Polymers with Tethered Anionic and Cationic Groups as Membranes for Fuel Cells

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Summary: Ionic clustering, water binding, and ion conductivity were studied in polymers functionalized with sulfonic acid and quaternary ammonium hydroxide groups. Small-angle x-ray scattering showed that no clustering occurred in the quaternary ammonium containing anion exchange membranes, while evidence of ionic clusters was present in both sulfonated poly(phenylene) and in Nafion, a poly(perfluorosulfonic acid). Interestingly, the water self-diffusion coefficients of the anion exchange membranes were generally greater than those observed for the sulfonated poly(phenylene)s, and moreover, the water self diffusion coefficients in anion exchange membranes were not a strong function of diffusion time. The water binding behavior lead to increased normalized conductivity in anion exchange membranes as compared to proton exchange membranes at the highest ion exchange capacities.

Keywords: anion exchange membrane; fuel cell; proton exchange membrane; states of water

Introduction

Fuel cells are an important energy conversion technology which have experienced much recent research activity in academic, industrial, and governmental settings. In proton exchange membrane (PEM) fuel cells, the cost of the oxygen reduction catalyst, platinum or a platinum group metal alloy, is a major barrier to widespread commercialization. Advancements in oxygen reduction catalysis in acidic environments have been made,[1,2] but the cost of a PEM fuel cell is still controlled to a large extent by the cost of the catalyst. Additionally, for liquid-fed fuel cells which are attractive for portable power applications, the diversity of liquid fuels is constrained by the oxidation kinetics of the fuel at low pH. Specifically, direct oxidation of ethanol is not currently possible at practical rates in the acidic environment of PEM fuel cells.

Alkaline membrane fuel cells (AMFC) have the advantage of operating at high pH where electrocatalysis, both oxygen reduction[3] and fuel oxidation[4], is significantly facilitated.[5] Membranes that enable operation at high pH may lead to fuel cells without platinum group metal catalysts, therefore significantly lowering the cost of the device. Also, direct oxidation of hydrocarbons and higher molecular weight alcohols may be possible under basic conditions, which leads to a wider selection of fuels for portable devices. Alkaline membrane fuel cells are enabled by polymers with attached quaternary ammonium functional groups.[6,7] Renewed interest in AMFCs has spurred the need for advanced materials development and further understanding of the controlling mechanisms that determine the performance of these devices.

In this report, the nanoscale structure and properties of sulfonated proton exchange membranes and quaternary ammonium containing anion exchange membranes will be compared. By contrasting the characteristics

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of each set of materials, we hope to form a deeper understanding of the structure-property relationships in ion-containing polymers, which may lead to improved, next-generation membranes for fuel cell applications.

Results and Discussion

Small-angle x-ray scattering curves for Nafion, sulfonated poly(phenylene) (SDAPP),[8] and a poly(sulfone) with attached quaternary ammonium groups (PS-AEM)[7] are shown in Figure 1. The measurements on dry membranes were performed on a Molecular Metrology SAXS equipped with a Cu target ($\lambda = 1.542$ Å). Typical counting times were 2 hours with typical membrane thicknesses on the order of 100 μm.

Nafion, with its more organized ionic nanophase structure showed more scattering than the sulfonated poly(phenylene) as evidenced by the increased intensity of the shoulder region around 0.07 Å^{-1}. The shoulder on the scattering curve for SDAPP was shifted to a higher scattering vector and was less intense, which indicates that smaller ionic features are present in SDAPP and than the structure is less well organized, e.g. the ionic phases do not undergo as strong a phase separation in SDAPP as in Nafion. These differences between the structure of Nafion and SDAPP have been observed previously in transmission electron microscopy studies.[9] The quaternary ammonium functionalized poly(sulfone), PS-AEM, showed a persistent decline in scattering intensity as a function of scattering vector with a slope of approximately -3.5 over the entire q-range investigated. This slope may indicate some fractal ordering of scattering or ionic species, but unlike the sulfonated membranes, larger clusters of ions that give rise to shoulders in the scattering curves do not seem to be present. Quantitative analysis of the x-ray and neutron scattering of these materials is an area of future research.

The normalized conductivity (σ_n) plotted against the effective water self diffusion coefficient (D_{eff}) measured using pulsed field gradient nuclear magnetic resonance for a series of each type of membrane at different ion exchange capacities are shown in Figure 2. The conductivity for SDAPP and Nafion was normalized to the dilute solution mobility of protons, 4.76.[10,11] The conductivity of the PS-AEMs was normalized to the dilute solution mobility of bicarbonate, 0.61,[10,11] since there is evidence that PS-AEMs left in contact with air rapidly undergo conversion from hydroxide form to carbonate and bicarbonate due to the presence of CO_2.

The σ_n of SDAPP membranes are significantly higher than for PS-AEMs at low

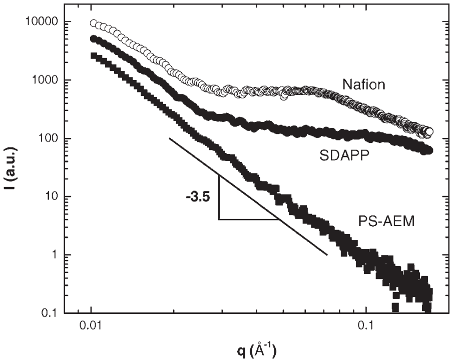

Figure 1.
SAXS intensities as a function of scattering vector for ion-containing polymer membranes, curves offset in intensity for clarity.

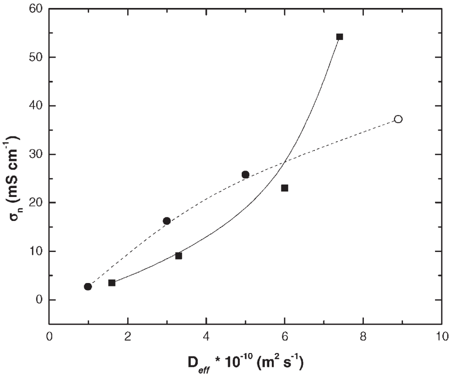

Figure 2.
Normalized conductivity for SDAPP (●), PS-AEM (■), and Nafion (○) as a function of water self diffusion coefficient ($\Delta = 50$ ms, where Δ is the time between gradient pulses).

D_{eff}. Additionally, the normalized conductivity of SDAPP membranes increases rapidly with increases in water self diffusion coefficient. This rapid increase in transport as the ion, and correspondingly water, content is increased may be evidence of percolated ionic pathways in SDAPP as observed from the SAXS. At higher water self diffusion coefficients, the normalized conductivity of the PS-AEM is greater than both SDAPP and Nafion. Under these conditions, the PS-AEM ions are surrounded by a large number of associated water molecules which probably coalesce to form facile ion transport pathways. At low degrees of functionalization in PS-AEMs where D_{eff} is suppressed, the normalized conductivity increases slowly. This slow increase, with much different shape than the curve for sulfonated membranes, may indicate an unpercolated ionic transport pathway in the PS-AEMs which is suggested from the scattering data.

As shown in Figure 3, the water self-diffusion coefficients were observed to be greater in PS-AEMs than in SDAPP membranes, which lead to a greater normalized conductivity once highly percolated ionic transport pathways are formed.

Monitoring the effective water self-diffusion coefficient as a function of the time between gradient pulses (Δ) can be used to probe different length scales within the materials. Nafion, with its highly phase separated ionic structure, seems to have a D_{eff} that is relatively independent of the time (or length) over which it is measured. The effective water self-diffusion coefficient for the PS-AEM samples declines only slightly with longer diffusion times. In SDAPP, the D_{eff} is strongly attenuated with increasing diffusion time which has been observed for other randomly sulfonated copolymers.[12] The dimensions probed by these PFG NMR experiments ($\langle z \rangle = \sqrt{2D_{eff}\Delta}$) range from 5 um to 30 μm. Therefore, the D_{eff} is an average of the different diffusion rates and binding environments experienced by the water over this length scale.

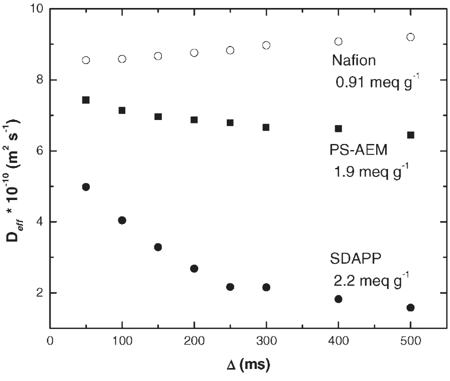

Figure 3.
Effective water self-diffusion coefficient for Nafion, PS-AEM, and SDAPP membranes as a function of the time between gradient pulses.

A series of effective water self-diffusion coefficients as a function of time between gradient pulses for PS-AEMs and SDAPP membranes is shown in Figure 4. In general, the D_{eff} values for the sulfonated poly(phenylene) membranes declined much more severely than for the quaternary ammonium containing poly(sulfone) membranes.

The decline in D_{eff} with diffusion time observed for SDAPP samples could be a result of a disorganized phase separated ionic morphology leading to highly tortuous pathways, or it could be due to the increased hydration energy of sulfonate groups as opposed to the quaternary ammonium groups. The increased hydration energy of the ionic groups would lead to tighter binding of water in the sulfonated membranes. At longer diffusion times more of these slower diffusing environments are encountered leading to the decrease in D_{eff}. As large ionic features were not observed for quaternary ammonium functionalized poly(sulfone) membranes, these membranes present the structure of a rather homogeneous material with dispersed ions throughout. This dispersed ionic structure would lead to length-scale independent D_{eff} as observed in Figure 4. For the lowest ion exchange capacity SDAPP sample, the water self-diffusion coefficient did not change greatly with diffusion time which could indicate that the ionic nanophase morphology was not interconnected at the low IEC and the material behaved more like a dispersed ionic system such as in the PS-AEMs.

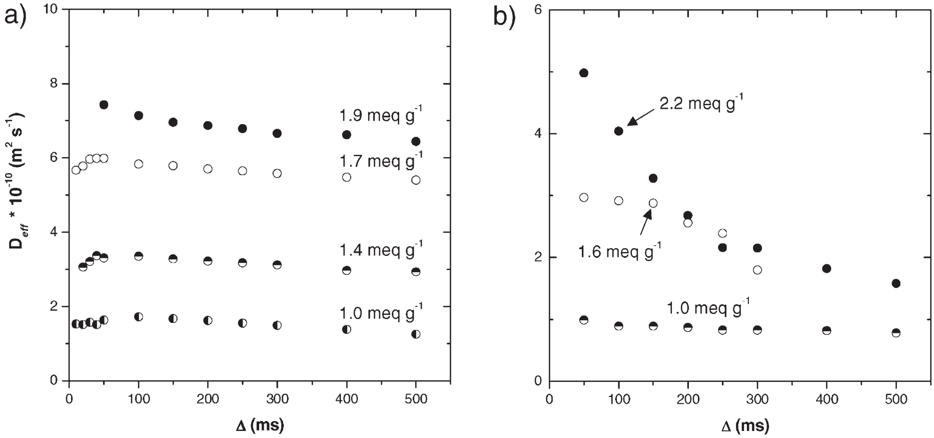

Figure 4.
Effective water self-diffusion coefficient for PS-AEM (a) and SDAPP (b) membranes as a function of the time between gradient pulses.

Conclusions

The ionic morphology and water binding properties greatly affect the transport within ion-conducting membranes. Poly(sulfone) functionalized with quaternary ammonium groups showed no detectable ionic domain formation by small-angle x-ray scattering whereas sulfonated membranes, SDAPP and Nafion, had distinct scattering features. The effective water self-diffusion coefficients were greater in PS-AEMs than in SDAPP and did not show a dependence on the diffusion time. At high IECs, the normalized conductivity of PS-AEMs was greater than that of the sulfonated membranes. These structural and transport measurements indicate that PS-AEMs, without a percolated ionic morphology, must have high ion contents to attain the high normalized conductivity observed in sulfonated membranes. Once a well-connected transport network is formed in PS-AEMs, their normalized conductivity is greater than the sulfonated polymers due to the weak water binding in quaternary ammonium functionalized membranes.

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[1] R. R. Adzic, J. Zhang, K. Sasaki, M. B. Vukmirovic, M. Shao, J. X. Wang, A. U. Nilekar, M. Mavrikakis, J. A. Valerio, F. Uribe, *Topics in Catalysis* **2007**, *46*(3–4), 249.

[2] V. Stamenkovic, B. S. Mun, K. J. J. Mayrhofer, P. N. Ross, N. M. Markovic, J. Rossmeisl, J. Greeley, J. K. Norskov, *Angew. Chem. Int. Ed.* **2006**, *45*(18), 2897.

[3] B. B. Blizanac, P. N. Ross, N. M. Markovic, *Electrochim. Acta* **2007**, *52*, 2264.

[4] M. C. Morin, C. Lamy, J. M. Léger, *J. Electroanal. Chem. Interf. Electrochem.* **1990**, *283*(1–2), 287.

[5] J. R. Varcoe, R. C. T. Slade, *Fuel Cells* **2005**, *5*(2), 187.

[6] T. N. Danks, R. C. T. Slade, J. R. Varcoe, *J. Mater. Chem.* **2003**, *13*(4), 712.

[7] M. R. Hibbs, M. A. Hickner, T. M. Alam, S. K. McIntyre, C. H. Fujimoto, C. J. Cornelius, *Chem. Mater.* **2008**, *20*(7), 2566.

[8] C. H. Fujimoto, M. A. Hickner, C. J. Cornelius, D. A. Loy, *Macromolecules* **2005**, *38*(12), 5010.

[9] M. A. Hickner, C. H. Fujimoto, C. J. Cornelius, *Polymer* **2006**, *47*(11), 4238.

[10] J. A. Dean, "*Lange's Handbook of Chemistry*", 15th ed., McGraw-Hill, New York **1999**.

[11] P. Vanysek, *Ionic conductivity and diffusion at infinite dilution*, in: "*CRC Handbook of Chemistry and Physics*", 83rd ed., D. R. Lide, Ed., CRC Press, Boca Raton **2002**.

[12] A. Roy, M. A. Hickner, X. X. Yu, Y. Li, T. E. Glass, J. E. McGrath, *J. Poly. Sci., B: Poly. Phys.* **2006**, *44*, 2226.