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

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/kWₑ

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
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 of 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 \( \lambda \), 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 or merit as shown
in Figure 4, which demonstrates a linear correlation in terms of the d-spacing and $\lambda$. 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$_3$Ni$_7$
  - 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**


**FY 2012 Presentations**


