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Investigating the Microstructure of Perfluorosulfonic Acid (PFSA) Ionomers used as Polymer Electrolyte Membranes (PEM)

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PFSA ionomers, that transport proton when fully hydrated, are the key component of an efficient PEM fuel cell. The main purpose of this study is to understand the microstructure and identify its relevant features that enable proton conduction. Small angle X-ray scattering (SAXS) experiments have revealed that the microstructure of the PFSA ionomers is known to vary with the level of hydration and molecular chemistry (i.e. equivalent weight (EW), side chain length)[1]. While these SAXS studies reveal the length scales of the features of the polymers, the complete microstructural information cannot be obtained, because of random chemical structure of the ionomers. This microstructure organizes into a fine phase separation between the hydrophobic polymer backbone and the aqueous domains containing the hydrated protons of only a few nanometers in dimension over a wide range of length scales.

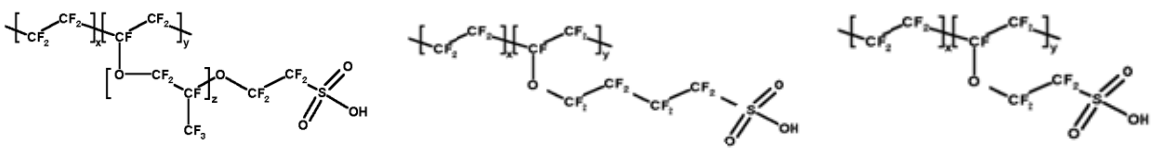
The chemical structure of PFSA ionomers is shown in Figure 1. The hydrophobic backbone is made of CF_2 units. The side chain has a sulfonic acid pendant group that is hydrophilic and is therefore, responsible for the proton conduction. We have investigated a number of these PFSA ionomers on lacey C grids, both as solutions and as 30 nm thick microtomed sections of a foil. We studied different EW and different side chain lengths using Z contrast and BF imaging. We determined the microstructure of hydrated/dry ionomers with and without ion-exchange. We have also used spatially resolved EELS and spectrum imaging to quantify the distribution of sulfur, oxygen, fluorine, carbon and water. VG Microscopes HB501UX STEM with 3rd order Nion aberration corrector and. Hitachi HF3300 (also for cryomicroscopy) was used for this study.

Wu et al have used Dissipative particle dynamics (DPD) simulations to evaluate the morphology of hydrated PFSA ionomers with different EW and side chain length [2]. The qualitative comparison in figure 2 shows clearly that the length scale of the simulations and the Z-contrast images of the unstained (no ion exchange) ionomers agree well. In a Z-contrast image the hydrophilic sulfonate side-chains are bright, as are the water molecules in the inverted simulation slices. The match between simulation and experiment is close enough to employ quantitative image comparison. For instance the fractal dimension of the simulation of the 3M ionomer with water uptake of 9 is 1.6, while the fractal dimension of the experimental images of 3M ionomer of similar EW is in average 1.8. Typical EELS spectrum of PFSA ionomers shown in figure 3 was obtained for a convergence angle (α) of 17.5° and a collection angle (β) of 12°. These spectra were quantified using the Duscher group's Quantifit program [3]. The loss of fluorine with dose within the composition is used as an indicator for electron beam damage, because the EELS quantification seems to be more sensitive to beam damage than Z-contrast imaging contrast changes. This work was supported by DOE BES (Contract No. DE-AC05-00OR22725), ORNL's SHaRE User Facility, sponsored by DOE BES, and SEERC.

References

1. *Haubold, H. G et. al., Electrochimica Acta* ***2001,*** *46 , 1559.*
2. *Wu, D. S.et. al., Energy & Environmental Science* ***2008,*** *1 , 284.*
3. *Gerd, D. Quantifit. http://web.utk.edu/~gduscher/Quantifit.*

1



(a) (b) (c)

Figure 1: Molecular Structure of PFSA ionomers- Nafion (a), 3M ionomer (b) and Solvay's Aquivion (c) with a sulfonic acid (SO_3H) pendant group in the side chain.

2

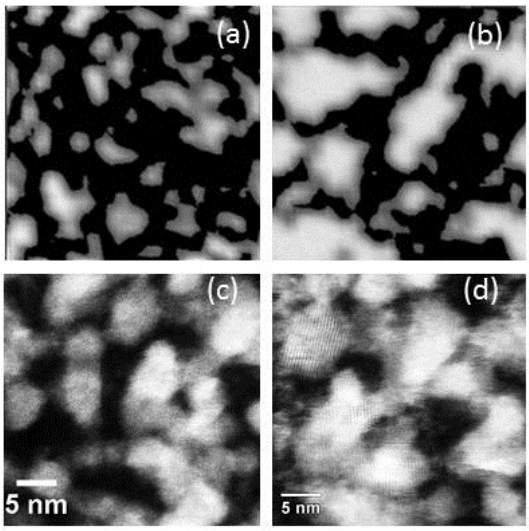


Figure 2: DPD Simulation of 3M 678 (a) λ = 9 and (b) λ =16 and Z contrast images (c) and (d) 3M 636 at the same scale as the simulation obtained at room temperature (dry).

3

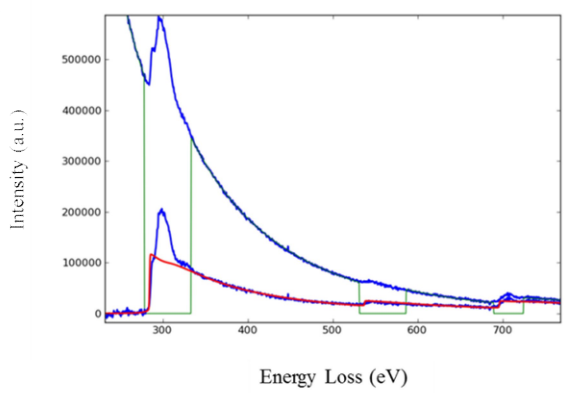


Figure 3: Typical EELS spectra of PFSA

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