

V.M.2 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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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. Specially,

- 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
 - Precious group metal (PGM) loading of 0.2 g/kW
- Cost: \$15/kW_e

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

Accomplishments

- Project initiated.
- Completed the water movement during shutdown mathematical model including cell-position effects.
- 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.
- Used dynamic scanning calorimetry to measure freeze kinetics and thermodynamics inside GDLs.
- Preliminary baseline cell studies finished including isothermal starts.



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 freeze 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 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). Figure 1 shows the approach of the project. As can be seen, 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

As fuel cells operate at low and subzero conditions, 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. This year, the focus was on the development of such diagnostic measurements. It is believed that one the key measurements for diffusion media is the capillary pressure – saturation relationship. We have developed an experimental methodology to measure such curves [1]. The results are shown in Figure 2 for both a standard SGL Group (SGL) GDL and a MPL. The MPL curve was obtained using a special layer provided by SGL in which a GDL was fully impregnated with an MP (as shown in the micrograph). The relationships clearly show that the MPL has a more hydrophobic signature, due both to its smaller pores and higher poly-tetrafluoroethylene (PTFE) weight fraction. What is interesting is that the MPL still exhibits the same intermediate wettability, where water is neither spontaneously imbibed or drained. These curves are now being used in modeling studies and going forward we aim to use this methodology to understand water distributions and the functioning of the MPL during operation [2].

Other diagnostics are aimed at determining what happens when water freezes in the various fuel cell layers. Figure 3 demonstrates measurements done with various GDLs using dynamic scanning calorimetry. For all GDLs, the crystallization temperature decreases as the PTFE content increases. Note that the SGL 24 and Toray (SGL) series GDLs follow a similar line, whereas water in the Toray (Fuel Cell Energy, FCE) GDL freezes at a higher temperature. One possible explanation is that the SGL 24 and Toray (SGL deposition) series GDLs have the same method of PTFE deposition, whereas the Toray (FCE) has a different method of PTFE deposition. This observation suggests that the method of PTFE deposition influences the crystallization

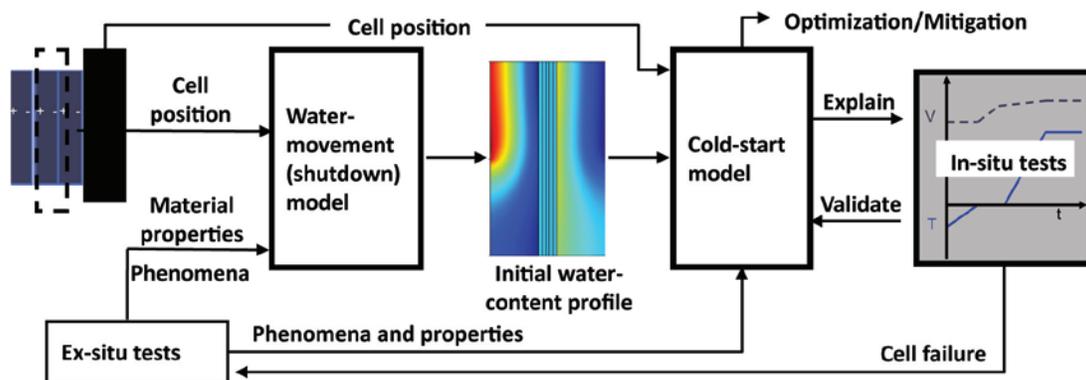


FIGURE 1. Information flow diagram of the project approach showing the various modeling scales and the experimental and modeling inputs/outputs.

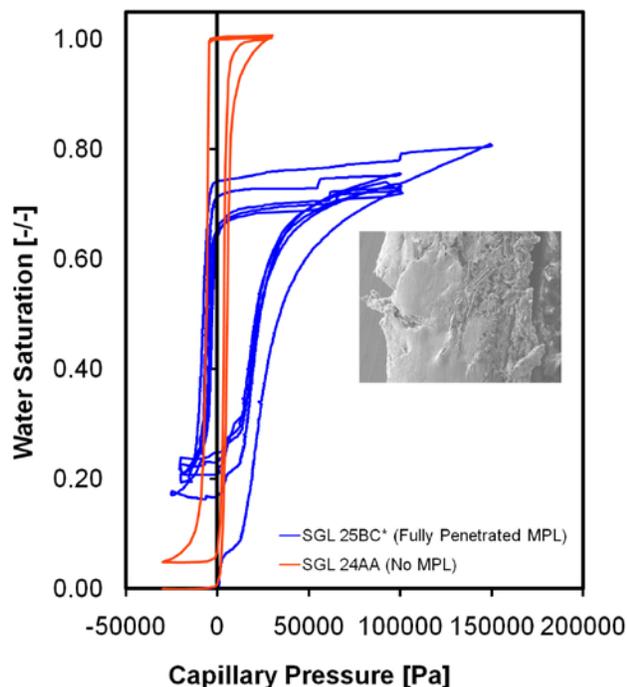


FIGURE 2. Saturation as a function of capillary pressure for a SGL 24AA (no MPL) and a SGL GDL with a fully impregnated MPL supplied by SGL. The inset is a SEM of the MPL impregnated GDL.

temperature. We hypothesize that addition of PTFE to the porous network changes the average internal ice/substrate wettability (i.e., contact angle), as well as the attainable level of water saturation, causing the decrease in crystallization temperature.

A plot of crystallization temperature and saturation versus PTFE content is shown for the Toray (FCE) series in Figure 3(b). For PTFE contents between 0 and 40 wt%, crystallization temperature decreases slightly with the addition of PTFE. Above 40 wt% PTFE, the crystallization temperature decreases more steeply. Between 0 and 40 wt% PTFE, water saturation remains relatively constant (within experimental error). However, those GDLs containing 50 and 60 wt% PTFE become increasingly difficult to saturate with water due to the need for increased capillary pressure. Consequently, saturation decreases abruptly. This suggests that at low enough fractions of PTFE, the saturation is constant and the average internal ice/substrate surface energy changes, while at larger fractions of PTFE, the attainable level of saturation also contributes to the decrease in crystallization temperature.

Ice formation in traditional catalyst layers was probed using a technique in which cyclic voltammetry is done under subzero conditions after isothermal starts reach zero volts. At very low temperature and current densities, the produced ice freezes immediately upon production, and this can be used to obtain a relationship

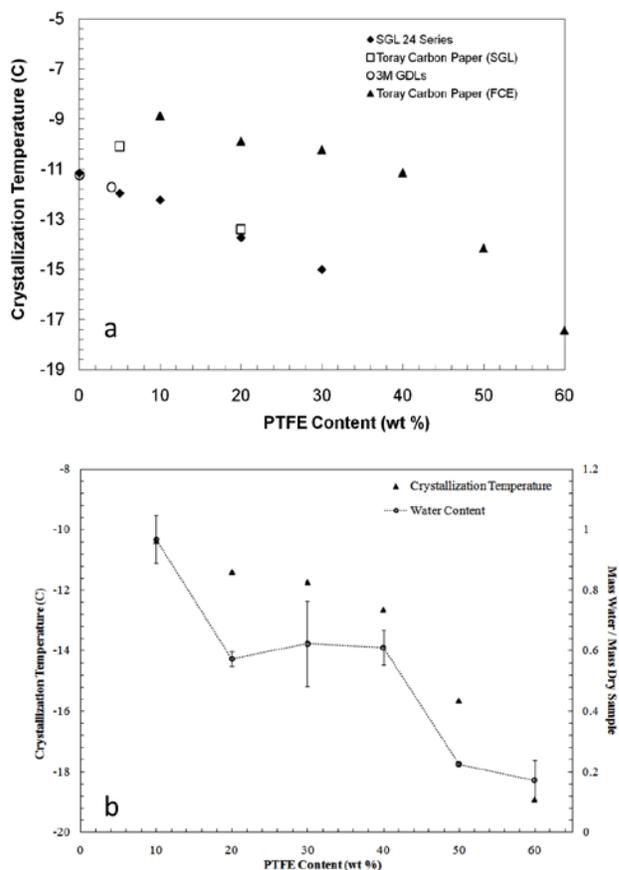


FIGURE 3. (a) Experimental data of the crystallization temperature as a function PTFE content for various GDLs. (b) Water content and crystallization temperature as a function of PTFE loading for Toray GDLs.

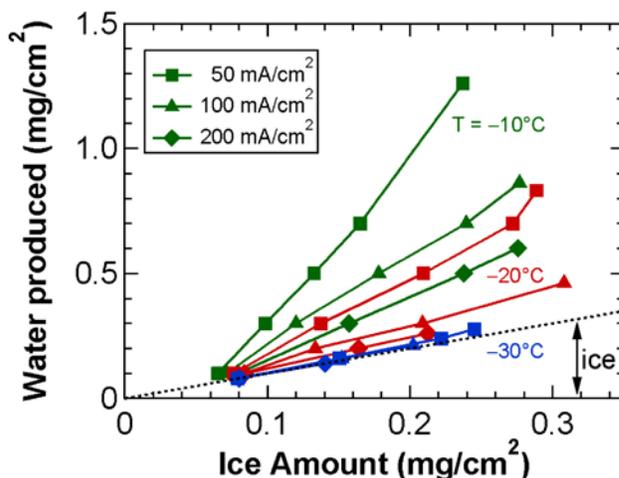


FIGURE 4. Experimental data of the fraction of liquid versus ice water for various isothermal startups at different current densities and temperatures. The line separating ice and liquid was fit to previous data.

as shown in the line in Figure 4. Then, the charge passed during isothermal starts can be plotted as shown in Figure 4. The figure shows the amount of the water produced that is in the ice phase versus liquid water. Thus, as the temperature is increased or the current density lowered, more product water can move away from the reaction site and does not freeze between the ionomer and catalyst particle. Knowing the amount of water in each phase will enable operation of the NSTF while meeting the DOE targets for survivability and cold start.

Conclusions and Future Directions

This project was initiated this year. Initial results are promising in guiding future directions and most of the year was spent on doing necessary diagnostic measurements and model development. The shutdown model clearly shows the redistribution of the water that occurs during long times and this can affect cell startup. Several novel experimental diagnostics for catalyst-layer ice, GDL freeze, and GDL liquid-related properties were developed and allow for better understanding of operation at low and subzero temperatures. In terms of future work, this can be summarized as:

- Cell performance:
 - Further testing of baseline and non-baseline assemblies.
 - Isothermal and adiabatic starts including cycling studies for tracking durability.
- Component characterization:
 - Consolidate/measure membrane properties at subzero conditions.
 - Diffusion media:
 - Neutron imaging of shutdown and water redistribution.
 - Capillary pressure – saturation relationships:
 - Impact of flowrate, temperature, injection sites (MPL analogs), materials
 - X-ray tomography for the water distribution
 - Measure effective gas diffusion coefficient and relative permeability versus saturation.
 - Measure and model freeze rate and ice-front propagation as a function of saturation.
- Modeling of shutdown, cold start, and isothermal start
- Stack studies for temperature distribution and performance characterization
- Understand and increase the operating window with thin-film catalyst layers

FY 2010 Publications/Presentations

1. Jeff T Gostick, Haluna P Gunterman, John Newman, and Adam Z Weber “ X-Ray tomographic study of liquid water distribution in GDLs under pressure-controlled capillary invasion and withdrawal”, ECS Transactions, Vegas ECS Meeting, 2010.
2. Thomas Dursch, Clayton J. Radke, and Adam Z. Weber, “Investigating Ice Formation in Gas-Diffusion Layers”, ECS Transactions, Las Vegas ECS Meeting, 2010.

References

1. J.T. Gostick, M.A. Ioannidis, M. W. Fowler and M.D. Pritzker, J. Power Sources, 194, 433 (2009).
2. A.Z. Weber, J. Power Sources, 195, 5292 (2010).