Project ID # FC41

Sub-Freezing Fuel Cell Effects

Yu Seung Kim
Rangachary Mukundan
Fernando Garzon
Bryan Pivovar (Point of Contact)

Los Alamos National Laboratory
Institute for Hydrogen and Fuel Cell Research

May 25, 2005

Overview

FY '05 Milestones (New Project)

- Nov 04: Hold Workshop on Sub-Freezing Effects.
  Status: Complete (Held February 1-2, 2005 Phoenix, AZ)
- Dec 04: Quantify conductivity of Nafion under subfreezing conditions.
  Status: Complete
- May 05: Prepare Draft R&D Roadmap based on Workshop Findings.
  Status: Initial Draft Completed
- June 05: Determine impact of freeze-thaw on electronic components.
  Status: Started
- Sep 05: Quantify interfacial impact due to freeze thaw cycling.
  Status: Significant Progress

Barriers Addressed

- **A. Durability**
- **D. Thermal, Air, and Water Management**
- **J. Startup Time/ Transient Operation**

Total Project Funding

- Funding in FY04: $0 K
- Funding for FY05: $500 K
- Non-cost shared

Collaborators

- Numerous Industrial, Academic and National Lab Workshop Participants (see following slides)

Objectives

- **To assist the DOE Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) 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.**

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

- **Perform research and development to address start-up and survivability concerns due to sub-freezing temperatures**

Sub-Freezing Effects Workshop

Fuel Cell Operations at Sub-Freezing Temperatures Workshop

- Workshop held in Phoenix, AZ, February 1-2, 2005
  - Baseline the current state of understanding on freeze related issues
  - Develop roadmap for pre-competitive research needs to meet DOE technical targets
- Draft report for DOE on freeze issues.

Table 3.4.4. Technical Targets: 80-kW_e (net) Transportation Fuel Cell Stacks Operating on Direct Hydrogen[a]

Characteristic	Units	2004 Status	2005	2010	2015
Cold startup time to 90% of rated power					
@ –20°C ambient temperature	sec	120	60	30	30
@ +20°C ambient temperature	sec	<60	30	15	15
Survivability[j]	°C	–40	–30	–40	–40

* Taken from http://www.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

Workshop Structure

Presentations

- DOE Program/Targets and Workshop Objectives, Nancy Garland, DOE Hydrogen Program
- Automotive PEM Stack Freeze Requirements & Suggested Fundamental Studies, Glenn Skala, General Motors
- Fundamental Issues in Subzero PEMFC Startup and Operation, Jeremy Meyers, UTC Fuel Cells
- PEMFC Freeze Start, Larry Blair (DOE consultant), for Ballard Power Systems
- Stationary Applications and Freeze/Thaw Challenges, Richard Gaylord, Plug Power
- Low Temperature Proton Conductivity, Tom Zawodzinski, Case Western Reserve University
- Membranes and MEAs at Freezing Temperatures, Phil Ross, Lawrence Berkeley National Lab
- MEA and Interfacial Issues in Low Temperature Fuel Cells, Bryan Pivovar, Los Alamos National Lab
- Startup of PEFC Stacks From Sub-Freezing Temperatures, R. K. Ahluwalia and X. Wang, Argonne National Lab

- Open Discussion of Freeze Related Issues, Doug Wheeler (moderator), National Renewable Energy Lab
  - A Study on Performance Degradation of PEMFC by Water Freezing, EunAe Cho, Korea Institute of Science and Technology
  - Fuel Cell Freeze Startup and Landscape of FC Freeze Patents, Ahmad Pesaran, Tony Markel, Gi-Heon Kim, Keith Wipke, National Renewable Energy Lab

Breakout Sessions

- Two groups discussing freeze related topics in parallel
- Identify effects of sub-freezing temperatures, identify and prioritize technical challenges, identify and prioritize pre-competitive research and development needs

*Presentations available at: http://www.eere.energy.gov/hydrogenandfuelcells/fc_freeze_workshop.html

Workshop Participants

LASTNAME	FIRSTNAME	ORGANIZATION
Abdel-Baset	Tarek	DaimlerChrysler
Adjemian	Kev	Arkema Inc.
Ahluwalia	Rajesh	Argonne National Laboratory
Balliet	Ryan	UTC Fuel Cells
Benjamin	Thomas	Argonne National Laboratory
Blair	Larry	DOE Consultant
Cho	Eunae	Korea Institute of Science and Technology
Cleghorn	Simon	W.L. Gore & Associates
Cornelius	Chris	Sandia National Laboratories
Datta	Ravindra	WPI, Department of Chemical Engineering
Debe	Mark	3M Company
DeCastro	Emory	E-TEK Division, De Nora N.A., Inc.
Donnelly	Paget	Energetics
Eisman	Glenn	Rensselaer Polytronic Institute
Epping	Kathleen	Department of Energy
Foure	Michel	Arkema
Fuller	Thomas	Georgia Institute of Technology
Garland	Nancy	Department of Energy
Gaylord	Richard	Plug Power, Inc.
Gronich	Sig	Department of Energy
Gupta	Nikunj	United Technologies Research Center
Hagans	Patrick	United Technology Research Center
Harmon	Marianne	GE Global Research
Herrera	LeeRoy	Los Alamos National Laboratory
Hickner	Michael	Sandia National Laboratories

LAST	FIRST	ORGANIZATION
Hirano	Shinichi	Ford Motor Company
Jonietz	Karl	Los Alamos National Laboratory
Kumar	Romesh	Argonne National Laboratory
Lightner	Valri	Department of Energy
McGrath	James	Virginia Tech
McQueen	Shawna	Energetics
Mench	Matthew	Pennsylvania State University
Meyers	Jeremy	UTC Fuel Cells
Mukundan	Rangachary	Los Alamos National Laboratory
Newman	John	Lawrence Berkeley National Laboratory
Onishi	Lisa	University of California Berkeley
Pesaran	Ahmad	National Renewable Energy Laboratory
Pivovar	Bryan	Los Alamos National Laboratory
Podolski	Walter	Argonne National Laboratory
Ross	Philip	Lawrence Berkeley National Laboratory
Schwiebert	Kathryn	DuPont Fuel Cells
Skala	Glenn	General Motors Corporation
Stroh	Kenneth	Los Alamos National Laboratory
Sverdrup	George	National Renewable Energy Laboratory
Van Zee	John	University of South Carolina
Weber	Adam	Lawrence Berkeley National Laboratory
Wheeler	Doug	National Renewable Energy Laboratory
Wipke	Keith	National Renewable Energy Laboratory
Zawodzinski	Thomas	Case Western Reserve University

49 participants including representatives from fuel cell manufacturers, university and national lab researchers, and government officials.

Workshop Findings

Evaluating the Effects of Sub-Freezing Temperatures

- Delayed fuel cell system startup and drive away.
- Temporary loss of fuel cell system performance.
- Irreversible and reversible performance degradation.
- Loss of fuel efficiency and increased fuel consumption.
- Physical degradation of membrane allowing crossover of gases.
- Lowered MEA transport and degraded kinetic properties.
- Clogging due to water and icing in pores and flow channels
- Reactant starvation and/or imbalance at low temperature operation.
- Increased mechanical stresses on fuel cell components and morphological changes.
- Loss of thermal and electrical interfacial contact.
- Adverse effects in balance of plant components, due to freezing water.
- Increased system costs due to the requirement for freeze mitigation strategies.

-***Causes:*** Large thermal mass, delamination or physical breakdown, ice formation.

Workshop Findings

Identifying the Technical Barriers/Challenges

- Startup Performance
  - -conductivity and kinetics at low temperatures, heat required for start up
- Stack Operation
  - -shut down protocols, relating stacks to single cells, degradation mechanisms
- Water Dynamics
  - -state of water, control of water, understanding of water (where and how)
- Performance Degradation
  - -where and how, freeze-thaw cycling vs. sub-freezing operation
- Thermal Management System
  - -reduced thermal mass, rapid heat up, better coolants, thermal expansion stresses
- Research Direction and Management
  - -models and validation, standardized test protocols, system integration issues
- Next Generation Materials
  - -wider operating range, more choices

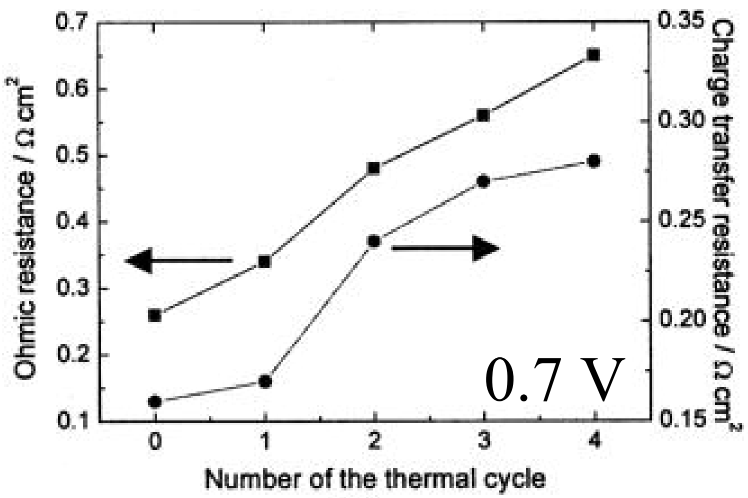
Workshop Findings

Research and Development Needs

- Improved System Designs (for rapid start-up)
- Define Failure Modes Associated with Freezing/Thawing (physical and chemical)
- Development of New (robust and dynamic) Materials
- Quantification of Water Movement (experimental and modeling)
- Better Characterization of Porous Media and Ionomers
- Characterization of Materials Properties at Lower Temperatures
- Understanding the State of Water within Ionomers

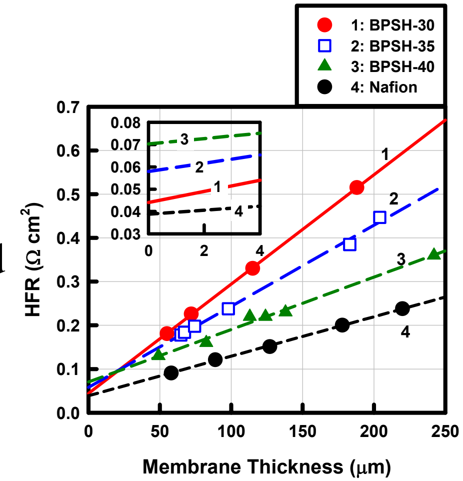
Technical Approach

- **Prior to (and based on the Workshop findings) we investigated 2 primary areas of subfreezing related concerns**
  - **Characterization of Nafion® under sub-freezing conditions**
    - Dry out cell before shutdown (US patent 6479177(Ballard), 6358637(GM))
    - Replace water with antifreeze solutions (Patent Application 20040224201 (Ballard) 6068941 (IFC), JECS 151(5)A661)
  - **Characterization of fuel cell performance and degradation due to freeze thaw cycling (particularly interfacial degradation)**



E. Cho et. al. *J. Electrochem. Soc.* **150**, A1667 (2003)

Literature reference suggested interfacial problems. We have significant experience with and have pioneered a technique to quantify membrane-electrode interfacial resistance.



Ref. FCP4 2005 OHFCIT Program Review

Characterization of Nafion®

- Use DSC and conductivity to explore state of water in Nafion® at low temperatures
  - Various levels of humidification
  - In contact with antifreeze solutions
- Studied literature for low temperature conductivity and DSC studies

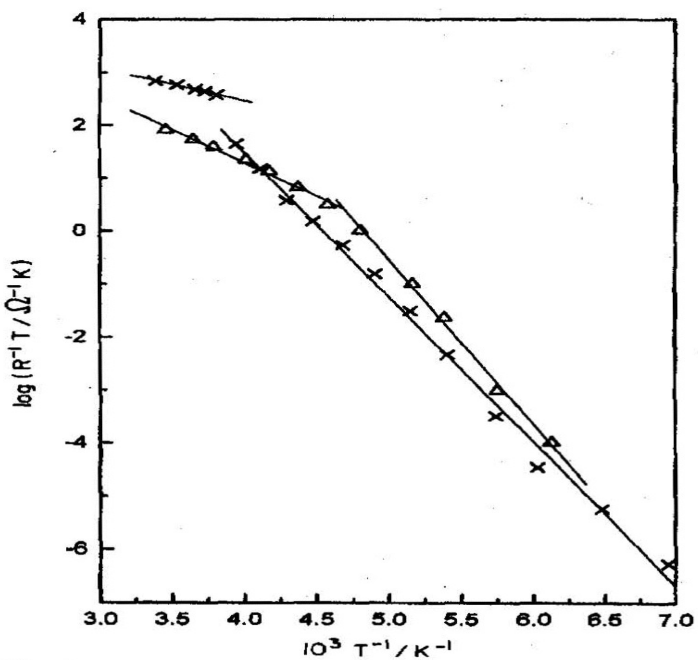
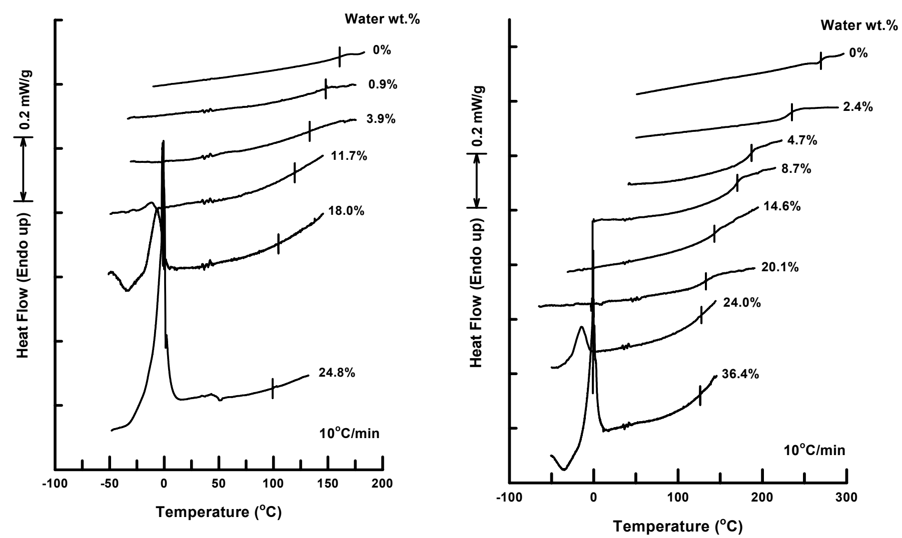


Fig. 4. Arrhenius plots of Nafion® membrane treated in nitric acid: (△) samples stored in air (B samples); (×) samples stored in water (C samples).

M. Cappadonia et. al, *J. Electroanal. Chem*, **376**,189 (1994)



Nafion-1135* **BPSH-40**

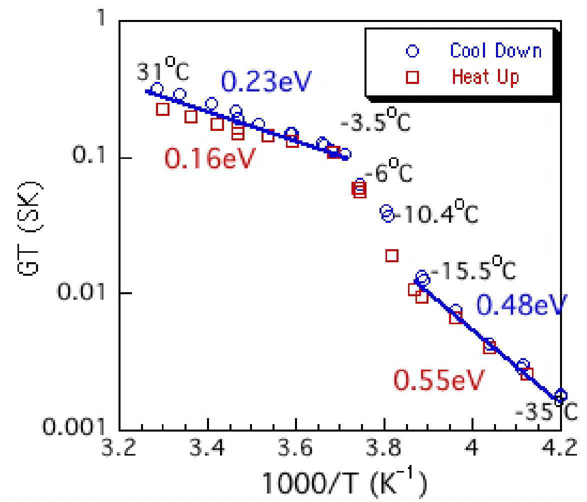
Y.S. Kim et. al, *Macromolecules*, 36, 17, 6181 (2003)

Liquid Water Immersed Nafion®

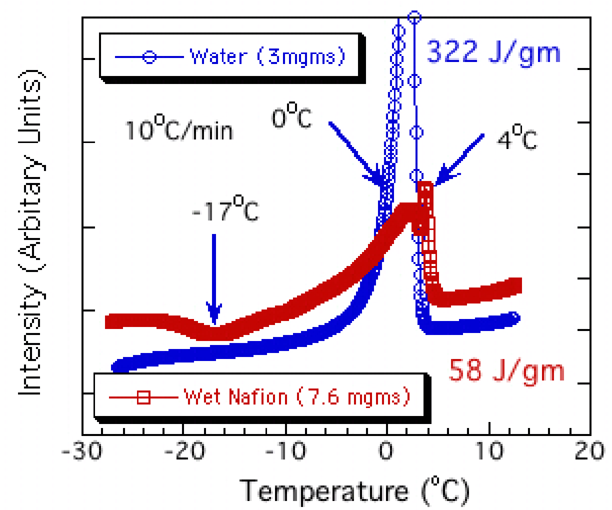
- Change in activation energy for conduction observed while freezing Nafion®.
- Changes in activation energies correlate to phase transition observed in the DSC.
- Low activation energy (≈ 0.2eV) in liquid water (> -3°C) and high activation energy (≈ 0.5eV) in ice (< -16°C)
- Consistent with ice formation in Nafion® and reports in the literature* (Data highly dependent on material pretreatment and measurement conditions)

*M. Cappadonia et. al, *Solid State Ionics* **77** (1995) 65
*M. Cappadonia et. al. *J. Electroanal. Chemistry* **376** (1994) 189
*N. Sivashinsky et. al. *J. Applied Polymer Science* **26** (1981) 2625

Conductivity of Nafion® (wet)



DSC of water and wet Nafion®

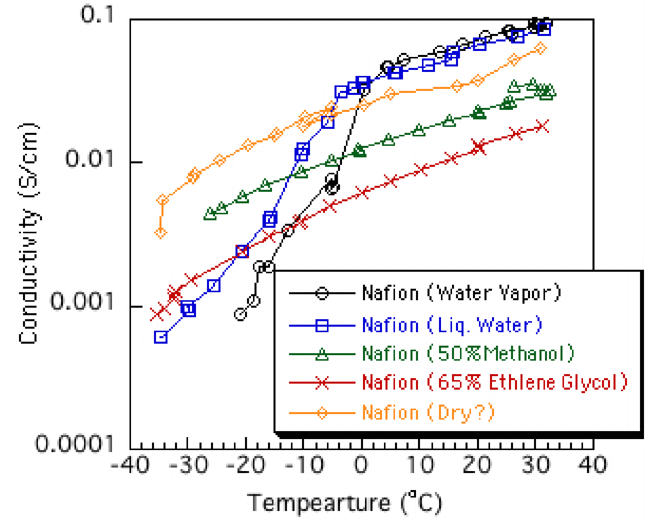


Nafion® under Various Conditions

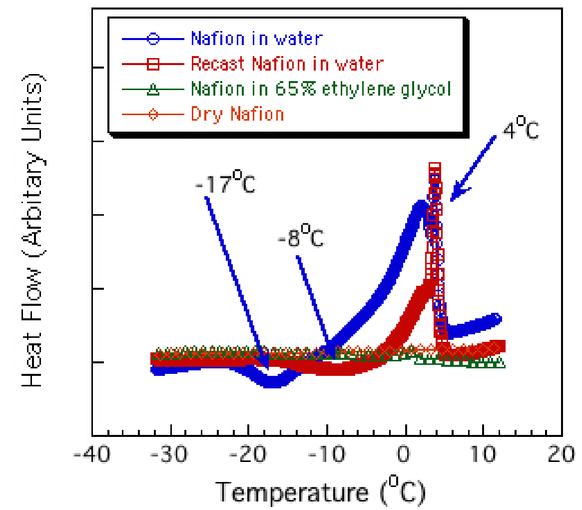
- Freezing (at > -40°C) can be avoided if the water is either dried sufficiently or replaced with antifreeze solutions.
- Freezing water leads to activation energy change and large drop in conductivity at lower temperatures.
- Of patented approaches, drying out leads to highest conductivities, perhaps has least adverse effects.
- Freezing water adds to latent heat necessary for rapid start-up.
- Controlled humidity and alternative ionomer experiments planned.

State of Water is Key!!!

Conductivity of Nafion®

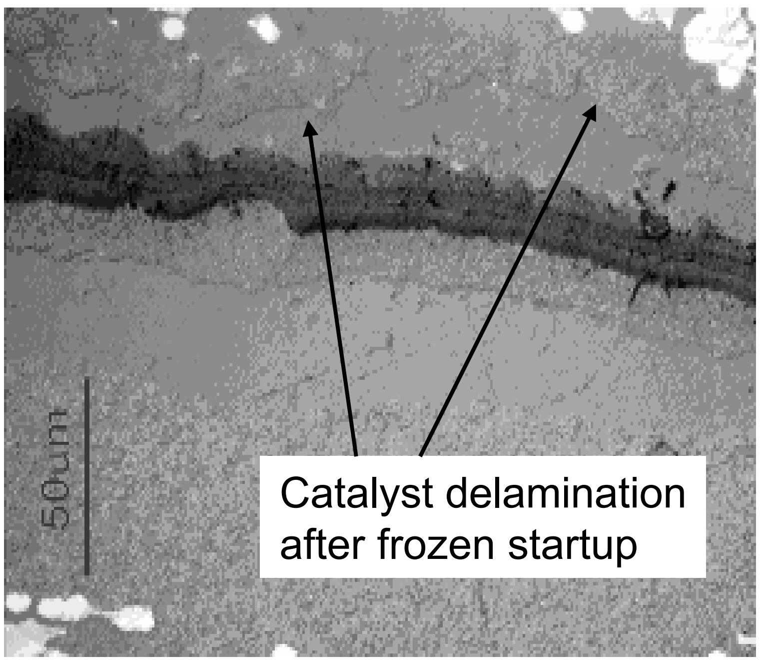


DSC of Nafion®

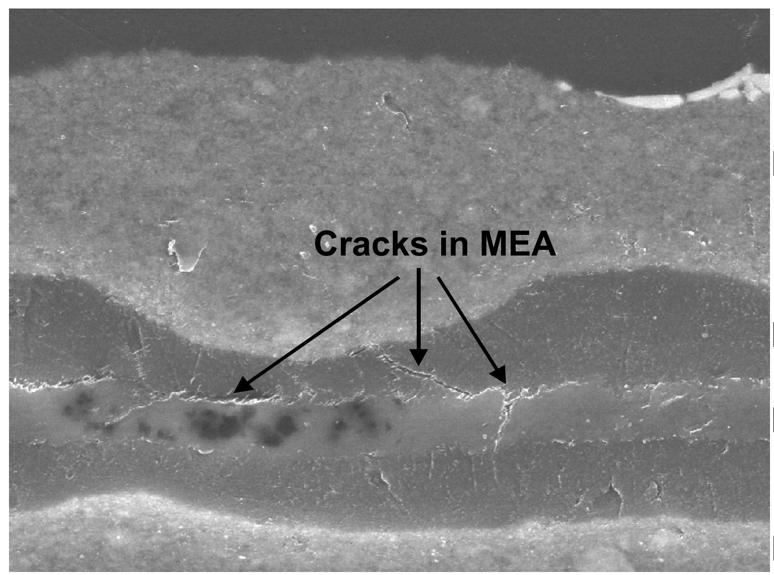


Fuel Cell Performance (Interfacial Degradation)

- Pioneers in quantifying membrane-electrode interfacial resistance and degradation over time.
- Literature evidence and SEMs suggest interfacial issues could be important.



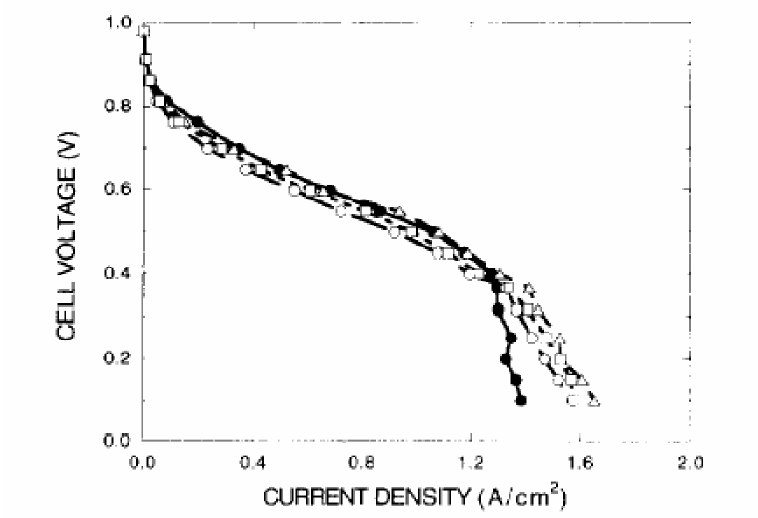
Commercial Pt/Pt MEA After 20 F/T Cycles



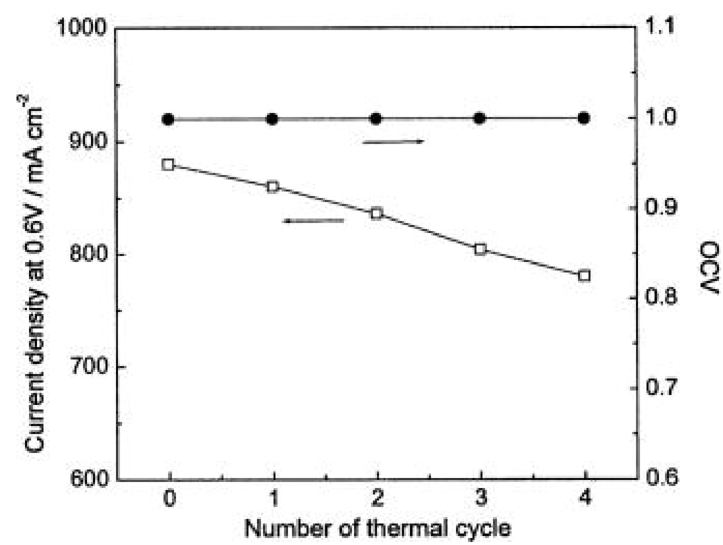
* Fundamental Issues in Subzero PEMFC Startup and Operation, Jeremy Meyers, Fuel Cell Operations at Sub-Freezing Temperatures Workshop, Feb 1, 2005, Phoenix, AZ, available at http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/03_meyers_distribution.pdf

Performance Degradation after Freeze/Thaw Cycling

- Two literature references report fuel cell performance as a function of freeze-thaw cycling (-10 to 80˚C).
- Significant differences in reported results with one study reporting no performance loss and the other reporting significant performance loss.
- We chose to focus on possible interfacial losses due to freeze-thaw cycling.



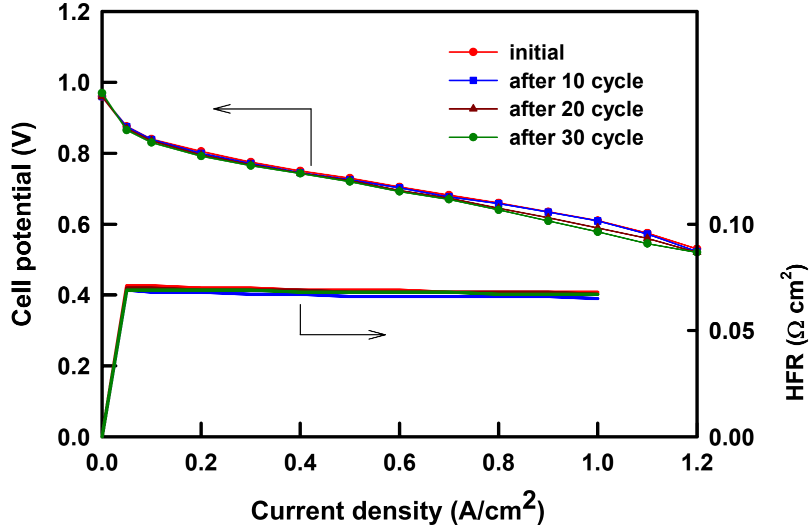
Wilson et al., *Electrochem. Acta*, **40**, 355, (1995)



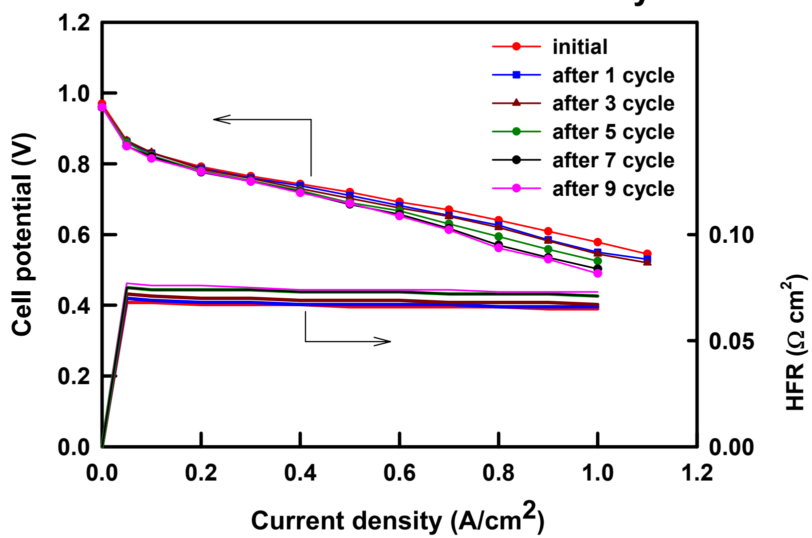
E. Cho et. al. *J. Electrochem. Soc*. **150**, A1667 (2003)

Performance Degradation after Freeze/Thaw Cycling

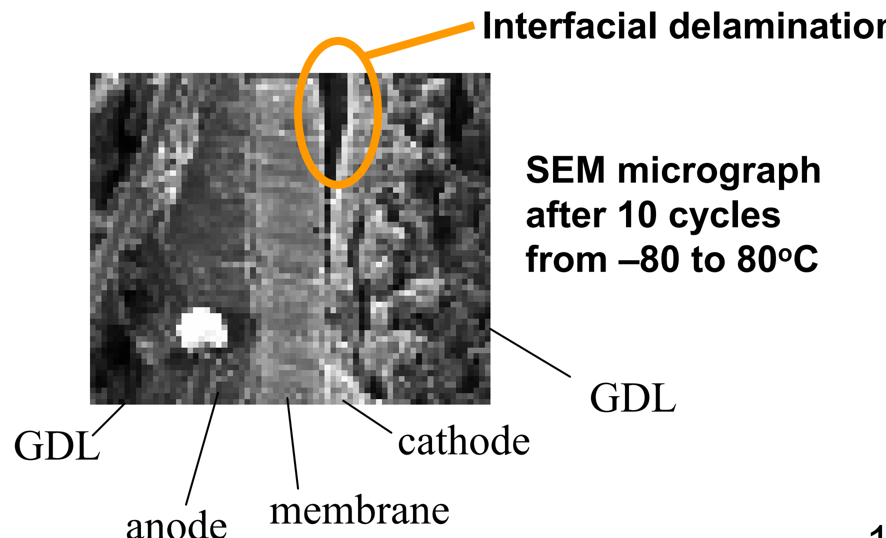
-5 to 80°C cycle



-80 to 80°C cycle



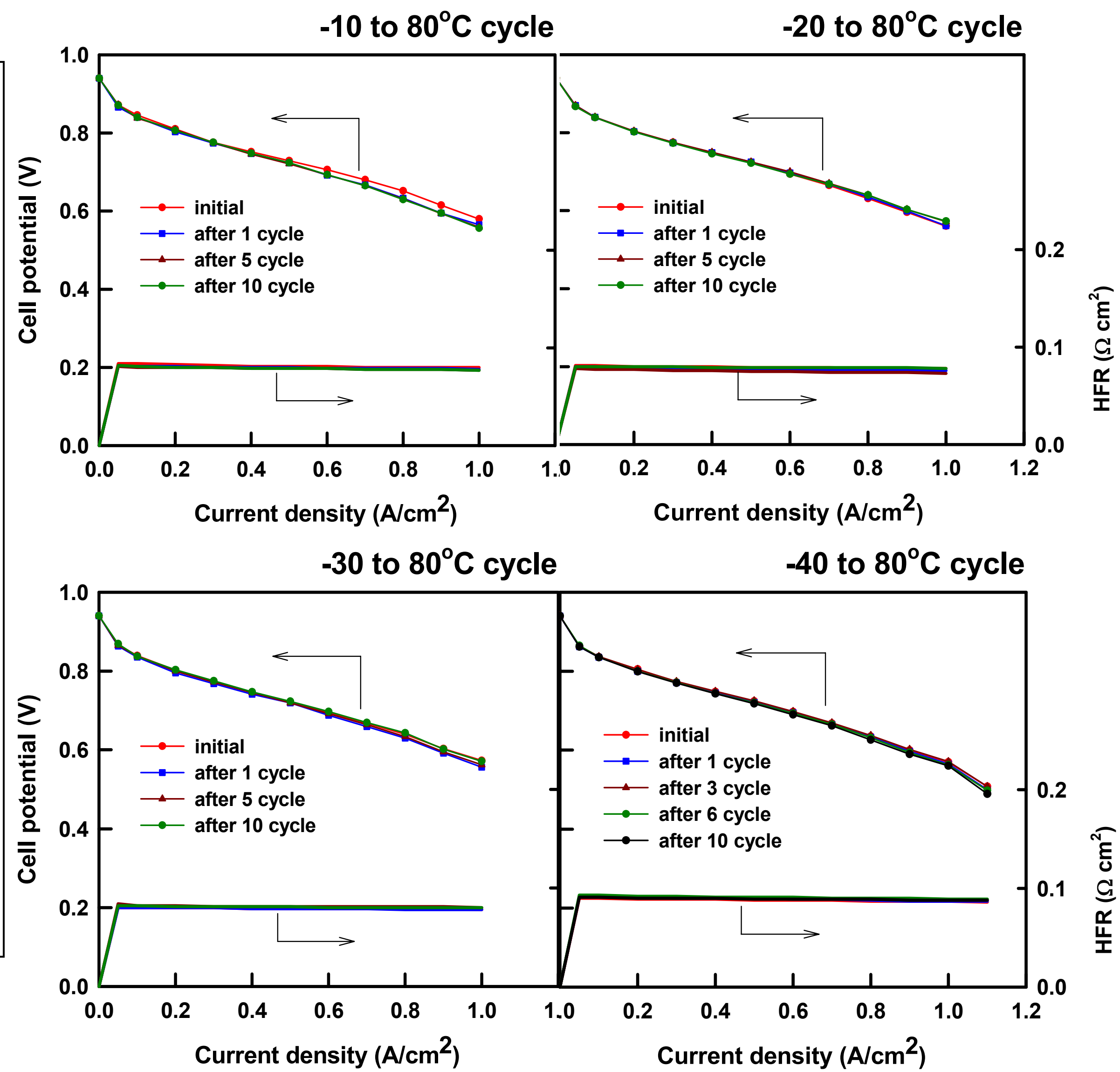
- Fuel cells stored under wet conditions (no attempt to dry).
- Freezing/Thaw cycling from -5 to 80°C gave no apparent performance degradation after >30 cycles.
- Freezing/Thaw cycling from -80 to 80°C quickly degraded performance. HFR increase and SEM study suggest interfacial degradation.



SEM micrograph after 10 cycles from –80 to 80°C

Effect of Freezing Temperatures on Cycling

- Based on initial results and Workshop initiated concerns about effects of temperatures, we systematically investigated freeze-thaw cycling.
- For the fuel cell tested in this study, no degradation was found with freeze-thaw cycling (10 cycles at each freezing temperature).
- Meets DOE survivability targets on a single cell basis.
- Still need to address start-up as well as survivability.



Comparison of Freeze/Thaw Cycling Results

	Cho et al.	*Wilson et al.*	*This work*	
Membrane	Nafion 115	Nafion 112	Nafion 112, Nafion 1135	
Electrode	20 wt% Pt/C (0.4 mg/cm^2)	20 wt% Pt/C (0.16 mg/cm^2)	20 wt% Pt/C (0.2 mg/cm^2)	
GDL	wet proofed carbon paper	hydrophobic carbon cloth	hydrophobic carbon cloth	
MEA processing	Catalyst ink sprayed on GDL / 140^{o}C hot pressing	Decal painting (TBA^+ form catalyst) /200^{o}C hot pressing	Decal painting (TBA^+ form catalyst) / 200^{o}C hot pressing	
F/T cycle	-10 to 80^{o}C (4 cycles)	-10 to 80^{o}C (3 cycles)	-5, -10, -20, -30, -40 to 80C (10 cycles)	-80 to 80^{o}C (9 cycles)
Results	Performance drop, HFR increase, catalyst loss	No performance loss	No performance loss	Performance drop, HFR increase

- Significantly more information is needed on other MEA processing conditions and materials (paper vs. cloth backings), and the effect of water content and temperature (time).

Future Plans

Remainder of FY 2004:

- **Fuel Cell Studies**
  - Effect of MEA fabrication conditions on interfacial degradation (include carbon paper studies).
  - Investigate impact of freeze-thaw on electronic components.
- **Fundamental study on state of water in ionomer**
  - Measurements of state of water for Nafion at controlled relative humidity.

FY 2005:

- **Fuel Cell Studies**
  - Oxygen reduction kinetics under freezing conditions
  - Investigate catalyst layers under freeze-thaw conditions
  - Cold start and/or transition behavior of fuel cells
- **Fundamental study on state of water in ionomer**
  - Alteration of state of water using specific interaction (e.g. inorganic/organic fillers, block copolymers)
  - Measurements of the state of water for Non-Nafion membranes at sub-zero temperature.

Publications and Presentations

- ***Presentation***

  1. MEA and Interfacial Issues in Low Temperature Fuel Cells, Bryan Pivovar, Fuel Cell Operations at Sub-Freezing Temperatures Workshop, February 1-2, 2005, Pheonix, AZ (available online at http://www.eere.energy.gov/hydrogenandfuelcells/fc_freeze_workshop.html)

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Hydrogen leak in the hydrogen supply leading to accumulation in the room with ignition leading to an explosive event.

Hydrogen Safety

Our approach to deal with this hazard is:

In labs with hydrogen supply from cylinder banks or from a hydrogen generator, hydrogen sensors have been installed and are interlocked with the hydrogen gas supply.

Two sensors are installed in every room for redundancy.

Sensors installed at ceiling level where accumulation is most severe.

H2 sets off the alarm at 10% of Lower Flammability Limit (LFL).

In rooms that use only bottled hydrogen, only a single cylinder is in the room at any given time and bottle sizes are limited to ensure being safely below the LFL of the room even with complete release of a full cylinder.

Work has been reviewed and approved through Los Alamos National Lab's safety programs:

Hazard Control Plan (HCP) - Hazard based safety review

Integrated Work Document (IWD) - Task based safety review

Integrated Safety Management (ISM)