VII.I.8 Investigating Failure in Polymer-Electrolyte Fuel Cells

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Start Date: December 2004
Projected End Date: September 2009

Objectives

- Understand and mitigate fuel cell failure mechanisms
- Experimentally characterize membrane properties as a function of temperature to understand operation and survivability at subzero temperatures
- Develop advanced mathematical models to predict fuel cell performance and failure through thermal-and-water management issues
- Optimize material properties and operating conditions to increase lifetime and durability

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
- C. Electrode Performance
- D. Thermal, Air, and Water Management

Technical Targets

This project is conducting fundamental studies of fuel cell failure mechanisms. This includes experiments aimed at meeting the operation and survivability targets at low and subzero temperatures:

- Survivability: –40°C
- Membrane conductivity at –20°C: 0.01 S/cm

In addition, mathematical models are being developed to improve performance and design against failure phenomena, allowing for the following DOE targets to be met:

- MEA performance at rated power: 1.28 W/cm^2
- Electrical energy efficiency at rated power: 50% (stack)
- Total catalyst loading: 0.30 g/kW
- Extent of performance degradation: 10%

Approach

- Develop mathematical models that consider the governing physical phenomena
- Validate the models both qualitatively and quantitatively

- Analyze simulation results to understand limiting phenomena and their impact on performance
- Optimize material properties and operating conditions to minimize the effects of failure mechanisms
- Conduct fundamental membrane property measurements at temperatures from ambient to subzero

Accomplishments

- Developed pseudo 2-D model to account for water-management issues
  - Determined physically consistent gas-channel/diffusion-medium boundary condition for two-phase flow
- Measured conductivity of Nafion® down to 0°C in both its vapor- and liquid-equilibrated forms
- Measured the peak freezing point of water in liquid-equilibrated Nafion® as a function of differential-scanning calorimetry (DSC) scan rate (–27 and –16°C at 10 and 1 °C/min, respectively)
- Examined air starvation effects through simulation

Future Directions

- Include non-isothermal effects in the current model
- Validate model further
- Optimize operating conditions and material properties to prevent thermal-and-water-management induced failure
- Examine membrane failure and degradation through chemical attack and mechanical properties
- Develop models to simulate high-temperature, low-relative-humidity fuel cell operation
- Measure water-uptake isotherms of Nafion® at subzero temperatures
- Measure water diffusion coefficients and electro-osmotic coefficients of Nafion® at subzero temperatures

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Introduction

A critical aspect of the hydrogen economy is the realization of fuel cell technology for the efficient conversion of hydrogen into electrical energy. Unfortunately, fuel cells are plagued by durability and lifetime issues that must be solved for the technology to move forward. Due to the complex and coupled nature of fuel cells, mathematical modeling is ideally suited to describe fuel cell operation, and allow for optimization of material properties and operating conditions such that the DOE technical targets can be met. Models require the governing physical phenomena and properties be known. Thus, fundamental experiments must be run to determine the relevant properties.

The lifetime issues that are addressed by this current work include experiments aimed at determining membrane properties and state of water at low and subzero temperatures, and modeling water-and-thermal management. The former is directly related to the DOE targets of operation down to –20°C and survivability to –40°C. The latter is related to the investigation of failure mechanisms such as flooding and hot-spot formation.

Approach

The overall approach is a combination of advanced mathematical model development and necessary fundamental experimentation. This approach allows one to study the relevant issues by developing physically-based macroscopic mathematical models. Using these models, simulations are run to identify those conditions that lead to fuel cell failure and to provide management schemes and design criteria that minimize failure. Along with the model development, fundamental measurement of membrane properties and behavior under subzero temperatures is undertaken so that the correct freeze phenomena and properties can be incorporated into the model.

Results

We have advanced and refined our previous models [1, 2] to be pseudo 2-D, where the compositional changes along the gas channel are explicitly accounted for, as shown in Figure 1. This new model allows for the examination of reactant depletion, as shown in Figure 2. For this simulation, the gas channel was divided into 20 segments, each of which ran the 1-D sandwich model. Figure 2 shows three polarization curves, corresponding to the inlet section (section 1), the outlet section (section 20), and the average. The outlet section demonstrates oxygen starvation on the cathode due to its depletion down the gas channel and flooding of the cathode diffusion medium. The results are consistent with experimental segmented-cell data [3], which also validates the model. The results are also relevant because, as shown in the figure, the average, or experimentally observed, polarization curve looks normal. The predicted existence of dead zones in the catalyst layer near the gas outlet can lead to side reactions such as carbon corrosion and be detrimental to lifetime. Subsequent analysis through modeling will optimize catalyst loading and operating conditions to prevent these dead zones. In addition, the along-the-channel changes result in non-uniform water production and mass-transfer effects, for example, the outlet section has higher dimensionless water flux from anode to cathode than the inlet section. Such distributions will again be a cause for durability concerns due to the heterogeneities they represent.

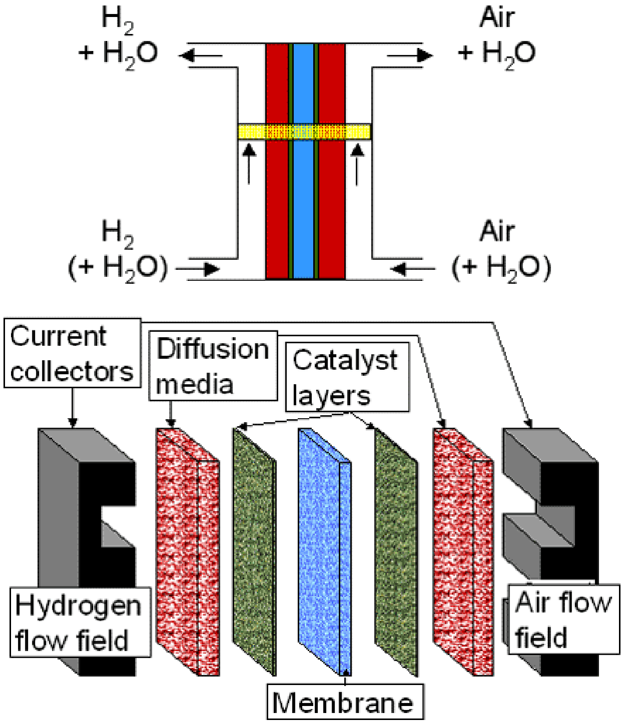

Figure 1. Schematic Showing the 1-D and Pseudo 2-D Modeling Domains

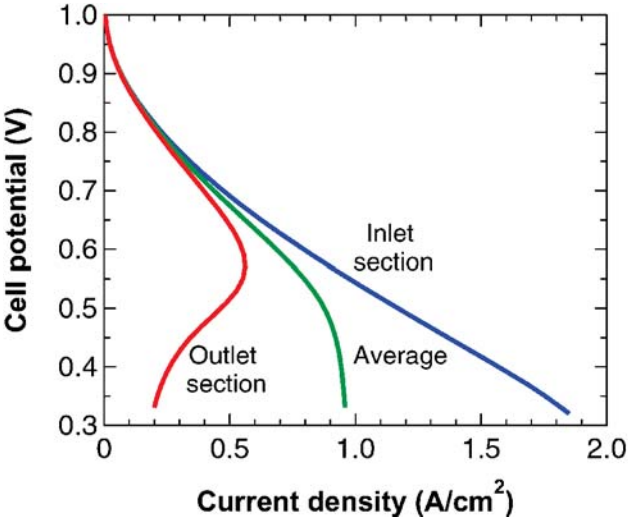

Figure 2. Simulation results showing the inlet section (section 1), average, and outlet section (section 20) polarization curves. The simulation conditions are: $T = 60°C$, Nafion® 112, fully humidified feeds at constant flow rates (fuel-to-air ratio of 0.75).

The current model is being modified to include non-isothermal effects and water movement through evaporation in the catalyst layers and condensation in the gas channel. However, there have been some numerical difficulties related to the exponentials of temperature in the vapor pressure and kinetic expressions, as well as the boundary conditions between the gas channel and the diffusion medium for both liquid water and water vapor. These conditions are crucial for predicting failure due to poor water management (i.e., flooding), and there is no consensus in the literature on the proper set of conditions.

The main problem deals with the assumption of local equilibrium (pore filling). For example, higher liquid pressures cause the large and then small hydrophobic pores to fill, and also increase the vapor pressure. For liquid water, if the liquid pressure is greater than or equal to the gas pressure, liquid water enters the gas channel with a pressure equal to that of the gas. For water vapor, a Danckwerts-Wehner-Wilhelm condition is used, which basically sets the flux of water vapor to that incoming with the gas stream, while also accounting for upstream diffusional effects. We believe these conditions to be superior to those sometimes used, like setting a value of saturation, in that they are physically consistent and mathematically rigorous.

As mentioned, to understand failure related to subzero temperature operation and freezing, there is a need to measure membrane transport and equilibrium parameters experimentally. Conductivity was measured with 4 probe AC impedance and is shown in Figure 3. The vapor-equilibrated conductivity is lower than the liquid-equilibrated one for all temperatures due to the higher water content in the liquid-equilibrated membrane. The vapor-equilibrated conductivity deviates from Arrhenius behavior due to changing water content with temperature, and the water-uptake isotherms are currently being measured.

In addition to conductivity, the state of water was studied. Figure 4 shows DSC curves at two different cooling rates. For both cases, the water in the membrane exhibits freezing-point depression, consistent with the notion of the water being in slightly hydrophobic pores and interacting with the membrane matrix. From the figure, the rate of cooling clearly has an impact on the freezing and melting points, which has system design consequences. Furthermore, the shift in melting point may indicate measuring kinetic and not thermodynamic phenomena. Finally, the results may be due to different membrane water contents, and this is now being explored.

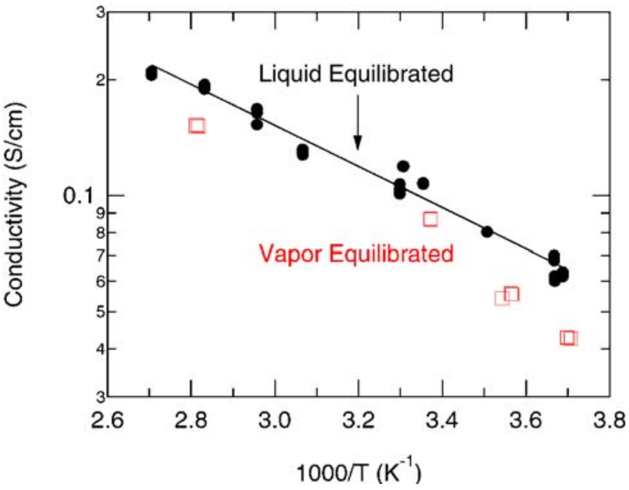

Figure 3. Arrhenius Plot of Experimental Membrane Conductivity for Both Vapor-Equilibrated (boxes) and Liquid-Equilibrated (circles) Membranes

Conclusions

- The control of membrane water content is crucial, especially at low temperatures
- The rate of cooling is important in understanding membrane freeze
- Starvation regions and dead zones may exist even if the overall polarization curve looks normal

FY 2005 Publications/Presentations

1. A. Z. Weber, Computational Fuel Cell Dynamics III, Banff International Research Station, March 2005.
2. J. Newman, Fuel Cell Gordon Research Conference, July 2005.
3. A. Z. Weber and J. Newman, "Effects of Water-Transfer Plates for Polymer-Electrolyte Fuel Cells," *J. Power Sources*, in preparation.
4. A. Z. Weber and J. Newman, "A Combination Model for Macroscopic Transport in Polymer-Electrolyte Membranes," in *Device and Materials Modeling of PEM Fuel Cells*, K. Promislow and S. Paddison, Editors, Springer (2005).

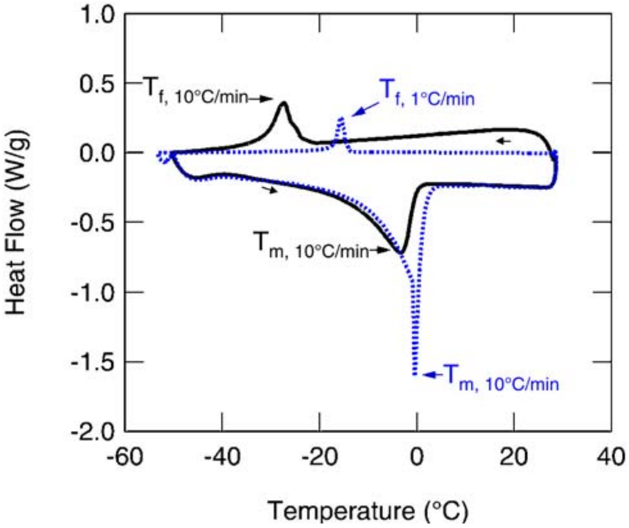

Figure 4. Experimental DSC showing the state of water in Nafion at two different cooling rates. The membrane was removed from liquid water, cooled, held at –50°C, and then heated at a rate of 10°C/min.

References

1. A. Z. Weber and J. Newman, *Chem. Rev.*, 104, 4679 (2004).
2. A. Z. Weber and J. Newman, *J. Electrochem. Soc.*, 151, A311 (2004).
3. M. M. Mench, C. Y. Wang, and M. Ishikawa, *J. Electrochem. Soc.*, 150, A1052 (2003).