

## Morphology and Swelling of Perfluorosulfonic-acid (PFSA) Ionomer Thin Films

Ahmet Kusoglu, Adam Z. Weber

Environmental Energy Technologies Division  
Lawrence Berkeley National Laboratory  
1 Cyclotron Road, Berkeley CA 94720, USA

Perfluorosulfonic-acid (PFSA) ionomers are commonly used as the proton-exchange membrane (PEM) in most solid-state energy-conversion and storage devices due to their exceptional ionic conductivity and good permselectivity. Ionomers have multiple functionalities in PEM fuel cells; in addition to their role as the ion-conducting membrane, they form a nanometer-thick electrolyte film within the catalyst-layers (CLs) wherein the electrochemical reactions occur.<sup>1</sup> Interactions of the ionomer with the CL interface as a membrane and within the CL as a thin film, result in highly complex material behavior that is highly dependent on the environmental conditions, ionomer thickness, and the material interactions, i.e., carbon, platinum, etc. Thus, characterization of the role of ionomer in fuel-cell catalyst layers requires an understanding the transport properties and water-uptake behavior throughout a wide thickness range.

Recent studies have shown that transport and uptake properties of Nafion thin films (< 200 nm thick) exhibit a significant deviation from bulk membranes.<sup>2-5</sup> Many of these studies found a decrease in water content (or swelling) when the ionomer is confined to nanometer-thick films, even though the magnitude of these changes depends on the processing conditions, thickness, and substrate. In any case, reduced water content of Nafion thin-films was found to be in agreement with the water content of the ionomers in fuel-cell CLs,<sup>1</sup> suggesting that thin-film ionomers can serve as model systems to study and elucidate the transport phenomena in CL ionomers.

In this work, we investigate the morphology and swelling of PFSA ionomers with various chemical structures (e.g., side-chain length, ion-exchange capacity) in an effort to expand our understanding of CL ionomer films. Time-resolved, small- and wide-angle Grazing-incidence X-Ray Scattering (GISAXS/GIWAXS) technique is employed to study the nanostructural changes in PFSA films due to environment, time, and humidity. Moreover, the swelling of the films under the same conditions and parameters are measured using ellipsometry to generate a structure-swelling relationship. It will be shown how the film thickness and humidity affect the phase-separation and swelling behavior when the chemical structure of the ionomer is altered. Our findings suggest that the confinement-driven structural reorganization of the water domains could change with the PFSA chemistry, which provides insight into the observed changes in the properties of fuel-cell CLs. Finally, we analyze our results for PFSA films in the light of our previous findings<sup>6</sup> on the structure-function relationship of bulk PFSA ionomers, and discuss the role of side-chain length and ion-exchange capacity in controlling the humidity-dependent structure-property relationship of PFSA ionomers throughout a wide thickness range (micrometer to nanometer). This work also provides a perspective for studying and modeling the transport phenomena at the membrane/electrode interface and has implications on CL optimization.

### Acknowledgement

We thank Steve Hamrock and Mike Yandrasits at 3M for providing ionomer solutions and discussion; Kyle Clark and John Kerr for help with bulk water uptake measurements; Eun Lim and Eric Schaible for facilitating the use of equipment at ALS; and Miguel M. Modestino and Gabriel Sanoja of UC Berkeley for their help with sample preparation. This work made use of facilities at the Advanced Light Source (ALS), supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy. This work was funded by the Assistant Secretary for Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office, of the U. S. Department of Energy under contract number DE-AC02—05CH11231.

### References

1. A. Kusoglu, A. Kwong, K. T. Clark, H. P. Gunterman and A. Z. Weber, *Journal of the Electrochemical Society*, **159**, F530 (2012).
2. S. A. Eastman, S. Kim, K. A. Page, B. W. Rowe, S. Kang, C. L. Soles and K. G. Yager, *Macromolecules*, **45**, 7920 (2012).
3. M. A. Modestino, D. K. Paul, S. Dishari, S. A. Petrina, F. I. Allen, M. A. Hickner, K. Karan, R. A. Segalman and A. Z. Weber, *Macromolecules* (2013).
4. S. K. Dishari and M. A. Hickner, *ACS Macro Letters*, **1**, 291 (2012).
5. M. A. Modestino, A. Kusoglu, A. Hexemer, A. Z. Weber and R. A. Segalman, *Macromolecules*, **45**, 4681 (2012).
6. A. Kusoglu, S. Savagatrup, K. T. Clark and A. Z. Weber, *Macromolecules*, **45**, 7467 (2012).