Characterizing Water Transport Properties of Hydrocarbon Block Copolymer Proton Exchange Membranes

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The proton exchange membrane (PEM) plays a critical role in transporting protons and provides a barrier to fuel crossover from PEM fuel cells. Perfluorosulfonic acid polymers (PFSAs), such as Nafion®, are the state-of-the-art PEM materials commercially available due to their good chemical stability, excellent mechanical properties and high proton conductivity. However, they have several drawbacks, such as high cost and unsatisfactory chemical durability.

Significant efforts have been devoted to developing alternative PEMs such as sulfonated aromatic statistical or block copolymers, poly(arylene ether sulfone)s (BPSHs), poly(ether ether ketone)s (SPEEKs), poly(arylene ether nitrile)s (SPAEBs), polyimides (SPIs) and polybenzimidazoles. Water transport properties (conductivity, diffusivity and electro-osmotic drag) of these membranes are vital to ensure the performance and stability of PEM fuel cells. These water transport properties are expected to be impacted by varied oligomer categories/properties, block lengths, ion exchange capacity (IEC) and membrane process conditions. The purpose of this work is to analyze how water transport properties of these block copolymer PEMs change with the above parameters and to further correlate the transport properties to the microstructures of these membranes.

The water diffusivity and electro-osmotic drag coefficient (EODC) of BPSH-hexafluoro bisphenol A benzonitrile (6FPAEB) membranes with various chain length segments, IEC and annealing temperature have been measured using our unique dynamic diffusivity and dead-ended EODC techniques [1, 2] (**See Figure 1** and **Figure 2**). Increasing blocklength increases domain size, diffusivity and EODC at a given RH. Higher IEC and annealing temperature have a similar effect. This was expected as the chain length increases, the scale of phase separation increases, and the water behaves more like "bulk water". Also seen is that water diffusivity and EODC of all the hydrocarbon-based ionomers characterized were significantly lower than those of Nafion®.

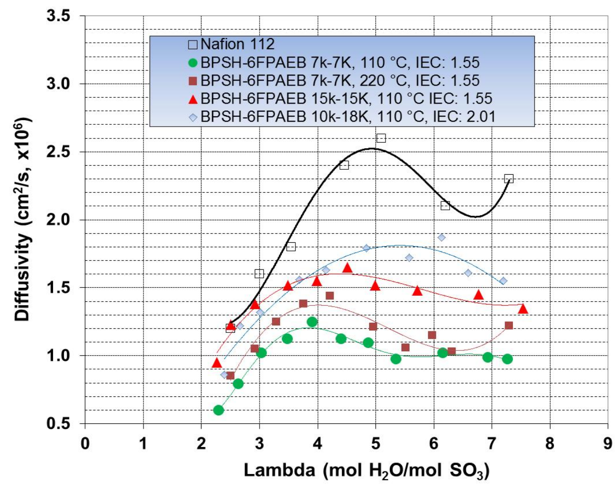

Figure 1: Diffusivity of the BPSH-6FPAEB of various block lengths, IEC and annealing temperature

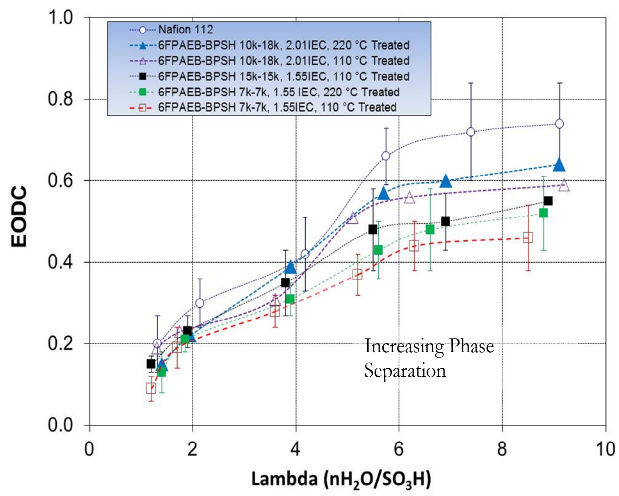

Figure 2: EODC of the BPSH-6FPAEB of various block lengths, IEC and annealing temperature

These membranes will be further characterized by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) and the structure-property relationship will be further elucidated towards better membrane design.

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Reference:

1. H. Xu, J. Ma, and C. Mittelsteadt, Novel System for Characterizing Electro-Osmotic Drag Coefficient of Proton Exchange Membranes", presented in 220th meeting of ECS, Abstract #1304, Honolulu, October (2012)
2. C. Mittelsteadt and J. Staser, Simultaneous Water Uptake, Diffusivity and Permeability Measurement of Perfluorinated Sulfonic Acid Polymer Electrolyte Membranes, ECS Transactions, 41 (1) 101-121 (2011)