flow is of significant interest [3,4].

The talk reviews a successful finite volume discretization strategy from semiconductor analysis [5,6] and discusses problem reformulations which allow for its application in the context of electrolyte modeling. Special emphasis is made on the proper reflection of qualitative properties of the physical model at the discrete level. Along with calculation results for benchmark examples, the influence of various model improvements is demonstrated.

A coupling strategy to the (Navier-) Stokes equations is discussed which – based on a discrete counterpart of the divergence constraint for the velocity – guarantees the preservation of fundamental properties of the transport problem including mass conservation, positivity and maximum principle [7].

[1] W. Dreyer, C. Guhlke, R. Müller, *Phys. Chem. Chem. Phys.* **15**, 7075-7086 (2013)
[2] M. Z. Bazant, B. D. Storey, A. A. Kornyshev, *Phys. Rev. Lett*. **106**, 046102 (2011)
[3] I. Rubinstein, B. Zaltsman, *J. Fluid Mech*. **579**, 173-226 (2007)
[4] L. J. Cheng, L. J. Guo, *Chem. Soc. Rev.* **39**, 923-938 (2010)
[5] D. L. Scharfetter, H. K. Gummel, *IEEE Trans Electron. Dev.* **16,** 64-77 (1969)
[6] K. Gärtner, *SIAM J. Sci. Comput.* **31**, 1347-1362 (2009)
[7] J. Fuhrmann, A. Linke, H. Langmach, *Appl. Num. Math*. **61**,540-554 (2011)

From water sorption to water management: X-ray and neutron scattering studies

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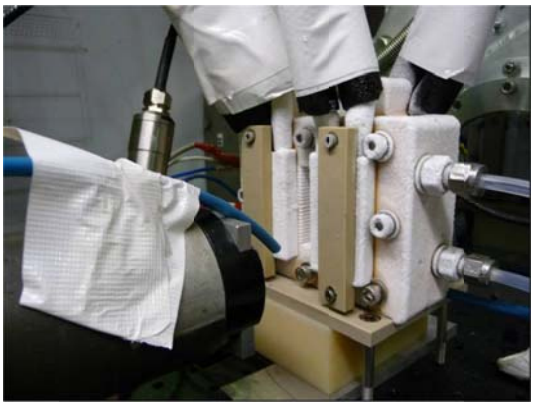
Abstract

The control of the water management in operating fuel cells is a key issue for improving the performance and durability. It is mainly controlled by the membrane transport properties namely the diffusion properties, the electroosmosis and the water transfer through the membrane interfaces. Small-angle neutron and X-ray scattering (SANS and SAXS) have been used to follow the kinetics of water sorption and desorption properties of the membrane [1,2]. Two different sorption processes have been evidenced for a membrane in contact with liquid water. The first one is thermo-activated and very fast (typically during the first 30 seconds). It corresponds to the water diffusion within the membrane. The second one is very slow since it occurs during several years and is attributable to the polymer matrix relaxation. This slow and never-ending process is also observed when the membrane is equilibrated with water vapor. The water sorption and desorption appear as similar processes which are not driven by the structure of the membrane interface but mainly by the external conditions. These results are confirmed by Nuclear Magnetic Resonance and gravimetric measurements. A specific method based on the determination of the water balance in the absence of concentration gradients has been developed for the determination of the electro-osmotic drag coefficient leading to values significantly smaller than the commonly accepted ones (typically below 1 instead of 3).

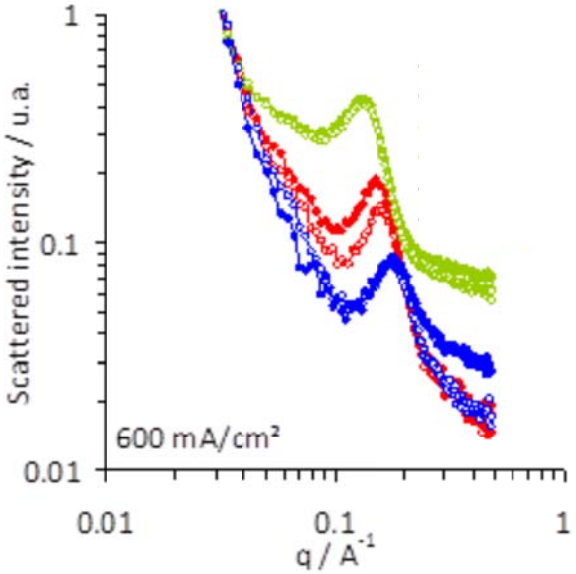
An efficient method based on the use of SANS experiments was developed and improved to extract the water concentration profiles across the membranes during fuel cell operation [3,4]. This technique was applied with success to analyze the effect of the most relevant parameters (current density, temperature, gas flow, gas distribution, nature of the electrodes, membrane thickness…).[4,8] Recent experiments were performed at sub-zero temperature in order to understand the difficulty encountered with the fuel cell cold start. The effect if the electro-osmosis and the back-diffusion can then be separated since only the diffusion is very sensitive to temperature. The effect of electroosmosis is no more counterbalanced by diffusion when the cell is operated at sub-zero temperature. Membrane dehydration is then observed when the current density is increased while the electrochemical reaction produces more and more water.[8] More recently both the spatial and time resolution were significantly improved. The spatial resolution permits to differentiate the membrane water content in front of the current collector ribs and gas distribution channels. The time resolution allows the study of the transient behaviors during on-off cycles or calls of current.

[1] G. Gebel, S. Lyonnard, H. Mendil-Jakani, A. Morin, *J. Physics: Condensed Matter* **23**, 234107 (2011)

[2] S. Lyonnard, G.K. Prajapati, Q. Berrod, L. Porcar G. Gebel, *ACS Macro Lett.* submitted.
[3] S. Deabate, G. Gebel, P. Huguet, A. Morin, G. Pourcelly, *Energy Environ. Sci.* **5**, 8824 (2012)
[4] F. Xu, O. Diat, G. Gebel, A. Morin, A. *J. Electrochem. Soc.* **154**, B1389 (2007)
[5] A. Morin, F. Xu, G. Gebel, O. Diat, O. *Int. J. Hydrogen Energy* **36**, 3096 (2011)
[6] G. Gebel, O. Diat, S. Escribano, R. Mosdale, *J. Power Sources* **179**, 132 (2008)
[7] A. Morin, F. Xu, G. Gebel, O. Diat, *Fuel Cells* **12**, 156 (2012)
[8] A. Morin, Z. Peng, J. Jestin, M. Detrez, G. Gebel, *Solid State Ionics,* in press



Fuel cell operating at low temperature on a SANS spectrometer



SANS spectra obtained during fuel cell operation at 600 mA/cm^2 under a counter-flow gas confirmation middle (green), top (red) and bottom (blue) of the cell. The data are recorded either in front of the gas distribution channels (empty symbols) or in front of the ribs (full symbols)

Water binding interactions in superacid proton exchange membranes

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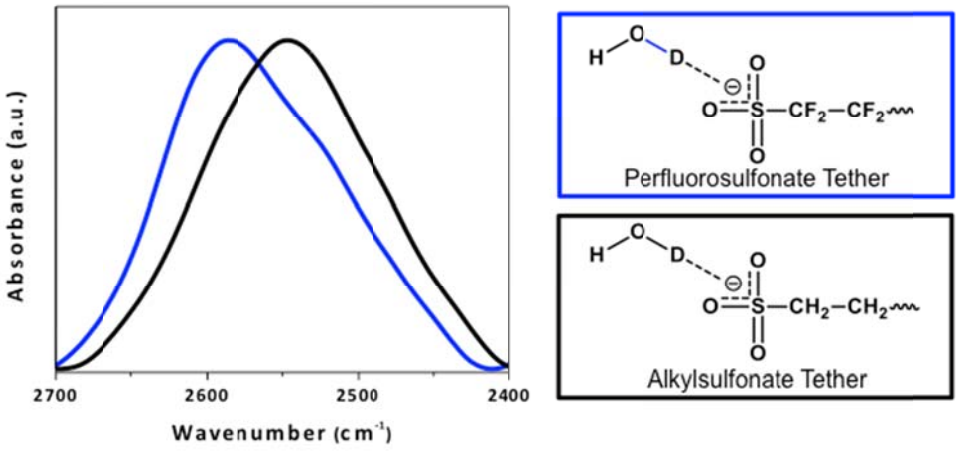
Abstract

The OD stretch of dilute HOD in H_2O in a series of sulfonated syndiotactic poly(styrene)[1] and poly(sulfone)[2] membranes was studied using FTIR spectroscopy to measure how the character of the sulfonate and backbone polarity influenced the water-membrane interactions. Using a three state model, the results yielded information about the amount of absorbed water participating in hydrogen bonds with the polymer-tethered aromatic, or perfluoro sulfonate groups versus the amount of water hydrogen bonding with other water molecules. The perflouroalkyl sulfonate moiety, which behaves as a superacid, consistently displayed the largest fraction of ionic headgroup-associated due to its strong ionic character. The OD stretch gave insight to the strength of the hydrogen bonds formed between water and the sulfonate groups. The superacid displayed an OD stretch peak position that was blueshifted by 39 cm^{-1} compared to the aryl OD stretching frequencies that were located at 2547 cm-1. The polarity of the polymer backbone also affected the OD stretch peak position. As hydration increased, the poly(styrene)-based membranes displayed a redshift from 2566 cm^{-1} to 2553 cm^{-1}, whereas poly(sulfone)-based membranes displayed no shift due to hydrogen bond acceptors in the poly(sulfone) backbone.



[1] Y. Chang, G. F. Brunello, J. Fuller, M. Hawley, Y. S. Kim, M. Disabb-Miller, M. A. Hickner, S. S. Jang, C. Bae, *Macromolecules* **44**, 8458-8469 (2011)
[2] Y. Chang, G. F. Brunello, J. Fuller, M. L. Disabb-Miller, M. E. Hawley, Y. S. Kim, M. A. Hickner, S. S. Jang, C. Bae, *Polym. Chem.* **4**, 272-281 (2013)

Atomic force microscopy studies of structure and conductivity of polymer electrolyte membranes

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Abstract

Solid polymer electrolytes are a key component in fuel cells. They are required to provide high ionic conductivity and adequate gas separation between the two electrochemical reactive electrodes and exhibit superior chemical stability. The membrane conductivity significantly determines the performance of the cells.

The conductivity of the common electrolyte membranes is typically based on a nanoscale phase separation that results in an ionic conductive network and a stabilizing matrix. In perfluorinated sulfonic acid membranes the acid groups are solvated and a hydrophilic proton conducting aqueous ionic phase is formed in a self-assembling process upon solidification of the membrane. The hydrophobic polymer back-bones which are perfluorinated as in case of Nafion-type molecules or aromatic as in case of multi-block copolymers provide mechanical stabilization.

Upon solidification of the polymer solution /dispersion a surface layer with a structure different from the bulk equilibrium structure is formed that depends on the surface energies of polymer and the adjacent material, i.e. humid air or platinum [1]. Consequently, the membrane properties at or close to the surface may differ from the bulk of the membrane and its structure and conductivity are crucial as interface between membrane and electrode/catalyst.

Different types of sulfonated membranes, perfluorinated Nafion® (**l**ong-**s**ide **c**hain molecules) and Aquivion® (**s**hort **s**ide **c**hain molecules) membranes, and aromatic multiblock copolymer membrane named JST (JSR Corp., Japan) have been investigated. Beside the investigation of surfaces freshly cut cross section from Nafion and Aquivion samples have been examined.

For analysis material-sensitive and conducting atomic force microscopy was used to map local adhesion forces, stiffness, deformation, conductivity and surface potential with nanoscale resolution. The following issues will be addressed:

1. Change of the conductivity upon current flow.
2. Size and distribution of conductive area at the surface for different membrane types.
3. Existence and thickness of a surface layer for different membranes.
4. Difference in membranes structure close to the surface (Fig. 1).
5. Ionic structure of the bulk for Nafion® and Aquivion®

6. Shape of aqueous phase in the bulk of Nafion® and Aquivion®.
7. Molecular structure of Nafion® (Fig. 2) and Aquivion®.
8. Deposition of platinum inside a Nafion® membrane after accelerated degradation (Fig. 3) [2].
9. Comparison of Nafion® nanostructure models with the AFM results.

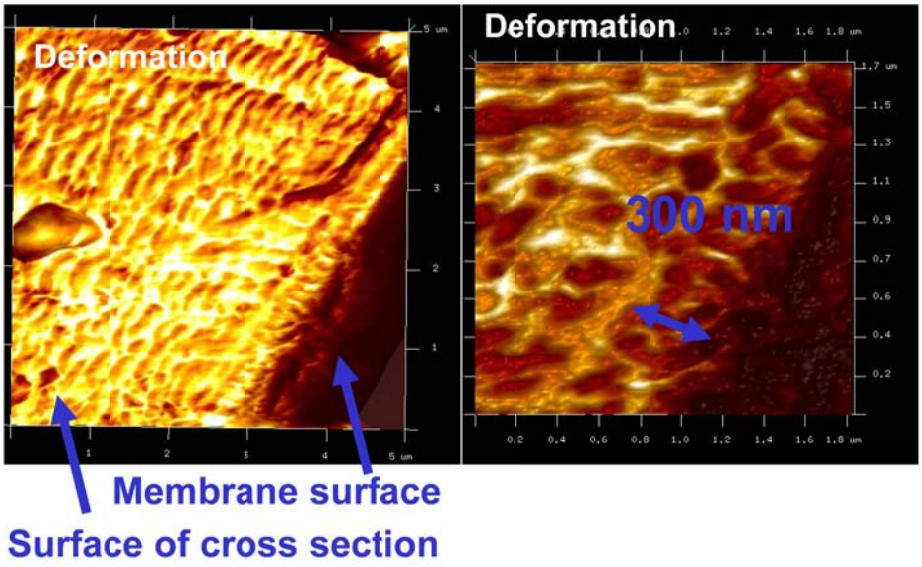

Figure 1: Cross section deformation image of Nafion® 112 and zoom into edge structure.

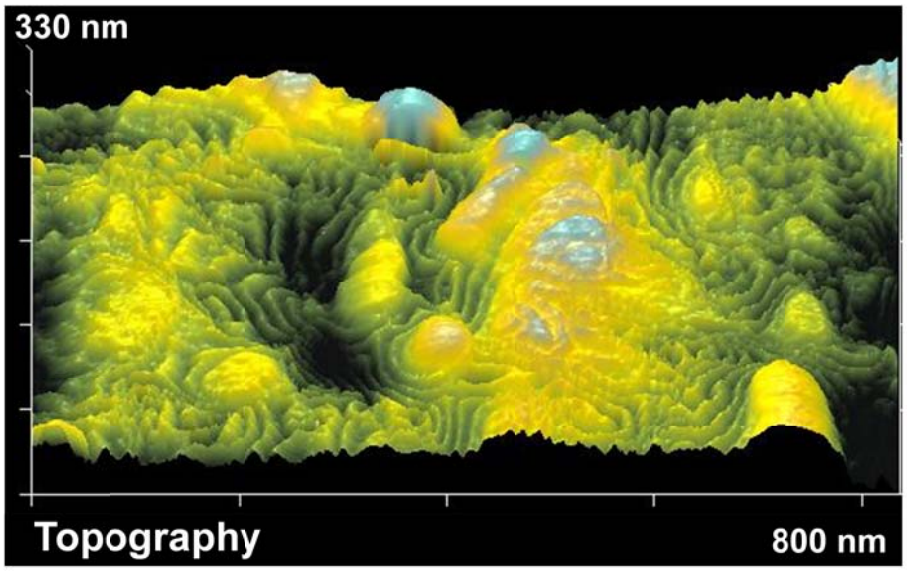

Figure 2: High resolution topography on cross section of Nafion® 112

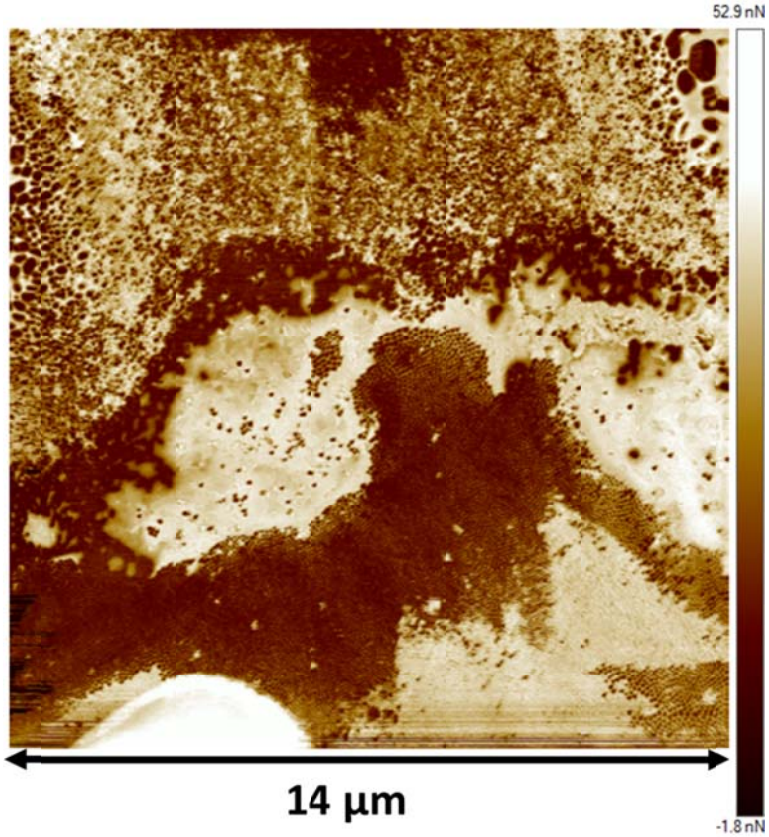

Figure 3: Adhesion image of cross section of Nafion® 112 membrane after 1600 h of accelerated degradation under open circuit voltage

[1] M. Bass, A. Berman, A. Singh, O. Konovalov, V. Freger, *J. Phys. Chem. B* **114**, 3784-3790 (2010)
[2] S. Helmly, R. Hiesgen, T. Morawietz, X.-Z. Yuan, H. Wang, K.A. Friedrich, *J. Electrochem. Soc.* **160**, F687-F69 (2013)

Water transport through PFSA and hydrocarbon ionomer membranes

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Abstract

Water permeability measurements are presented and analyzed in the context of fuel cell water balance measurements. Water transport data is obtained for membranes exposed to either liquid or vapour phases of water, or, both, wherein a chemical potential gradient is developed across the membrane by either controlling the differential humidity in the case of water vapour or hydraulic pressure in the case of liquid water. The analysis is extended to hydrocarbon ionomers and aged PFSA ionomer membranes.

Thermal osmosis and thermoelectric potentials in polymer electrolyte fuel cell membrane materials

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Abstract

The theory of non-equilibrium thermodynamics, as extended to heterogeneous systems, provides a systematic basis for description of membrane transport phenomena [1]. We show how thermal osmosis and thermoelectric phenomena can benefit from this theory in experimental design and interpretation of measurements. The excess entropy production of an interface dictates the form of equation, in this case for the transport of heat, water and charge (protons) at boundaries. Equations are illustrated with experimental results and simulations for fuel cell materials. We consider first a Nafion membrane surrounded by Sigracet layers exposed to temperature- and water vapor pressure gradients [2]. The next case is a concentration cell with hydrogen electrodes and a membrane-electrode assembly, standardly used in fuel cells.

We shall see how the hydrophilic or hydrophobic nature of the membrane material can change the direction of water transport in sandwiched layers exposed to a temperature difference. Experimental results and simulations indicate a need for better knowledge on the mechanism of water diffusion in the Nafion membrane [2]. Self-diffusion of water in the Nafion membrane does not account for the observations.

The concentration cell with hydrogen electrodes can be used to determine single electrode Peltier heat effects in the fuel cell from Seebeck coefficient determinations [3]. A major part of the heat produced in a reversible manner in the fuel cell is produced at the anode, due to disappearance of hydrogen gas, and due to transported entropy through the membrane [3]. Practical consequences of these results can be pointed out for salt power plants using reverse electro-dialysis or of for power production from friction electricity [4,5].

[1] S. Kjelstrup and D. Bedeaux, *Non-equilibrium Thermodynamics for heterogeneous Systems,* Ser. Stat. Mech., Vol. 16, World Scientific, Singapore (2008)
[2] K. Glavatskiy, J. G. Pharoah, S. Kjelstrup, *J. Membrane Sci.* **431**, 96-104 (2013)
[3] S. Kjelstrup, P. J Vie, L. Akyalcin, P. Zefaniya, J. G Pharoah, O. Burheim, *Electrochimica Acta* **99,** 166-175 (2013)
[4] K. Sandbakk, A. Bentien, S. Kjelstrup, *J. Membrane Sci*. **434,** 10-17 (2013)
[5] A. Bentien, T. Okada, S. Kjelstrup, *J. Phys. Chem. C* (2013)

Structure/transport interplay in perfluorinated membranes and model surfactants systems probed by scattering techniques

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Abstract

The synthesis and manufacturing of polymer electrolyte membranes with improved functional properties such as high proton conductivity and chemical stability is an actual challenge to increase the performances of Proton Exchange Membrane Fuel Cells. To achieve this goal, a microscopic understanding of the relation between the primary chemical nature of the electrolyte, the morphology, the proton transfer / water diffusion mechanisms, and the effective properties is essential. In this presentation we will show the suitability of scattering techniques to investigate the structure/transport interplay at microscopic scales in PFSA membranes and model surfactants systems. We report on SANS studies performed to investigate polymer microstructure [1]. In complement, proton and water dynamics were obtained in Nafion/Hyflon membranes by Quasi-Elastic Neutron Scattering (QENS)[2]. Two types of protons coexist at all hydrations: localized non-diffusive slow protons (strongly interacting with acid groups), and diffusive hydration protons confined in ionic channels. To get further insights into the diffusion mechanisms, we investigated self-assembling perfluorosulfonic surfactants as model systems [3]. At low hydration in PFSA membranes, the local proton dynamics is well described by a semi-lamellar geometry, as predicted by the Nafion ribbon model [4] and confirmed by the comparison with lamellar self-assembled surfactants model systems. Molecular Dynamics simulations performed on hydrated ionic surfactants will be shortly presented, as a complementary approach to the scattering experiments.

[1] S. Lyonnard *et al.*, *European Physical Journal* **213**, 195-211 (2012)
[2] J-C. Perrin, S. Lyonnard *et al.*, *J. Phys Chem C* **111**, 3393-3404 (2007)
[3] S. Lyonnard *et al.*, *European Physical Journal* **189**, 205-216 (2010)
[4] L. Rubatat *et al.*, *Macromolecules* **37**, 7772-7783 (2004**)**

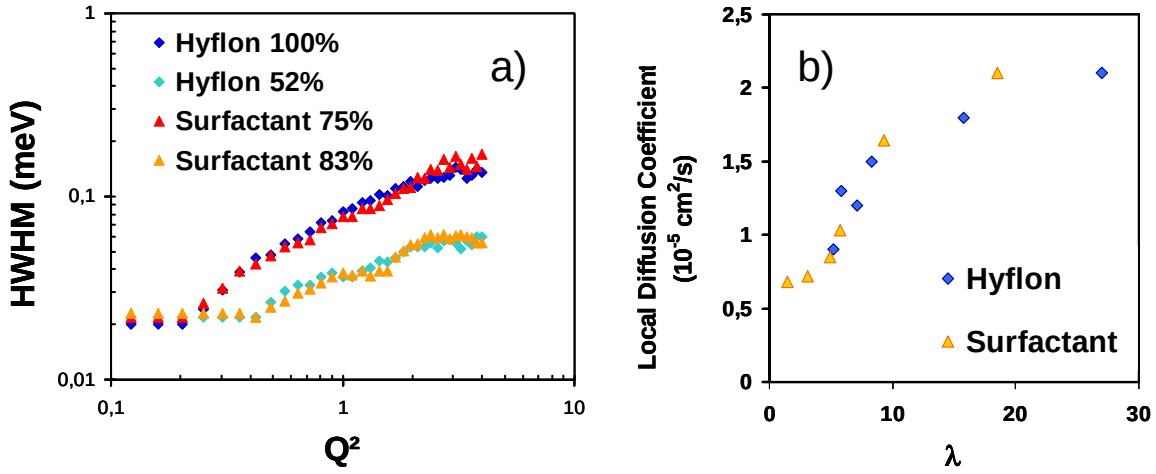

Figure 1. a) Half-Width at Half Maximum (HWHM) of the quasielastic broadening measured by neutron scattering on Hyflon membranes (52 and 100% Relative Humidity), compared to perfluorosulfonated surfactants (75% and 83% w/w). b) Proton diffusion coefficients extracted from the HWHM analysis in the framework of confined motion models, as a function of the hydration number $\lambda = n[H_2O]/[SO_3^-]$.

Perfluoro-sulfonimide ionomer for PEFCs

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Abstract

"Ionomers", the electrolytes contained in catalyst layers, have crucial roles in the PEFC system: binding the catalyst powder to form a catalyst layer and bonding the catalyst layer with an electrolyte membrane, and carrying proton to/from the membrane from/to reaction sites, Pt catalysts. However, they also have negative impacts: hindering transportation of reactants (H_2 or O_2) from the gas phase to the catalyst surface [1] and blocking active sites on Pt catalyst to slow down the kinetics of oxygen reduction reaction (ORR) [2].

Although perfluorinated sulfonic acid polymers (e.g. Nafion), which have been almost exclusively used as the ionomer for commercialized PEFCs, possess reasonably good properties in all the above-mentioned aspects plus its high chemical stability, further improvements are highly required for realizing high-temperature low-humidity operable high-power low-cost (low Pt content) PEFCs for automotive application

To address this issue, we have developed bifunctional perfluoro-sulfonimide ionomers, which are non-crosslinked and alcohol-soluble unlike our previously reported crosslinked perfluoro-sulfonimide membrane [3]; this property is essential as a binder.

The perfluoro-sulfonimide ionomers were synthesized by amidating a sulfonyl fluoride-ending perfluoro-polymer and reacting the obtained sulfonamide polymers with $FO_2S(CF_2)_3$-SO_2Rf (Fig. 1), which were generated from the condensation reaction of $FO_2S(CF_2)_3SO_2F$ and HRf (Rf = OH, $NHSO_2CF_3$, and $NHSO_2C_4F_9$.

The protonic conductivity and oxygen permeability of the ionomers were measured in conventional manners using thick casted membranes. Those polymers have superior protonic conductivity (Fig. 2) and oxygen permeability (Fig. 3) to conventional Nafion probably because of their bifunctionality and perfluorocarbon terminal, respectively.

Electrochemical measurement was carried out using a Pt(111) single crystal. Cyclic voltammograms in an inert condition shows that adsorption is clearly weaker by the new ionomer than by the sulfonic acid counterpart (Fig. 4). While the effect on ORR activity is minimal at 0.9V (vs. RHE), the improvement is widen at 0.82V (Fig.5). First principles theory calculation also showed a less-adsorptive nature of the new ionomer.

[1] N. Nonoyama, *et al*., *J. Electrochem. Soc*. **158**, B416 (2011)
[2] R. Subbaraman *et al.*, *ChemPhysChem* **11**, 2825 (2010)
[3] M. Kawasumi *et al.*, *Electrochemical Soc*. Meet. Abstr. #927, MA2005-02:927 (2005)

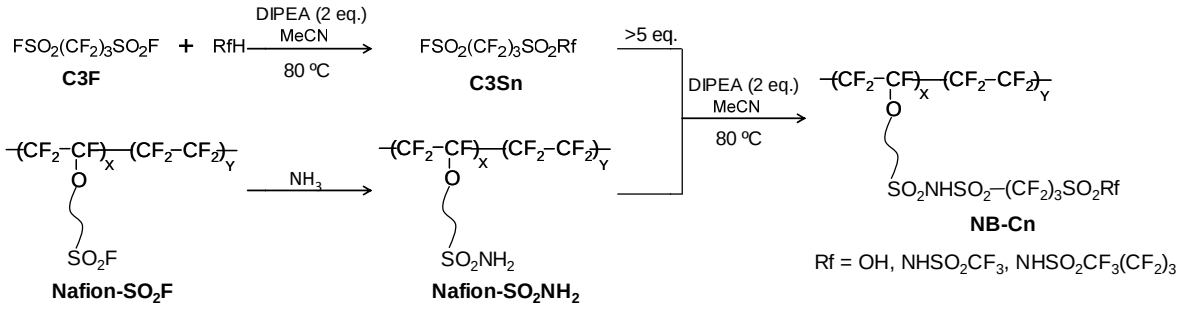

Fig.1 Synthesis of perfluoro-sulfonimide ionomer

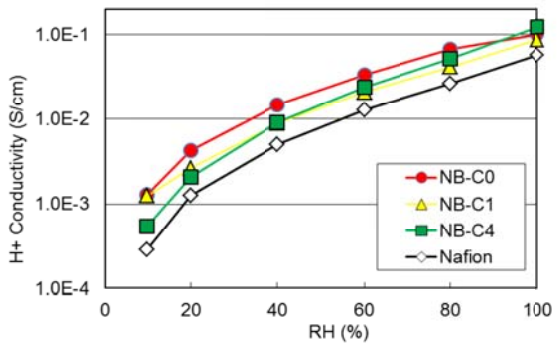

Fig.2 Protonic conductivity of ionomers

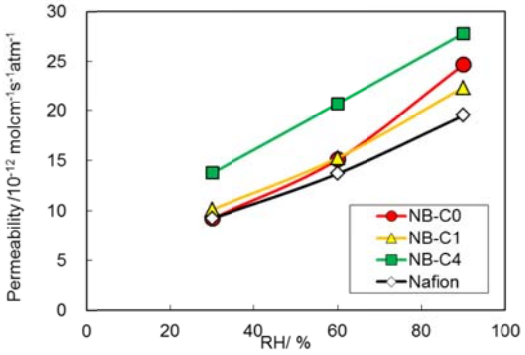

Fig.3 Oxygen permeability of ionomers

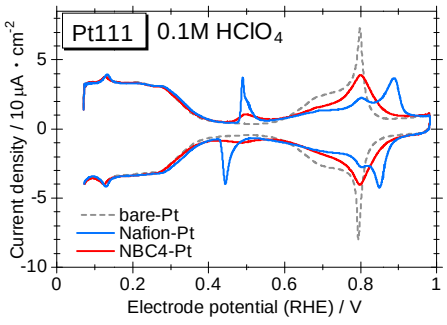

Fig.4 Cyclic voltammograms of Pt(111) covered with ionomers in N_2-saturated perchloric acid.

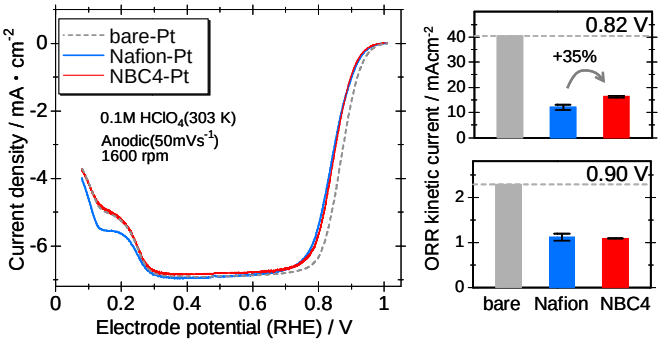

Fig.5 Linear sweep voltammograms of Pt(111) covered with ionomers in oxygen-saturated perchloric acid and ORR activities at 0.82 V and 0.9 V.

Ionomer in catalyst layers and its influence on the transport properties

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Abstract

For zero-emission leadership, Nissan has been developing both battery electric vehicles (BEVs) and fuel cell electric vehicles (FCEVs). Cost reduction is the primary concern associated with commercialization of FCEVs. Downsizing and reducing platinum usage of proton exchange membrane fuel cell (PEMFC) stacks are essential for the cost reduction. In order to lower the platinum amount of a membrane electrode assembly (MEA) without sacrificing its performance and durability, mass transport of reactants should be significantly improved as well as kinetics of the catalyst. Catalyst layer (CL) of the MEA is a key component, because it contains platinum and both mass transport and electrochemical reaction occur simultaneously. Due to the difficulty of analyzing its complicated microstructure and formation process from ink, and phenomena there, both physical modeling and nano-scale characterization have been applied to reveal them so far [1-4]. Great efforts have been made to analyze morphology and properties of thin-film ionomer that can affect the performance of CL significantly [5-9] as well as electrocatalysts.

In Nissan, we also have been analyzing CLs from characterization and modeling aspects to design low platinum-loaded CL [10-14]. In this presentation, microstructure of ionomer in ink and CL, and its influence on the transport properties will be introduced with experimental and simulation results.

[1] M. Uchida, Y. Aoyama, N. Eda, and A. Ohta, *JES* **142**, 4143 (1995)
[2] M. Eikerling, *JES* **153**, E58 (2006)
[3] K.C. Neyerlin, W. Gu, J. Jorne, A. Clark, Jr., H.A. Gasteiger, *JES* **154**, B279 (2007)
[4] N. Nonoyama, S. Okazaki, A.Z. Weber, Y. Ikogi, T. Yoshida, *JES* **158**, B416 (2011)
[5] T.Navessin, M.Eikerling, Q.Wang, D.Song, Z.Liu, J.Horsfall, K.V.Lovell, S.Holdcroft, *JES* **152**, A796 (2005)
[6] T. Masuda, H. Naohara, S. Takakusagi, P.R. Singh, K. Uosaki, *Chem. Lett.* **38**, 884 (2009)
[7] D.D. Borges, K. Malek, S. Mossa, G. Gebel, A.A. Franco, *ECS Trans.* **45**, 23 (2013)
[8] Z. Siroma, T. Ioroi, N. Fujiwara, K. Yasuda, *Electrochem. Comm.* **4**, 143 (2002)
[9] K. Kudo, Y. Morimoto, *ECS Trans.* **50**, 1487 (2013)
[10] T. Mashio, A. Ohma, S. Yamamoto, K. Shinohara, *ECS Trans.* **11**, 529 (2007)
[11] H. Iden, A. Ohma, K. Shinohara, *JES* **156**, B1078 (2009)
[12] K. Sato, A. Ohma, K. Yamaguchi, K. Shinohara, *ECS Trans.* **19**, 39 (2009)
[13] T. Mashio, K. Malek, M. Eikerling, A. Ohma, H. Kanesaka, K. Shinohara, *J. Phys. Chem.* C **114**, 13739 (2010)

[14] Y. Ono, T. Mashio, S. Takaichi, A. Ohma, H. Kanesaka, K. Shinohara, *ECS Trans.* **28**, 69 (2010)

Continuum models of network formation in ionomer membranes

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Abstract

Ionomer membranes, in particular Nafion, are well-known to be hysteric materials which display long time-scales associated with transient behavior, time-scales that are far outside the reach of even the most coarse-grained particle based simulations. Moreover an understanding of the mechanisms behind the transients states of Nafion is most readily obtained by the development of relatively simple models, based upon a dissipation of a free energy, which resolves the competition between various morphological states.

The Functionalized Cahn-Hilliard free energy incorporates solvation energy of pendant ionic groups against interfacial bending energy and various contributions to the solvent-phase pressure, to develop an diffuse-interface expression for the interfacial free energy within functionalized-polymer/solvent mixtures. We present this free energy, and show the results of time-dependent simulations of the solvent phase morphology, as well as identifying several possible scaling regimes for these most complex materials.

Polymer electrolyte membranes (PEM) as key component of batteries and fuel cells: Recent developments

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Abstract

FuMA-Tech “Functional Membranes and Plant Technology” combines the important tasks of providing energy and water. As a member of BWT Best Water Technology Group, the leading water technology group in Europe, FuMA-Tech is engaged in the field of battery, fuel cell and membrane separation technology. The company has 20 years’ experience in polymer and membrane production and in membrane separation technology. Polymer synthesis, manufacturing experience in membrane production as well as the operation of these membranes in industrial products have provided the know-how for the development and serial production of ion-conductive polymers and membranes for all known electro membrane applications including electrodialysis, acid and base dialysis, electrolysis, batteries and fuel cells.

Polymer electrolyte membranes (PEM) are key components of batteries and fuel cells. The state-of-the-art PEMs are commonly based on fluorinated polymers such as our perfluorosulfonic acid (PFSA) ionomer fumion® F (FuMA-Tech) which shows the required electrochemical and mechanical stability.

In recent years a number of alternative ionomers have been developed, among which are sulfonated aromatic polymers as promising candidates due to their commercial availability and processability. The research interest at FuMA-Tech focused on hydrophilic–hydrophobic multiblock copolymers that self-organize into phase-separated nanostructures which allow for high ion-conductivity in the hydrophilic domains and optimal membrane properties based on the hydrophobic domains.

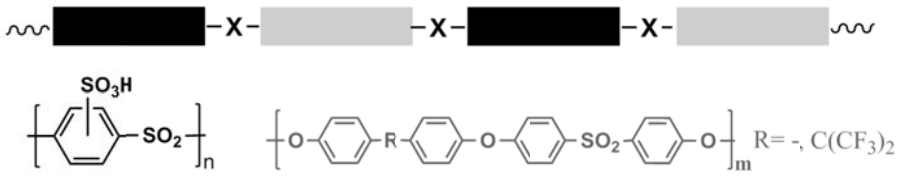

Fig. 1 Structure of multiblock copolymer based on polysulfone.

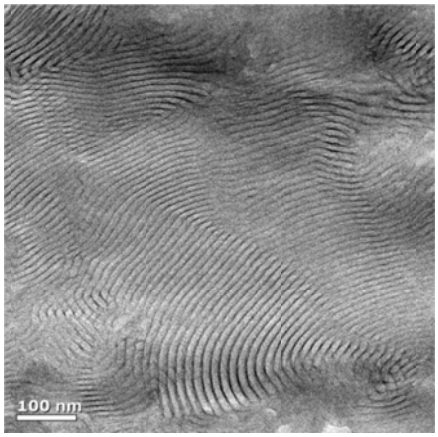

Fig. 2 Morphology of multiblock copolymer with correlation lengths around 15 and 30 nm.

Membranes' development that includes lately also membranes for battery applications (such as vanadium redox battery) and other electrochemical applications will be discussed as well.

Acknowledgement
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[1] M. Schuster *et al*., *Macromolecules* **40**, 598 (2007)
[2] G. Titvinidze *et al.*, *Adv. Funct. Mater*. **22**, 4456 (2012)

Multiscale simulation to explore the effects of water in Nafion

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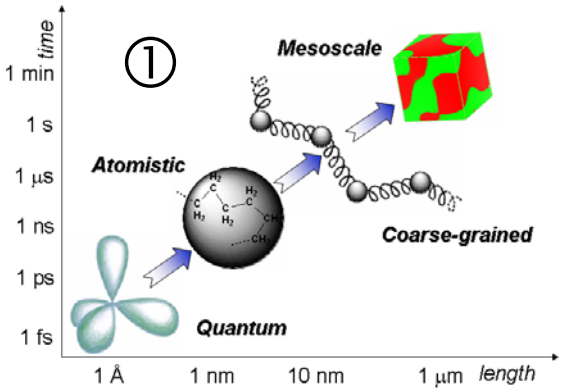
Abstract

To describe the role of water molecules in proton exchange membrane, for use in fuel cells (PEMFC), molecular simulation has become an essential tool. It usefully complements experiments and theoretical models. Molecular simulation can actually be considered as an experiment performed in a computer through a code. It aims to reveal properties at the molecular level. However, to efficiently probe molecular events, and thus to reveal the vast domain of length and time scales related to interactions between water molecules and membranes, molecular simulation must be split into different levels. This separation refers to multiscale simulation [1]. During this presentation, three levels are discussed. They are schematically shown in Figure 1. The ultimate challenge is actually to uncover the perplexing link between molecular structures and macroscopic phenomena. Each scale is exemplified by a study involving water molecules and Nafion®. The lowest level, the quantum level, is governed by the Schrödinger equation. Agreement between simulated and experimental IR spectra of Nafion® with different water uptakes allowed probing of structural changes occurring during proton dissociation [2]. Molecules can then be designed in order to specifically reproduce such features [3]. Ultimately, using quantum methods is problematic for complex systems, and Schrödinger's equation cannot be applied to unravel physical properties such as the glass transition. Atoms are then depicted by particles which interact with other atoms through the use of a force field. This atomistic scale is governed by Newton's laws. The influence of water in determining the value of the glass transition temperature in Nafion® membrane is studied at this level [4]. As the number of atoms, or the time that is covered by simulation increases, dissipative effects must be taken into account. This coarser scale refers to the mesoscale domain which is governed by Langevin's equation. Shearing effects and the spinodal transition with regards to polydispersity are specifically examined [5].



[1] H.J.C. Berendsen, Simulating the physical world: hierarchical modeling from quantum mechanics to fluid dynamics, Cambridge University Press (2007)
[2] P. Laflamme, A. Beaudoin, T. Chapaton, C. Spino, A. Soldera, *J. Comput. Chem*. **33**, 1190-1196 (2012)
[3] P. Laflamme, A. Beaudoin, T. Chapaton, C. Spino, A. Soldera, *J. Membr. Sci.* **401-402**, 56-60 (2012)
[4] A. Soldera, *Mol. Simul*. **38**, 762-771 (2012)
[5] A. Soldera, Y. Qi, W.T. Capehart, *J. Chem. Phys*. **130**, 064902 (2009)

The role of the interface in controlling transport phenomena in PFSAs

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Abstract

Perfluorosulfonic-acid (PFSA) membranes are the most widely studied ionomer for proton-exchange-membrane-fuel-cell applications, with Nafion® still considered to be the benchmark material. Its exceptional proton conductivity along with good thermo-mechanical stability make it suitable for most electrochemical devices. The performance of a fuel-cell membrane is controlled by its transport properties and sorption behavior, which are strongly correlated through the interactions between chemical structure and morphology. In this talk, our recent work on PFSA materials including Nafion and the short-side-chain PFSA by 3M will be discussed with the hope of answering and opening up for debate key questions remaining in terms of the impact, nature, and existence of interfacial morphology and its resultant resistance on transport, differences due to dynamic versus steady-state transport and generating models for such transport, and correlations between structure and transport properties. A key focus area is understanding the impact of the interface on getting water into the membrane such that the universal chemical \ mechanical energy balance for water uptake can be applied. While the majority of the talk will focus on bulk membranes, the extension towards ionomer thin films that exist in the fuel-cell catalyst layer will also be made.

Acknowledgements

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‘Thermodynamics’ of water/solution-PEM interactions: New targets, methods, data and analysis

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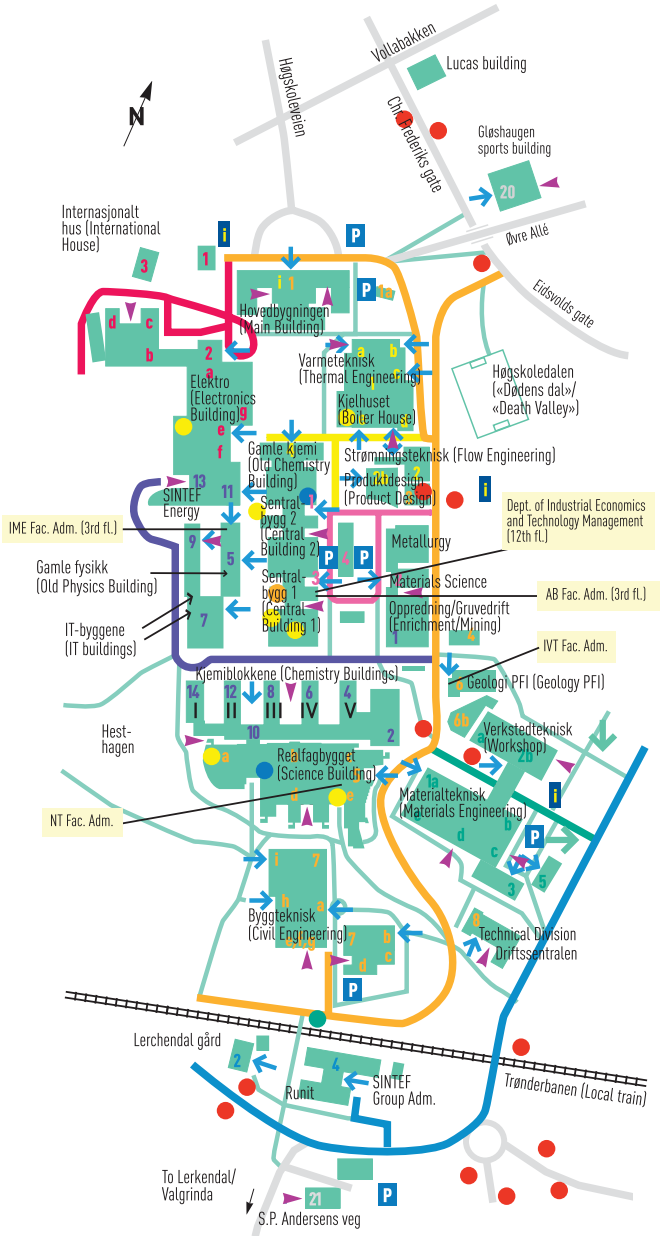
Abstract

The uptake and transport of water and other species in proton exchange membranes and in other types of membranes is an essential feature of their performance in applications related to fuel cells and a host of other electrochemical and membrane-based systems. (We note in passing that the study of polymer membrane processes is generally undertaken at a well-defined steady-state, rather than at true thermodynamic equilibrium.) While studies of such properties are rooted in fundamentals discussed half a century ago and the applications of these materials have exploded in the past two decades, detailed work adding to available data has been piecemeal. A more inclusive and complete set of thermodynamic data for membranes as well as a more complete analysis is desirable.

In this contribution, we will highlight new measurement methods and results obtained from the study of water, acid and ion uptake by a range of different membranes. Acid and ion uptake has become important in the context of applications such as redox flow batteries. New methods and data sets to be discussed include density measurements with partial molar volume analysis, isothermal calorimetry measurements to elucidate interaction enthalpies, and combinations of the above with other thermodynamic data from sorption measurements. In addition, acid and ion partitioning into the membrane will be discussed in the context of Donnan equilibrium effects.

Based on this data and analysis, we will discuss the relative importance of various properties of the polymer system (mechanical and chemical aspects) in determining the energetics of processes described by the data.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Vollabakken
Lucas building
Høgskoleløypen
Gløshaugen sports building
Øvre Allé
Internasjonalt hus (International House)
Hovedbygningen (Main Building)
Eidsvolds gate
Varmeteknisk (Thermal Engineering)
Høgskoledalen («Dødens dal»/ «Death Valley»)
Elektro (Electronics Building)
Kjelhuset (Boiler House)
Gamle kjemi (Old Chemistry Building)
Strømningsteknisk (Flow Engineering)
Produktdesign (Product Design)
SINTEF Energy
Sentral-bygg 2 (Central Building 2)
Dept. of Industrial Economics and Technology Management (12th fl.)
IME Fac. Adm. (3rd fl.)
Metallurgy
Gamle fysikk (Old Physics Building)
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Oppredning/Gruvedrift (Enrichment/Mining)
IT-byggene (IT buildings)
IVT Fac. Adm.
Kjemiblokkene (Chemistry Buildings)
Geology PFI (Geology PFI)
Hest-hagen
Verkstedteknisk (Workshop)
Realfagbygget (Science Building)
Materialteknisk (Materials Engineering)
NT Fac. Adm.
Byggteknisk (Civil Engineering)
Technical Division Driftssentralen
Lerchendal gård
Trønderbanen (Local train)
Runit
SINTEF Group Adm.
To Lerkendal/ Valgrinda
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