VII.I.6 Fundamental Science for Performance, Cost and Durability

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

Objectives

- Apply phenomenological models to the development of a robust reference electrode and the study of membrane-electrode delamination.
- Investigate the effect of water relative humidity (RH) on oxygen reduction.
- Study electrolytes that can function at higher pH than currently employed ionomers (improved oxygen reduction reaction and catalyst stability).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section 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

Technical Targets

This project is conducting fundamental studies for cost, performance and durability. Insights gained from these studies will be applied toward the design and synthesis of fuel cell materials that meet the following DOE 2010 targets (Table 3.4.4):

- Precious metal loading: 0.3 g/kW
- Cost: $30/kW$_e$
- Durability with cycling: 5,000 hours

Approach

- Develop and verify a reference electrode design that gives relevant and reproducible results.
- Develop a phenomenological and computational fluid dynamics (CFD) model to explain observed membrane-electrode resistance based on electrode delamination.
- Investigate the oxygen reduction reaction as a function of RH as it would relate to lower humidity operation of fuel cell cathodes.

- Explore proton conduction in imidazole "buffered" electrolytes to explore proton conductivity through a range of pH.

Accomplishments

- Developed and verified a reference electrode that gave relevant and reproducible results.
- Demonstrated model addressing membrane-electrode delamination with qualitative agreement with experimental data.
- Investigated effect of temperature and relative humidity on the oxygen reduction reaction using microelectrodes.
- Investigated conductivity of imidazole-based high pH proton conductors.

Future Directions

- Validate and refine delamination model with experimental data.
- Use microelectrodes to study oxygen reduction and peroxide generation.
- Study oxygen reduction in high pH conductors.
- Elucidate proton conduction in high pH systems.

Introduction

Fuel cells will need to address issues of cost, durability and performance in order to meet commercialization requirements. The goal of this project is to provide the fundamental understanding of processes necessary to assist the DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program meet DOE milestones for cost, performance and durability.

Approach

The approach of this project is four-pronged. First, develop and validate a reliable reference electrode. This approach explores three different geometries for reference electrodes and uses CFD models to validate observed results. Second, develop a model to interpret performance losses due to membrane-electrode delamination. This model combines phenomenological and CFD models in an attempt to validate membrane-electrode delamination as a degradation mechanism. Third, explore the effects of relative humidity on oxygen reduction. The oxygen reduction reaction is explored using microelectrodes (platinum) and thin layers of Nafion® in order to determine the effects of relative humidity and temperature on performance. Fourth, investigate conductivity of imidazole buffered solutions for high pH proton conduction. High pH is known to be beneficial for catalysis. Our approach involves investigating these systems using quantum mechanical models and conductivity and nuclear magnetic resonance measurements of solutions to elucidate proton conduction.

Results

Reference electrode modeling and development is essentially complete. We have successfully demonstrated a reference electrode that gives reliable operation and validated its positioning by our CFD model. Figure 1 shows the reference electrode schematically, and Figure 2 shows the resulting

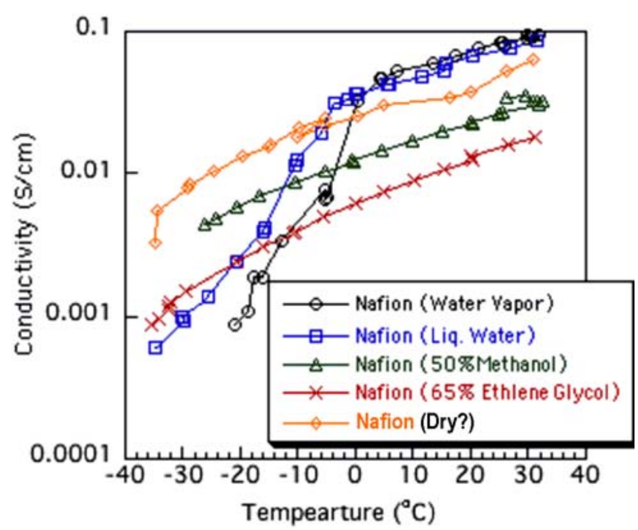

Figure 1. Schematic of Well Performing Reference Electrode

performance obtained using the reference electrode on hydrogen and air. A model of membrane-electrode delamination has been developed. Results shown in Figure 3 show the effect of delamination size based on 30% of the membrane-electrode interface being delaminated. The results of this work qualitatively agree with experimentally observed performance and high frequency resistance. Further work looks to investigate the size of delaminations and the fraction of the surface delaminated.

Figure 4 shows the response to oxygen reduction using microelectrodes as a function of relative humidity. At low overpotentials (~0.9V vs. forming gas hydrogen electrode [FGHE]) only modest changes in current are witnessed. At much higher overpotentials (~0.3 V vs. FGHE) significant differences in current are witnessed. These results suggest RH plays a minor role on catalyst performance, but need further investigation. Figure 5 shows the energy barriers for proton transport between water molecules (dashed lines) and imidazole molecules (solid lines) for quantum mechanical calculations based on separation distance. It is apparent that energy barriers for proton transport in both cases are roughly equivalent for the geometry presented here. Table 1 shows conductivity of high pH (8) solutions containing imidazole and triflic acid. The difference between conductivity in protonated and dueterated water suggest proton hopping plays a significant role in conductivity, suggesting these materials might be reasonable proton conductors for fuel cell applications.

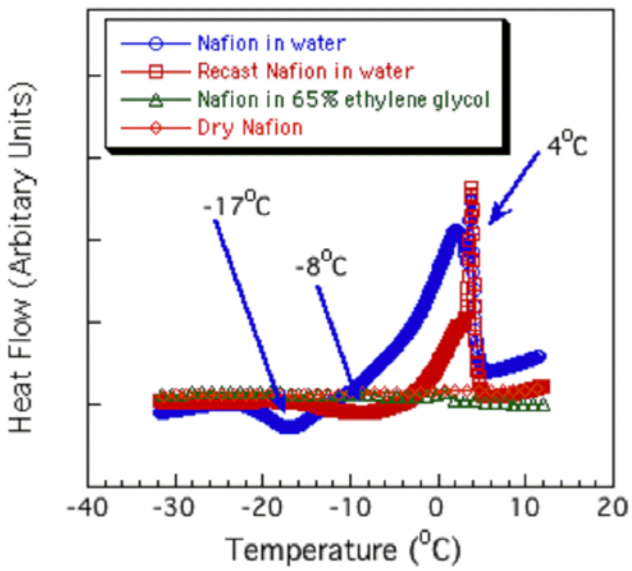

Figure 2. Validation of Reference Electrode Performance

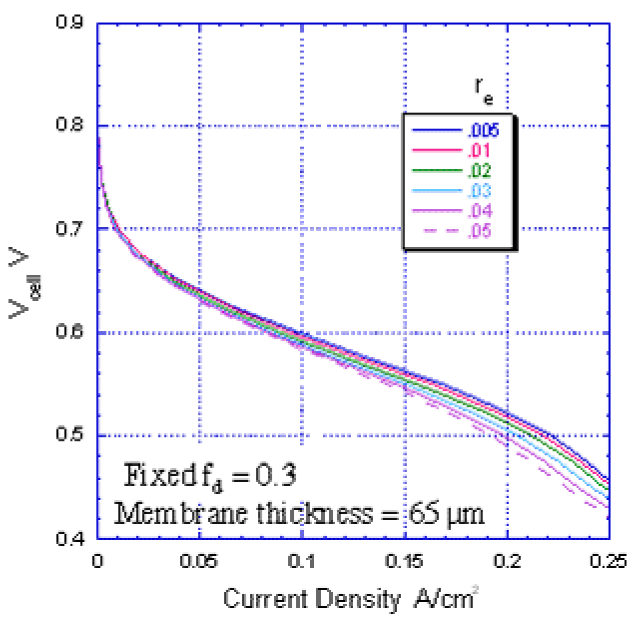

Figure 3. Results of Delamination Model Performance as a Function of Delamination Size for 30% Delamination and 65 Micron Membrane Thickness

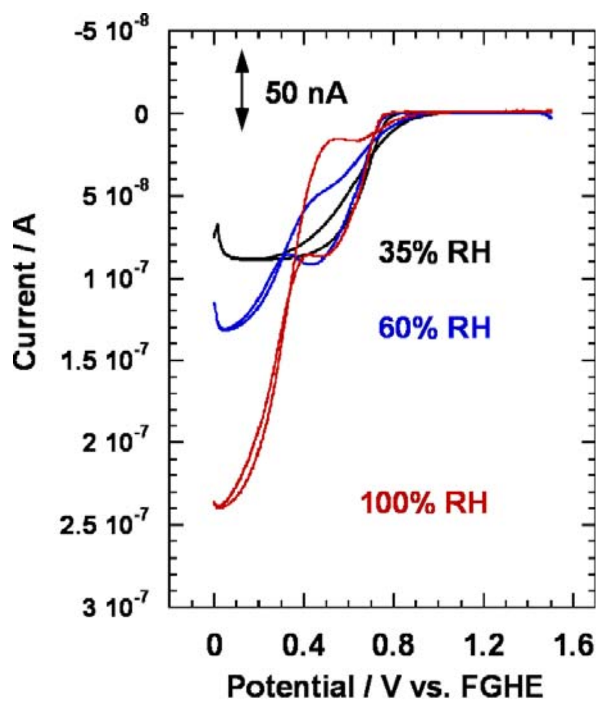

Figure 4. Current vs. Potential for ORR at 20°C and Various Levels of RH

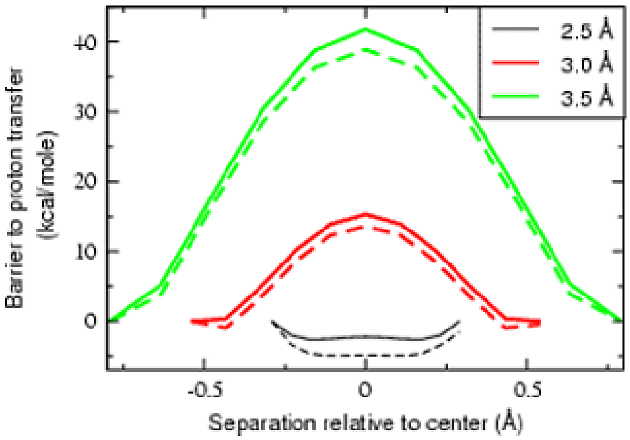

Figure 5. Barrier to Proton Transfer Calculated by Quantum Mechanical Model as a Function of Separation Distance for Water (dashed) and Imidazole (solid)

Table 1. Properties of Imidazole Buffered Triflic Acid Solution in Protonated and Dueterated Water

Sample	pH	Conductivity (mS/cm)
2 M imidazole 1 M CF_3SO_3H in D_2O [estimated from NMR]	8	58 (at 22°C) 65 (at 30°C) [80 (at 30°C)]
2 M imidazole 1 M CF_3SO_3H in H_2O	8	68 (at 22°C) 79 (at 30°C)

Conclusions

A reference electrode has been developed that will allow accurate determination of potential at the anode and cathode of an operating fuel cell. This data is important in investigating catalyst stability and durability. A model for membrane-electrode delamination has been developed and has shown qualitative agreement with experimentally observed degradation. Oxygen reduction reaction (ORR) on platinum microelectrodes has been investigated as a function of temperature and RH. Finally, evidence has been found that suggests reasonable proton conductivity can be achieved in a high pH electrolyte.

FY 2005 Publications/Presentations

1. "Direct Measurement of *iR*-Free Individual-Electrode Overpotentials in PEFC," P. Piela, T.E. Springer, M.S. Wilson, J. Davey and P. Zelenay, in *Proton Conducting Membrane Fuel Cells IV*, M. Murthy, (Ed.), Proceedings of the 206th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 3 – 8, 2004; Electrochemical Society, Pennington, New Jersey, submitted.
2. "Direct Measurement of *iR*-free Individual-Electrode Overpotentials in PEFC," Piotr Piela, Tom Springer, Mahlon Wilson, John Davey and Piotr Zelenay, 206th Meeting of The Electrochemical Society Honolulu, Hawaii, October 3-8, 2004.