Sub Freezing Fuel Cell Effects

Fernando Garzon
Yu Seung Kim
Rangachary (Mukund) Mukundan [Point of contact]
Bryan Pivovar

Los Alamos National Laboratory

May 18th 2006

Project ID # FC30

This presentation does not contain any proprietary or confidential information

LA-UR-06-2943

Overview

Timeline

Start : FY 05
Status : Ongoing

Budget

FY 05 : $ 500K
FY 06 : $ 650K
No cost share

Partners

Sandia National Laboratory

Lawrence Berkeley National Laboratory

GM and GE (Data sharing)

Barriers

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

Targets

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
Transient response (time for 10% to 90% of rated power)	sec	1	2	1	1
Cold startup time to 90% of rated power @ –20°C ambient temperature @ +20°C ambient temperature	 sec sec	 120 <60	 60 30	 30 15	 30 15
Survivability[f]	°C	–40	–30	–40	–40

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

Objectives

- Overall
  - **Assist the DOE-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 (-20^{o}C, 30 sec, 5 MJ) and survivability (-40^{o}C)**
- **FY 05**
  - **Establish baseline research and future research needs for fuel cell operation and survivability at sub freezing temperatures**
  - **Initiate research and development based on workshop findings to address start-up and survivability concerns at sub-freezing temperatures**
- **FY 06**
  - **Identify degradation mechanisms (freezing and cold start-up)**
  - **Quantify materials properties at sub-freezing temperatures**

Approach

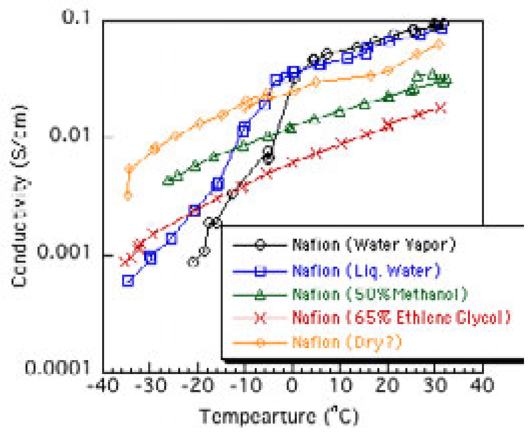
- Characterization of water in ionomer, catalyst, and gas diffusion layers
  - State of water in Nafion® and conductivity — 100% complete
  - State of water and conductivity in non-Nafion® electrolytes, electrodes and GDLs — 10% complete
- Identification of degradation mechanisms
  - Freeze/thaw cycling (Ice formation) — 90% complete
    - Interfacial degradation in fully humidified fuel cells
  - Startup and shutdown — 30% complete
    - Measure transient response from -20°C to 80°C
  - Subject components to thermal cycling — 5% complete
    - Characterize mechanical/electrical properties

State of water in Nafion® (FY 05)

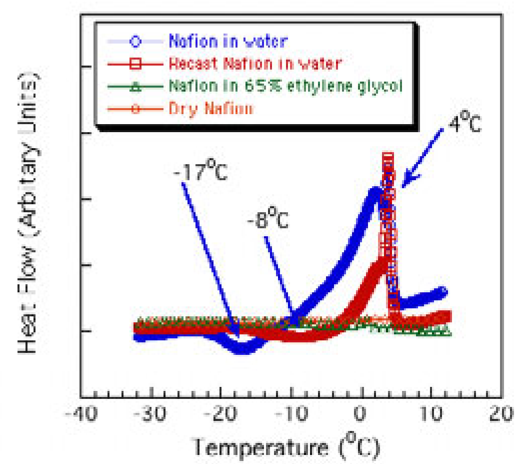
- Freezing (at > -40°C) can be avoided if the water is either dried sufficiently or replaced with antifreeze solutions.
- Freezing water leads to activation energy change and large drop in conductivity at lower temperatures.
- Of patented approaches, drying out leads to highest conductivities, perhaps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

<u>State of Water is Key!!!</u>

Conductivity of Nafion®



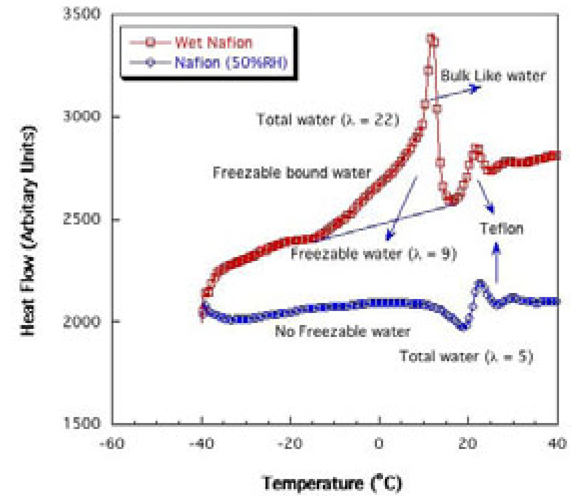
DSC of Nafion®

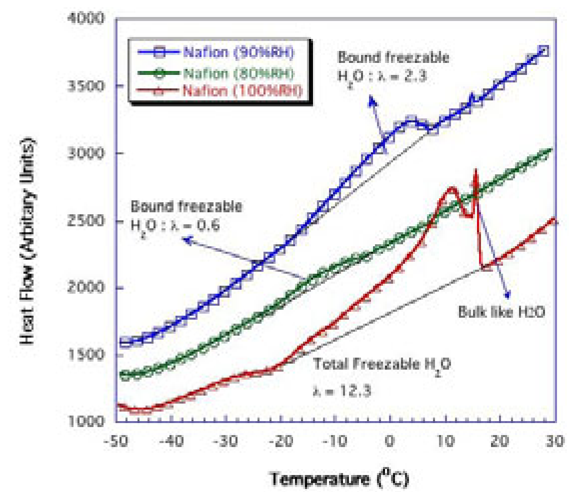


State of water in Nafion®

- Effect of varying RH
  - Nafion® in liquid water and 100%RH shows bulk like water, bound-freezing water and non-freezing water
  - Nafion® in equilibrium with 90%RH and 80%RH shows only bound-freezing water and non-freezing water
  - Nafion® in equilibrium with < 50%RH shows only non-freezing water

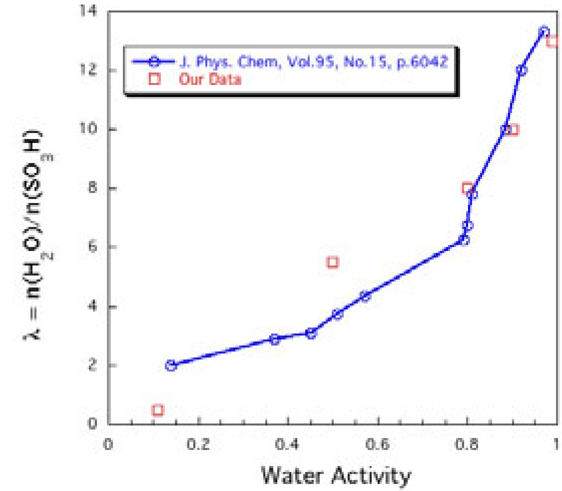
Condition	T = 30°C
Water	λ = 22
Water Vapor	λ = 13±4
90% RH	λ = 10±2
80%RH	λ = 8±1
50%RH	λ = 5.5±1
11%RH	λ = 0.4±0.1

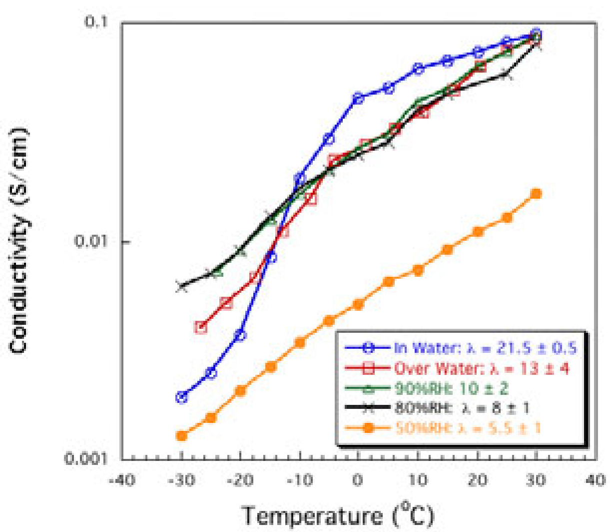


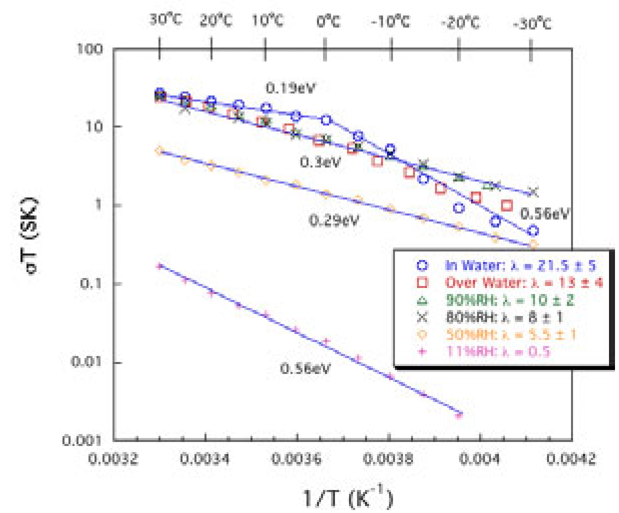


Conductivity of Nafion®

- Sample equilibrated @ 80-90%RH ($7 < \lambda < 12$) has optimal conductivity (corresponds to absence of bulk-like water)
- Dry/Frozen activation energy (0.5 - 0.6eV); wet activation energy (0.2 - 0.3eV)
- Avoiding bulk-like water may also help alleviate degradation mechanisms (ice formation at $0^{o}C$)







State of water in alternate membranes

	Total water(λ)	Tightly bound (non freezing) water (λ)	Loosely bound (sub-freezing) water (λ)	Free water (0^oC freezing) water (λ)
Nafion	20	2	13	5
6F-30	9	7	2	0
6F-40	15	7	8	0
BPSH-30	12	4	8	0
BPSH-40	18	5	11	2

Non-Nafion® membranes exhibited lower number of freezable water!!

Degradation : Freeze/Thaw cycling (FY 05)

	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

Degradation : Freeze/Thaw cycling

Materials used

Membrane: Nafion® 1135

Catalyst: Pt/C E-Tek (20% pt loading), or Pt black (JM HiSpec 1000)

GDL: SGL carbon paper (Low permeability,20% PTFE, standard MPL; SGL 30DC)

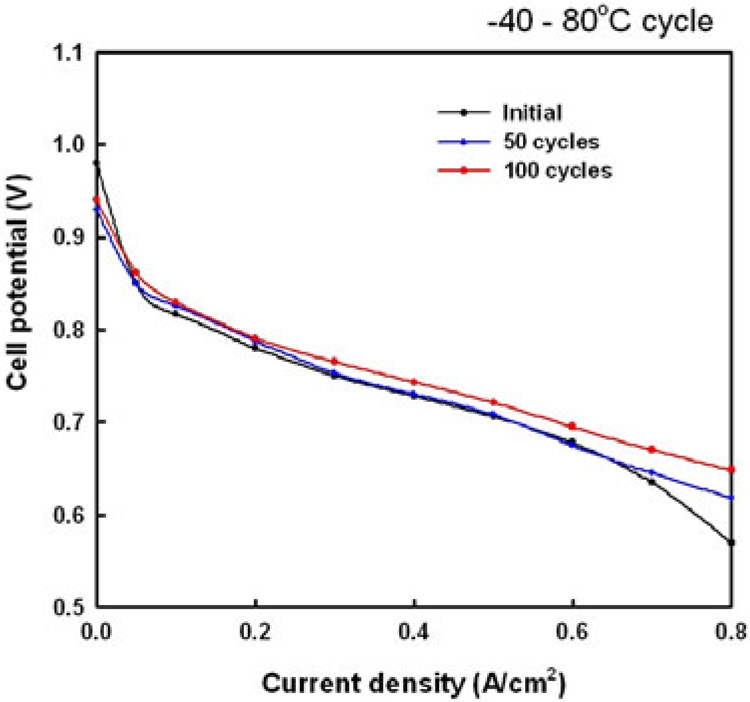
or E-Tek carbon cloth (double side PTFE coating; v.2.02)

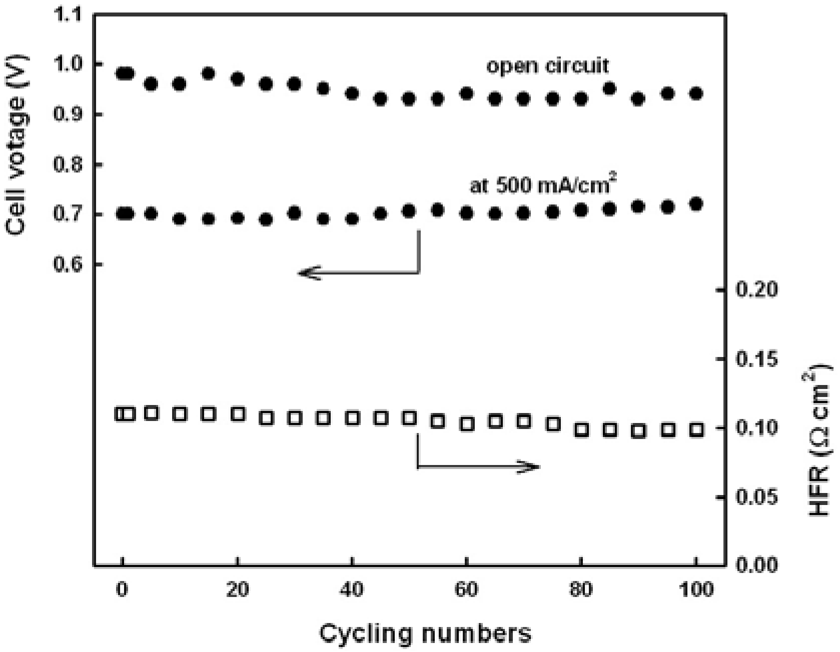
Catalyst	Application	Hot pressing	Initial performance	After F-T cycle (-40°C - +40°C, 15+ times)
Pt/C or Pt black	Painting on GDL	At 140°C At 220°C	Poor (less than 80 mA/cm² at 0.7 V)	No Exp.
Pt/C or Pt black	Painting on membrane	No At 140°C	Good (greater than 500 mA/cm² at 0.7V)	No performance loss
Pt/C or Pt Black	Decal transfer	At 140°C At 220°C		
Pt black	Half painting on GDL and membrane	At 140°C		

Degradation : Freeze/Thaw cycling

- 100 Freeze/Thaw cycles from -40°C

GDL: carbon cloth (E-tek)
Active area: 22 cm^2



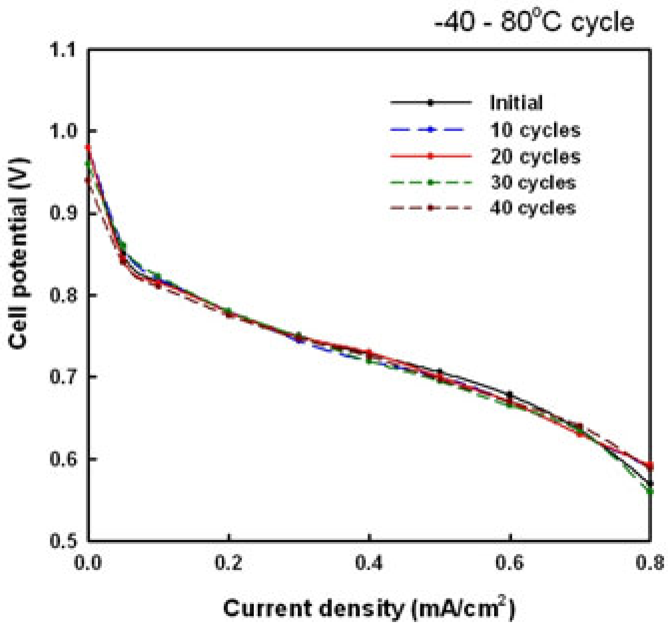


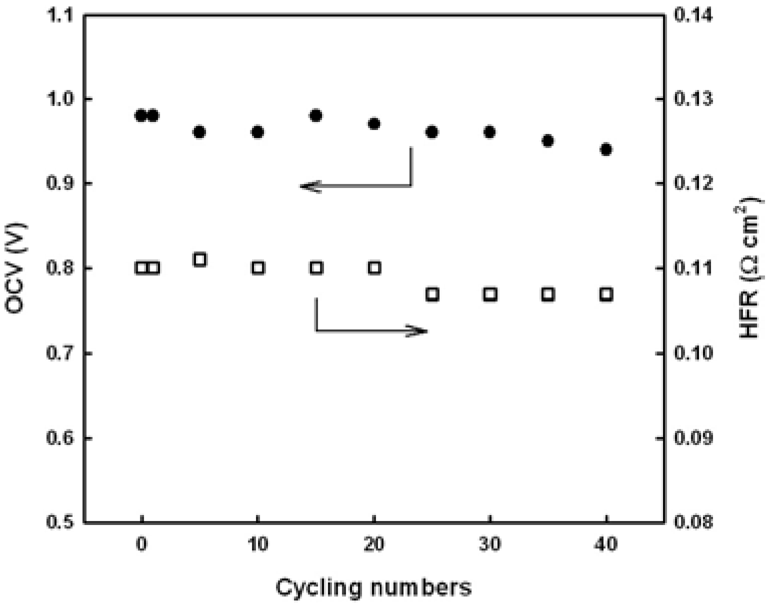
No Systematic Degradation Observable

Slight decrease in OCV associated with decrease in HFR
Could be due to membrane thinning and/or improvement in membrane conductivity
results in slightly improved performance

Degradation : Freeze/Thaw cycling

GDL: carbon paper (SGL), Active area: 5 cm^2





- No systematic degradation observed up to 45cycles
- Mechanical Failure @ 45 cycles
- More tests initiated to investigate failure mechanisms

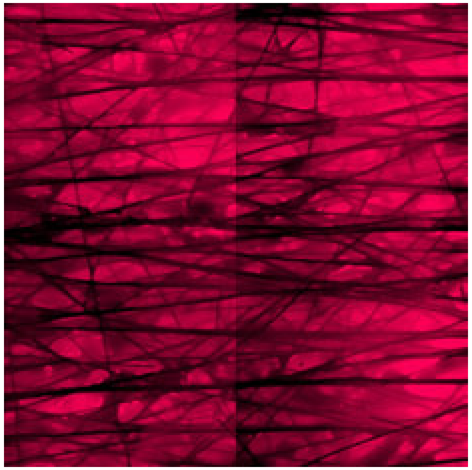
Characterization of GDL

Confocal Laser Imaging

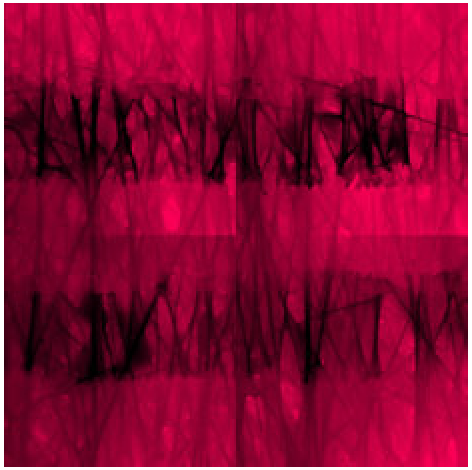
Dr. Mike Hickner (Sandia National Laboratory)

GDL: carbon paper (SGL) with microporous layer

After Fuel Cell operation



Compressed GDL in anode
No aging
Image scale is 3.73 mm on a side



Compressed GDL in anode
45 F/T cycles from 80°C to -40°C
Image scale is 3.73 mm on a side

Channel Space in anode GDL
45 F/T cycles from 80°C to -40°C
Image scale is 0.92 mm on a side

Evidence for breakage of fibers at the land/channel edge of flow field

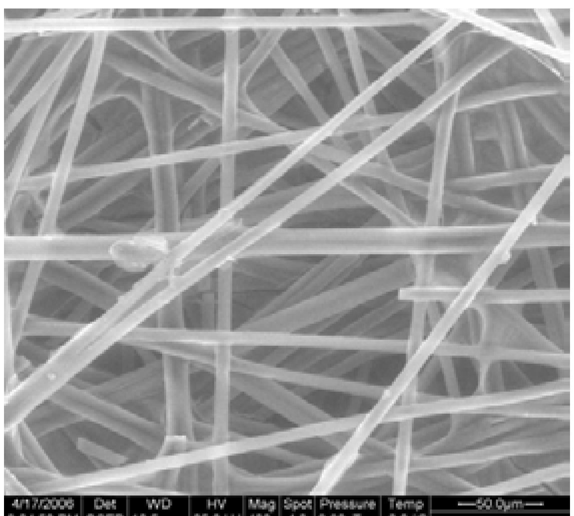
- Could be due to heaving of the membrane while freezing
- More prominent at the anode than at the cathode

GDL Imaging (ESEM)

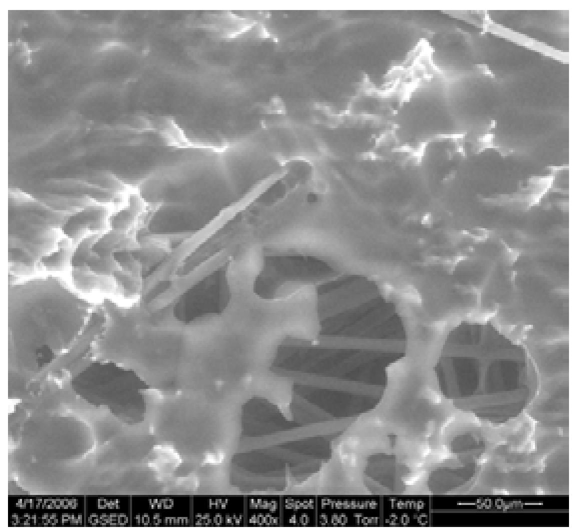
- *Ex situ* monitoring of ice formation
- Control of P_{H2O}(0-100% RH) and T (-40^{o}C to +40^{o}C) during imaging
- Freeze/thaw cycling at various RH while imaging

- Mount samples in cross-section (stage being machined)
- Examine interfaces during freeze/thaw cycling (GDL/MEA; catalyst/membrane)

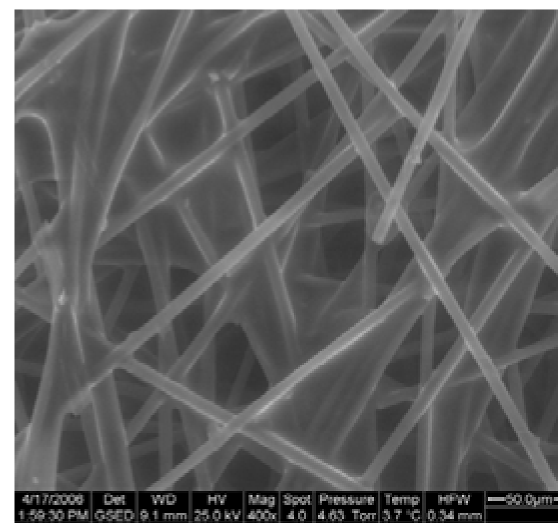
Untreated GDL (SGL)



Ice (T = -2^{o}C; P_{H2O} = 3.8torr)

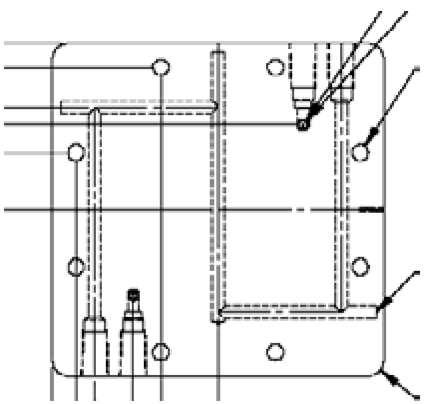


Water (T = 3.7^{o}C; P_{H2O} = 4.63 torr)



Performance during start up

- Have cell with ability to operate between -10^{o}C and +80^{o}C
- The end plates have flow channels through which fluid can flow
- These are connected to a chiller with propylene glycol/water mixtures
- Currently using 5cm^2 cells with a Neslab RTE 740 chiller
- Will have capability to cool 50cm^2 cells down to -20^{o}C with ULT -80 chiller

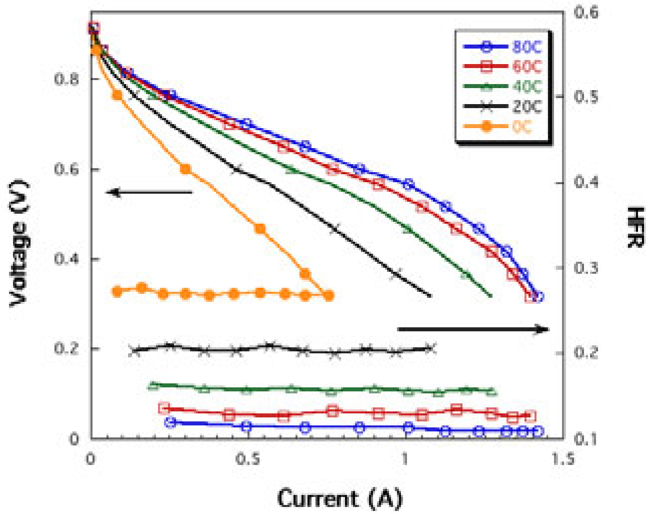


End Plate With flow channels

Chiller connected to end plates

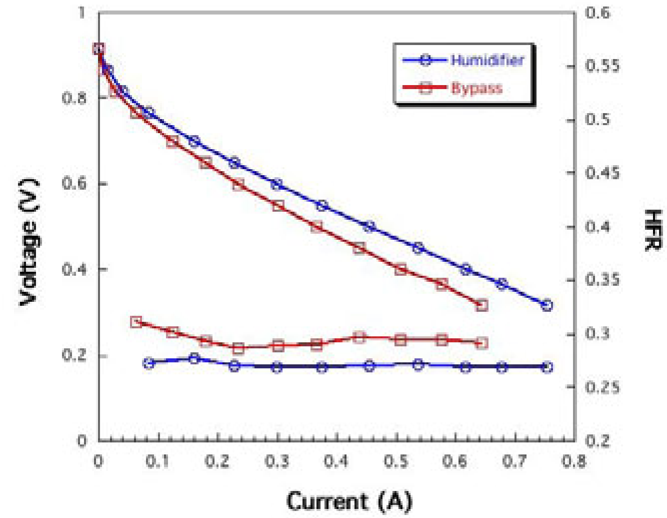
Performance during start up

Fully humidified



E-Tek carbon cloth (double side PTFE coating; v.2.02)

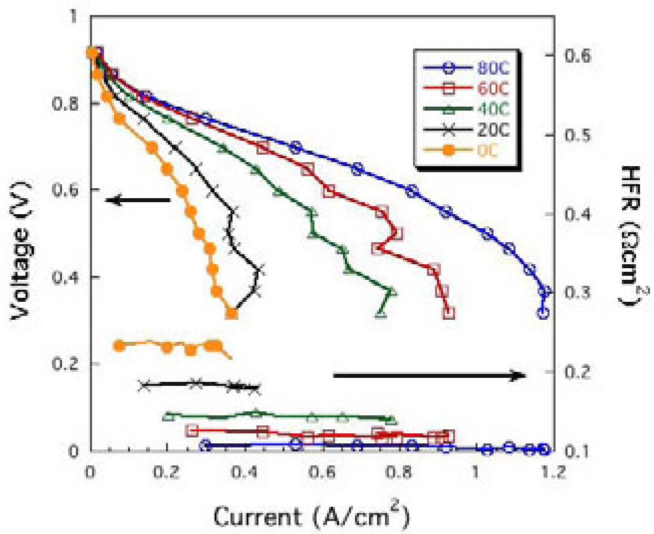
0^0C operation



- Operation at various temperature and humidity conditions to study start-up characteristics
- High Frequency resistance correlates with *ex situ* conductivity measurements
- Problems with operation below 0^oC
  - Clogging of anode flow due to ice formation

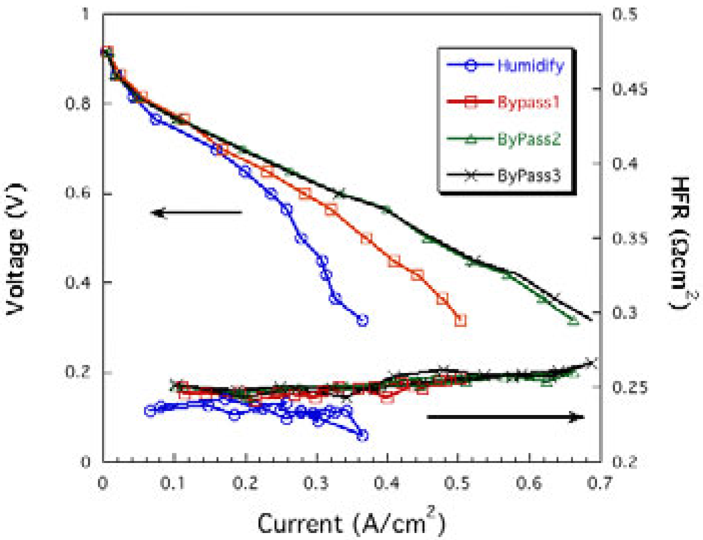
Performance during start up

Fully humidified



SGL carbon paper (Low permeability,20 % PTFE, standard MPL; SGL 30DC)

0^0C operation



- Performance at low temperatures extremely dependant on GDL
  - At 0^0C, performance improves with drying gases
  - Mass transport limitations at high humidity
- Start up will have to consider hydrophobicity of GDL for optimal performance

Component Degradation

- Currently setting up environmental chamber
  - Measurement of mechanical properties at low temperatures
  - Change in mechanical properties due to thermal cycling
  - Capable of independent operation
    - Freeze/thaw cycling of various components and cells
    - Will be equipped with *in situ* electrical property measurements

SPECIFICATIONS	
Temperature Rating	-70 to +350 ° C
Internal Height	560 mm
Internal Width	240 mm
Internal Depth	230 mm

Future Work

- Remainder of FY 06
  - Conductivity in non-Nafion® membranes
  - Transient response during cold start/stops
  - Component degradation due to freeze/thaw cycling
    - Mechanical/Electrical/Thermal properties (Sept 06)
- FY 07
  - Electrode and GDL conductivity at low temperatures
    - Ionic and electronic conductivity (transport numbers)
  - Mechanical and thermal properties at low temperatures
  - Degradation mechanisms during cold start/stop cycling

Project Summary

Goal

- Help DOE meet survivability (-40°C) and start up (from -20°C in 30 sec with < 5MJ energy) targets

Achievements

- Characterize state of water and conductivity in Nafion® membranes
- Established durability of MEA to 100 freeze/thaw cycles to -40°C
- Identified GDL (carbon paper) failure as potential degradation mechanism

Future Work

- Characterize component (mechanical/electrical/thermal) properties at low temperatures and degradation
- Identify degradation mechanisms due to start/stop cycling from low temperatures

Response to Reviewer's comments

- "Need to do more thermal cycles (>100) to look for high cycle failure modes
  - Added 100 cycles to our testing
  - E-Tek cloth had no problems while SGL paper may have problems due to carbon fiber breakage (further testing initiated)
- "Should add structural issues : impact of frozen water on membrane"
  - Purchased and installed an environmental chamber on our Instron
  - We are on track to meet our Sept 06 milestone for characterization of component degradation after 100 freeze/thaw cycles
- "Good and clear presentation of future plans"
  - Achieved all milestones and expanded research in problem areas identified by initial research

Response to Reviewer's comments

- "Workshop was an excellent means of initiating collaborations"
  - Have continued interactions with conference calls and data sharing to keep the work relevant and complementary to industry
- "Good initial fundamental studies of water in membranes as a function of subfreezing temperature"
  - This work is 90% complete and has been published and presented
- "Take care that one doesn't a priori assume that a phase change of water in a membrane will necessarily cause problems"
  - The fundamental properties are being measure at the low temperatures (will be useful for any modeling effort)
  - Degradation mechanisms if any are being identified
  - Research is being focused only on those areas that present a problem

Publications and Presentations

- 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"

- 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)

- 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)

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

Critical Assumptions and Issues

- Operation of fuel cell below 0^0C
  - Problem with ice formation in the anode side
  - Will have to modify (enlarge) the anode flow channels similar to that on the cathode side where we do not have this problem
- Would like to add neutron imaging
  - NIST is planning to add a Z-direction imaging (tomography) capability this year
  - Once our hardware and their upgrade is completed we expect to use their facility