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# Direct Methanol Fuel Cell Performance Using Sulfonated Poly(arylene ether sulfone) Random Copolymers as Electrolytes

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## Abstract

Sulfonated poly(arylene ether sulfone) random copolymers are a new series of sulfonic acid containing polymers that have shown promise as fuel cell electrolytes. Here, we report on direct methanol fuel cell (DMFC) performance of this class of polymers at sulfonation levels ranging from 40 to 60% (monomer basis). The DMFC performance of these polymers is compared to that of Nafion 117, the long standing standard in fuel cell testing. These polymers show a higher selectivity for protons over methanol for all the sulfonation levels tested, with the 40% sulfonated polymer showing 2.5 times the selectivity of Nafion. While the higher sulfonated forms (50 and 60%) did show a higher selectivity, only the lower sulfonation levels (40 and 45%) have shown improved performance in DMFC testing. The results of these experiments will be discussed in terms of the relevant test conditions, and experimentally determined membrane properties. The relevant DMFC properties of these polymers will be discussed in terms of sulfonation level and compared to those of Nafion 117.

## Introduction

Direct methanol fuel cells (DMFCs) are currently being investigated for a wide number of applications because methanol has reasonable electrochemical activity, high energy density, and is an easily handled liquid under moderate conditions. Sulfonated poly(arylene ether sulfone)random copolymers (PBPSH), a new class of polymer electrolytes, were studied as a replacement for Nafion in DMFCs. Polymer films, ranging in sulfonation level from 40% (PBPSH-40) to 60% (PBPSH-60) on a monomer basis, were examined in terms of DMFC performance and relevant fuel cell characteristics.

Nafion, a perfluorosulfonic acid ionomer, has been the primary membrane used due to its good chemical and mechanical stability, high proton conductivity and the ability to be made into membrane electrode assemblies with high performance. However, for DMFC applications, Nafion has high methanol permeability, and typically suffers from high methanol crossover, leading to both the loss of potential energy from the methanol reacting at the cathode, and the overpotential losses associated with methanol oxidation at the cathode.

Even though fuel utilizations near 90% have been reported for DMFC systems based on Nafion (1), these values are only for fixed points of operation and suffer greatly when not operated under optimal conditions. An improved DMFC membrane would allow for higher fuel utilizations and a greater dynamic operating range. Furthermore, a high efficiency Nafion system is typically limited to very low methanol concentrations (<.5M), and for system considerations higher feed concentrations would often be preferred.

While there has been great interest in developing new membranes for use in DMFCs, there has been little success demonstrated in this area using membranes other than Nafion or similar polymers. Here, we present the results of PBPSH in DMFC testing which shows promising performance when compared to Nafion 117.

## Experimental

### *Synthesis of Membrane Electrode Assemblies (MEAs)*

MEAs were prepared from standard catalyst inks containing either unsupported platinum or platinum-ruthenium, and water and Nafion 1200 solution. These inks were sonicated and then applied to the membranes by direct painting. So that all the membranes tested have identical electrodes. Nafion 117 films were pretreated by boiling in peroxide and acid, and sulfonated poly(arylene ether sulfone)random copolymers (PBPSH - XX) membranes were converted to the acid form by boiling in acid (the XX designation refers to the percent sulfonation of the monomer, for example PBPSH – 40 refers to a 40% sulfonated poly(arylene ether sulfone)random copolymer). Further details of polymer synthesis/structure and membrane casting have been reported elsewhere (2). Thickness of the dry membranes was determined using a micrometer prior to catalyst application.

### *Fuel Cell Experiments*

The resulting MEAs were tested in fuel cell hardware to determine membrane properties and DMFC performance. Relevant DMFC membrane properties such as methanol permeability, proton conductivity and electro-osmotic drag were obtained from these experiments.

Fuel cell test results reported here are for tests run in 5 $cm^2$ cells at 60C with 1M methanol at a flow rate of 2 mL/min, and an air flow rate of 250 sccm at 30 psig backpressure. Polarization curves were obtained under these conditions, and proton conductivities were determined from high frequency resistance measurements.

By operating the cell at a constant current, we were able to determine both the water flux through the membrane and the methanol crossover as a function of current density, from an analysis of the cathode effluent. In this experiment, the water in the cathode exhaust was collected in a Drierite filled U-tube, and the $CO_2$ content of the dry effluent was determined using a nondispersive linearized $CO_2$ sensor. While, the details of this experiment are described in greater detail elsewhere (3), from the data obtained we were able to extract the methanol permeability (from crossover data in the absence of current) and the electro-osmotic drag coefficient of the membrane. Additionally, the crossover data and polarization curves were used to determine cell efficiency as a function of current density using a method also described in greater detail elsewhere (4).

## Results and Discussion

Figure 1 shows DMFC polarization curves for the five different membranes tested: PBPSH at 40, 45, 50 and 60% sulfonation, and Nafion 117. Under the conditions tested (1M methanol, 60C), the PBPSH-40 membrane showed the best performance at low current density, and the PBPSH-45 membrane showed the best performance at high current density, with up to a 100mV improvement over Nafion 117. The PBPSH-50 and 60 membranes showed very similar performance, although much poorer than that of Nafion 117.

The methanol crossover of the above cells is shown in Figure 2 as a function of current density. The PBPSH-40 membrane showed by far the lowest crossover of any of the cells tested, a four times lower than that of Nafion 117. While, the other PBPSH membranes showed methanol crossover rates even higher than of Nafion 117, with the PBPSH-45 membrane showing the highest crossover rate. At first glance these results seem counterintuitive, because one expects that crossover rates should increase as the sulfonation level and water uptake of the membranes increase. However, the membranes tested here were of varying thickness, and when interpreting crossover rates membrane thickness is a key parameter.

Membrane thickness, along with open circuit methanol crossover, high frequency resistance and electro-osmotic drag coefficient, of the test membranes can be found in Table 1. From these measured data, methanol permeability and proton conductivity were calculated, along with selectivity and relative selectivity, see Table 2. The calculated methanol permeability and proton conductivity of these membranes are dependent not only on the open circuit methanol crossover or high frequency resistance, but also highly sensitive to the measured membrane thickness. However, the selectivity of these membranes is independent of membrane thickness, and only depends on the directly measured methanol crossover and high frequency resistance.

Once membrane thickness is accounted for, the methanol permeability of the PBPSH system of polymers does follow the trend of increasing permeability with increasing sulfonation level as expected. The least methanol permeable membrane PBPSH-40 is less than 1/5 as permeable as Nafion 117, and even PBPSH-60, the most permeable PBPSH polymer tested, is 40% less permeable than Nafion 117, and the crossover data shown in Figure 2 is reasonable.

Proton conductivity would be expected to follow a similar trend of increasing conductivity with sulfonation. In fact this trend has been shown on measurements of freestanding PBPSH membranes using AC impedance (2). However, the proton conductivity of these measurements shows a minimum at 45% sulfonation is these fuel cell tests. This minimum can be explained in terms of the experimental measurement and our treatment of the data. The high frequency resistance measurement that is used to determine the proton conductivity takes into account not only membrane resistance, but also other resistances associated with current collectors, catalyst/backing layers and interfaces. The resistance obtained is normalized by the thickness of the membrane; therefore, the thinner the membrane the more important these added resistances become. For a relatively thick membrane like Nafion 117, where interfacial resistances between the catalyst layer and membrane are likely to be small because Nafion has been used in the catalyst layer eliminating a dissimilar polymer interface, these resistances can usually be safely ignored when interpreting proton conductivity data. However, for dissimilar polymers and thin membranes (in this study the PBPSH-45 membrane was 16% the thickness of Nafion 117) these resistances can play an important role in high frequency resistance data.

We can interpret polarization curves for these polymers in terms of methanol crossover and high frequency resistance. PBPSH-40 has the best performance at low current and also the lowest methanol crossover. The decreased crossover could easily lead to a reduced overpotential at the cathode and therefore increased performance at low current. PBPSH-45 has the best performance at high current, and this can be explained because it has the lowest high frequency resistance of any of the membranes tested. Its performance at low current is somewhat surprising due to the high crossover rates exhibited. PBPSH-50 and 60 have very similar curves with poor performance. This poor performance may be attributed partially to the high methanol crossover rates through the polymer, but other factors certainly contribute. It may be that the electrodes of these MEAs were of poor quality or that an interaction between the polymers contributed this decrease in performance. These data were taken from single experiments and as with any experimental membrane, supply and reproducibility are factors and are being pursued.

The selectivity of the membranes, a ratio of the proton conductivity to the methanol permeability of a membrane, are found in Table 2 and from these values a relative selectivity, a ratio of a membrane's selectivity normalized by the selectivity of Nafion 117, were determined, also in Table 2. Relative selectivity is a useful standard, because Nafion 117 has a relative selectivity of 1, and a membrane with a value greater than one has a chance of being an improved DMFC electrolyte, with the greater the number the greater the potential improvement. The PBPSH system of polymers shows a trend of increasing selectivity with decreasing sulfonation level for the range tested here, 40 to 60% sulfonation. Even the least selective membrane, PBPSH-60, has a selectivity 10% higher than that of Nafion 117, while the most selective membrane, PBPSH-40, has a selectivity 2.5 times that of Nafion 117.

The electro-osmotic drag coefficient of the PBPSH system of polymers increased as the level of sulfonation increased (water uptake also increased in this range (2)). The electro-osmotic drag ranged from 1.5 waters/ proton for PBPSH-40 to 3.0 waters/ proton for PBPSH-60 at 60C. Figure 3 is a graph for electro-osmotic drag coefficient versus relative selectivity for all the membranes tested. Interestingly, Nafion 117 seems to follow the general trend of the PBPSH polymers of decreasing selectivity with increasing electro-osmotic drag coefficient. This suggests that selectivity and electro-osmotic drag may be related in ionomer systems as has been suggested elsewhere (5,6).

Overall efficiencies of these cells are shown in Figure 4 for each of the membranes tested as a function of current density. PBPSH-50 and 60 show poor performance in terms of overall efficiency when compared to Nafion 117. But, both PBPSH-40 and 45 show promise when compared to Nafion 117. PBPSH-45 shows similar maximum efficiency to Nafion 117, but at increased current. PBPSH-40 is the most interesting of the group, showing a greatly increased efficiency over all the other membranes tested, as might be expected because it was also the most selective membrane. While lowering the methanol feed concentration would increase the efficiency of Nafion, and lessen the difference in efficiency between Nafion and PBPSH-40. PBPSH-40 should still give better performance in fuel cell tests due to its higher selectivity.

## Conclusions

While there has been great interest in developing new membranes for use in DMFC applications, there has been little success demonstrated in this area using membranes other than Nafion or similar polymers. Here, we have demonstrated the use of PBPSH with a significant improvement compared to Nafion 117 DMFCs both in terms of current/voltage response and fuel utilization, with the best performance coming from the least sulfonated polymer tested PBPSH – 40. This polymer also shows a significantly decreased electro-osmotic drag coefficient, and the results presented here suggest a relationship between electro-osmotic drag and selectivity in polymer electrolytes. While, the results presented here are encouraging, further work needs to be done to understand the role of electrode structure on performance and of interfacial resistances, as well as studies on the reproducibility of these experiments and the stability of PBPSH polymers in these systems.

## Acknowledgements

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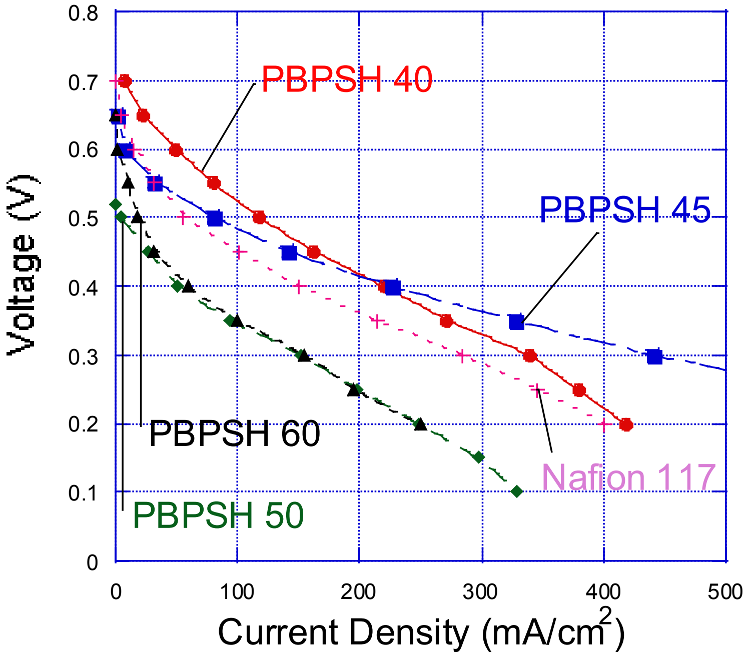

Figure 1: DMFC polarization curves for PBPSH-40, 45, 50 and 60 and Nafion 117. Anode: 1M methanol, 2mL/min. Cathode: 250 sccm air, humidified to 65C, 30 psig backpressure. Cell 60C.

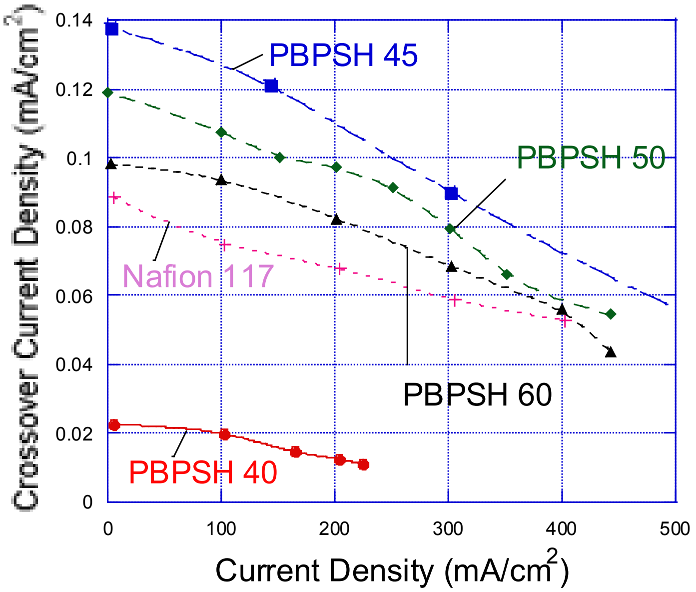

Figure 2: Methanol crossover current as a function of current density for PBPSH-40, 45, 50 and 60 and Nafion 117.

| Membrane | Open Circuit Methanol Crossover (mA/cm$^2$) | High Frequency Resistance Ohm cm$^2$ | Membrane Thickness (µm) | Electro-osmotic Drag Coefficient |
|---|---|---|---|---|
| Nafion 117 | 89 | 0.21 | 178 | 3.3 |
| PBPSH-40 | 23 | 0.33 | 127 | 1.5 |
| PBPSH-45 | 138 | 0.09 | 30 | 1.9 |
| PBPSH-50 | 118 | 0.12 | 48 | 2.5 |
| PBPSH-60 | 99 | 0.17 | 89 | 3.0 |

Table 1: DMFC measured open circuit methanol crossover, high frequency resistance, and electro-osmotic drag coefficient for PBPSH-40, 45, 50 and 60 and Nafion 117. Membrane thickness of the test membranes has also been included.

| Membrane | Methanol Permeability x10$^6$ (cm$^2$/s) | Proton Conductivity mS/cm | Selectivity x10$^{-6}$ (mS s /cm$^3$) | Relative Selectivity |
|---|---|---|---|---|
| Nafion 117 | 2.73 | 84.7 | 31.0 | 1.00 |
| PBPSH-40 | 0.50 | 38.5 | 76.3 | 2.46 |
| PBPSH-45 | 0.73 | 33.9 | 46.6 | 1.50 |
| PBPSH-50 | 0.98 | 40.2 | 40.9 | 1.32 |
| PBPSH-60 | 1.52 | 52.3 | 34.4 | 1.11 |

Table 2: Relevant DMFC membrane properties (methanol permeability, conductivity and selectivity) calculated from experimental data found in Table 1.

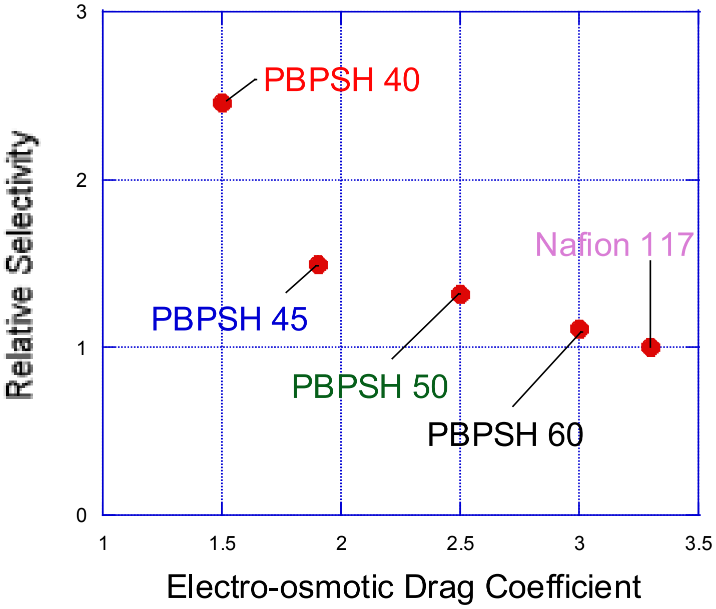

Figure 3: Relative selectivity versus electro-osmotic drag coefficient for PBPSH-40, 45, 50 and 60 and Nafion 117.

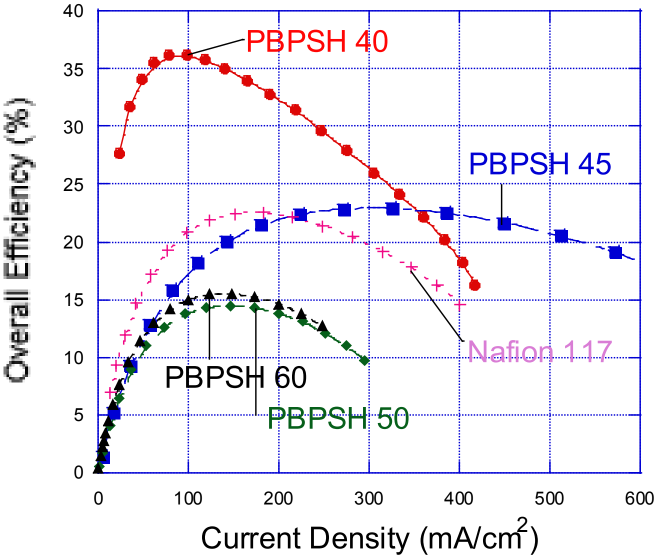

Figure 4: DMFC overall cell efficiency as a function of current density for PBPSH-40, 45, 50 and 60 and Nafion 117.