V.G.17 Sub-Freezing Fuel Cell Effects

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Objectives

- Quantify materials properties of fuel cell components (e.g. conductivity of Nafion®) under sub-freezing conditions.
- Identify degradation mechanisms due to freeze/thaw cycling (ice formation and startup/shutdown).
- Determine impact of freeze-thaw cycling on fuel cell component properties.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(D) Thermal, Air, and Water Management
(J) Startup Time/Transient Operation

Technical Targets

This project is conducting fundamental studies of sub-freezing effects on fuel cells. Insights gained from these studies will be applied toward the DOE start-up and survivability targets.

LANL Progress Toward Meeting DOE Low Temperature Requirements (Table 3.4.4)

Characteristic	Units	2010 Target	LANL
Start-up time from -20°C	sec	30	n/a
Survivability	°C	-40	-40 (100 cycles)

Accomplishments

- Quantified the conductivity of, and state of water in Nafion® in the temperature range (-40°C to +30°C). Discovered that the optimal conductivity under sub-freezing conditions is obtained when $7 < \lambda < 12$ in Nafion®. The water content is expressed in terms of the hydration number (λ) or the amount of water per sulfonic acid group in the membrane (H_2O/SO_3^-).
- Demonstrated durability of fully humidified single cells to 100 freeze/thaw cycles down to –40°C.
- Identified carbon fiber breakage in the gas diffusion layer (GDL) as a potential failure mechanism during freeze/thaw cycling.

Introduction

Fuel cells will need to be operated and stored under sub-freezing conditions in order to reach commercialization in most transportation markets. The goal of this project is to assist the DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program in understanding the role sub-freezing temperatures play on fuel cell performance and durability in order to meet DOE milestones for sub-freezing startup and survivability.

Approach

A workshop with 49 participants including representatives from fuel cell manufacturers, university and national lab researchers, and government officials was organized in Phoenix, AZ on February 1-2, 2005 to quantify sub-freezing issues in fuel cells. This workshop identified several key areas of research that need to be addressed for the successful commercialization of fuel cells. Based on the results of this workshop we have focused this project on two key areas: 1) the characterization of mechanical, electrical and thermal properties and the state of water in the various fuel cell component materials under sub-freezing conditions; and 2) the identification of degradation mechanisms during freeze/thaw cycling.

The component characterization under sub-freezing temperatures will include 1) alternating current (AC) impedance measurements of the conductivity, 2) differential scanning calorimeter (DSC) measurements of the state of water, and 3) mechanical properties measurement. The degradation mechanisms that are operational during freeze/thaw cycling will be evaluated by studying: 1) the effect of ice formation on membrane electrode assembly (MEA) integrity, 2) the effect of start/stop cycles on fuel cell performance, and 3) the effect of freeze/thaw cycling on the component properties including electrical conductivity and mechanical strength.

Results

The conductivity of Nafion® in the temperature range –40ºC to +30ºC is illustrated in Figure 1. Nafion® immersed in liquid water and equilibrated over water (100% relative humidity, RH) showed a low activation energy (≈ 0.2 eV) at T > 0°C and a high activation energy (≈ 0.5 eV) at T < -15°C. This change in activation energy is consistent with that reported by Cappadonia et al. and corresponds to the freezing of the water in the membrane [1]. This change in activation energy was not observed for the Nafion® membranes that were equilibrated at 90% RH and 80% RH. Moreover, these experiments revealed that at lower temperatures (< -10ºC), a gain in the overall conductivity could be achieved by an actual decrease in the water content of the membrane. However, it should be noted that at further lower water contents (< 50% RH) the conductivity starts to drop dramatically. These conductivity results are consistent with the DSC curves shown in Figure 2. It is seen that there is "bulk-like water" freezing in the membrane saturated with water vapor and liquid water (not shown in Figure 2) that is absent in the membranes equilibrated at 90% RH and 80% RH ("bulk like water" is free water with a sharp phase transition from ice to water at 0°C). Moreover, the membranes equilibrated with RH >50% possess bound-freezable water whose content increases with increasing RH. The increase in conductivity with increasing RH is related to the increase in water content while the change in activation energy is associated with the freezing of bulk-like water. Therefore, the optimal conductivity at low temperatures (<-10ºC) is achieved for membranes equilibrated at 80-90% RH with no bulk-like water present.

The performance of a fuel cell prepared using E-Tek (v2) double-sided wetproofed carbon cloth subjected to 100 freeze/thaw cycles down to –40°C is shown in Figure 3a. It is seen that there is no degradation in the performance of this cell, and in fact there is a slight improvement in performance associated with this freeze/thaw cycling. This improvement is consistent with the slight decrease in high frequency resistance (HFR) and open circuit voltage (OCV) shown in Figure 3b that could either be related to the thinning of the membrane or to morphological changes occurring in the membrane leading to higher conductivities and permeabilities [2]. Another cell with the same Pt loading (0.2mg/cm^2 at both anode and cathode) but

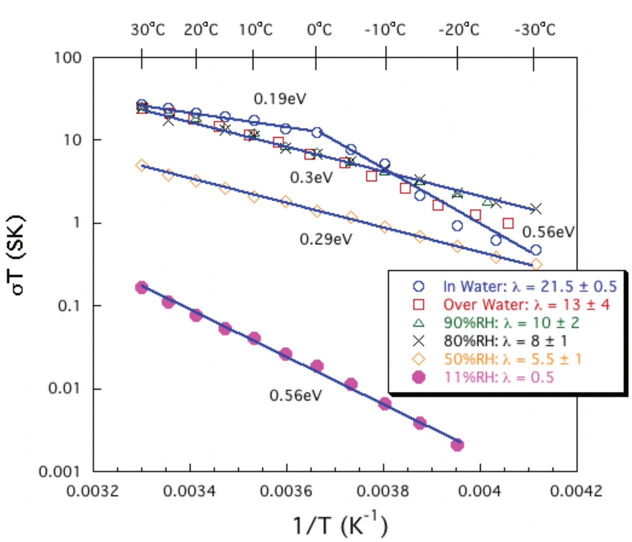

FIGURE 1. Conductivity of Nafion® 117 membranes equilibrated at various relative humidities.

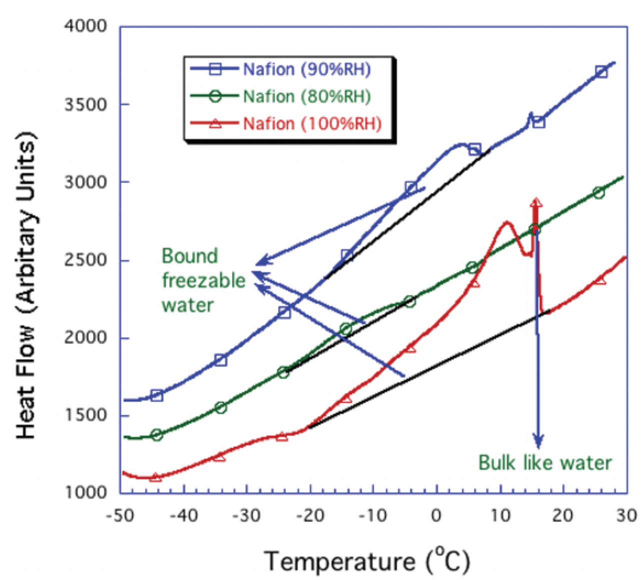

FIGURE 2. DSC of Nafion® 117 membranes equilibrated at various relative humidities.

with a SGL Carbon Group carbon paper GDL with attached microporous layer failed at 45 cycles to -40°C. Confocal laser imaging of the carbon paper performed at Sandia National Laboratories by Dr. Mike Hickner (Figures 4a and b) revealed that there was significant breakage of the carbon fibers at the flow channel edges. These experiments indicate that while interfacial failure is unlikely as long as the cooling/heating rates are not excessive, carbon fiber breakage in the GDL at the land/channel edges could be a potential failure mechanism. We have initiated environmental SEM (ESEM) work to further characterize the breakage of fibers and identify its correlation to ice formation.

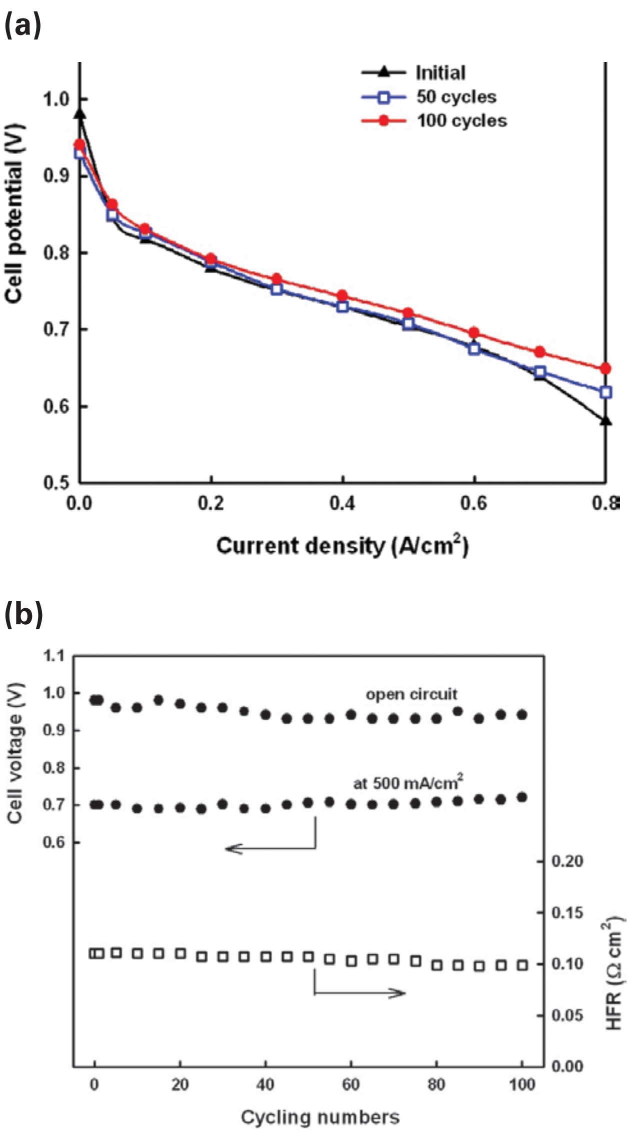

FIGURE 3. Performance of a 22 cm^2 fuel cell (with E-TEK carbon cloth GDL) subject to 100 freeze/thaw cycles from -40°C: a) Polarization curves, and b) HFR, OCV and voltage at 500 mA/cm^2.

The low temperature (0°C) performance characteristics of fuel cells using carbon cloth and carbon paper GDLs are illustrated in Figures 5a and 5b, respectively. It is seen that in both cells the HFR is high (> 0.2 Ωcm^2) when compared to the cell operated at 80°C (≈ 0.1 Ωcm^2). Moreover, the HFR also increases with increasing humidification of the inlet gases. Both these results can be correlated with the measured conductivity of the Nafion® membrane under these

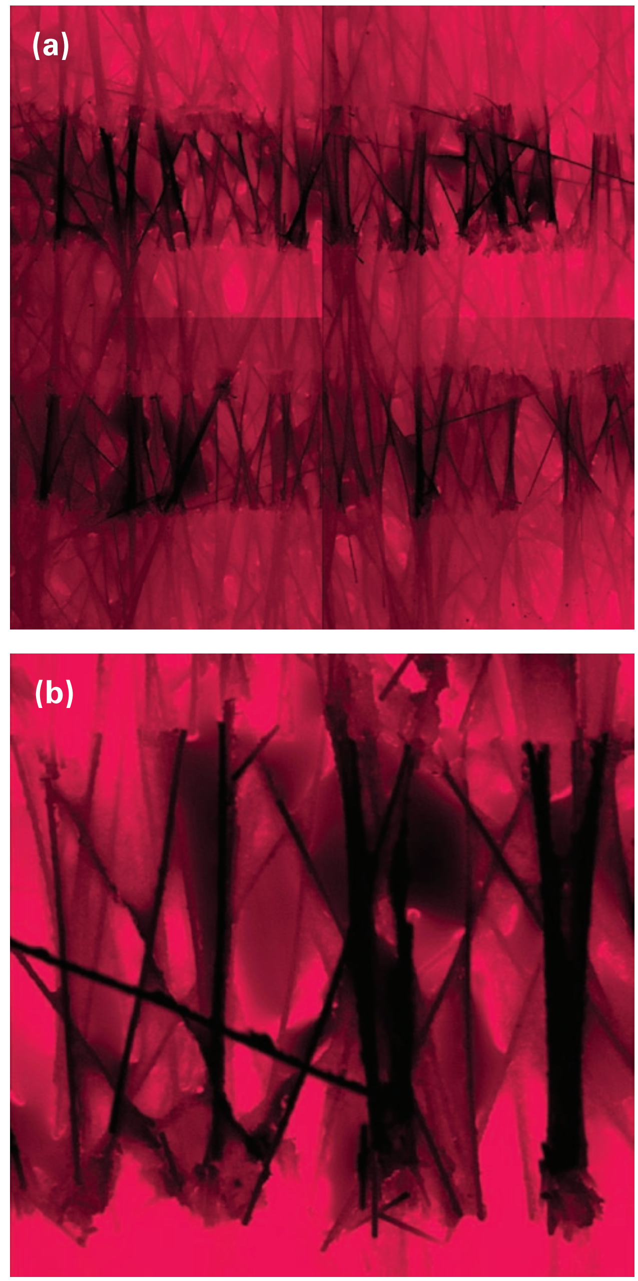

FIGURE 4. Confocal laser microscopy image of the carbon paper GDL at the anode of a fuel cell subjected to 45 freeze/thaw cycles: a) image scale is 3.73 mm on a side, and b) image scale is 0.92 mm on a side.

RHs and temperatures. It is also seen in Figure 5b that the performance of the fuel cell with the carbon paper GDL improves as the humidity decreases. This is due to the flooding associated with the low temperatures and higher humidities which is not observed in the cell with the carbon cloth GDL (Figure 5a). Therefore, the sub-freezing start-up characteristics of fuel cells will have to be considered while optimizing the GDL materials for fuel cells.

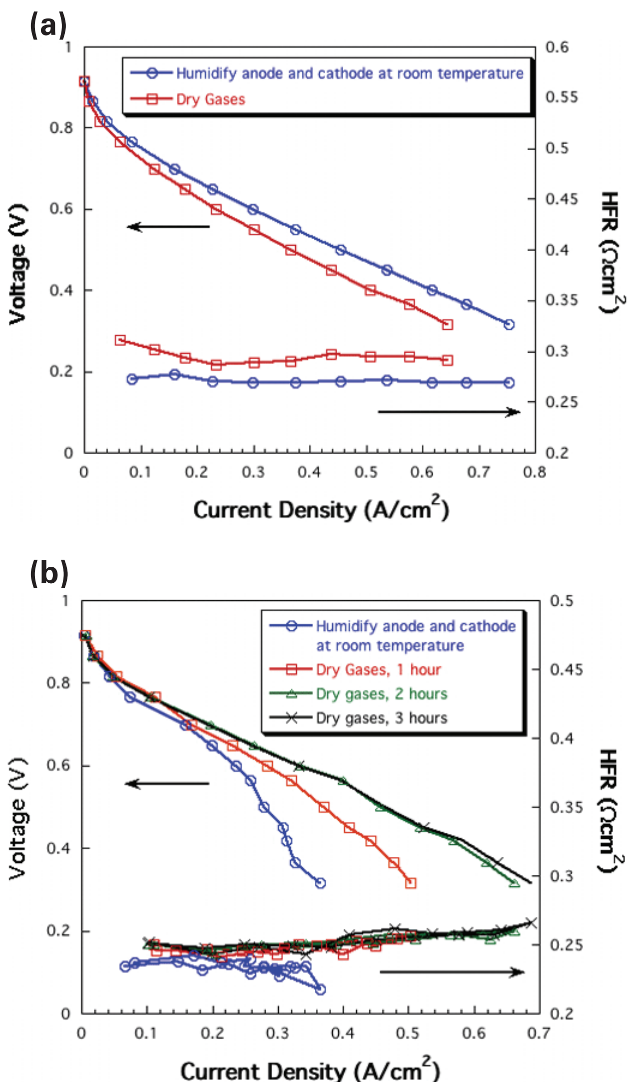

FIGURE 5. Polarization curves and HFR of fuel cells operated at 0°C under various RHs: a) using E-Tek (v2) double sided wetproofed carbon cloth GDL, and b) using SGL carbon paper GDL with attached microporous layer.

Conclusions and Future Directions

- Discovered that the optimal conductivity of Nafion® under sub-freezing conditions is obtained when $7 < \lambda < 12$.
- Demonstrated durability of fully humidified single cells using carbon cloth GDL to 100 freeze/thaw cycles down to –40°C.
- Identified carbon fiber breakage in the GDL at the land/channel edges as a potential failure mechanism during freeze/thaw cycling.
- Designed single fuel cells capable of operating under sub-freezing temperatures.
- Identified importance of GDL and water management in improving fuel cell performance at low temperatures.
- Carbon paper failure during freeze/thaw cycling will be further examined using ESEM.
- The performance of fuel cells under sub-freezing conditions will be characterized and additional degradation mechanisms (during start-up/shut-down) if any will be identified.
- The change in mechanical properties of fuel cell components due to freeze/thaw cycling will be evaluated.

FY 2006 Publications/Presentations

1. R. Mukundan, Y. S. Kim, F. H. Garzon and B. Pivovar, "Freeze/Thaw effects in PEM fuel cells" Accepted for publication in "ECS Transactions" Volume 1, "Durability and Reliability of Low-Temperature Fuel Cells Systems."

2. R. Mukundan, Y. S. Kim, F. H. Garzon and B. Pivovar, "Freeze/Thaw effects in PEM fuel cells" Presented at the 208th meeting of the Electrochemical Society, Abstract #1208, Los Angeles (2005).

3. Y.S Kim, F. Garzon, R. Mukundan, B. S. Pivovar, "The role of membrane-electrode interface on fuel cell performance", 2005 Fuel Cell Seminar, Palm Springs, CA, Nov 14-18 (2005).

4. R. Borup, "Durability and freeze/thaw effects in fuel cells" Presentation at Korean Institute of Science and Technology (KIST), (2005).

References

1. M. Cappadonia, J. W. Erning, S. M. Saberi Niaki, and U. Stimming, *Solid State Ionics*, **77**, 65 (1995).

2. R. C. McDonald, C. K. Mittelsteadt, and E. L. Thompson, Fuel Cells, 4(3), 208 (2004).