V.E.2 Fuel-Cell Fundamentals at Low and Subzero Temperatures

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Subcontractors
- Los Alamos National Laboratory (LANL), Los Alamos, NM
- United Technologies Research Center (UTRC), East Hartford, CT
- 3M Company, St. Paul, MN

Project Start Date: September 21, 2009
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Fundamentally understand transport phenomena and water and thermal management at low and subzero temperatures
- Examine water (liquid and ice) management with thin-film catalyst layers (CLs), such as 3M's nanostructured thin film (NSTF) 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) 2015 Objectives

- Use validated mathematical model to explore water-out-the-anode scheme for NSTF CLs
- Measure water content and resistance of traditional CLs
- Examine materials properties for low equivalent weight (EW) ionomer membranes and thin films
- Explore water distributions for and impacts of various gas diffusion layers (GDLs) and microporous layers (MPLs)

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells 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 enable various metrics to be met or exceeded. These include those related to durability, performance, and cost. Specially,

- Durability
  - 5,000 h (automotive) and 40,000 h (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 loading of 0.2 g/kW
- Cost: \$15/kW_e

FY 2015 Accomplishments

- Combined modeling and experiment to understand low-temperature performance of NSTF showing how the critical factor is removing liquid water through the anode
- Examined transient operation showing how the membrane properties and GDL interface are the most sensitive parameters for water-out-of-the-anode scheme

- Increased water out the anode lowers cathode flooding and is driven by morphological features that decrease GDL surface adhesion force
- Developed along-the-channel model to correlate spatially varying results
- Investigated water movement and existence in diffusion media including under compression where water-imbibition front and CL water content were imaged
- Examined operation of novel MPLs containing hydrophilic additives
- Investigated traditional CL resistance and importance of ionomer mass-transport resistance at low catalyst loadings

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. 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 CLs, 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 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 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 (2D) cell model is developed and validated by comparison of measured in situ cell performance in both single cells under a variety of cell assemblies and architectures in order to highlight specific controlling phenomena. To explore 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 problem is exacerbated in thin-film CLs such as NSTF CLs as shown previously with single cell, low-temperature operation. To improve performance, it is thought that one needs to reduce the amount of water within the thin-film cathode, and thus increase it out of the anode as was shown previously. This year, the 2D model was used to examine the impact of the water-out-the-anode scheme. As shown in Figure 1a, the model correctly predicts this trend by changing the liquid water pressure boundary condition (Figure 1c). The change in condition is related to the adhesion force and droplet detachment values that we measure. Figure 1b shows the impact of GDL permeability, which is not a strong impact compared to the pressure (Figure 1c), highlighting that interfacial phenomena are key in determining water removal impacts.

The above analysis is for a NSTF cell, but, in practice, platinum on carbon (Pt/C) CLs are traditionally used that are thicker, thus minimizing the impact of water flooding. However, to reach such thicknesses, these electrodes contain ionomer that provides proton conduction throughout the layer. To explore impacts of this ionomer, various diagnostic tests were conducted. Using a hydrogen pump setup, we were able to measure both the CL and dry GDL and MPL resistances to gas transport. As shown in Figure 2, the CL resistance dominates, even though the test uses hydrogen and does not generate water. Furthermore, this resistance increased with lower Pt loadings, which is consistent with previous reported observations and shows a key limiting factor in decreasing catalyst loading. Currently we are working to explore these resistances by measuring gas permeation coefficients in the ionomer thin-film and correlating them to the structure of the film such that ways can be found to minimize its effect.

It is important as well to visualize water to understand where it exists and thus improve models as well as elucidate governing phenomena. Figure 3 shows two such visualizations. In the top figure, high-resolution neutron imaging was used to visualize the water content of cells with thick CLs in order to collect enough data points. As seen, the cathode CL behaves quite differently than the anode one. Furthermore, the impact of phase-change-induced flow is clearly seen in that the water content decreases in the cathode and increases at the cathode GDL boundary as a function of increasing temperature due to the temperature gradient across the GDL. In the bottom figure, X-ray computed

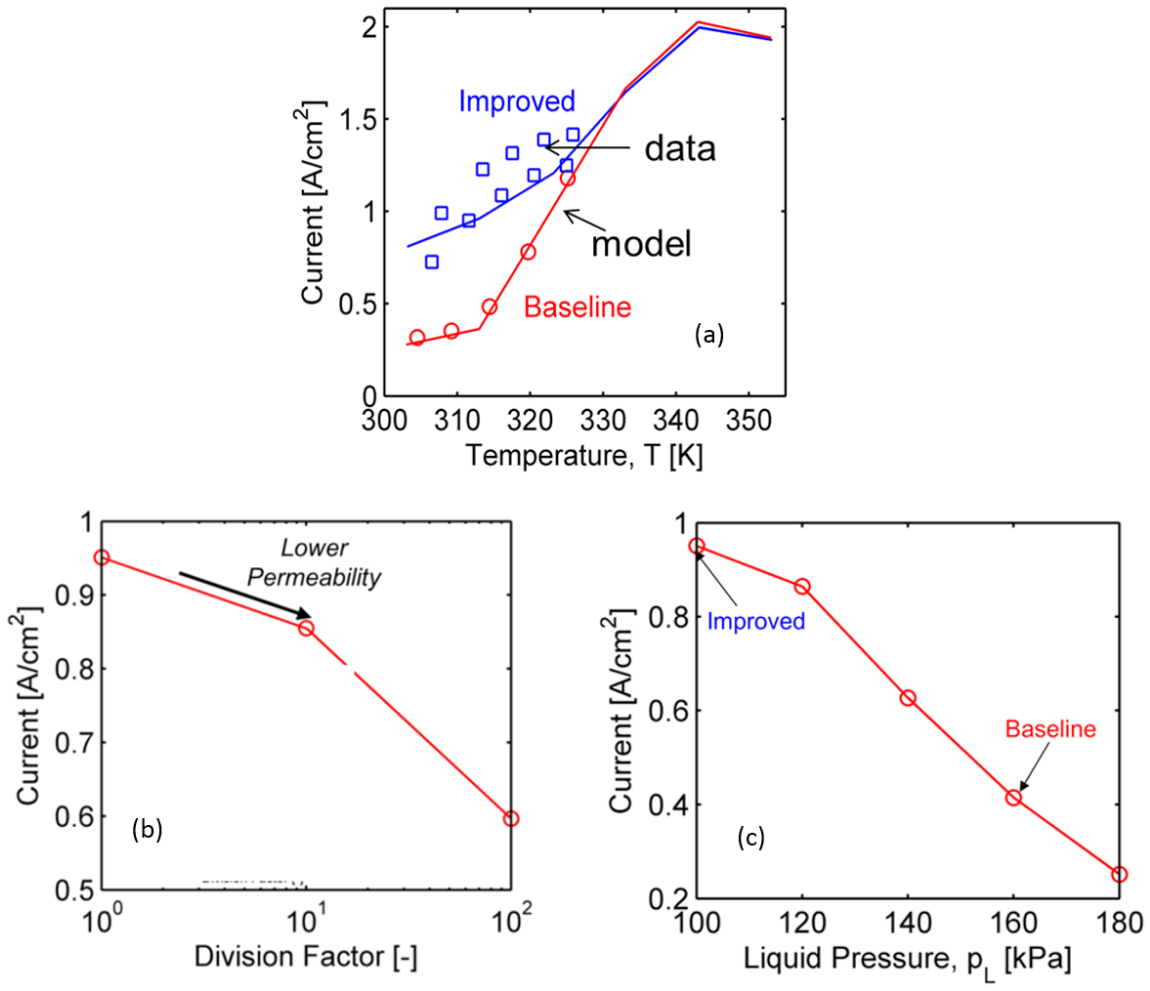

FIGURE 1. (a) Cell voltage (at 0.25 A/cm^2) as a function of temperature with 100% relative humidity feeds at 150 kPa for an NSTF cell with a baseline or improved anode GDL including both data (points) and 2D model results (lines). Sensitivity study for (b) GDL permeability and (c) GDL/channel liquid pressure boundary condition on cell voltage at 40°C and 0.25 A/cm^2.

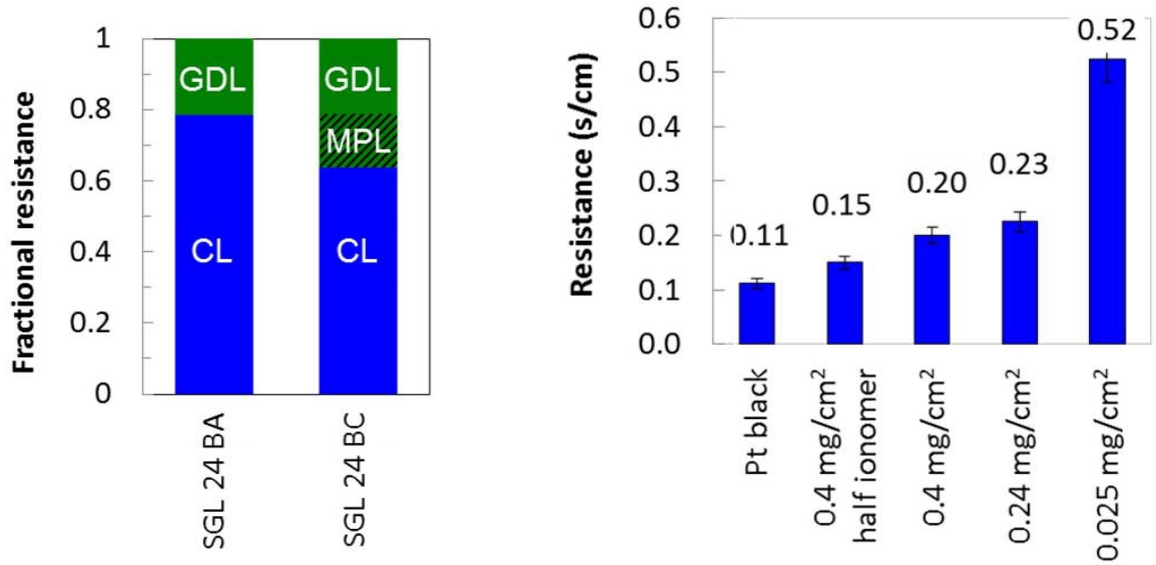

FIGURE 2. Normalized gas-phase effective resistance as measured by hydrogen pump limiting current for GDL, MPL, and traditional Pt/C catalyst layer. Measured transport resistance as a function of catalyst-layer type and loading.

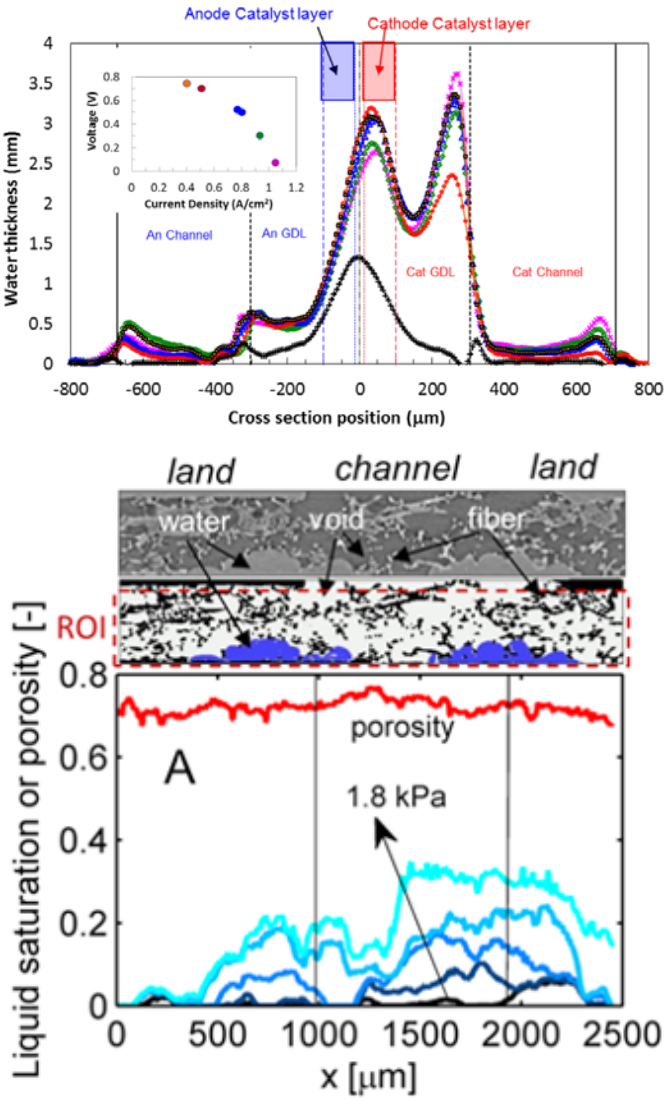

FIGURE 3. (top) Water thickness from neutron imaging with thick catalyst layers at 80°C; the inset shows the polarization performance. (bottom) Liquid saturation of a GDL as measured by X-ray computed tomography showing the water saturation in-plane as a function of inlet pressure from 0 to breakthrough.

tomography at the Advanced Light Source was used to ascertain the position and structure of water imbibition into the GDL. It is clearly seen that water exists as a front partway through the GDL but then capillary fingering occurs. Thus, models that use volume-averaged quantities such as saturation will not be accurate since they cannot capture the stochastic nature of water percolation.

CONCLUSIONS AND FUTURE DIRECTIONS

The project focus this year was on developing and utilizing diagnostic methods for fuel cell components at low temperatures to elucidate routes for performance improvement. Such activities also include incorporating the experimental observations into a transient performance model that can describe the observed changes. Several novel methods were developed and measurements for membranes, GDLs, and CL ionomer were made. The results allow for a better understanding of liquid formation and movement within the cell, as well as limitations due to ionomer films at low catalyst loadings. In addition, single-cell testing of cells containing traditional CLs was accomplished including segmented cells with transient data, adiabatic cells, and thick CLs for neutron imaging.

Future work is summarized as follows:

- Cell Performance
  - Run cool and cold starts using adiabatic cell hardware (UTRC)
  - Examine possible interlayers and multilayer electrodes
  - Run NSTF and Gore cells with different diffusion media and operating conditions (LANL)
  - Perform imaging: segmented cell and NIST imaging including thick CLs
- Component Characterization
  - Measure transport resistance, especially for low Pt loadings
  - Measurement of key GDL properties, including PSD, liquid-water pathways, and adhesion force, for new GDLs
  - Measure transport properties of ionomer films, especially low EW ones
  - Characterize reinforced membranes
- Modeling
  - Exercise model to determine critical properties and guide material development and provide design targets
  - Incorporate more advanced interfacial and kinetic models
  - Examine pore-scale models and new GDL model possibilities
- Understand and increase the operating window with thin-film CLs
  - Focus on solutions and strategies derived from the integrated model and cell and component studies
- Solicit input and advice from original equipment manufacturers and material companies on cell performance

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Adam Z. Weber, Charles W. Tobias Award of the Electrochemical Society.

2. Adam Z Weber, Kavli Fellow, of the National Academy of Sciences.

FY 2015 PUBLICATIONS

1. Ahmet Kusoglu, Douglas Kushner, Devproshad K. Paul, Kunal Karan, Michael A. Hickner, and Adam Z. Weber, 'Impact of Substrate and Processing on Confinement of Nafion® Thin Films,' *Advanced Functional Materials*, **24** (30), 4763–4774 (2014).

2. Anthony D. Santamaria, Prodip K. Das, James C. MacDonald, and Adam Z. Weber, 'Liquid-Water Interactions with Gas-Diffusion-Layer Surfaces,' *J. Electrochem. Soc*., **161** (12), F1184–F1193 (2014).

3. Adam Z. Weber, Rodney L. Borup, Robert M. Darling, Prodip K. Das, Thomas J. Dursch, Wenbin Gu, David Harvey, Ahmet Kusoglu, Shawn Litster, Matthew Mench, Rangachary Mukundan, Jon P. Owejan, Jon Pharoah, Marc Secanell, and Iryna Zenyuk, 'A Critical Review of Modeling Transport Phenomena in Polymer-Electrolyte Fuel Cells,' *J. Electrochem. Soc*., **161** (12), F1254–F1299 (2014).

4. Adam Z. Weber and Ahmet Kusoglu, 'Unexplained transport resistances for low-loaded fuel-cell catalyst layers,' *J. Materials Chemistry A*, **2** (42), 17207–17211 (2014). *(highlight)*

5. Frances I. Allen, Luis R. Comolli, Ahmet Kusoglu, Miguel A. Modestino, Andrew M. Minor, and Adam Z. Weber, 'Morphology of Hydrated As-Cast Nafion® Revealed through Cryo Electron Tomography,' *ACS Macro Letters*, **4**, 1–5 (2015). (*Cover, ACS Editors Choice article*)

6. Iryna V. Zenyuk, Dilworth Y. Parkinson, Gisuk Hwang, and Adam Z.Weber, 'Probing water distribution in compressed fuel-cell gas-diffusion layers using X-ray computed tomography,' *Electrochemistry Communications*, **53**, 24–28 (2015).

7. Pablo A. García-Salaberri, Gisuk Hwang, Marcos Vera, Adam Z. Weber, and Jeffrey T. Gostick, 'Effective diffusivity in partially-saturated carbon-fiber gas diffusion layers: Effect of through-plane saturation distribution,' *International Journal of Heat and Mass Transfer*, **86**, 319–333 (2015).

FY 2015 PRESENTATIONS

1. Adam Weber, "Understanding Transport in Fuel-Cell Ionomer," Chemical Engineering Colloquium, Colorado School of Mines (invited).

2. I.V. Zenyuk, D.Y. Parkinson, G. Hwang, A.Z. Weber "Understanding Water Transport in Compressed Gas Diffusion Layers of Polymer-Electrolyte Fuel Cells Using X-ray Computed Tomography," 2015 MRS Spring Meeting & Exhibit, 2015.

3. A.Z. Weber, A. Kusoglu, A. Hexemer, "Structure of Nafion® Thin Films on Gold." APS Meeting, San Antonio, 2015.

4. A. Kusoglu, A.Z. Weber, "Structure/Property Relationship of PFSA in Thin Film regime," SSPC17, Seoul, 2014.

5. A.Z. Weber, A. Kusoglu, S. Shi, M. Tesfaye, "Understanding ionomer thin films," ACS Meeting, Denver, 2015.

6. A. Kusoglu, A.Z. Weber, "Structure-Function Relationship of PFSA Thin Films," ISPE14 Meeting, Australia, 2014.

7. P.A. García-Salaberri, J.T. Gostick, G. Hwang, M. Vera, A.Z. Weber, "Pore-Scale Calculations of Effective Diffusivity in Partially-Saturated GDLs: Application to PEFC Continuum Models," MODVAL 12, Germany, 2015.

8. M. Tesfaye, A. Kusoglu, B.D. McCloskey, A.Z. Weber, "Impact of Structure on Transport Properties of Bulk and Thin-film Ionomers," Advances in Fuel Cells, Asilomar, 2015.

9. A. Kusoglu, A. Crothers, A.Z. Weber, "Understanding and Modeling Water Transport in Proton-Exchange Membranes," ISE Meeting, Lausanne, 2014.

10. P.K. Das, A.Z. Weber, "Role of GDL Surface Wettability and Operating Conditions in Liquid-Water Removal from NSTF Catalyst Layers," IMECE, 2014.

11. A. Kusoglu, A.Z. Weber, "Study of PFSA Ionomers using X-Ray Scattering Techniques," ACS Meeting, San Francisco, 2014 (invited).

12. T.J. Dursch, G.J. Trigub, R. Lujan, R. Mukundan, C.J. Radke, A.Z. Weber, "Ice-Crystallization Kinetics During Fuel-Cell Cold-Start," ECS Meeting, Orlando, 2014 (award talk).

13. A.Z. Weber, "Understanding Transport Phenomena in Polymer-Electrolyte Fuel Cells," ECS meeting, Cancun, 2014 (award talk).

14. D.L. Jacobson, D. O'Kelly, D.S. Hussey, D. Spernjak, A.Z. Weber, R. Mukundan, J. Fairweather, J.S. Spendelow, and R.L. Borup, "Using neutron radiography to accurately quantify the through-plane water content of a proton-exchange membrane," ACNS, 2014.

15. M.L. Perry, "Characterization of Polymer Electrolyte Fuel Cells with Ultra-Low Catalyst Loadings," ECS Meeting, Cancun, 2014 (invited).

16. A. Weber, "Understanding Transport in Fuel-Cell Ionomer," Chemical Engineering Colloquium, Tufts University, 2014 (invited).

17. I.V. Zenyuk, A. Santamaria, P.K. Das, A. Steinbach, R. Mukundan, R.L. Borup, A.Z. Weber, "Water Management with Thin-Film Catalyst Layers," CARISMA, South Africa, 2014.

18. A. Kusoglu, A.Z. Weber, "Critical role of the interface in controlling transport in PFSA membranes," ACS Meeting, San Francisco, 2014.