V.F.1 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

Project Start Date: September 21, 2009
Project End Date: September 30, 2014

Overall 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 (CLs)
- 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

Fiscal Year (FY) 2013 Objectives

- Develop and validate model for NSTF CLs showing impact of different diffusion media and temperature
- Quantify performance changes with NSTF at different temperatures, material sets, and compression
- Develop diagnostic methods for critical properties for operation with liquid water
- Examine freeze kinetics and ionomer morphology in traditional CLs and thin-film model systems

Technical Barriers

This project addresses the following technical barriers from the fuel cell section of the Fuel Cell Technologies Office 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

Technical Targets

This project is conducting fundamental investigations into fuel cell operation at low and subzero temperatures. The knowledge gained will provide valuable insight necessary to devise material and mitigation strategies to meet DOE targets. 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
  - Platinum-grade metal loading of 0.2 g/kW
- Cost: \$15/kW_e

FY 2013 Accomplishments

- Elucidated impact of anode gas-diffusion layer (GDL) on low-temperature performance utilizing both modeling and experiments, which showed increased performance with GDLs that promoted more water movement out of the anode side of the cell with less flooding.
- Examined in-depth the underlying membrane structure/ function relationships including direct visualization of water profiles demonstrating importance of membrane interface on transport phenomena.
- Analyzed polarization curves showing perhaps significant ionic-conduction limitations in NSTF CLs at low-temperature operation.
- Developed mechanical stress model.

- Studied ionomer thin films on different substrates showing impact of film thickness, thermal history, and substrate interactions.
- Measured effective gas diffusivities in partially saturated gas-diffusion layers.

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 understand and eventually optimize 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 CLs such as the NSTF developed by 3M Company 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 at low precious metal loadings. This project directly focuses on the above aspects of operation at lower temperatures with both NSTF and traditional CLs with the goal that improved understanding will allow for the DOE targets to be met with regard to cold start, survivability, performance, and cost.

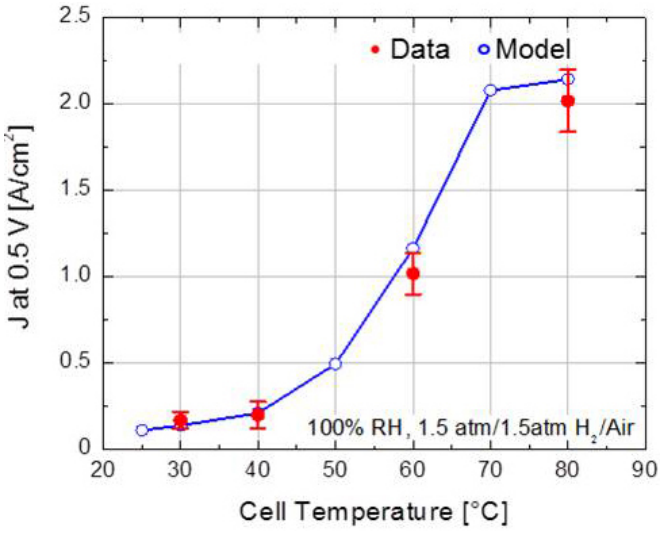
APPROACH

The overall approach is to use a synergistic combination of cell, stack, and component diagnostic studies with advanced mathematical modeling conducted 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 two-dimensional (2-D) 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 in order 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 advanced 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 is probably exacerbated in thin-film CLs such as NSTF CLs. As an example of this, Figure 1 shows the impact of temperature on baseline NSTF cells (3M 2009 "Best in Class"). As the cell temperature decreases such that vapor-phase removal is not sufficient and liquid water forms, the performance drastically decreases. This change in performance is also captured in the developed, physics-based 2-D mathematical model for this cell that utilized findings and properties from the advanced diagnostics developed in this project.

In Figure 2a, possible routes to performance increase are shown by use of the model. It is clear that development of schemes in which water is moved out the anode and hence minimize flooding of the cathode should increase performance. Indeed, removal of the MPL from the anode GDL should show significant performance increases. In Figure 2b, it is seen that the experimental data justify this supposition in that the lower temperature performance increases as the MPL thickness is decreased. However, one must be cognizant that thinner or no MPLs can promote shorting of the cell during assembly due to carbon fiber penetration into the GDLs, thus a minimum thickness is probably required. Beyond just the MPL, another possible route for low-temperature performance increase is using different anode GDLs. This possibility is shown in Figure 3, where it is clear that some anode GDLs perform significantly



RH - relative humidity

FIGURE 1. Current density at 0.5 V cell potential from data and model predictions of an NSTF cell as a function of cell temperature with fully humidified feeds.

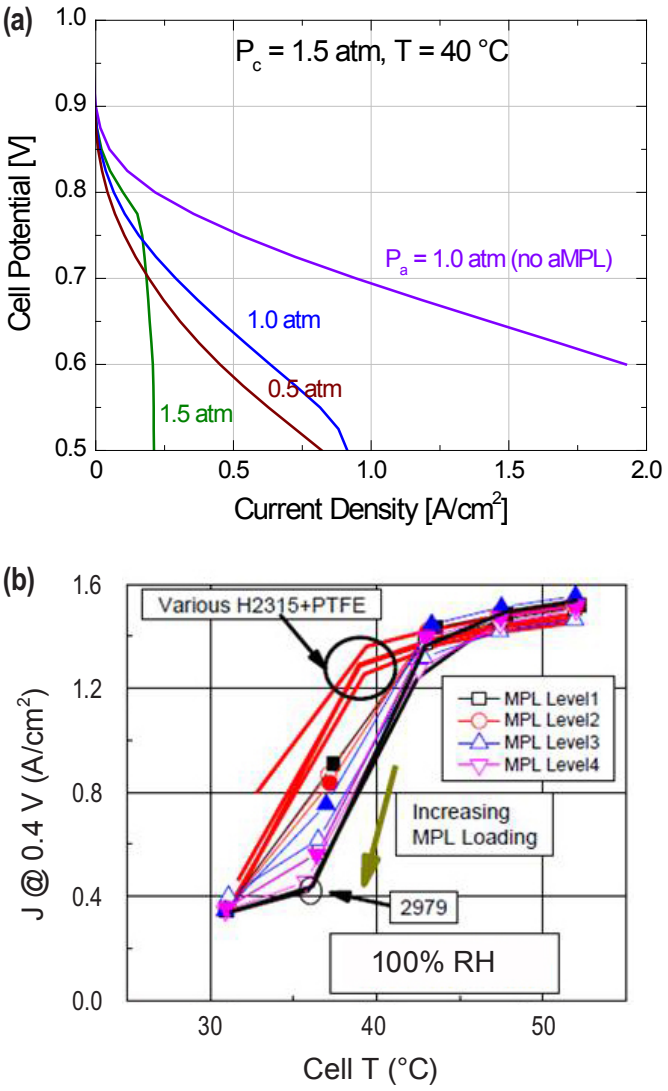


FIGURE 2. (a) Predicted polarization curves using the mathematical model and different anode diffusion media and pressure conditions. (b) Experimental data showing impact of MPL thickness (loading) on cell current density at 0.4 V as a function of cell temperature.

better at lower temperatures than others. To investigate this in more detail, neutron imaging results, shown in Figure 3b, demonstrate that the better performing GDLs seem to reduce the anode and cathode water contents, perhaps by providing routes for water to leave the cell and promoting water transport from cathode to anode. The exact reasons for this behavior are currently under investigation. Finally, Figure 3a also shows the impact of cell compression on performance. As the GDL becomes compressed, the contact resistance between the GDL and bipolar plate is decreased, resulting in better performance. However, continued compression reduces the GDL porosity and causes mass-transport limitations and increased heterogeneity of GDLs under lands and channels. From this study, it appears that 5-10% compression is optimal.

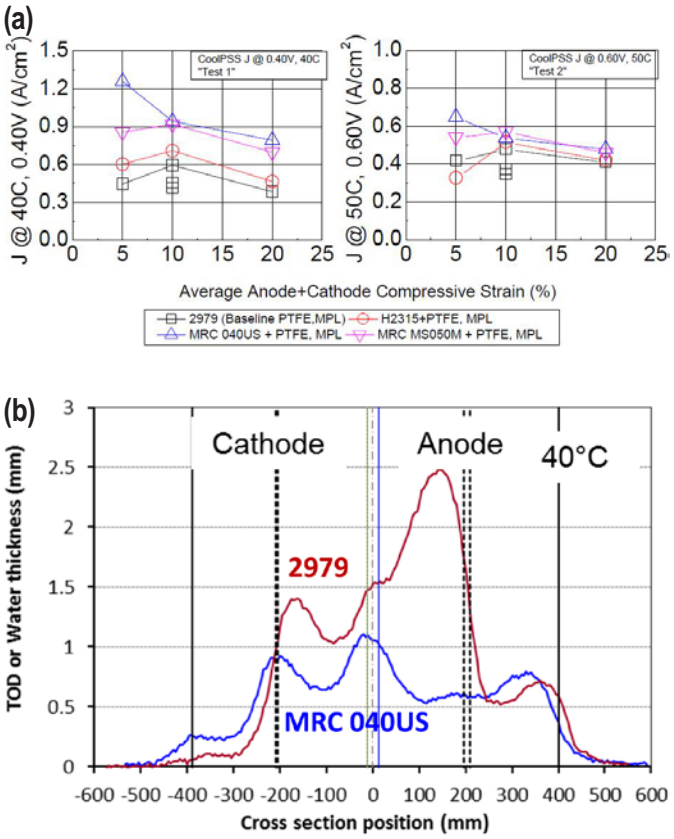


FIGURE 3. (a) Impact of cell compression and different GDLs on cell current density at two different temperatures and potentials. (b) Neutron-imaging water content for NSTF cells at 0.3 V with different GDLs; the lines in the middle denote the MEA.

A key issue in operating at lower temperatures is water removal from and build-up in the cell. This accumulation of water in the porous diffusion media will impede the transport of reactant gases from the channels to the active sites. Previously, it was unknown how the saturation, the volume fraction of water in the pore space, impacts the gas diffusion coefficient. This year, we developed a hydrogen pump limiting current setup to measure this relationship. The results, as shown in Figure 4, demonstrate an almost cubic dependence of the gas diffusion coefficient on both the porosity and liquid saturation for a carbon-paper GDL, where the effective gas diffusion coefficient is a product of the two expressions: $\frac{\langle D \rangle}{D} = f(\varepsilon) f(S_L)$. This cubic dependence is quite different than the often assumed 1.5 power (so-called Bruggemann expression), and incorporation of these results into the model enabled the good agreement shown in Figure 1. This diagnostic will further increase understanding of transport phenomena at low temperatures and is being refined and utilized for more fuel cell layers and prospective materials.

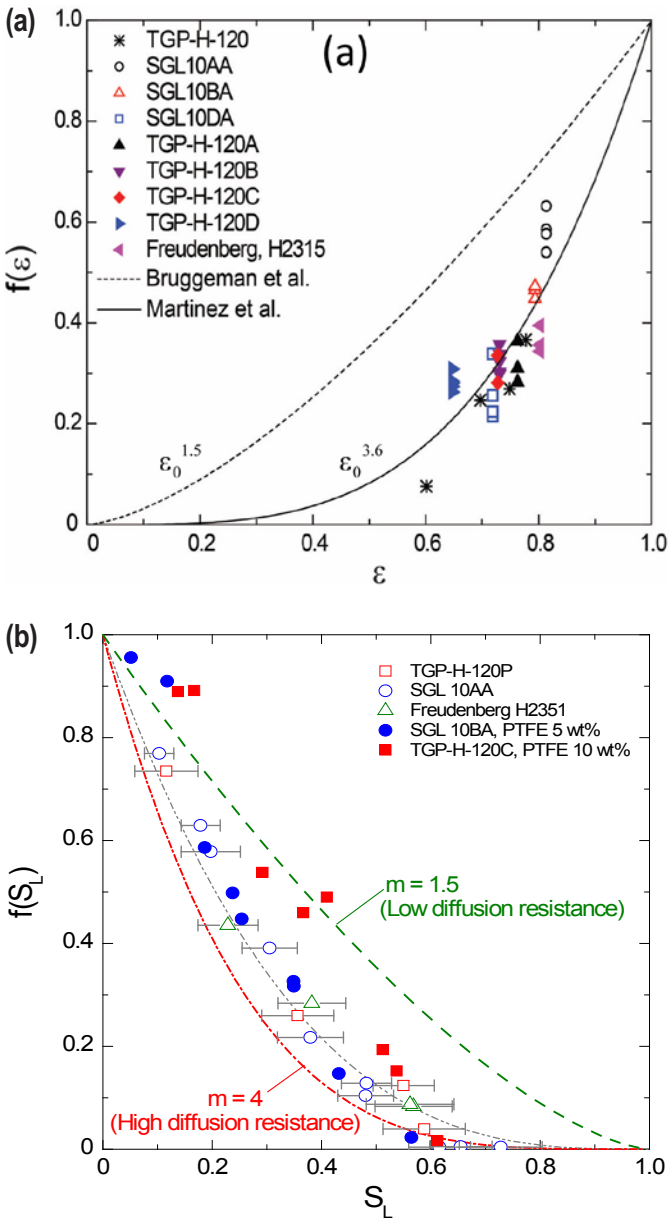


FIGURE 4. Measured effective diffusivity of hydrogen as a function of porosity (a) (normalized to bulk diffusivity) and saturation (b) (normalized to effective dry diffusivity) for different GDL papers.

CONCLUSIONS AND FUTURE DIRECTIONS

The project focus this year was on developing and utilizing diagnostic methods for fuel cell components at low temperatures and incorporating them into a performance model that can describe observed changes. To this end, several novel methods were developed, and measurements for membranes, GDLs, and CL ionomer were made. The results allow for a better understanding of liquid and ice formation and movement within the cell, as well as limitations due to ionomer films at low catalyst loadings. In addition, single-cell testing of NSTF cells was accomplished with the model able to replicate performance decrease as a function of anode GDL and temperature.

In terms of future work, this can be summarized as:

- Cell Performance
  - United Technologies Research Center to run cool and cold starts including adiabatic and temperature transients:
    - NSTF and low-loaded traditional CLs
    - Run hybrid water transport plate cells
  - Los Alamos National Laboratory to run NSTF cells including various tests:
    - Segmented cell
    - Power transients
    - National Institute of Standards and Technology high and higher resolution neutron imaging
  - 3M to run cells to determine water balance and impact of NSTF structure
- Component characterization
  - Traditional CLs
    - Examine thin-film membrane morphology
  - NSTF CLs
    - Proton migration on platinum
  - GDLs
    - Liquid-water movement out of the GDLs by droplets
    - Measurement of effective diffusivities, thermal conductivities, and relative permeabilities
  - MPLs: how do they work with liquid water?
  - Membrane
    - Interfacial resistance and membrane morphology with different environments
- Modeling
  - Use data from all partners to understand the anode GDL and water-out-the-anode scheme for NSTF CLs
  - Develop transient model and examine CL water capacity versus water removal fluxes as a function of CL thickness
  - Optimize schemes and structures to increase low-temperature performance
- Examine failed MEAs and cyclical isothermal cold starts for durability concerns
- Understand and increase the operating window with thin-film CLs

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1. 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).

2. Ahmet Kusoglu, Anthony Kwong, Kyle T. Clark, Haluna P. Gunterman, and Adam Z. Weber, 'Water Uptake of Fuel-Cell Catalyst Layers,' *Journal of the Electrochemical Society*, **159** (9), F530-F535 (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*, **421-422**, 283-291 (2012). doi:10.1016/j.memsci.2012.07.027.

4. Gi-suk Hwang and Adam Z. Weber, 'Effective-Diffusivity Measurement of Partially-Saturated Fuel-Cell Gas-Diffusion Layers,' *Journal of the Electrochemical Society*, **159** (11), F683-F692 (2012).

5. Ahmet Kusoglu, Suchol Savagatrup, Kyle T. Clark, and Adam Z. Weber, 'Role of Mechanical Factors in Controlling the Structure/Function Relationship of PFSA Ionomers,' *Macromolecules*, **45** (18), 7467-7476 (2012). doi: 10.1021/ma301419s.

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8. Miguel A. Modestino, Devproshad K. Paul, Shudipto Dishari, Stephanie A. Petrina, Frances I. Allen, Michael A. Hickner, Kunal Karan, Rachel A. Segalman, and Adam Z. Weber, 'Self-assembly and transport limitations in confined Nafion films,' *Macromolecules*, **46** (3), 867-873 (2013).

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11. Thomas J. Dursch, Monica A. Ciontea, Gregory J. Trigub, Clayton J. Radke, and Adam Z. Weber, 'Ice-Crystallization Kinetics and Water Movement in Gas-Diffusion and Catalyst Layers', *ECS Transactions*, **50** (2), 429-435 (2012).

12. Ahmet Kusoglu and Adam Weber, 'Role of Chemical-Mechanical Energies in Understanding Structure and Properties of Aged and Degraded Membranes', *ECS Transactions*, **50** (2), 961-965 (2012).

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1. T.J. Dursch, G.J. Trigub, C.J. Radke, A.Z. Weber, 'Isothermal Ice-Crystallization Kinetics in Catalyst Layers of Proton-Exchange-Membrane Fuel Cells,' *86th Colloid and Surface Science Symposium*, Montreal, Canada, June 2012.

2. Ahmet Kusoglu, Adam Z. Weber, Michael Hickner, Kunal Karan 'Understanding Confinement Effects on PFSA Ionomer,' ACS Materials in Fuel Cells, Asilomar, California, February 2013.

3. Ahmet Kusoglu, Adam Z. Weber, Michael Hickner, Kunal Karan 'Water Uptake and Transport in Nafion,' ACS Materials in Fuel Cells, Asilomar, February 2013. (invited talk)

4. Gi Suk Hwang, Dilworth Y. Parkinson, Ahmet Kusoglu, Alastair A. MacDowell, and Adam Z. Weber, 'Understanding Water Uptake and Transport in Polymer-Electrolyte Membrane Fuel Cells Using X-Ray Micro-tomography,' *245th ACS National Meeting & Exposition,* New Orleans, Louisiana, April 2013.

5. Prodip K Das and Adam Z. Weber, 'Understanding Water Management as a Function of Catalyst-Layer Thickness,' *222nd Meeting of the Electrochemical Society*, Honolulu, Hawaii, October 2012.

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7. T.J. Dursch, M.A. Ciontea, G.J. Trigub, C.J. Radke, A. Z. Weber, 'Ice-Crystallization Kinetics and Water Movement in the Gas-Diffusion and Catalyst Layers of a Proton-Exchange-Membrane Fuel Cell,' *222nd Meeting of the Electrochemical Society*, Honolulu, Hawaii, October 2012.

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12. Adam Z. Weber, 'Understanding Ionomer-Related Transport and Morphology in Polymer-Electrolyte Fuel Cells,' *Princeton Chemical Engineering Colloquium*, October, 2012.

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14. Ahmet Kusoglu, and Adam Z Weber, 'Mechanical/Chemical Energy Balance in Perfluorinated Sulfonic Acid Membranes,' *SSPC13 Meeting,* Grenoble, France, September 2012. (invited talk)

15. Prodip Das and Adam Z. Weber, 'Understanding Water Management as a Function of Fuel-Cell Catalyst-Layer Thickness,' *International Society of Electrochemistry Annual Meeting*, Prague, Czech Republic, August 2012.

16. Prodip K. Das, Sophia E.M. Haussener, Anthony Kwong, Gi-suk Hwang, Haluna P. Gunterman, Adam Z. Weber, 'Physicochemical Characterization of Fuel-Cell Diffusion Media,' *ASME 2012 10th International Conference on Nanochannels, Microchannels and Minichannels,* Puerto Rico, July 2012.

17. Prodip K. Das and Adam Z. Weber, 'Water-Droplet Adhesion Force on Fuel-Cell Gas-Diffusion Layers: Beyond Contact-Angle Measurements,' *ASME 2012 10th International Conference on Nanochannels, Microchannels and Minichannels,* Puerto Rico, July 2012.