

## The Importance of Interfaces in Membrane Optimization for DMFCs

Yu Seung Kim<sup>1</sup>, J.E. McGrath<sup>2</sup> and Bryan S. Pivovar<sup>1</sup>

<sup>1</sup>Electronic and Electrochemical Materials and Devices, MST-11, MS-D429, Los Alamos National Laboratory, Los Alamos, NM 87545

<sup>2</sup>Department of Chemistry and Materials Research Institute, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

Methanol resistant membranes based on disulfonated poly(arylene ether sulfone) copolymers (BPSH-XX, where XX refers to the degree of disulfonation) were developed at Virginia Tech.<sup>1,2</sup> The performance of these copolymers has been optimized in terms of membrane selectivity (i.e. the ratio of proton conductivity to methanol permeability).<sup>3</sup> Recently, we found that the interfacial compatibility between membrane and electrode could have a significant influence on performance and durability depending on methanol feed concentration<sup>4</sup> and copolymer composition.<sup>5</sup> In this presentation, the performance of the BPSH copolymers is investigated in terms of interfacial resistance rather than membrane selectivity.

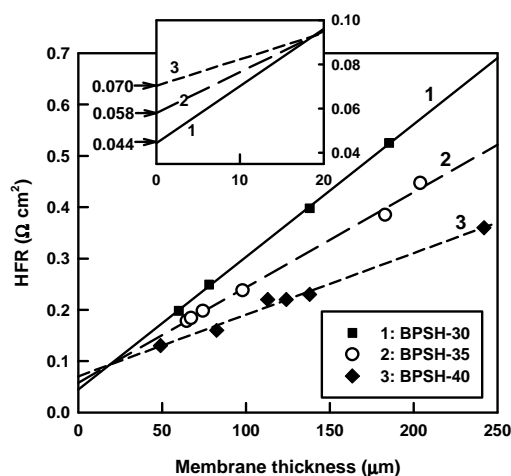
Figure 1 shows cell resistance as a function of membrane thickness. From this plot, we derive the membrane resistivity (slope) and nonmembrane resistance (y-intercept).<sup>5</sup> The conductivity of the membrane is the inverse of the resistivity and the interfacial resistance is estimated by subtracting electronic resistances from the nonmembrane resistance. Figure 1 shows that cell resistivity increased (membrane conductivity decreased) with decreasing disulfonation level, as expected, but the interfacial resistance decreased. An interesting result occurs when extrapolating values from Figure 1 to membranes of 20  $\mu\text{m}$  thickness. At this membrane thickness the HFR from all three disulfonation levels are identical, because tradeoffs between interfacial resistance and membrane resistance are equal. These results illustrate the importance of interfacial effects on observed HFR.

Figure 2 presents DMFC performance using thin membranes of BPSH-30, -35 and Nafion (~ 60  $\mu\text{m}$  thick). This figure clearly shows that the BPSH-30 MEA outperformed the BPSH-35 and Nafion control MEAs. The differences in performance are attributed to methanol crossover and the quality of the interfaces. These results will be discussed in detail, with further investigation into the effects of membrane acidification, methanol concentration, and long-term stability.

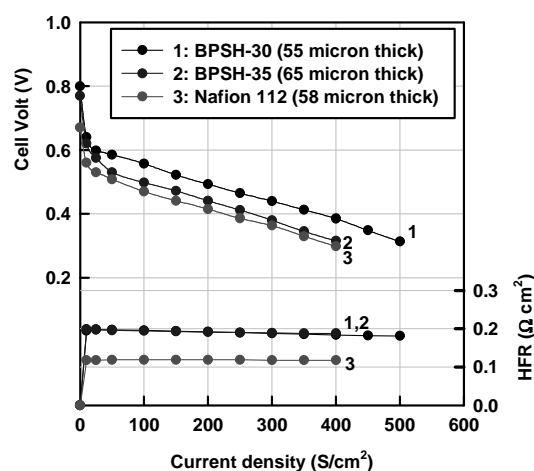
### References

1. F. Wang, M. Hickner, Y. S. Kim, T. Zawodzinski, and J. E. McGrath, *Journal of Membrane Science*, 197 (2002), 231-242.
2. W. Harrison, F. Wang, J. B. Mechem, V. Bahanu, M. Hill, Y. S. Kim, and J. E. McGrath, *Journal of Polymer Science, Part B: Polymer Chemistry* 41 (2003), 2264-2276.
3. Y. S. Kim, M. Hickner, L. Dong, B. S. Pivovar, J. E. McGrath, *Journal of Membrane Science*, in print (2004).

4. Y. S. Kim, B. S. Pivovar, 206<sup>th</sup> Meeting of the Electrochemical Society, Honolulu, Oct. 3-8, (2004).
5. Y. S. Kim, B. S. Pivovar, 204<sup>th</sup> Meeting of the Electrochemical Society, Orlando, Oct. 12-16, (2003).



**Figure 1.** The effect of copolymer composition of BPSH on HFR at 80°C under DMFC conditions; arrows in the small box indicate the non-membrane resistance



**Figure 2.** Polarization curve of BPSH-30 MEA under optimized membrane thickness; feed methanol concentration: 2 M.

### Acknowledgment

The BPSH copolymer tested in this study was supplied by Hydrosize Technologies, Inc. (Raleigh, NC) based on procedures developed at Virginia Tech. Expressed appreciation to the U.S. Department of Energy.