

V.F.2 Fuel Cell Fundamentals at Low and Subzero Temperatures

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Subcontractors:

- 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 exceeding. 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 loading of 0.2 g/kW
- Cost: \$15/kW_e

Fiscal Year (FY) 2012 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
- Develop diagnostic methods for critical 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:

(A) Durability

(C) Performance

- Cell Issues
- Stack Water Management
- System Thermal and Water Management
- System Start-Up and Shut-Down Time and Energy/Transient Operation

FY 2012 Accomplishments

- Site baseline data converged and systematic cell testing was initiated which showed possible ohmic-limitations with NSTF at lower temperatures.
- Measured adhesion forces accurately and representatively for droplets on the gas diffusion layer (GDL) surface.
- Isothermal data demonstrated low ice capacity of NSTF but superb durability.
- Examined in-depth the underlying membrane structure/function relationships.
- Examined water uptake in traditional catalyst layers:
 - Low uptake in ionomer due to interfacial character and morphology
 - Slow freeze kinetics
 - Some hydrophilicity which depends strongly on existence of cracks



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 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 of operation at lower temperatures with both NSTF and traditional catalyst layers 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 are used to quantify transport properties and to delineate phenomena that are used in the modeling. The one plus two-dimensional cell model is developed and validated by comparison of measured in situ cell performance in single cells under a variety of cell assemblies and architectures to highlight specific controlling phenomena. Durability is 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 is accomplished including the development of a suite of ex situ diagnostics that measure and evaluate the various critical material properties and transport-related phenomena.

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. It is also expected that this probably is exacerbated in thin-film catalyst layers such as NSTF. To test the limitations in NSTF cells, baseline cells (3M 2009 “Best in Class”) were studied using polarization-curve analysis at different temperatures. First, the cells must be properly broken-in using thermal cycling, which consists of fixed-flow polarization curves at 70°C (for 40 min), followed by open-circuit cool down by liquid-water injection (for 40 min). These cycles help remove contaminants and establish water pathways through the system. Once conditioned, hydrogen-pump experiments were carried out at different temperatures and the results compared to those obtained using traditional Pt/C catalyst layers. To

analyze the results, the change in polarization at different temperatures and humidities are plotted as shown in Figure 1. The analysis follows that of Perry and coworkers where the sharp increase at the lower humidity is seemingly due to mass-transport and probably ionic-transport limitations, which agrees with similar oxygen-reaction-order analysis (not shown). Also, at lower temperatures, the NSTF cell shows a kinetic loss indicative of the slow change in potential after dropping temperature. These simple characterization measurements can help to delineate what is limiting in the cell, and focus optimization and further diagnostic efforts.

While understanding performance is important, durability issues are also critical for the eventual use in applications. To study and compare different catalyst layers in terms of durability issues related to low temperatures, freeze/thaw experiments were conducted. These experiments were done both within a cell as well as in an environmental scanning electron microscope (ESEM). For the former, Figure 2(a,c) shows that the NSTF demonstrated negligible decay in polarization performance after 10 freeze/thaw cycles, whereas the traditional catalyst layer did exhibit a performance decrease. These results can be explained by Figure 2(b,d), where freeze/thaw cycling in the ESEM demonstrated that the traditional catalyst layer develops substantially more cracks than the NSTF one. The reason for this is that the traditional catalyst layer has ice that forms in between the catalyst particles which forces the layer apart, whereas for the NSTF, the water forms mainly on the surface. In addition, the NSTF itself is a stronger layer due to the underpinning of the substrate and the existence of the Pt-extended surface.

A key issue in operating at lower temperatures is water removal from the cell. This removal is most often accomplished by liquid droplets entering the gas channels in the flowfield. The way in which the droplets detach has been modeled previously using a force balance. However, the

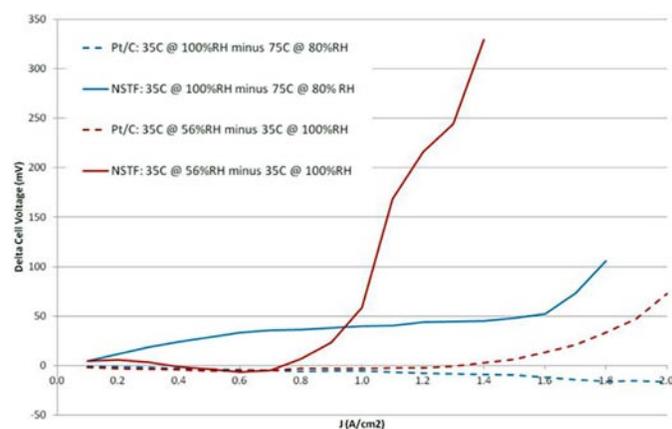


FIGURE 1. Polarization-performance changes for both traditional and NSTF catalyst layers at different temperatures or relative humidities

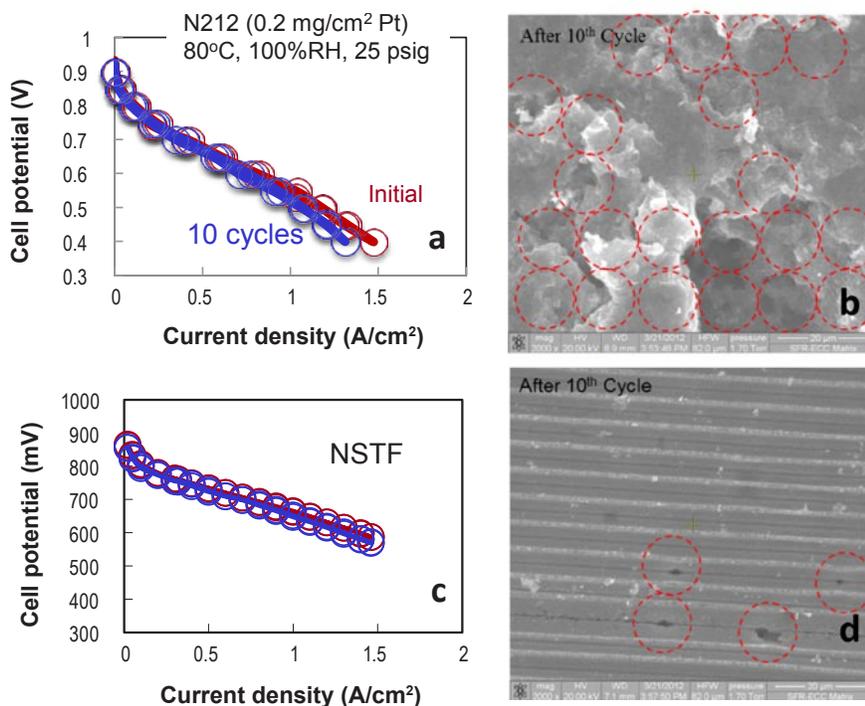


FIGURE 2. Polarization performance both initial and after 10 freeze/thaw cycles for a traditional (a) and NSTF (c) catalyst layer; and the resulting ESEM profiles after 10 freeze/thaw cycles in the ESEM for traditional (b) and NSTF (d) catalyst layers, where the circles denote existence of cracks

droplet adhesion force or force to remove the droplet from the surface was taken either from experiments of droplets placed on the surface or through ancillary studies like droplet contact-angle hysteresis. In the last year, we utilized a custom-built goniometer to calculate directly the adhesion force of droplet injected through the GDL. The apparatus functions by injecting a droplet of a given volume through the GDL, and then rotating the whole apparatus and measuring the angle at which the droplet falls off as shown in Figure 3 (a and b). This angle is then used to calculate the gravity force to remove the droplet, which, when normalized for the wetted diameter of the droplet on the surface, is the adhesion force. Resulting measurements are shown in Figure 3 (c and d) for the top placement and bottom injection. As shown, the adhesion force is a function of poly-tetrafluoroethylene (PTFE) content, where some minimal content is required to lower it (i.e., make it easier to remove the droplets). Also, the bottom injection demonstrates a much higher adhesion force due to the underlying water column attached to the droplet, something that has been ignored in previous analyses. This test and these forces will allow for a more complete picture of water-droplet removal to emerge and better modeling and understanding of low-temperature fuel cell operation.

Other diagnostics are aimed at determining what happens when water freezes in the various fuel cell layers. Last year, we developed a rate expression for freeze kinetics and data using nucleation theory and dynamic scanning

calorimetry. This year we adapted this to catalyst layers with the results that catalyst layers freeze slower than GDLs at the same subcooling, which we believe is due to nucleation on a small spherical particle instead of a long fiber. Also, this year we examined water uptake in traditional catalyst layers in more detail showing that the capillary properties of the catalyst layer are similar but slightly more hydrophilic than GDLs. However, this behavior depends strongly on cracking where cracked samples are more hydrophilic. In addition, we also confirmed and expanded the study of water uptake into catalyst-layer ionomer, showing that it is not a diffusive process but dominated probably by polymer relaxation, and also results in much lower water uptake than in bulk ionomer.

In terms of the last point, a lot of work was done to understand better the structure/function relationships of ionomer membranes. To this end, we developed a relatively straightforward energy-balance approach for predicting membrane water uptake. This approach is based on equating the chemical energy of solvation with that of the mechanical energy on the polymer (either external or internal) to keep it from dissolving. The multiscale model relies on information from both the macroscale (i.e., water uptake and λ , moles of water per sulfonic acid group) and the nanoscale (i.e., distance between ionomer domains or d-spacing). To understand the latter, small-angle X-ray scattering (SAXS) studies were done using the Advanced Light Source at LBNL. These studies revealed a figure of merit as shown

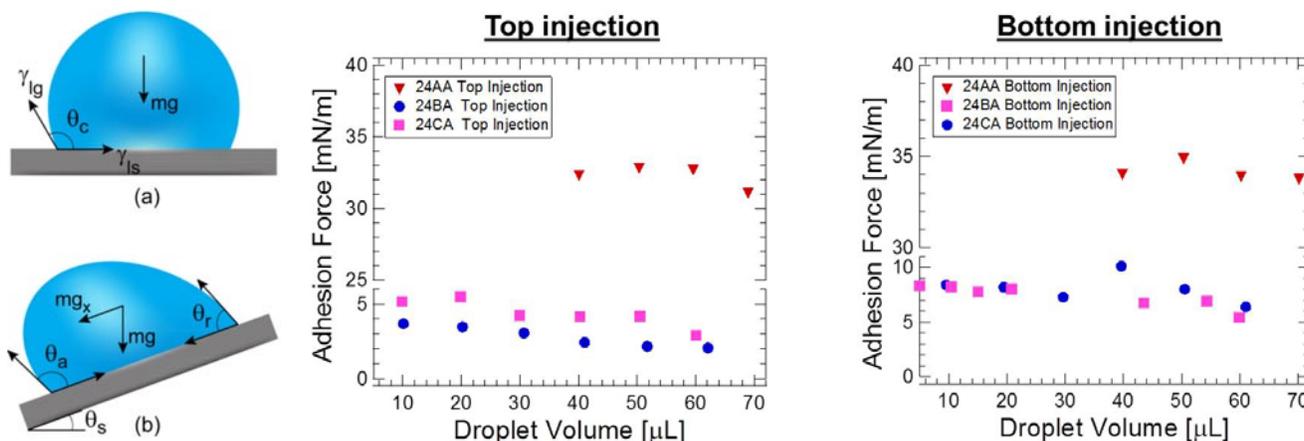


FIGURE 3. Schematic of a droplet on a GDL surface both sessile (a) and at the critical sliding angle (b); and droplet adhesion force as a function of droplet volume for three GDLs of different PTFE content (A=0, B = 5%, C = 10%) for both a top placement (c) and bottom injection (b) of the droplet

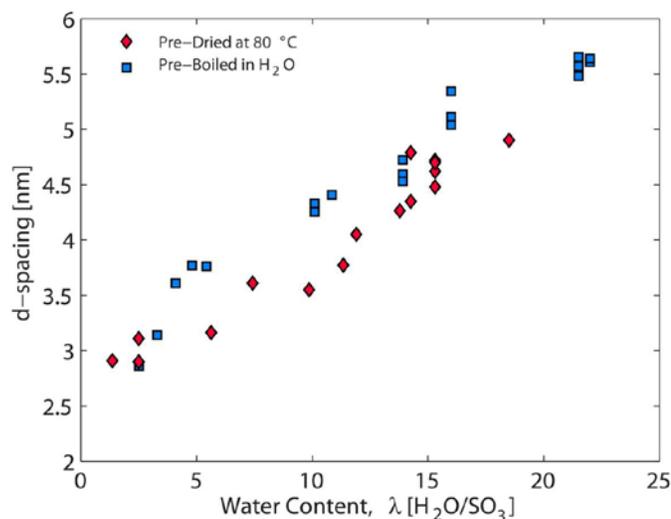


FIGURE 4. Hydrophilic domain spacing as a function of water content for a preboiled and pre-dried or as-received Nafion® 212 membrane

in Figure 4, which demonstrates a linear correlation in terms of the d-spacing and λ . Furthermore, as also shown, while the swelling changes with water content are similar for both an as-received or pre-dried membrane and a pre-boiled membrane, the actual values are different which demonstrates that the morphology and underlying structure/function relationship are also different. We have also shown that this difference can probably be attributed to a change in the structure of the ionic domains with more cylindrical domains existing for the preboiled sample. In addition, other SAXS studies explored how the drying or annealing of the membrane results in backbone crystallinity and this changes the mechanical energy which results in lower uptake. Throughout, the model and the studies underline the importance in reporting membrane conditions and any pretreatment when reporting experimental data.

Conclusions and Future Directions

The project focus this year was on developing and utilizing diagnostic methods for fuel cell components at low temperatures. To this end, several novel methods were developed and measurements for both traditional and NSTF catalyst layers made. The results allow for a better understanding of liquid and ice formation and movement within the cell. In addition, single-cell testing of NSTF cells was accomplished and site-to-site agreement obtained, where the latter is dependent on the way in which the cells are thermally cycled or conditioned before testing. In terms of modeling, both component-level models (e.g., membrane) and multidimensional models were developed and examined, with the latter showing that a two-dimensional framework is sufficient for modeling the critical transport-related phenomena. In terms of future work, this can be summarized as:

- Cell Performance
 - Testing of non-baseline assemblies
 - Examine low-temperature behavior and conditioning for NSTF Pt_3Ni_7
 - Impact of anode GDLs
 - Adiabatic starts including NSTF and low-loaded traditional membrane electrode assemblies
 - Temperature and power transients including neutron-imaging analysis
- Component Characterization
 - Catalyst Layers
 - More data on water-related properties including ionomer morphology, freeze, water uptake, and gas diffusion
 - Study proton migration along NSTF whiskers
 - Diffusion Media

- Measure effective gas-diffusion coefficient as a function of saturation
- Determine how liquid water gets out of the GDL (boundary condition)
- Membrane
 - Structure/function relationships, especially with reinforced membranes and impact of environment
- Modeling
 - Use data from all partners and understand the anode GDL and water-out-the-anode scheme for NSTF
 - Develop transient model and examine catalyst layer water capacity versus water removal fluxes or resistances as a function of catalyst layer thickness
 - Mechanical stress model and its impacts on performance
- Examine failed membrane electrode assemblies and cyclical isothermal cold starts for durability concerns
- Understand and increase the operating window for thin-film catalyst layers

Awards

1. The PI of this project was awarded the Supramaniam Srinivasan Young Investigator Award of the Energy Technology Division of the Electrochemical Society.
2. Work on the catalyst-layer diagnostics was awarded a Best Poster Paper at the 2012 Grove Fuel Cell Science and Technology Conference in Berlin.

FY 2012 Publications

1. Ahmet Kusoglu and Adam Z. Weber, 'Water Transport in Nafion Membranes,' in *Polymers for Energy Storage and Delivery: Polyelectrolytes for Batteries and Fuel Cells*, Kirt A. Page, Christopher L. Soles, and James Runt, Editors, ACS Symposium Series, 175-199 (2012).
2. Daniel S. Hussey, Dusan Spornjak, Adam Z. Weber, Rangachary Mukundan, Joseph Fairweather, Eric L. Brosha, John Davey, Jacob S. Spendelow, David L. Jacobson, and Rodney L. Borup, 'Accurate measurement of the through-plane water content of proton-exchange membranes using neutron radiography,' *J. Appl. Phys.*, submitted (2012).
3. Ahmet Kusoglu, Alexander Hexemer, Ruichun Jiang, Craig S Gittleman, and Adam Z. Weber, 'Effect of Compression on Conductivity and Morphology of PFSA Ionomers,' *J. Membrane Science*, in press (2012).
4. Miguel A. Modestino, Ahmet Kusoglu, Alexander Hexemer, Adam Z. Weber, and Rachel A. Segalman, 'Controlling Nafion Structure and Properties via Wetting Interactions,' *Macromolecules*, **45** (11), 4681-4688 (2012).
5. Prodip K. Das, Adam Grippin, Anthony Kwong, and Adam Z. Weber, 'Liquid-Water-Droplet Adhesion-Force

Measurements on Fresh and Aged Fuel-Cell Gas-Diffusion Layers,' *Journal of The Electrochemical Society*, **159** (5), B489-B496 (2012).

6. Thomas J. Dursch, Monica A. Ciontea, Clayton J. Radke, and Adam Z. Weber, 'Isothermal Ice-Crystallization Kinetics in the Gas-Diffusion Layer of a Proton-Exchange-Membrane Fuel Cell,' *Langmuir*, **28** (2), 1222-1234 (2012).
7. Ahmet Kusoglu, Miguel A. Modestino, Alexander Hexemer, Rachel A. Segalman, and Adam Z. Weber, 'Subsecond Morphological Changes in Nafion during Water Uptake Detected by Small-Angle X-Ray Scattering,' *ACS Macro Letters*, **1**, 33-36 (2012).
8. Ahmet Kusoglu, Brian L. Kienitz, and Adam Z. Weber, 'Understanding the Effects of Compression and Constraint on Water Uptake of Fuel-Cell Membranes,' *J. Electrochem. Soc.*, **158** (12), B1504-B1514 (2011).
9. Gi Suk Hwang, Massoud Kaviani, Jeffrey T. Gostick, Brian Kientiz, Adam Z. Weber, and Moo Hwan Kim, 'Role of Water States on Water Uptake and Proton Transport in Nafion using Molecular Simulations and Bimodal Network,' *Polymer*, **52**, 2584-2593 (2011).
10. Haluna P. Gunterman, Anthony Kwong, Jeff T. Gostick, Ahmet Kusoglu, and Adam Z. Weber, 'Water Uptake in PEMFC Catalyst Layers,' *ECS Transactions*, **41** (1), 647 (2011).
11. Prodip K. Das, Adam Grippin, and Adam Z. Weber, 'Detachment of Liquid-Water Droplets from Gas-Diffusion Layers,' *ECS Transactions*, **41** (1), 459 (2011).
12. Adam Z. Weber, 'Macroscopic Modeling of the Proton-Exchange-Membrane Fuel-Cell Catalyst Layer' *ECS Transactions*, **42** (1), 71-84 (2012).

FY 2012 Presentations

1. Adam Z. Weber, 'Macroscopic Modeling of the Proton-Exchange-Membrane Fuel-Cell Catalyst Layer,' *221st Meeting of the Electrochemical Society*, Seattle, Washington, May 2012. (invited talk)
2. Ahmet Kusoglu and Adam Z. Weber, 'Modeling Water Uptake in Fuel-Cell Membranes,' ModVal 9, Sursee, Switzerland, April 2012.
3. Ahmet Kusoglu, Anthony Kwong, Kyle Clark, Haluna Gunterman, and Adam Z. Weber, 'Water Uptake in Fuel-Cell Catalyst Layers,' *Fuel Cells 2012 Science & Technology*, Berlin, Germany, April 2012.
4. Ahmet Kusoglu and Adam Z. Weber, 'Understanding Schroeder's Paradox,' *March APS Meeting*, Boston, Massachusetts, March 2012.
5. Ahmet Kusoglu and Adam Z. Weber, 'Water Sorption and Related Structure-Function Properties of Nafion at Multiple Time- and Length-Scales,' *220th Meeting of the Electrochemical Society*, Boston, Massachusetts, October 2011 (invited talk).
6. Prodip K. Das and Adam Z. Weber, 'Detachment of Liquid-Water Droplets from Gas-Diffusion Layers,' *220th Meeting of the Electrochemical Society*, Boston, Massachusetts, October 2011.
7. Ahmet Kusoglu, Ruichun Jiang, Craig S Gittleman, and Adam Z. Weber, 'Effect of Compression on Conductivity and Morphology of PFSA Membranes,' *242nd ACS National Meeting & Exposition*, Denver, Colorado, August 2011.

8. Prodip Das, Haluna Gunterman, and Adam Z. Weber, 'Understanding Water Removal from Fuel-Cell Gas-Diffusion Layers,' *European Fuel Cell Forum 2011*, Lucerne, Switzerland, June 2011.

9. Adam Z. Weber, Wonseok Yoon, and Prodip Das, 'Continuum Modeling of Fuel-Cell Transport Phenomena,' *219th Meeting of the Electrochemical Society*, Montreal, May 2011 (invited talk).

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

11. Adam Z. Weber, Prodip K. Das, Haluna P. Gunterman, Anthony Kwong, Gisuk Hwang, Kyle T. Clark, and Ahmet Kusoglu, 'Liquid-Water Uptake and Removal in PEM Fuel-Cell Components,' *2011 Fuel Cell Seminar*, Orlando, November 2011.