Nafion versus Sulfonated poly(arylene ether sulfone)s: A comparison of the methanol diffusion behavior.

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Direct methanol fuel cells (DMFCs) may potentially be used for portable power applications. The limitation with such fuel cells however, is the permeation of methanol through the fuel cell membrane. This permeation not only results in an inefficient use of the fuel, but also creates a mixed potential at the cathode, thereby limiting the overall cell efficiency. As with most polymer electrolytes, Nafion does not sufficiently inhibit methanol crossover, thus warranting the development of new membranes that will perform better in a direct methanol fuel cell.

In this work, we studied the methanol diffusion behavior for two fuel cell membranes; Nafion 117 (Du Pont) and a sulfonated poly(arylene ether sulfone) (BPSH-40), produced at Virginia Tech. The BPSH-40 membrane was previously shown to be a good proton conductor and performs admirably in a direct methanol fuel cell[1]. Permeability measurements also suggest that this membrane material is relatively impermeable to methanol, and thus may be a suitable candidate to replace Nafion in DMFCs[1]. The aim of this study was to examine the effect of methanol concentration (0.5 to 8M) and temperature on the diffusion behavior of methanol within these membranes.

The diffusion coefficients were determined with the use of novel nuclear magnetic resonance (NMR)[2]. This method enables the diffusion of methanol to be determined while the membrane is immersed in a methanol solution. The effect of methanol concentration on the diffusion of methanol within the two membranes is shown in Figure 1. Overall, the diffusion coefficients are similar. However, while there is a steady increase in the diffusion of methanol in Nafion as the concentration increases, the diffusion of methanol in BPSH-40 shows a dramatic decrease between 2 and 4M before leveling out. This behavior was quite surprising upon first examination, as it seems that the BPSH-40 membrane becomes more impermeable to methanol as the concentration of methanol increases. One possible explanation for this observation is that the water and methanol uptake into the membrane are tightly coupled. Therefore, at lower methanol concentrations where the water activity is high, and thus the water uptake is high, the methanol more readily permeates the membrane. As the methanol concentration decreases, so to does the water content and consequently there is less tendency for the water to assist in the methanol uptake.

To probe the validity of this hypothesis, the membranes were immersed in methanol solutions of different concentrations and weighed to determine the total amount of solvent absorbed by the membrane. The results are shown in Figure 2 and the mass is normalized to the largest total weight. For Nafion, there is a steady increase in the solvent uptake as the methanol concentration increases. This is consistent with the previously observed 'equipartitioning' of water and methanol into the membrane. With the BPSH-40 membrane, however, the mass decreases before leveling out at concentrations above 4M. This may indicate that the water content is dropping but the methanol is still effectively excluded by BPSH. In other words, the solubility of methanol in BPSH is most responsible for the increased 'selectivity' coefficient. This is also consistent with our observation that the diffusion coefficient of methanol in the membrane is comparable to that in Nafion even though the permeability is comparatively lower. The implication of these results is that the BPSH-40 membrane may be more suited for DMFC applications given the relatively low uptake of methanol, particularly at the higher methanol concentrations.

1. B. S. Pivovar, M. Hickner, F. Wang, J. McGrath, P. Zelenay and T. A. Zawodzinski, AIChE Fuel Cell Technology: Opportunities and Challenges, 535 (2002)
2. H. A. Every and T. A. Zawodzinski, AIChE Fuel Cell Technology: Opportunities and Challenges, 558 (2002).

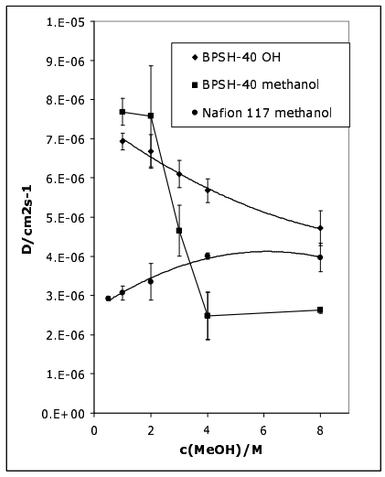

Figure 1 The effect of concentration on the methanol diffusion properties.

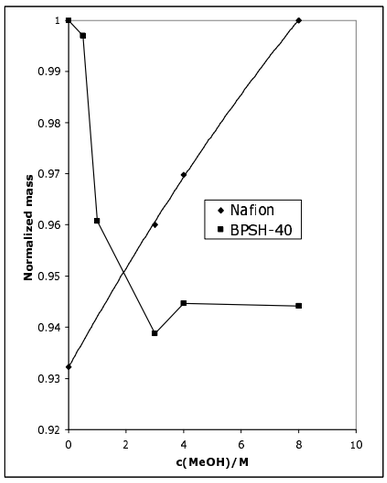

Figure 2 The effect of methanol concentration on solvent uptake in the membrane.