

V.G.1 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
- McGill University, Montreal, Quebec, Canada

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 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

Fiscal Year (FY) 2014 Objectives

- Develop transient models and use it to examine NSTF start-up performance as compared to experimental data
- Quantify performance changes with NSTF and at different temperatures and material sets
- Develop diagnostic methods for critical properties for operation with liquid water including analysis of gas diffusion layers (GDLs) and micro-porous layers (MPLs)
- Examine impact of freeze kinetics and ionomer morphology with traditional catalyst layers and thin-film model systems

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:

- 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 loading of 0.2 g/kW
- Cost: \$15/kW_e for 80-kW_e fuel cell stack operating on direct hydrogen

FY 2014 Accomplishments

- Analyzed NSTF performance with different anode GDLs to ascertain the mechanisms of improved performance at lower temperature due to more water out of the anode due to GDL structure and changes in droplet adhesion force
- Explored mechanism of liquid water movement through an MPL by development of MPL analogues, which is due to specific sites that are partially in liquid contact

- Measured current distribution using segmented cell for model validation and analysis
- Measured Nafion® morphology by direct imaging using cryo-transmission electron microscopy tomography
- Demonstrated that improved freeze kinetics predicts measured delay of cell failure in isothermal freeze experiments
- Measured and modeled isothermal and adiabatic cell performance, showing that NSTF cells can startup and operate better within a stack environment due to the different thermal boundary conditions
- Systematically investigated various casting and thermal treatment conditions on the morphology, swelling, and water-uptake behavior of ionomer thin films on various substrates



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 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 two-dimensional cell model is developed and validated by comparison of measured in situ cell performance using a variety of cell assemblies and 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 is exacerbated in thin-film catalyst layers such as NSTF catalyst layers (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. Such an analysis is shown in Figure 1a, where we plot the cell voltage at 0.25 A/cm² for different operating temperatures as a function of the fraction of water being removed from the anode. As can be seen, the larger the fraction removed, the better the performance at lower temperatures. Also, the performance decreases as temperature decreases. Shown in Figure 1 are cell test results with the cell having two different anode GDLs. The one with the improved GDL allows better performance at lower temperatures that is seemingly correlated to the ability of that anode GDL to remove more water. Characterization of the GDLs has shown that the improved one has a banded structure, and the main variable that this is seemingly impacting is the ease of water removal from its surface as shown in Figure 1b. Here, we developed a technique to measure the flow velocity in a channel needed to remove a water droplet from the GDL's top surface that was formed through bottom-inject of the water. Figure 1b shows that the improved GDL has a lower detachment velocity, thus meaning that for a given flowrate water can be more easily removed, which correlates with more water out of the anode and the improved performance seen in Figure 1a.

The above analysis is for a single cell, but in practice fuel cells are operated within a stack. To mimic such an impact, a single-cell fixture with limited thermal mass was designed since one major difference between a single cell and a cell within a stack is the thermal boundary condition. As shown in Figure 2a, the measured startup performance for such an adiabatic cell (i.e., one within a stack where the other cells insulate it) compared to the traditional isothermal one (i.e., where the temperature boundaries remain constant) shows that the cell has better transient and steady-state performance. To explore this, the LBNL two-dimensional performance model was made transient and the adiabatic and isothermal conditions compared. As shown in Figure 2b, the temperature increase provided by the adiabatic cell allows for the catalyst-layer water content to decrease since more can be removed in the vapor phase. The model can now be

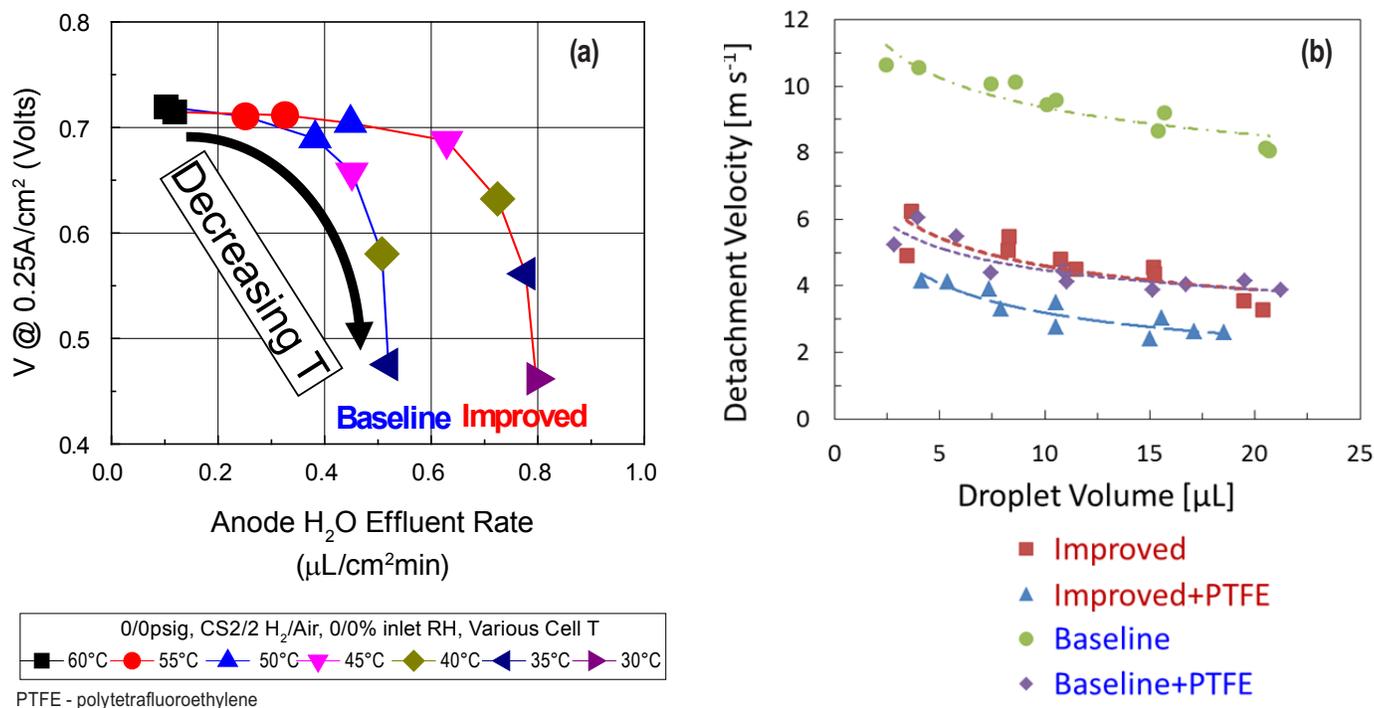


FIGURE 1. (a) Cell voltage at 0.25 A/cm² for an NSTF cell as a function of amount of water leaving the anode for two different anode GDLs. The different points correspond to different cell temperatures, and the cell conditions are no humidity or back pressure. (b) Measured detachment velocity as a function of droplet volume for a droplet emerged from different GDLs.

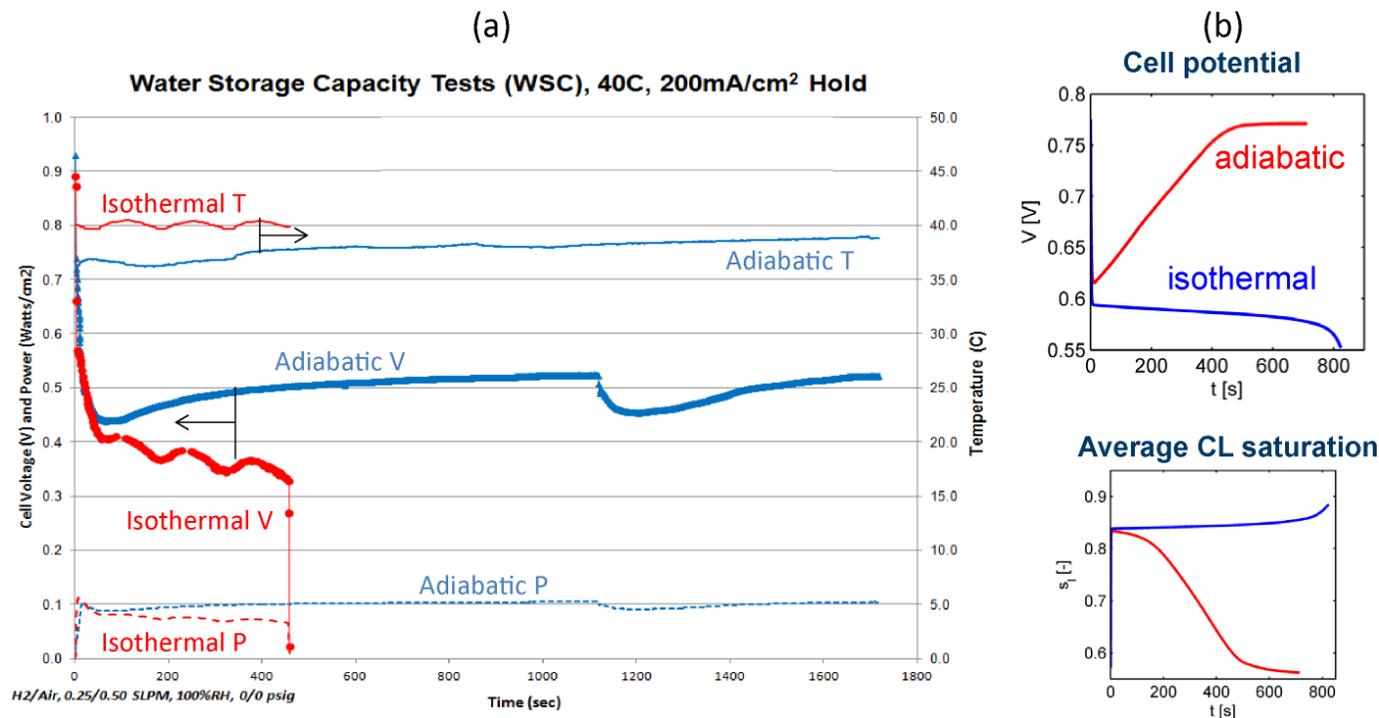


FIGURE 2. (a) Cell voltage as a function of time for both an isothermal and adiabatic single cell with NSTF catalyst layers. One can see that the adiabatic cell allows for increased performance and startup. (b) Transient two-dimensional simulation results for adiabatic and isothermal boundary conditions in terms of both cell potential and average catalyst-layer saturation as a function of time.

validated with the data and used to explore the importance of the thermal boundary condition (e.g., cell location in a stack) on performance and startup.

To understand further the emergence of water droplets and liquid water through the fuel cell porous backing layers (MPL and GDL), a setup was designed to measure the liquid-pressure response of the system rather than visualizing the liquid-water behavior. The droplet growth-detachment cycle and resultant pressure profile contains valuable information about the water configuration inside the GDL and MPL. This potential was explored more closely by studying GDLs with and without an MPL. Attempts are also made to mimic the behavior of the MPL using various water-impermeable masks with a variety of hole arrays, to mimic the cracks and blemishes typically found in real MPLs and elucidate the underlying transport mechanisms. To help interpret the observed experimental behavior, a model was developed that explains the sawtooth pressure profiles as seen in Figure 3. The figure shows that the model can accurately reproduce the experimental data, where a GDL has multiple entry sites whereas the MPL has a limited number of entry sites but also a small reservoir that is accessed through the changing liquid/vapor interfaces of the smaller domains. With the

gained knowledge, better models and understanding can be obtained for liquid-water transport through these important layers.

Figure 4 shows the impact of subcooling or subzero temperature on isothermal-start experiments. As the subcooling becomes lower (i.e., temperature approaches 0°C), the time for cell failure (i.e., 0 V), drastically increases. As shown in the figure, a simple model of water and thermal transport through the cathode side of the cell captures this behavior when using our previously measured ex situ freeze kinetics in both the GDL and catalyst layers. The reason is that as the subcooling becomes less than 15°C or so, the formation of ice becomes nucleation limited. Furthermore, such behavior is not reproduced when using a traditional thermodynamic-based rate expressions, showing the importance of accounting for the ice-formation kinetics.

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 including changing the anode GDL. Such

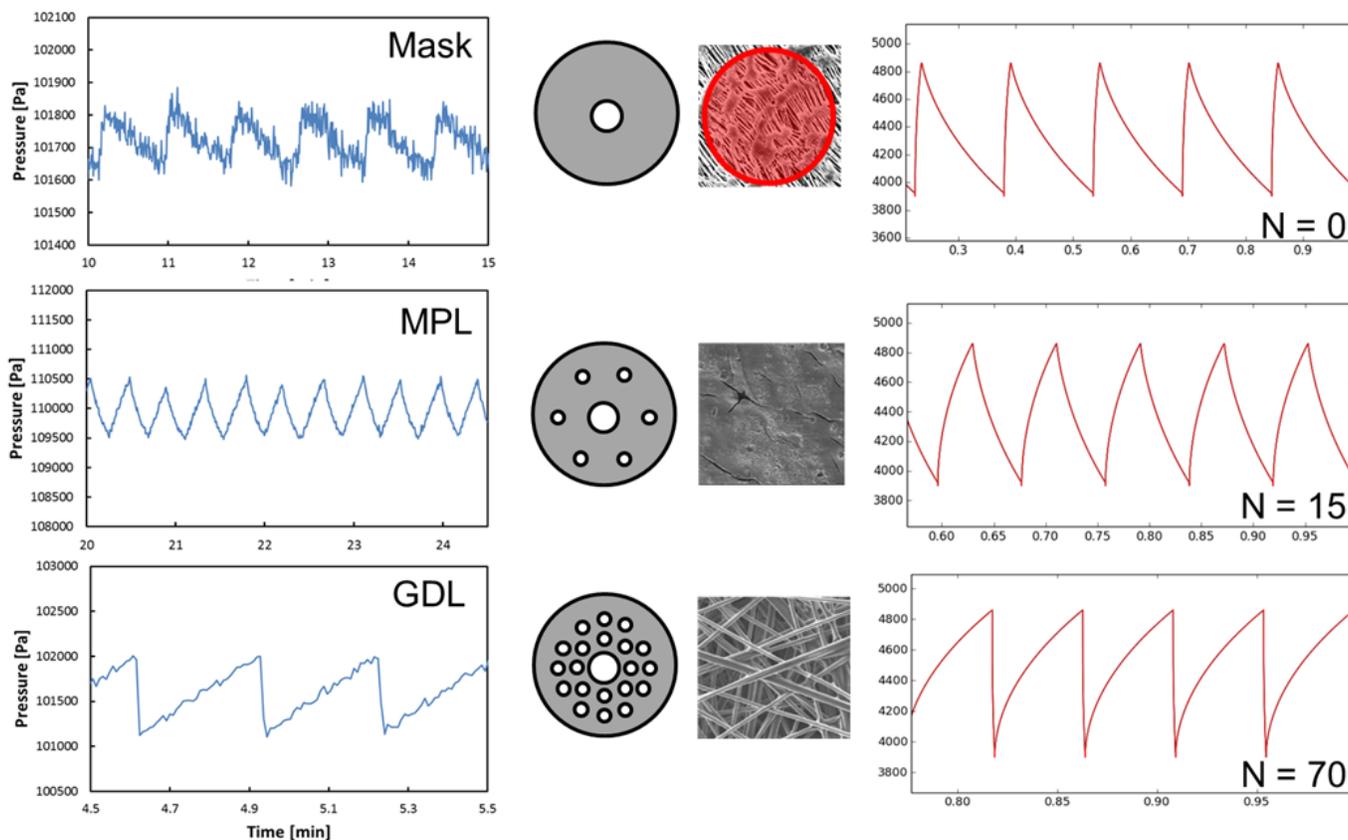


FIGURE 3. Analysis of liquid-water pressure as a function of time for a pendant droplet being formed and removed (by gravity) through different porous media of a mask/GDL, MPL/GDL, and bare GDL. The left side shows the pressure data, the middle shows the morphology used in a simple water-flow model used to generate the data on the right side. The model shows that a simple analysis of water entry points and interfacial reservoirs can explain the experimental data.

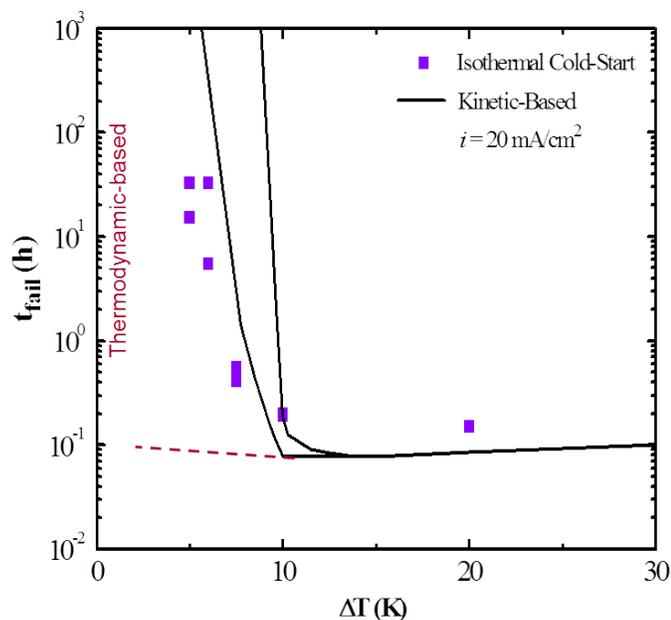


FIGURE 4. Measured isothermal cold-start data for single cells as a function of subcooling (temperature below 0°C), where the data are time to cell failure. The solid lines correspond to a simple water and thermal model using measured ice-formation kinetics, and the dotted lines to the typically used thermodynamic-based rate equation for ice formation.

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 catalyst-layer 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 NSTF cells was accomplished with varying thermal boundary conditions to mimic cells within a stack.

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

- Cell Performance
 - UTRC to run tests with cool and cold starts including adiabatic and temperature transients
 - Both NSTF and low-loaded traditional CLs
 - LANL to run tests with both NSTF and traditional CL Gore cells with different GDLs and operation conditions
 - Segmented cell
 - Power transients
 - NIST high(er)- and low- (transient) resolution imaging
- Component Characterization
 - Traditional CLs

- Examine gas-phase transport properties and uptake with low-equivalent weight ionomer and ionomer thin films
- NSTF CLs
 - Determine proton conductivity on platinum
- GDLs
 - Study the impact of bipolar plate structures on liquid-water movement out of the GDL
 - Measure effective transport properties (e.g., diffusivity, permeability, thermal conductivity)
 - Produce images of liquid water within and on the surface of the GDL
- Membrane
 - Correlate interfacial resistance and membrane morphology in different environments

- Modeling
 - Use data from all partners to refine transient model
 - Develop bilayer or alternate approach for NSTF CLs
 - Develop down-the-channel model (two-dimensional + 1)
- Understand and increase the operating window with thin-film CLs
 - Focus on possible solutions and strategies as derived from the integrated model, as well as cell and component studies
- Solicit input and advice from original equipment manufacturers regarding areas to focus on and key issues they face with regard to low-temperature operation

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Adam Z. Weber, Presidential Early Career Award for Scientists and Engineers (PECASE)

FY 2014 PUBLICATIONS

1. Gi Suk Hwang, Dilworth Y. Parkinson, Ahmet Kusoglu, Alastair A. MacDowell, and Adam Z. Weber, 'Understanding Water Uptake and Transport in Nafion using X-Ray Microtomography,' *ACS Macro Letters*, **2**, 288-291 (2013).

2. Ahmet Kusoglu, Kyu Taek Cho, Rafael A. Prato, and Adam Z. Weber, 'Structural and Transport Properties of Nafion in Hydrobromic-Acid Solutions,' *Solid State Ionics*, **252**, 68-74 (2013).

3. Thomas J. Dursch, Greg J. Trigub, J. F. Liu, Clayton J. Radke, and Adam Z. Weber, 'Non-isothermal Melting of Ice in the Gas-Diffusion Layer of a Proton-Exchange-Membrane Fuel Cell,' *International Journal of Heat and Mass Transfer*, **67**, 896-901 (2013).

4. Thomas J. Dursch, Greg J. Trigub, Rodger Lujan, J. F. Liu, Rangachary Mukundan, Clayton J. Radke, and Adam Z. Weber, 'Ice-Crystallization Kinetics in the Catalyst Layer of a Proton-Exchange-Membrane Fuel Cell,' *Journal of the Electrochemical Society*, **161** (3), F199-F207 (2014).
5. 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).
6. Kirt A. Page, Ahmet Kusoglu, Christopher M. Stafford, Sangcheol Kim, R. Joseph Kline, and Adam Z. Weber, 'Confinement-driven Increase in Ionomer Thin-Film Modulus,' *Nano Letters*, **14**, 2299-2304 (2014).
7. Thomas J. Dursch, Jianfeng F. Liu, Greg J. Trigub, Clayton J. Radke, and Adam Z. Weber, 'Ice-Crystallization During Cold-Start of a Proton-Exchange-Membrane Fuel Cell,' *ECS Transactions*, **58** (1), 897-905 (2013).
8. Adam Z. Weber, 'Macroscopic Modeling of Porous Electrodes,' in *Electrochemical Engineering*, Trung Nguyen, Editor in encyclopedia of applied electrochemistry, Robert Savinell, Ken-Ichiro Ota, Gerhard Kreysa, Editors, Springer, in press (2014). doi: 10.1007/978-1-4419-6996-5.
9. Adam Z. Weber, 'Thermal Effects in Electrochemical Systems,' in *Electrochemical Engineering*, Trung Nguyen, Editor in encyclopedia of applied electrochemistry, Robert Savinell, Ken-Ichiro Ota, Gerhard Kreysa, Editors, Springer, in press (2014). doi: 10.1007/978-1-4419-6996-5.
10. Fairweather J. D., D. Spornjak, J. Spindelow, R. Mukundan, D. Hussey, D. Jacobson, and R. L. Borup, 'Evaluation of Transient Water Content During PEMFC Operational Cycles by Stroboscopic Neutron Imaging,' *ECS Transactions* (2013)
11. J. Mishler, Y. Wang, R. Lujan, R. Mukundan, and R.L. Borup, 'An experimental study of polymer electrolyte fuel cell operation at sub-freezing temperatures,' *J. Electrochem. Soc.*, **160**, F514-F521 (2013).
4. Ahmet Kusoglu, Adam Z. Weber, "Morphology and Swelling of Perfluorosulfonic-acid (PFSA) Ionomer Thin Films," ECS meeting, San Francisco.
4. Prodip K. Das and Adam Z. Weber, 'Water-Management in PEMFC with Ultra-Thin Catalyst-Layers,' ASME Fuel Cell Conference, Minneapolis (2013).
5. T.J. Dursch, G.J. Trigub, J.F. Liu, C.J. Radke, A.Z. Weber, "Effect of External Vibrations on Non-isothermal Ice-Nucleation Rates," AIChE meeting, San Francisco.
6. Thomas J. Dursch, Jianfeng F. Liu, Greg J. Trigub, Clayton J. Radke, and Adam Z. Weber, 'Ice-Crystallization Kinetics During Cold-Start of a Proton-Exchange-Membrane Fuel Cell,' ECS meeting, San Francisco.
7. Rangachary Mukundan, Dusan Spornjak, Roger Lujan, Daniel Hussey, David Jacobson, Andy Steinbach, Adam Weber, and Rodney L. Borup, "Neutron imaging and performance of PEM fuel cells with nanostructured thin film electrodes at low temperatures," ECS meeting, San Francisco.
8. Gi-suk Hwang, Joseph Grant, and Adam Z. Weber, "Effective Diffusivity Measurement of Partially-Saturated Diffusion Media," ECS meeting, San Francisco (2013).
9. Adam Z. Weber, Ahmet Kusoglu, "The Role of the Interface in Controlling Transport Phenomena in PFSA's," Water Phenomena in PEM Workshop, Norway (invited).
10. Rachid Zaffou, Mike L. Perry, Zhongfen Ding, "Performance of Polymer-Electrolyte Fuel Cells with Ultra-Low Catalyst Loadings under Low Temperature Operation," ECS Meeting, Toronto (2013).
11. Adam Weber, "Understanding Transport in and Properties of Nafion Across Length Scales," MII Symposium, Virginia Tech (invited).
12. Ahmet Kusoglu, Alex Hexemer, Adam Weber, "Interfaces, Bulk, and Confinement in Nafion," Golden Gate Polymer Forum, San Francisco (invited).
13. Adam Z Weber, "Macroscopic Modeling of Performance Concerns in Proton-Exchange-Membrane Fuel-Cell Catalyst Layers," IPAM Fuel Cell Modeling, Los Angeles (invited).
14. Prodip K Das, Anthony Santamaria, Adam Z. Weber, "Understanding liquid water and gas-diffusion layers," Grove Fuel Cell Science and Technology Conference, Amsterdam, (2014).
15. Ahmet Kusoglu and Adam Weber, "Impact of Interfacial Conditions on Perfluorosulfonic-acid (PFSA) Membranes and Thin Films," ECEE conference, Shanghai (2014). (invited)

FY 2014 PRESENTATIONS

1. A. Kusoglu, G.S. Hwang, and A.Z. Weber, "Water Uptake in PFSA Membranes," ECS Meeting, Toronto (2013). (invited tutorial).
2. Thomas J. Dursch, Clayton J. Radke, and Adam Z. Weber, "Phase Change and Water Movement in Fuel-Cell Porous Media," ASME Heat Transfer Conference, Minneapolis (2013). (invited keynote).
3. Adam Z Weber and Ahmet Kusoglu, "Structure/Function Relationships in Perfluorinated Sulfonic Acid Membranes," Solid State Ionics, Kyoto, (2013).