V.G.8 Investigation Failure in Polymer-Electrolyte Fuel Cells

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Start Date: December 2004
Projected End Date: September 2009

Overall goal: Understand and mitigate fuel cell failure mechanisms.

Objectives

- Experimentally characterize membrane properties as a function of temperature to understand operation and survivability at subzero temperatures.
- Experimentally correlate membrane degradation to relative humidity and oxygen crossover rates.
- 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 (3.4.4.2) 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 and fundamental experiments are being developed to improve performance and design against failure phenomena, allowing for the following DOE targets to be met:

- Lifetime of 5,000 hours
- MEA performance at rated power: 1.28 W/cm^2
- Electrical energy efficiency at rated power: 35%
- Total catalyst loading: 0.33 g/kW
- Extent of performance degradation: 10%

Accomplishments

- Developed nonisothermal pseudo 2-D model to account for water- and thermal-management issues.
  - Includes modeling of crossflow configuration
- Analyzed temperature-gradient effects on performance.
- Measured conductivity of Nafion® down to -20°C for liquid-equilibrated and 0°C for vapor-equilibrated membrane.
- Measured the freezing point of water in liquid-equilibrated Nafion® as a function of differential scanning calorimeter (DSC) scan rate (–23 and –21°C at 5 and 1 °C/min, respectively).
- Determined the amount of freezable water from DSC in liquid-equilibrated Nafion® for different scan rates.
- Measured and compared the freezing temperature of pure water droplets and water in Nafion®.
- Measured water content of 100% relative humidity (RH) vapor-equilibrated Nafion® with varying air pressures at 29°C to investigate Schröder's paradox.
- Measured water content at 100% RH for vapor-equilibrated membrane between 0 to 80°C to investigate Schröder's paradox and the effect of temperature cycling.
- Measured membrane fluoride emissions and changes in membrane structure upon accelerated aging and open-circuit conditions.
- Began investigation into mechanically-related failure with a focus on membrane stress effects.

Introduction

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 and correlations.

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 experimentation of membrane properties and behavior is undertaken so that the correct freeze and degradation phenomena and properties can be incorporated into the model.

Results

We have advanced and refined our previous models [1,2] to allow for crossflow and to include nonisothermal phenomena. This new model allows for the examination of the interplay between water and thermal management, as shown in Figure 1. The figure shows polarization curves at two different operating or coolant temperatures and as a function of external heat-transfer coefficient. As seen, the inclusion of nonisothermal effects typically results in worse performance mainly due to reactant depletion by the higher water vapor pressure. In addition, the temperature gradients in the cell sandwich result in a situation where the incoming reactant gases have to diffuse against the water vapor that is moving down the temperature gradient, similar to a heat-pipe effect. Furthermore, although the oxygen-reduction reaction generates the most heat, the balanced evaporation and condensation reactions actually consume and generate over 2.5 times the amount of energy as the oxygen-reduction reaction.

Modeling also allows for optimization analysis to be conducted, as shown in Figure 2. From the curves, it is obvious that extraordinary heat-transfer is not required for optimum performance. In fact, conduction through a typical graphite bipolar plate to a coolant stream correlates to a heat-transfer coefficient of around 1 W/cm^{2}K. The shown optimization is for ambient

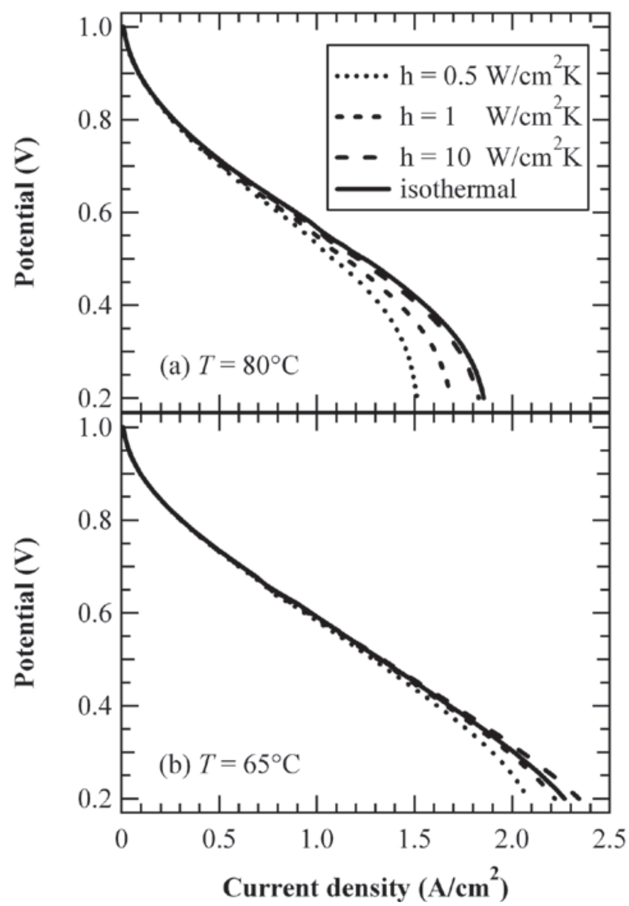

FIGURE 1. Polarization Curves for Isothermal Operation and Three Cases of Nonisothermal Operation with Different Heat-Transfer Coefficients (The temperatures for (a) and (b) signify both the inlet and coolant temperatures.)

pressure and saturated feeds, and higher optimum temperatures are realized with lower humidity feeds and higher operating pressures. Modeling is ideally suited for studying the tradeoffs associated with fuel cell operation.

As mentioned, to understand failure related to subzero operation and freezing, there is a need to measure membrane transport and equilibrium parameters experimentally. Conductivity was measured (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 decreasing water content with increasing temperature at 100% RH. In addition, the liquid-equilibrated conductivity changes activation energy at 0°C. The effect of temperature cycling on water uptake is currently being measured between 0 and 80°C.

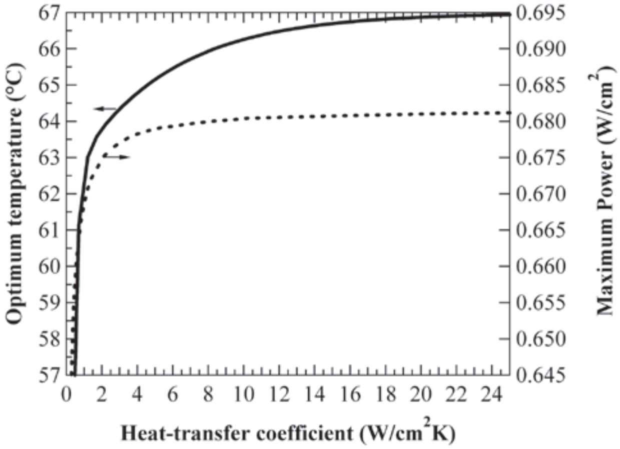

FIGURE 2. Optimum Coolant and Feed Temperature as a Function of Heat-Transfer Coefficient (The optimization is done for the optimum maximum power, which is also given in the figure.)

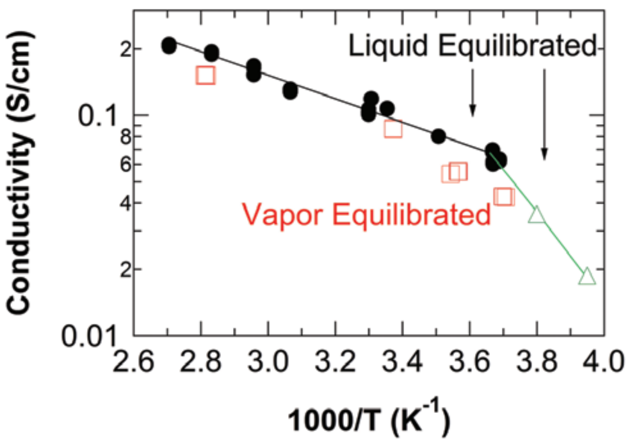

FIGURE 3. Arrhenius Plot of Experimental Membrane Conductivity for both Vapor-Equilibrated (squares) and Liquid-Equilibrated (diamonds and triangles) Membranes

The state of water was studied for different scan rates as well. The amount of freezable water was determined to be about $\lambda = 10$ for originally liquid-equilibrated Nafion®, assuming a heat of fusion of pure water. The freezing temperature of pure water and water in Nafion® were approximately –20°C for the same scan rates. Interestingly, these two situations give close to the same freezing-point depression. For fast scan rates, the freezing and melting temperatures of water in Nafion were lower than for slow scan rates. The rate of cooling clearly has an impact on the freezing and melting points, which has system-design consequences.

Conclusions and Future Directions

- Rate of cooling is important in understanding membrane freezing.
- Conductivity exhibits a change of activation energy at 0°C.
- Vapor-equilibrated water content was lower at 30°C after temperature cycling to 80°C than before cycling.
- Pure water droplets and water in Nafion® freeze at about -20°C for scan rates as low at 1°C/min.
- The amount of originally liquid-equilibrated membrane freezable water is about λ=10.
- There is a strong interplay between water and thermal management.
- Temperature gradients reduce mass transfer due to a heat-pipe effect where water vapor moves down the gradient and against the reactant flow.
- Extraordinary heat transfer is not required for optimum performance.
- Optimum operating temperature for peak power is around 65°C for saturated feeds and 1 bar operation.
- Develop mechanically-related failure model with a focus on detailed stress distributions within the membrane.
- Collaborate to validate the mathematical models.
- Include countercurrent flow in the model.
- Develop models to simulate high-temperature, low-relative-humidity fuel-cell operation.
- Measure water-uptake isotherms of Nafion® at subzero temperatures.
- Experimentally measure water content at subambient to operating temperatures to investigate and understand Schröder's paradox.
- Measure water diffusion coefficients and electro-osmotic coefficients of Nafion® at ambient to subzero temperatures through developed apparatus.

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).

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2. A. Z. Weber and J. Newman, "Modeling Gas-Phase Transport in Polymer-Electrolyte Fuel Cells," 208th Electrochemical Society Meeting, Los Angeles, CA, October 2005.

3. A. Z. Weber and J. Newman, “Modeling Nonisothermal Effects in Polymer-electrolyte Fuel Cells,” 208th Electrochemical Society Meeting, Los Angeles, CA, October 2005.

4. L. Onishi and J. Newman, “Low Temperature Membrane Properties,” 208th Electrochemical Society Meeting, Los Angeles, CA, October 2005.

5. A. Z. Weber and J. Newman, “Effects of Heterogeneities in Polymer-Electrolyte Fuel Cells,” 209th Electrochemical Society Meeting, Denver, CO, May 2006.

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