V.B.7 Non-Nafion® Membrane Electrode Assemblies

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Objectives

Develop low-cost, high performance and durable alternative membrane electrode assemblies (MEAs).

- Explore MEA operating window dependence on architecture.
- Evaluate the performance of non-Nafion® binder under H_2/air conditions.
- Demonstrate H_2/air long-term (2,000 h) performance of non-Nafion® membranes under cycling conditions.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost
(C) Electrode Performance
(D) Thermal, Air, and Water Management
(J) Startup Time/Transient Operation

Technical Targets

This project is developing alternative non-Nafion® membranes and electrode ionomers. Major technical targets for proton exchange membrane and MEA are as follows:

- Performance @ ¼ power (0.8 V): 320 mW/cm^2
- Durability with cycling at operating temperature of ≤80°C: 5,000 h
- Durability with cycling at operating temperature of >80°C: 2,000 h
- Inlet water vapor partial pressure: 1.5 kPa (abs)

Accomplishments

- Fluorinated poly(arylene ether sulfone) membranes were developed which exhibited excellent compatibility with Nafion®-bonded electrodes and better water utilization upon proton conduction compared to a previously developed wholly aromatic polysulfone system. [Power density at 0.8 V of the fluorinated poly(arylene ether sulfone) membranes was 200 and 240 mW/cm^2 at 80 and 95°C, respectively.]
- Preliminarily testing showed no catastrophic membrane failure observed in H_2/air fuel cell mode for ~400 h at 80°C under start/stop cycling conditions. Two thousand hour life test will be completed by September 30, 2006.
- Non-Nafion® ionomer-catalyst ink dispersion was prepared using an alcohol/water mixture. The performance of non-Nafion® ionomer-bonded electrodes reached 272 mW/cm^2 (0.8 V) at 95°C and 65% relative humidity (RH).

Introduction

Current perfluorinated copolymer proton exchange membranes such as Nafion® are undesirably expensive and unstable at elevated temperature. Thus, advanced and low-cost polymer materials that have improved performance and preferably operation at >80°C and low hydration levels are needed. In addition, the new materials must have good mechanical and chemical stability under highly oxidizing conditions, which would maintain their fuel cell performance in the aggressive environment.

In FY 2004, we developed wholly aromatic polysulfone copolymers (BPSH) which are thermal-oxidatively stable and highly proton conductive (ca. ~0.1 S/cm at room temperature) [1]. However, these copolymers have relatively poor interfacial compatibility with Nafion®-bonded electrodes which lead to continuous performance degradation over time [2]. Therefore, in FY 2005, we have started to develop new types of hydrocarbon-based copolymers which have desirable interfacial compatibility with Nafion®-bonded electrodes. In FY 2006, we not only continued to develop alternative polymer electrolyte but also made efforts to develop non-Nafion® ionomers which may enhance the interfacial compatibility with non-Nafion® membranes. Initial and extended term performance of new electrolyte and electrode materials are evaluated.

Approach

Relatively poor interfacial compatibility between BPSH and Nafion®-bonded electrodes originated from a dimensional mismatch between membrane and electrode under dehydrated/hydrate cycling conditions, lack of adhesion, and water transport/electro-osmotic drag difference. Thus, the technical approaches in this project include (1) alternative membranes which are interfacially compatible with Nafion®-bonded electrodes and (2) alternative electrodes which are interfacially compatible with non-Nafion® membranes.

For membrane development, the chemical structure of BPSH is modified using various functional groups such as hexafluoro bisphenol-A, benzonitrile, and phenyl phosphine oxide (PPO) groups. A qualitative relationship between the chemical structure and interfacial compatibility is established. Based on the interfacial study, H_2/air fuel cell performance of a few selected interface compatible non-Nafion® membranes are demonstrated at 80°C or higher temperature. Durability tests under various cycling conditions have been performed and remain as on-going tasks. For the electrode binder development, an appropriate catalyst ink formulation is prepared from alcohol/water mixture. Electrochemical analysis and electrode optimization are performed using some selected non-Nafion® ionomers. Finally, the performance of non-Nafion® bonded electrocatalyst is reported.

Results

Previous studies indicated that the interfacial incompatibility of our polysulfone systems were impacted by membrane volume change due to hydration and temperature change, suggesting that reducing dimensional mismatch between membrane and electrode would improve interfacial compatibility [3]. Thus, our experiments focus on developing low-water swollen alternative polymer electrolytes while maintaining high proton conductivity for the Nafion®-bonded electrodes in order to meet the DOE membrane durability target.

The chemical structure of BPSH was modified by introducing fluorine moieties or other polar functional groups such as benzonitile or phenyl phosphine oxide (PPO) in the copolymer backbone. Membrane water uptake has been carefully measured based on wet volume instead of the conventional dry weight basis, in which membrane density and water volume fraction were considered. The modified polysulfone membranes with incorporation of hexafluoro bisphenol A and other polar groups (e.g. benzonitrile groups) showed a reduced water uptake compared to BPSH (Figure 1a and 1b, respectively). The reduced water uptake significantly improved the interfacial compatibility which was confirmed by the accelerated long-term tests (i.e. in direct methanol fuel cell mode). Strong polar group incorporation, however, resulted in a decreased proton conductivity which adversely impact fuel cell performance, while fluorinated systems showed improved proton conductivity compared to BPSH, probably attributed to a greater degree of phase separation. Figure 2 shows the H_2/air fuel cell performance of a selected fluorinated system at 80 and 95°C. Power density at 0.8 V of this system reached to 200 and 240 mW/cm^2 at 80 and 95°C, respectively,

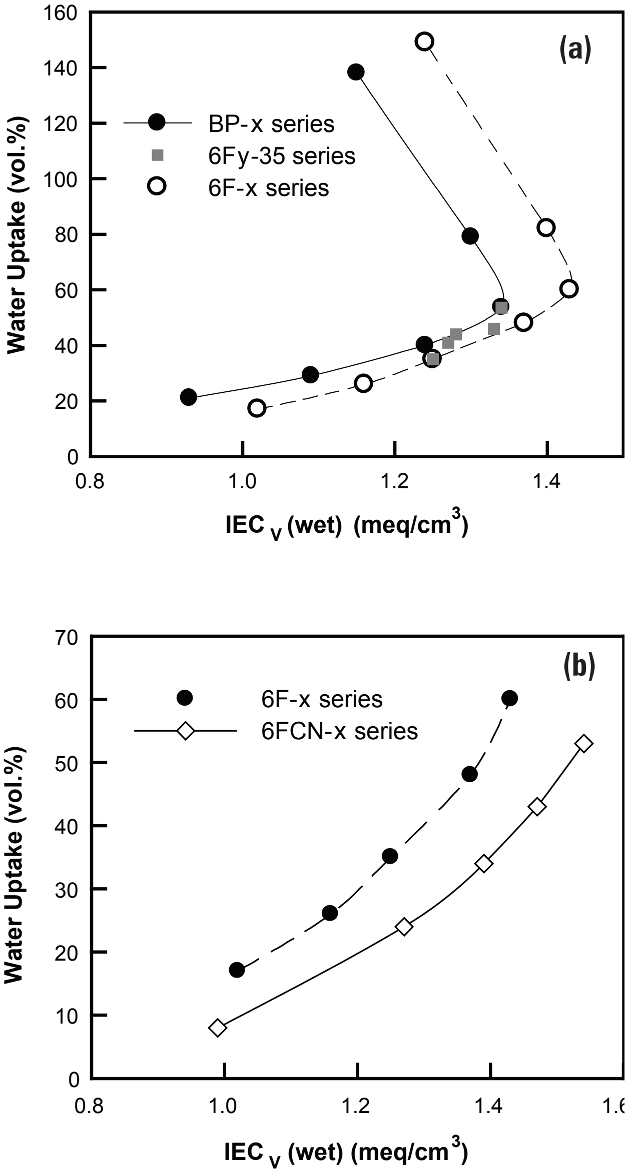

FIGURE 1. Effect of (a) Fluorine and (b) Polar Group (benzonitrile) of Sulfonated Polysulfones on Water Uptake

which was approaching to the 2010 DOE target (i.e. 320 mW/cm^2). Preliminary results from the long-term H_2/air fuel cell test showed stable performance for at least 400 h under start/stop cycling which was in stark contrast with the continuous performance decrease of the previous BPSH system that over time (Figure 3). Further life test using this copolymer system is on-going.

The other way to improve the membrane-electrode interface is to use non-Nafion® ionomer as the electrode binding material. Previous studies (FY 2003-2004) indicated that the ionomer dispersion made from polar solvents such as DMAc poisoned the electrocatalyst, resulting in decreasing electrochemically available catalyst surface area and electrochemical activity [4]. In the FY 2006, we were able to prepare an alcohol-based catalyst ink formulation. Figure 4 compares the cyclic voltamograms of non-Nafion® and Nafion®-bonded electrodes. It was noted that the available electrochemical surface area for the non-Nafion®-bonded Pt catalyst was slightly greater than that of the Nafion®-bonded catalyst, possibly due to better ionic contact with the catalyst particles. Hydrogen oxidation and reduction occur at very similar rates with a noticeable difference in the hydrogen desorption and oxidation peak shapes. The change in the onset of platinum oxidation (~800 mV) gives further evidence that the polymer/catalyst interfaces of these two materials are significantly different. Further investigation of this non-Nafion® bonded electrode elucidated that limited mass transfer, probably due to the flooding, would be the main cause for the relatively inferior fuel cell performance which could be diminished with less humidified conditions. Figure 5 shows the polarization curve using a non-Nafion® bonded cathode of which the power density reached to 272 mW/cm^2 (80% of DOE 2010 target) at 95°C, and 65% RH.

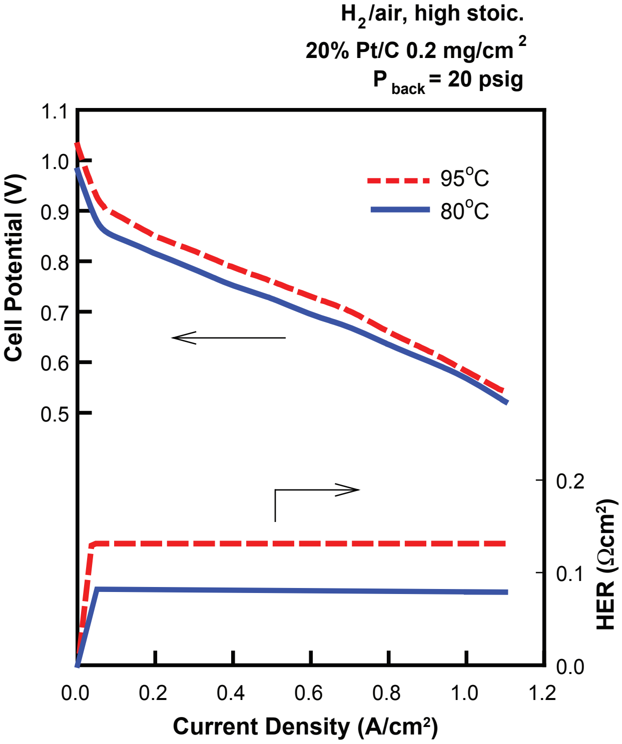

FIGURE 2. H_2/air Fuel Cell Performance of Fluorinated Polysulfone at 80 and 95°C

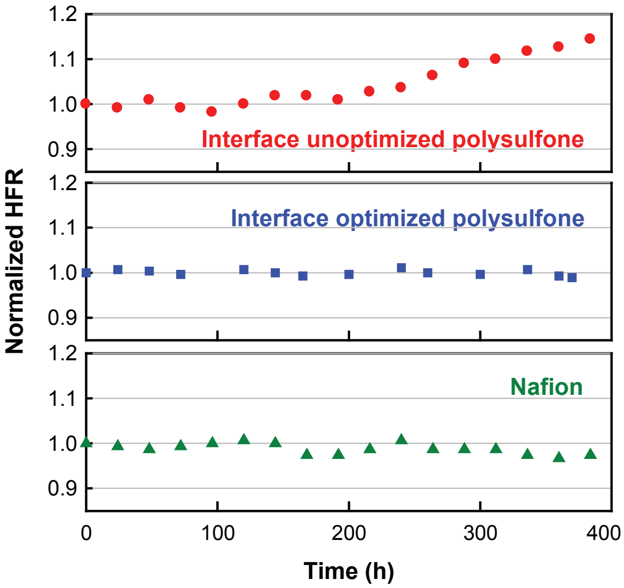

FIGURE 3. Cell High-Frequency Resistance Change during Life Test with Start-Stop Cycling

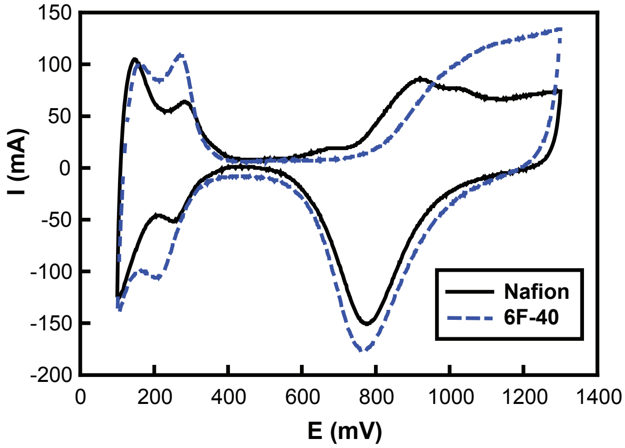

FIGURE 4. Comparison of Cyclic Voltamograms of Nafion®- and Sulfonated Polysulfone-bonded Pt Catalyst

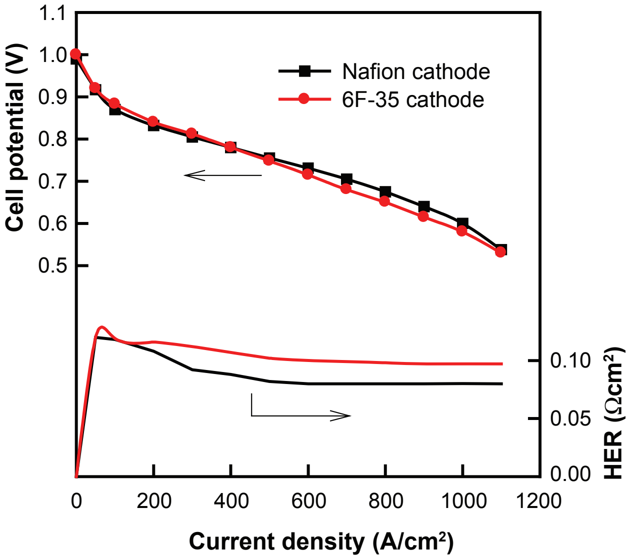

FIGURE 5. H_2/air Performance of Non-Nafion®-bonded Cathode at 95°C, 65% RH

Longer-term stability of this new ionomer is under investigation.

Conclusions and Future Directions

- A new fluorinated polysulfone electrolyte showed good membrane-electrode interfacial compatibility, leading to promising H_2/air fuel cell performance. Further long-term H_2/air life testing (e.g. 2,000 h with start/stop cycling) will be completed by September 2006.
- Nobler non-Nafion® membranes are planned to be synthesized using multi-block architecture, aiming at improved fuel cell performance at lower inlet water partial pressure.
- Non-Nafion®-bonded electrodes prepared from an alcohol/water dispersion showed encouraging H_2/air performance at low relative humidity. Further results will be needed to verify the stability and appropriate water transfer.
- A systematic approach for ensuring membrane and electrode ionomer durability at elevated temperature (~100°C) and low relative humidity (<50% RH) is needed.

FY 2006 Publications/Presentations

1. Yu Seung Kim and Bryan Pivovar, "Polymer Electrolyte Membranes for Direct Methanol Fuel Cells," in Advances in Fuel Cells (Ed. Tim S. Zhao), Elsevier, Oxford, 2006 to appear.

2. Yu Seung Kim, Brian Einsla, Mehmet Sankir, William Harrison, and Bryan S. Pivovar, "Structure-property-performance Relationships of Sulfonated Poly(Arylene Ether Sulfone)s as a Polymer Electrolyte for Fuel Cell Applications," *Polymer*, 47, 4026 (2006).

3. W.L. Harrison, Y.S. Kim, M. Hickner, and J.E. McGrath, "Poly(Arylene Ether Sulfone) Copolymers from Sulfonated Monomers Building Blocks: Synthesis, Characterization and Performance –A Review," *Fuel Cells*, 5, 2, 201-212 (2005).

4. B.S. Pivovar "An Overview of Electro-osmosis in Fuel Cell Polymer Electrolytes" *Polymer*, 47, 4194 (2006).

5. B.R. Einsla, Y.S. Kim, M.A. Hickner, Y.T. Hong, M.L. Hill, B.S.Pivovar, J.E. McGrath, "Sulfonated Naphtahlene dianhydride Based Polyimide Copolymers for Proton Exchange Membrane Fuel Cells" *J. Memb. Sci.* 15, 255, 141 (2005).

6. A. Siu, B. Pivovar and S. Holdcroft, "Dependence of Methanol Permeability on Morphology and Nature of Water in Graft Copolymers for Proton Exchange Membranes", *Journal of Polymer Science B*, in press (2006).

7. Y.S. Kim, B.S. Pivovar, "Utilizing Alternative Polymers in Fuel Cell Applications: Advantages, Difficulties, and Opportunities", Pacific Polymer Conference IX, Dec. 11-14, Hawaii (2005).

8. Y.S. Kim, B.S. Pivovar, "Alternative Polymer Performance in Direct Methanol Fuel Cells", 46th Battery Symposium, Nagoya, Japan, Nov. 16-18 (2005).

9. Y.S. Kim, F. Garzon, R. Mukundan, B.S. Pivovar , "The Role of the Membrane-Electrode Interface on Fuel Cell Performance", 2005 Fuel Cell Seminar, Palm Springs, CA, Nov. 14-18 (2005).

10. Y.S. Kim, B. Pivovar, "Durability of Membrane-Electrode Interface under DMFC Operating Conditions", 208th Meeting of the Electrochemical Society, Los Angeles, CA, Oct. 16-21 (2005).

11. M. Sankir, Y. S. Kim, W. L. Harrison, A. S. Badami, and J. E. McGrath, "Proton Exchange Membrane Fuel Cells: II. Synthesis and Characterization of Partially Fluorinated Disulfonated Poly (Arylene Ether Benzonitrile) Copolymers", Division of Fuel Chemistry, 231th ACS National Meeting, Washington, D.C., August 22-26 (2005).

12. Y.S. Kim, M. Sankir, J. Chlistunoff, J. E. McGrath, B. Pivovar, "Non-Nafion Catalyst Binders for Proton Exchange Membrane Fuel Cells", 209th Meeting of the Electrochemical Society, Denver, CO, May 7-11 (2006).

References

1. Bryan S. Pivovar, Y.S. Kim, 2004 DOE Annual Review.

2. Y.S. Kim, A. Siu, B.S. Pivovar, 2005 DOE Annual Review.

3. Y.S. Kim, B.S. Pivovar, Meeting of the Electrochemical Society, Abs No. 1073, Orlando, FL, October 12-16, 2003.

4. M. Hickner, B.S. Pivovar, unpublished data 2003.