

VII.B.9 Non-Nafion[®] Membrane Electrode Assemblies

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Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Develop a low-cost, high performance and durable alternative membrane electrode assembly (MEA)
- Investigate effect of membrane-electrode interface
- Design interface optimized MEA
- Develop non-Nafion[®] MEA
- Evaluate non-Nafion[®] electrode performance
- Optimize MEA structure for high temperature and/or low humidity operations

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

Table 1. Los Alamos National Laboratory (LANL) Progress Toward Meeting DOE Membrane and MEA Requirements (Tables 3.4.12 and 3.4.14)

| Characteristic | Units | 2005 Target | LANL |
|--|-------------------|-------------|--------------------|
| Membrane Conductivity at: | S/cm | | |
| Operating Temperature | | 0.10 | 0.10 |
| Room temperature | | 0.07 | 0.05 |
| -20°C | | 0.01 | n/a |
| Operating temperature | °C | 120 | 100 |
| Durability with cycling at operating temperature of 80°C | hours | 2,000 | 3,000 ^a |
| Cost | \$/m ² | 50 | n/a |

Table 1. Los Alamos National Laboratory (LANL) Progress Toward Meeting DOE Membrane and MEA Requirements (Tables 3.4.12 and 3.4.14)

| Characteristic | Units | 2005 Target | LANL |
|--|--------------------|-------------|------|
| Performance @ ¼ power (0.8V) | mA/cm ² | 250 | 250 |
| | mW/cm ² | 200 | 200 |
| Performance @ rated power | mW/cm ² | 800 | 600 |
| Extent of performance degradation over lifetime | % | 10 | n/a |
| Thermal cyclability in presence of condensed water | | Yes | Yes |

^a Operation at 80°C without cycling.

This project is an on-going study developing non-Nafion[®] membranes and electrode ionomers. Some achievements listed above were obtained in 2004.

Approach

- Understand performance degradation mechanism for non-Nafion[®] membranes.
- Increase knowledge of structure-property-performance relationship.
- Prepare membranes that show stable long-term performance.
- Systematically investigate electrode structure using non-Nafion[®] ionomer.

Accomplishments

- Quantified interfacial resistance between non-Nafion[®] membrane and Nafion[®]-bonded electrodes.
- Identified the impact of interfacial incompatibility on initial and long-term fuel cell performance.
- Designed novel polymer electrolytes having improved interfacial compatibility.
- Optimized catalyst/ionomer composition using alternative polymer binder.
- Demonstrated long-term fuel cell performance of the interface optimized membrane.

Future Directions

- Evaluate H₂/air long-term performance of non-Nafion[®] membranes under various conditions (e.g., stop/start cycling, potential cycling, and controlled humidity).
- Optimize MEA structure for high temperature and/or low humidity operations.
- Investigate thermal, air, and water management of non-Nafion[®] system.
- Systematic study of non-Nafion[®] ionomer stability in catalyst layers (i.e., peroxide effects).

Introduction

Fuel cells will need advanced and low-cost polymer electrolytes that have improved performance and preferably operate at 120°C and low hydration levels. The goal of this project is to assist the DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program by performing the enabling science that will produce high performance MEAs out of alternative polymeric electrolytes.

Approach

Current, critical issues in non-Nafion[®] electrolytes used as fuel cell membranes include membrane-electrode interfacial incompatibility and resultant performance degradation. We have isolated interfacial degradation from other degradation sources using a novel *in-situ* single cell high frequency resistance (HFR) measurement. The factors contributing to interfacial degradation are explored as a function of the chemical structure of

the polymer studied. This allowed for elucidation of degradation mechanisms and the development of systems with improved performance. For improved electrode structures, reaction kinetics and air/water transport of a non-Nafion[®] binder system were investigated with systematic variation of catalyst/non-Nafion[®] composition.

Results

Research into the characterization of membrane-electrode interfacial resistance and its impact on long-term performance is shown in Figures 1 and 2. Figure 1 shows that interfacial resistance of non-optimized alternative polysulfone membranes is higher than Nafion[®] and increases with degree of sulfonation. Figure 2 shows that performance degradation over time is proportional to the initial interfacial resistance. Systematic study using various alternative membranes indicated that dimensional mismatch due to increased water swelling of the membrane (compared to the electrodes) was the major cause for interfacial failure. Figure 3 shows the correlation between membrane water uptake and

HFR increase after 100 h of fuel cell operation. Based on this observation, we designed high performance non-Nafion[®] membranes having greater hydrophobicity. The membrane presented here showed not only promising electrochemical properties (conductivity = 0.1 S/cm at 80°C and performance = 200 mW/cm² at 0.8 V), but also improved the long-term stability (i.e., stable cell resistance over 2,500 h under harsh direct methanol fuel cell [DMFC] operating conditions), as shown in Figure 4. Currently, long-term tests under various H₂/air operating conditions are ongoing.

We were able to achieve comparable electrode performance for MEAs in which Nafion[®] was replaced in the electrode (see Figure 5). Figure 6 shows an example of how a non-Nafion[®] electrode improved fuel cell performance at elevated temperatures. In this MEA design, the non-Nafion[®]

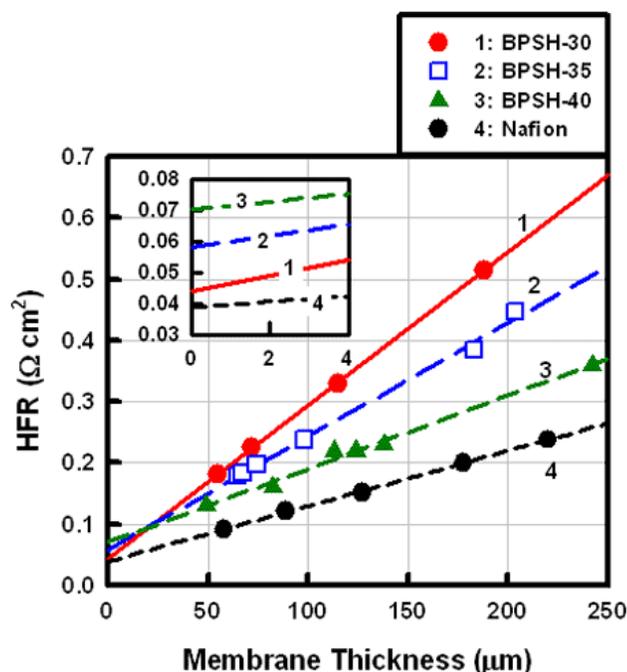


Figure 1. Effect of Degree of Sulfonation of Sulfonated Polysulfone Membranes (BPSH-30, -35, and -40 are hydrocarbon based polysulfones with -30, -35, and 40% degree of disulfonation, respectively).

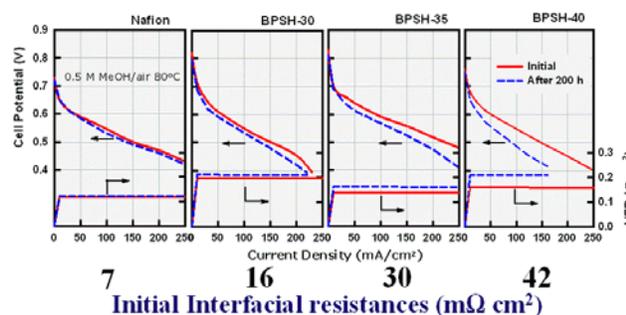


Figure 2. Influence of Interfacial Compatibility on Long-Term Performance

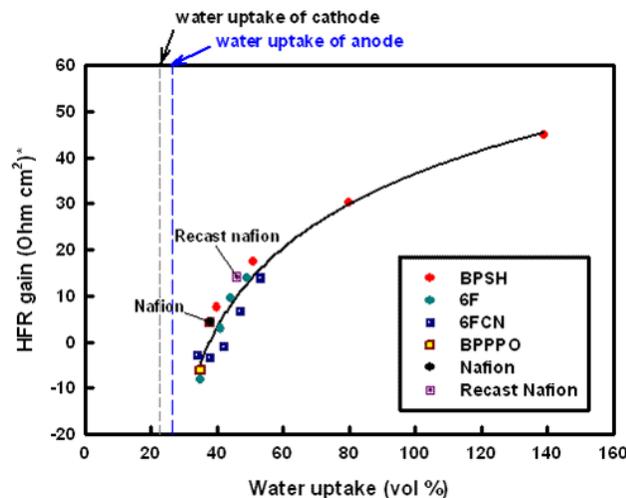


Figure 3. Correlation between Membrane Water Uptake and HFR Gain After 100 h Life Test

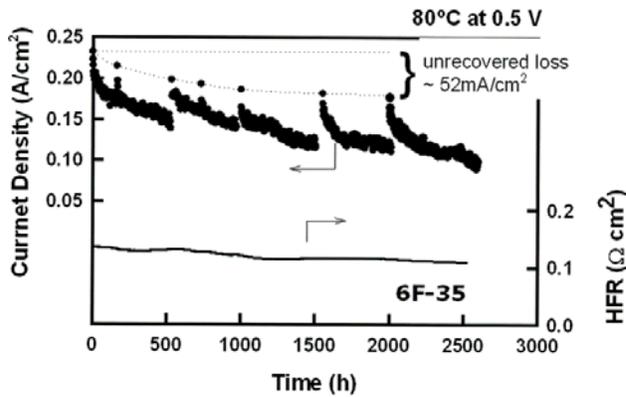


Figure 4. Long-term (2,500 h) Stability of Interface Optimized Non-Nafion Membrane Under 80°C DMFC Operating Conditions

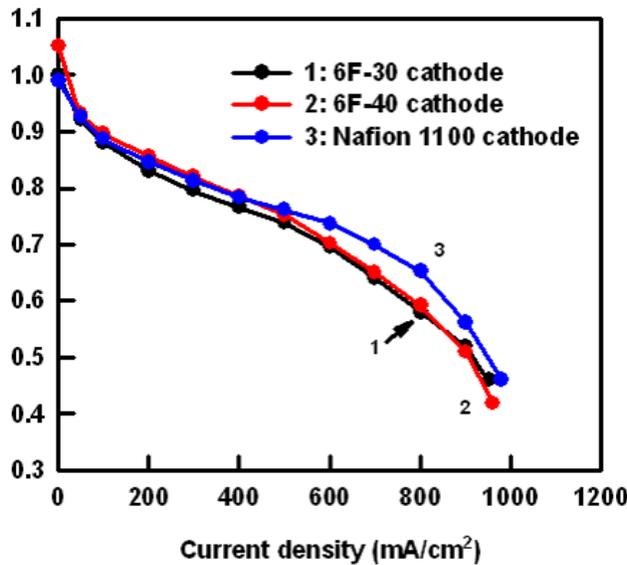


Figure 5. Cathode Performance of Non-Nafion® Binder (6F-30 and 6F-40 are fluorinated polysulfones with 30 and 40% degree of disulfonation, respectively).

binder improved water management, by preventing water from being transported out of the membrane through the cathode, due to lower electro-osmotic drag of the non-Nafion® ionomer.

Conclusions

Non-Nafion® membranes developed through this project have shown comparable initial performance with currently used Nafion® membrane (meet current DOE target in terms of performance). Long-term stability was greatly improved by optimizing

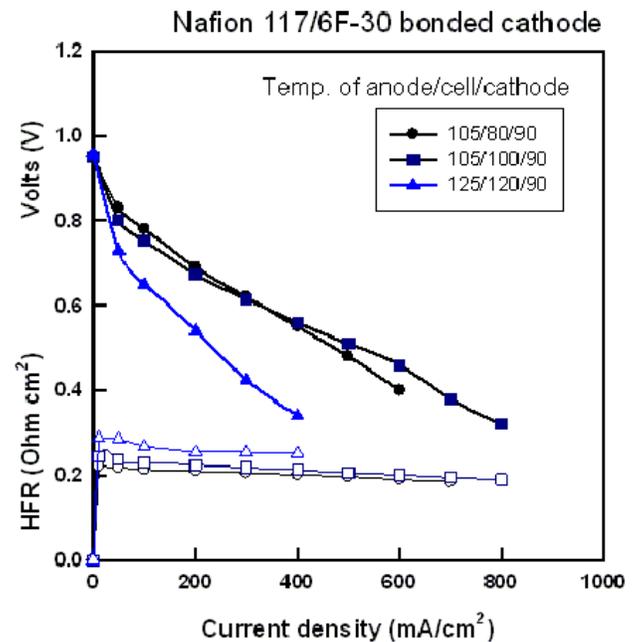
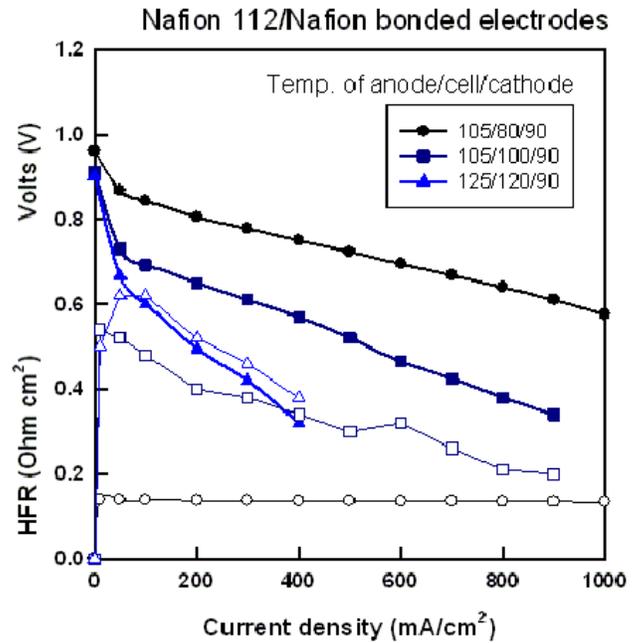


Figure 6. H₂/Air Performance of Non-Nafion® Electrode Under Elevated Temperature Operation

the membrane-electrode interface. New interfaced optimized membrane showed stable long-term performance up to 3,000 h under DMFC conditions. Electrodes using non-Nafion® polymers showed comparable catalytic activity but reduced water transport that enabled hydration to be maintained under elevated fuel cell operating conditions. Future research will focus on studying long-term stability

with start/stop cycling, further optimizing MEA structure and studying non-Nafion[®] membrane stability in catalyst layers.

Special Recognitions & Awards/Patents Issued

1. Y. S. Kim, Honorable Mention for a distinguished postdoctoral award, LANL, 2005.
2. Advanced Membrane Electrode Assemblies for Fuel Cells, Yu Seung Kim and Bryan S. Pivovar, Patent Application, S104819, 2005.

FY 2005 Publications/Presentations

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2. Yu Seung Kim, Michael Hickner, Limin Dong, Bryan Pivovar and James E. McGrath, *Journal of Membrane Science*, **243**, 317-326 (2004).
3. Brian R. Einsla, Yu Seung Kim, Michael Hickner, Young-Taik Hong, Melinda L. Hill, Bryan Pivovar, and James E. McGrath, *Journal of Membrane Science*, **255**, 141-148 (2005).
4. M.J. Sumner, W.L. Harrison, R.M. Weyers, Y.S. Kim, J.E. McGrath, J.S. Riffle, A. Brink, M.H. Brink, *Journal of Membrane Science*, **239**, 2, 199-211 (2004).
5. Michael Hickner, Hossein Ghassemi, Yu Seung Kim, Brian Einsla, and James E. McGrath, *Chemical Reviews*, **104**, 4587-4612 (2004).
6. W.L. Harrison, Y.S. Kim, M. Hickner, J.E. McGrath, *Fuel Cells*, **5**, 2, 201-212 (2005).
7. Yu Seung Kim, Bryan S. Pivovar, Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2005, Asilomar Conference Grounds, Pacific Grove, CA, Feb. 20-23 (2005)
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