V.F.7 Fuel Cell Fundamentals at Low and Subzero Temperatures

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• Los Alamos National Laboratory, Los Alamos, NM
• United Technologies Research Center, East Hartford, CT
• 3M Company, St Paul, MN
• The Pennsylvania State University, State College, PA

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Fiscal Year (FY) 2011 Objectives

- Fundamentally understand transport phenomena and water and thermal management at low and subzero temperatures.
- Examine water (liquid and ice) management with nano-structured thin-film (NSTF) catalyst layers.
- Enable operational and material optimization strategies to be developed to overcome observed performance bottlenecks.
- Characterize and measure critical transport properties for operation with liquid water.
- Elucidate the associated degradation mechanisms due to subzero operation and enable mitigation strategies to be developed.

Technical Barriers

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

(C) Performance
(A) Durability
(D) Water Transport within the Stack
(E) System Thermal and Water Management
(G) Start-Up and Shut-Down Time and Energy/Transient Operation

Technical Targets

This project is conducting fundamental investigations into fuel cell operation at low and subzero temperatures. The knowledge gained will enable various metrics to be met or exceeded. These include those related to durability, performance, and cost. Specifically,

- Durability
  - 5,000 hr (automotive) and 40,000 hr (stationary).
  - Thermal cycling ability with liquid water.
- Performance
  - Unassisted start from -40°C.
  - Cold start to 50% power in 30 seconds and with 5 MJ or less energy.
  - Efficiency of 65% and 55% for 25% and 100% rated power, respectively.
  - Stack power density of 2 kW/kg.
  - Platinum group metal (PGM) loading of 0.2 g/kW.
- Cost: $15/kW_e

FY 2011 Accomplishments

- Completed cold-start model and demonstrated that proton limitations may exist during isothermal cold starts as ice lenses build up near the membrane interface.
- Determined impact of membrane thickness, catalyst-layer thickness, and ionomer-to-carbon ratio on isothermal cold-start behavior.
- Developed capabilities and experimental protocols for measuring capillary-pressure–saturation relationships for both gas diffusion layers (GDLs) and microporous layers (MPLs). Demonstrated that this relationship is critical and can be used to explain water transport throughout the material. Also designed a test fixture for measuring water distributions using X-ray tomography.
- Developed rate expression from theory and fit to experimental data showing kinetic freezing phenomena inside GDLs.
- Measured water properties in a traditional catalyst layer including ionomer water uptake and capillary-pressure saturation relationship.

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Introduction

Polymer electrolyte fuel cells experience a range of different operating conditions. As part of that range, they are expected to be able to survive and start at low and subzero temperatures. Under these conditions, there is

a large amount of liquid and perhaps frozen water due to the low vapor pressure of water. Thus, water and thermal management become critical to understanding and eventually optimizing operation at these conditions. Similarly, durability aspects due to freezing and low temperatures are somewhat unknown and need further study in order to identify mechanisms and mitigation strategies. In addition, it is known that thin-film catalyst layers such as the NSTF developed by 3M have issues with large amounts of liquid water due to their thinness. These layers provide routes towards meeting the DOE cost targets due to their high catalytic activities. This project directly focuses on the above aspects with the goal that improved understanding will allow for the DOE targets to be met with regard to cold start, survivability, performance, and cost.

Approach

The overall approach is to use a synergistic combination of cell, stack, and component diagnostic studies with advanced mathematical modeling at various locations (national laboratories, industry, and academia). Ex situ diagnostics will be used to quantify transport properties and to delineate phenomena that are used in the modeling. The multiscale modeling will account for stack position through boundary conditions that are fed to a pseudo three-dimensional or one plus two-dimensional cell model. This model will be used during shutdown to predict the water profile during the subsequent cold start. The model will be validated by comparison of measured in situ cell performance in both stacks and single cells. Durability will be probed by doing cycling and other stress tests as well as taking failed cells from the in situ testing and duplicating their failure ex situ. To understand controlling phenomena and the impact of various layers, a systematic investigation at the component scale will be accomplished. After initial baseline cell assemblies have been tested and explored, various components will be switched to understand the impact of each one on both performance and durability.

Results

When fuel cells operate at low and subzero temperatures, liquid water and water management become more important. Thus, there is a need to study properties of the porous fuel cell layers in the presence of liquid water. As noted last year, the capillary pressure–saturation relationship is critical in understanding the two-phase properties of fuel cell layers. This year, we used this technique to examine the properties of a catalyst layer. For this study, an extra thick (about 30 microns) catalyst layer was made using the tradition ink painting process. This layer was then tested using our capillary pressure apparatus [1], and the results are shown in Figure 1a. As can be seen, the layer is about 60% hydrophilic, which is much different than the results of a GDL, which shows hydrophobic behavior on imbibition and a mixed wettability response. Similarly, we tested the water uptake of these catalyst layers using dynamic vapor sorption
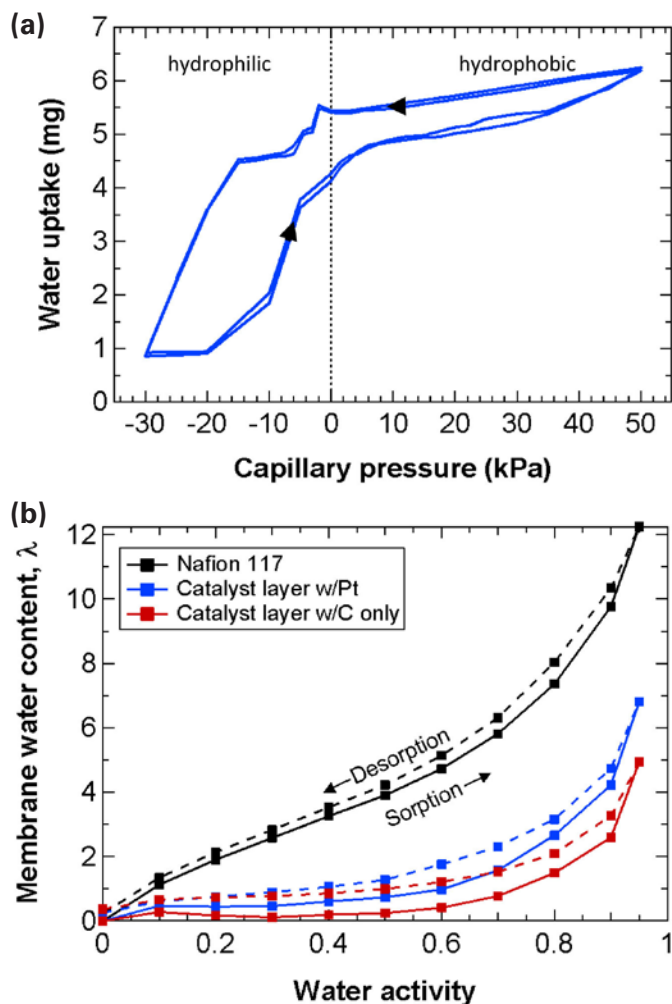

FIGURE 1. (a) Capillary pressure–saturation relationship for a traditional Pt/C catalyst layer. (b) Membrane water content for a Pt/C and C only catalyst layer as a function of humidity (bulk Nafion® is shown as a reference).

apparatus (SMS Instruments). As Figure 1b demonstrates, the water uptake of the ionomer in the catalyst layer is less than that of a bulk ionomer, thereby suggesting a depression of its transport properties as well. Interestingly, samples with Pt/C and not just C show increased water uptake which may be due to the fact that the sulfonic acid sites bind to the Pt (in agreement with results from Oak Ridge National Laboratory), which opens up the membrane morphology to accept more water.

Other diagnostics are aimed at determining what happens when water freezes in the various fuel cell layers. Using nucleation theory and dynamic scanning calorimetry, we were able to develop a rate expression for water freezing inside of a GDL. This expression was used to predict the onset of freezing under different subcoolings as shown in Figure 2. It is interesting to note that ice will not form in GDLs until substantial subcooling has occurred, even over long periods of time. However, that is not to say that freezing will not occur in other components, especially flow fields.
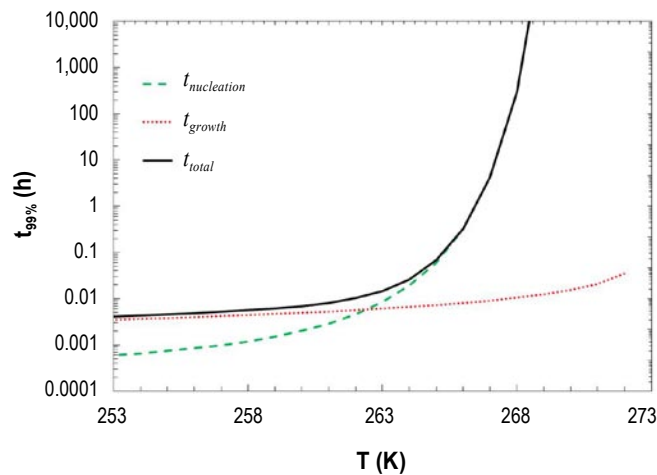
FIGURE 2. Prediction of time to freeze in a GDL as a function of subcooling using experimentally fit and theoretically derived rate expression.

To understand ice formation as a function of MEA properties, isothermal cold-start experiments were undergone. The main variables altered were the catalyst-layer thickness, membrane thickness, and ionomer to carbon ratio. Figure 3a shows the results of changing the membrane thickness, where thicker membranes allow for more water production as long as the temperature is high enough. The reason is that at lower temperatures, there is not a sufficient diffusion flux for water to get into the membrane and saturate it. Figure 3b shows the impact of catalyst-layer thickness, where thinner catalyst layers do not seem to have enough storage capacity to allow for more water generation before failure. This could be critical for NSTF and is something being investigated for next year. Finally, Figure 3c shows the impact of ionomer to carbon ratio. At low values, there is not enough ionomer to provide good proton conductivity and thus the water production before failure is low. However, at high ionomer-to-carbon-ratio contents, the ionomer begins to fill in the pore space of the catalyst layer, thereby limiting oxygen transport and storage capacity of the produced water.

Mathematical modeling was used to understand both isothermal and nonisothermal cold start. The nonisothermal cases demonstrate that starting either at lower voltages or with drier membranes lead to better performance. For isothermal cold start, the simulations demonstrate that the entire pore capacity of the catalyst layer may not be used during the start, especially at high current densities. The reason for this is that an ice front forms and propagates from the membrane interface towards the interface with the GDL as shown in Figure 4. The ice-front propagation is driven by the nonuniform reaction-rate distribution that occurs at high current densities, which is why it is not seen in the case of lower current densities which have a more uniform reaction-rate distribution. The end result of the ice front is that at higher current densities, the cell becomes ohmically limited
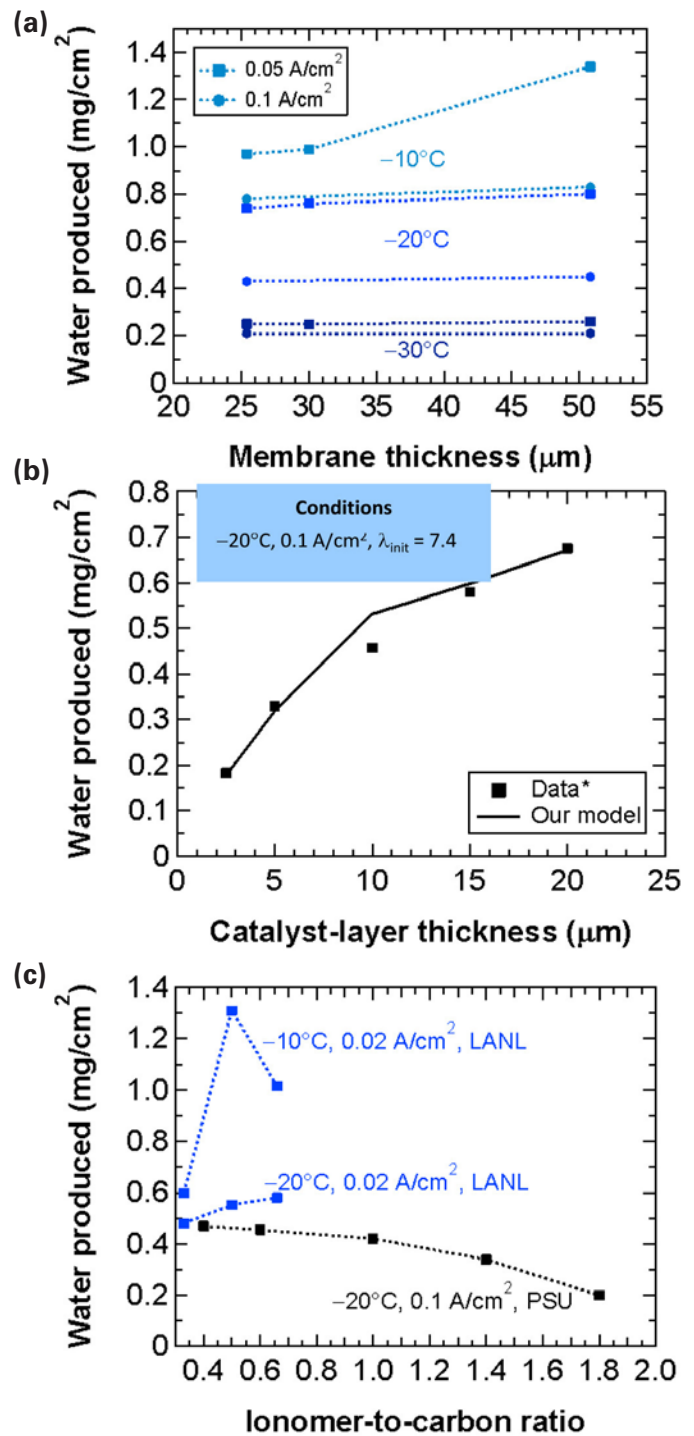

FIGURE 3. Isothermal cold-start data showing water produced before zero volts as a function of (a) membrane thickness, (b) catalyst-layer thickness, and (c) ionomer-to-carbon ratio.

since the protons cannot reach the reaction site as it goes further from the membrane. Thus, the zero cell voltage is not due to a true limiting current and zero oxygen concentration, but due to proton conduction limitations. Understanding these interplays and phenomena will allow for optimum
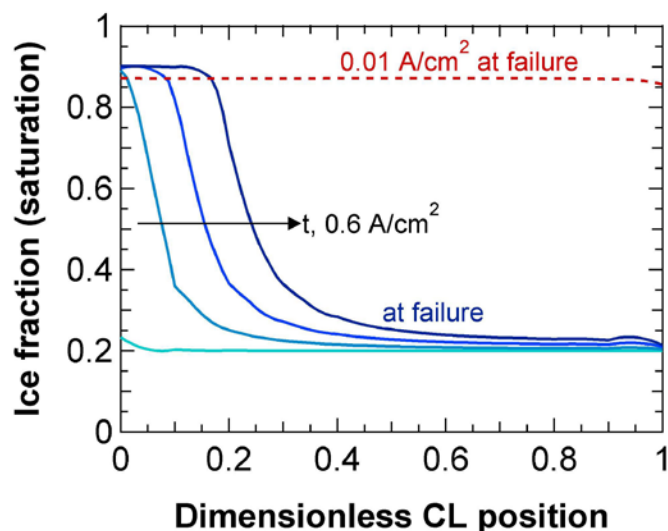
FIGURE 4. Isothermal cold-start simulation results showing ice-fraction profile as a function of time for two current densities.

starting conditions and material properties to be determined such that DOE targets for cold start can be met.

Conclusions and Future Directions

The project focus this year was on exploring liquid and ice formation in traditional catalyst layers and GDLs. The experiments demonstrated the hydrophilicity of the catalyst layer although some hydrophobic character remains; reduced water uptake in catalyst-layer ionomer; the need to subcool GDLs to induce freezing; and that thicker catalyst layers with around 0.4 ionomer-to-carbon ratio provide the best chance to cold start due to their increased water capacity and sufficient ionic conductivity. In addition, the cold-start model was finished, with results helping to explain experimental observations with both isothermal and nonisothermal cold starts including the fact that ohmic and not oxygen mass-transfer limitations can become limiting during cold start at higher current densities. In terms of future work, this can be summarized as:

- Cell Performance
  - Testing of non-baseline assemblies.
  - Isothermal and adiabatic starts including cycling studies for tracking durability.
  - Provide model-validation data.
- Component Characterization
  - Catalyst layers
    - More data on water-related properties.
    - Examine ice generation and form using infrared thermography and X-ray tomography.
  - Diffusion media
    - Capillary pressure – saturation relationships.

Impact of flowrate, temperature, injection sites (MPL analogs), materials.

  - Measure effective gas-diffusion coefficient as a function of saturation.
- Modeling of Cold Start
  - Examine interplay between water storage and movement for transient and startup.
  - Develop three-dimensional to two-dimensional downscaling correlations.
  - Model the low-anode-pressure and alternative-GDL results that 3M has obtained.
- Stack studies for temperature distribution and performance characterization.
- Understand and increase the operating window with thin-film catalyst layers.

FY 2011 Publications/Presentations

1. T.J. Dursch, C.J. Radke, and A.Z. Weber, 'Crystallization Kinetics of Ice in the Gas-Diffusion Layer of a PEMFC,' Langmuir, submitted (2011).

2. G.-S. Hwang, M. Kaviany, J.T. Gostick, B. Kientiz, A.Z. Weber, M.H. Kim, 'Role of Water States on Water Uptake and Proton Transport in Nafion using Molecular Simulations and Bimodal Network,' Polymer, 52, 5284 (2011).

3. Nobuaki Nonoyama, Shinobu Okazaki, Adam Z. Weber, Yoshihiro Ikogi, and Toshihiko Yoshida, 'Analysis of Oxygen-Transport Diffusion Resistance in Proton-Exchange-Membrane Fuel Cells', J. Electrochem. Soc., 158, B416 (2011).

4. Y. Wang, P.P. Mukherjee, J. Mishler, R. Mukundan, R.L. Borup, 'Cold start of PEFCs', Electro. Acta, 55, 2636 (2010).

5. Thomas J. Dursch, Clayton Radke, and A. Weber, 'Ice Formation in Gas-Diffusion Layers', ECS Transactions, 33 (1), 1143 (2010).

6. Jeff T. Gostick, Haluna Gunterman, Brian Kienitz, JohnxNewman, Alastair MacDowell, and A. Weber, 'Tomographic Imaging of Water Injection and Withdrawal in PEMFC Gas Diffusion Layers', ECS Transactions, 33 (1), 1407 (2010).

7. T.J. Dursch, M.A. Ciontea, C.J. Radke, and A.Z. Weber, 'Isothermal Crystallization Kinetics in the Gas-Diffusion Layer of a Fuel Cell,' 85th Colloid and Surface Science Symposium, Montreal, Canada, June 2011.

8. Ahmet Kusoglu and Adam Z. Weber, 'Dynamic Water Sorption Behavior of PFSA Membranes,' 241st American Chemical Society Meeting, Anaheim, April 2011.

9. B. Kienitz, J. Gostick, A. MacDowell, and A. Weber, 'Investigating Nafion Water Content Using X-ray Radiography,' 218th Meeting of the Electrochemical Society, Las Vegas, October 2010.

10. J.T. Gostick, H. Gunterman, A. MacDowell, J. Newman, and A. Weber, 'Imaging Water Distribution in GDLs Using X-ray

Tomography,' 218th Meeting of the Electrochemical Society, Las Vegas, October 2010.

11. A. Kusoglu, J. Park, and A. Weber, 'Effect of Constraint on the Sorption Behavior of Fuel-Cell Membranes,' 218th Meeting of the Electrochemical Society, Las Vegas, October 2010.

12. H. Gunterman, J. Gostick, J. Newman, and A. Weber, 'Measurement of Air-Water Capillary-Pressure Curves of Microporous Layers,' 218th Meeting of the Electrochemical Society, Las Vegas, October 2010.