VII.J Cold Operation

VII.J.1 Sub-Freezing Fuel Cell Effects

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Start Date: October 1, 2004
Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Hold workshop on sub-freezing effects.
- Quantify conductivity of Nafion® under sub-freezing conditions.
- Prepare draft research and development roadmap based on workshop findings.
- Determine impact of freeze-thaw on electronic components.
- Quantify interfacial impact due to freeze thaw cycling.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section 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

Table 1. Los Alamos National Laboratory (LANL) Progress Toward Meeting DOE Low Temperature Requirements (Table 3.4.4)

Characteristic	Units	2005 Target	LANL
Startup time from -20°C	sec	60	n/a
Survivability	°C	-30	-40 (40 cycles)

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

Approach

- Organize and co-host (with DOE) a workshop on sub-freezing effects in fuel cells.

- Perform research and development to address startup and survivability concerns due to sub-freezing temperatures.

Accomplishments

- Held Fuel Cell Operations at Sub-Freezing Temperatures Workshop February 1-2, 2005, Phoenix, AZ.
- Prepared draft report based on workshop findings for DOE; expect final report to be posted to web in near future.
- Quantified conductivity of Nafion at sub-freezing temperatures and in various states suggested by the patent literature for improved freeze tolerance.
- Demonstrated survivability for 40 sub-freezing cycles down to -40^{o}C using cloth gas diffusion layers.

Future Directions

- Evaluate the effect of fabrication conditions on tolerance to freeze cycling.
- Investigate catalyst layers and gas diffusion layers under freeze-thaw conditions.
- Measure conductivity and determine the state of water for non-Nafion membranes at sub-zero temperatures.

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

The approach of this project is two-pronged. First, organize and co-host (with DOE) a workshop on sub-freezing effects in fuel cells. Second, perform research and development to address startup and survivability concerns due to sub-freezing temperatures.

The workshop goals are to baseline the current state-of-understanding on freeze related issues, and to help DOE develop a roadmap for pre-competitive research needs to meet DOE technical targets. Research and development was started prior to the workshop; workshop findings were incorporated into the research and development at a later date. Two areas were focused on: characterization of Nafion under sub-freezing conditions and characterization of fuel cell performance and degradation due to freeze-thaw cycling (particularly interfacial degradation).

Results

A workshop was held in Phoenix, Arizona February 1-2, 2005, to quantify sub-freezing issues in fuel cells. The workshop had 49 participants including representatives from fuel cell manufacturers, university and national lab researchers, and government officials. The workshop included invited speaker and breakout sessions. A report of the workshop findings will be posted in the near future on the web at http://www.eere.energy.gov/hydrogenandfuelcells/fc_freeze_workshop.html. This website also contains presentations from the workshop.

Research into the characterization of Nafion under sub-freezing conditions is summarized in Figures 1 and 2. Figure 1 shows the conductivity of Nafion under various sub-freezing conditions suggested by the patent literature and Figure 2 shows differential scanning calorimetry (DSC) data relating the state of water to the conductivity trends found in Figure 1. Comparisons of Figures 1 and 2 show an inflection point in conductivity for samples that exhibit a phase change by DSC measurement. This represents freezable water in the sample, which has detrimental effects for conductivity and for the amount of energy needed to complete melting. Patented approaches do not show freezable water. Fuel cell performance was investigated for survivability by freeze-thaw cycling of fuel cells to

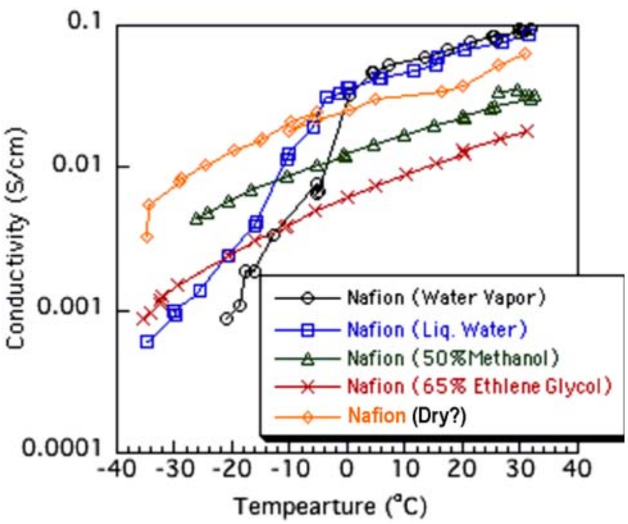

Figure 1. Conductivity of Nafion under Various Sub-Freezing Conditions Suggested by the Patent Literature

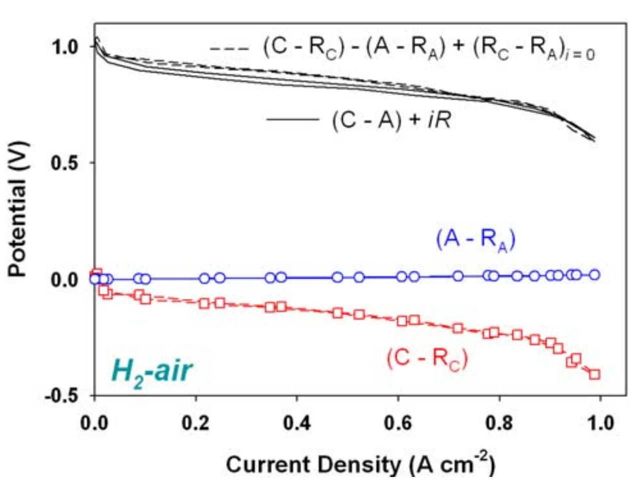

Figure 2. DSC Data at Sub-Freezing Temperature Relating to the State of Water in Nafion

various conditions. Figure 3 shows the detrimental effects of cycling to -80^{o}C. Under these conditions, fuel cell performance degrades after only a few cycles. Increases in high frequency resistance measurements and scanning electron microscopy (SEM) micrographs suggest interfacial delamination plays a major role in performance loss (Figure 4). Figure 5 shows fuel cell performance of a sample taken through 40 freeze-thaw cycles down to -40^{o}C (only final 10 cycles are shown). Under these conditions no performance degradation was found, meeting DOE survivability targets for this particular composition and preparation (further investigation of composition and preparation still needed).

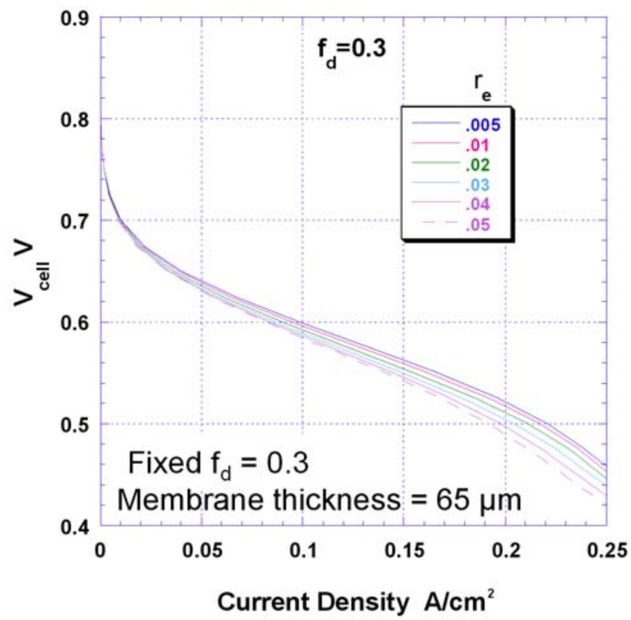

Figure 3. Fuel Cell Performance after Freeze-Thaw Cycling to -80^{o}C

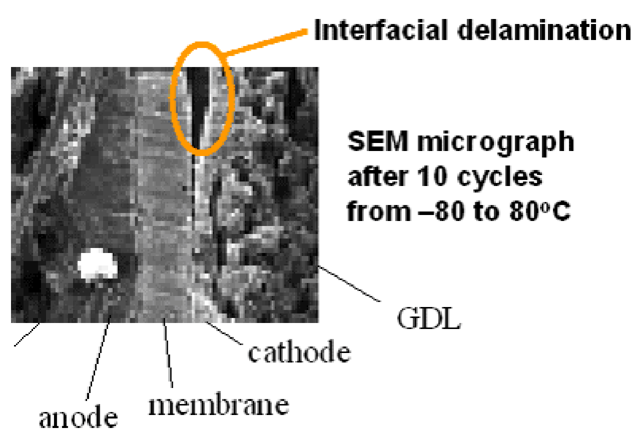

Figure 4. SEM Sample of Membrane Electrode Assembly after Freeze-Thaw Cycling to -80^{o}C

Conclusions

Sub-freezing temperatures have been shown to have detrimental effects on fuel cell performance. A workshop report in draft form has been prepared and will soon be finalized and posted to the web. Initial experiments into conduction in Nafion reveal that patented approaches prevent ice formation within the membrane. Survivability has been demonstrated using specific composition and processing techniques. Future work will focus on studying the impact of freezing on gas diffusion and catalyst layers, studying the effects in alternative ionomers and investigating other compositions and processing techniques.

FY 2005 Publications/Presentations

1. "MEA and Interfacial Issues in Low Temperature Fuel Cells," Bryan Pivovar, Fuel Cell Operations at Sub-Freezing Temperatures Workshop February 1-2, 2005, Phoenix, AZ.

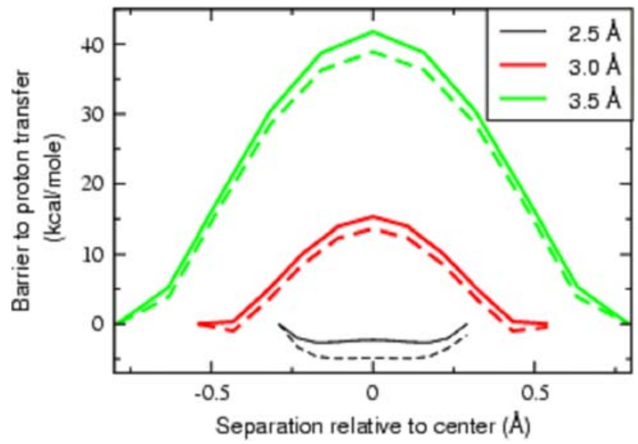

Figure 5. Fuel Cell Performance after Cycling to -40^{o}C