2007 DOE Hydrogen Program

PEM Fuel Cell Freeze Durability and Cold Start Project

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United Technologies Corporation

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Project ID # FCP5

Overview

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Timeline

- Project start date: 5/1/2006
- Project end date: 4/30/2007
- Percent complete: 100%

Barriers

- Start-up and shut-down time and energy
- Water transport within the stack
- Durability

Budget

- Total project funding
  - $990K DOE
  - $247K UTC Power

Partners

- United Technologies Research Center (UTRC)

Objectives

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- **Improve cold-start, or Boot-Strap Start, ("BSS") time by investigating the effects of cell properties and start procedures**
- **Subject a short stack to freeze/thaw cycling between - 40ºC and + 20ºC to investigate any possible damage mechanisms**
- **Subject single cells and/or short stacks to repeated cold starts (BSS), measure performance degradation, and investigate the mechanisms of any performance degradation**

Approach

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- Task 1: Cold Start (BSS) Decay Studies
  - Investigate the effect of freeze and cold start (BSS) procedures on performance decay
  - Alternative cell materials will be evaluated for their resistance to performance loss with repeated cycles.
- Task 2: Cold Survivability
  - Conduct freeze/thaw cycling of short stack to -40 ºC
  - Conduct teardown analysis to characterize failure modes
- Task 3: Rapid Cold Start (BSS) Characterization
  - Investigate the effect of freeze and cold start procedures on BSS capability
  - Investigate effect of alternate cell materials on BSS capability

UTC's PEM fuel-cell technology

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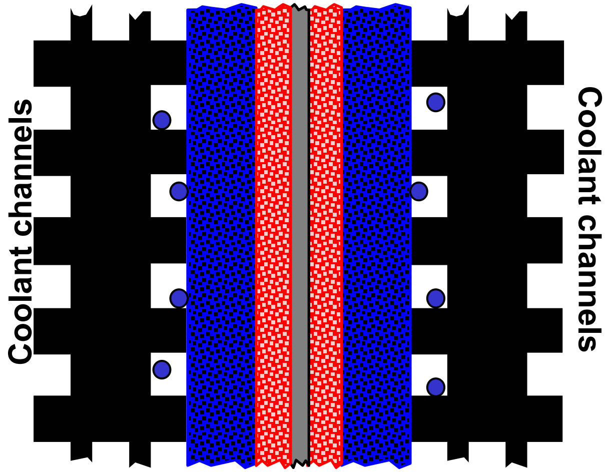
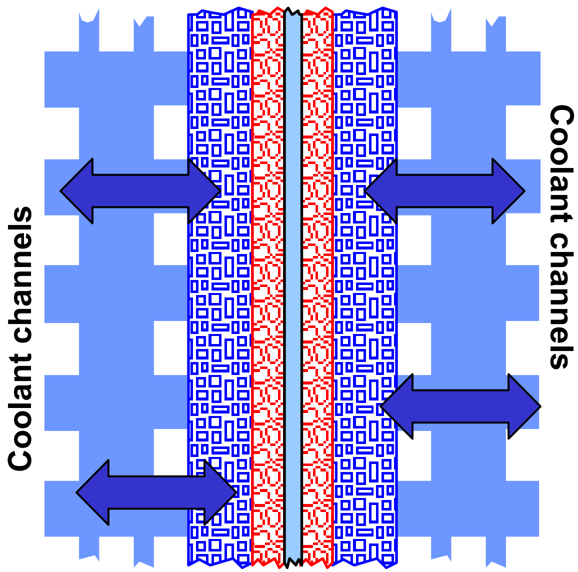
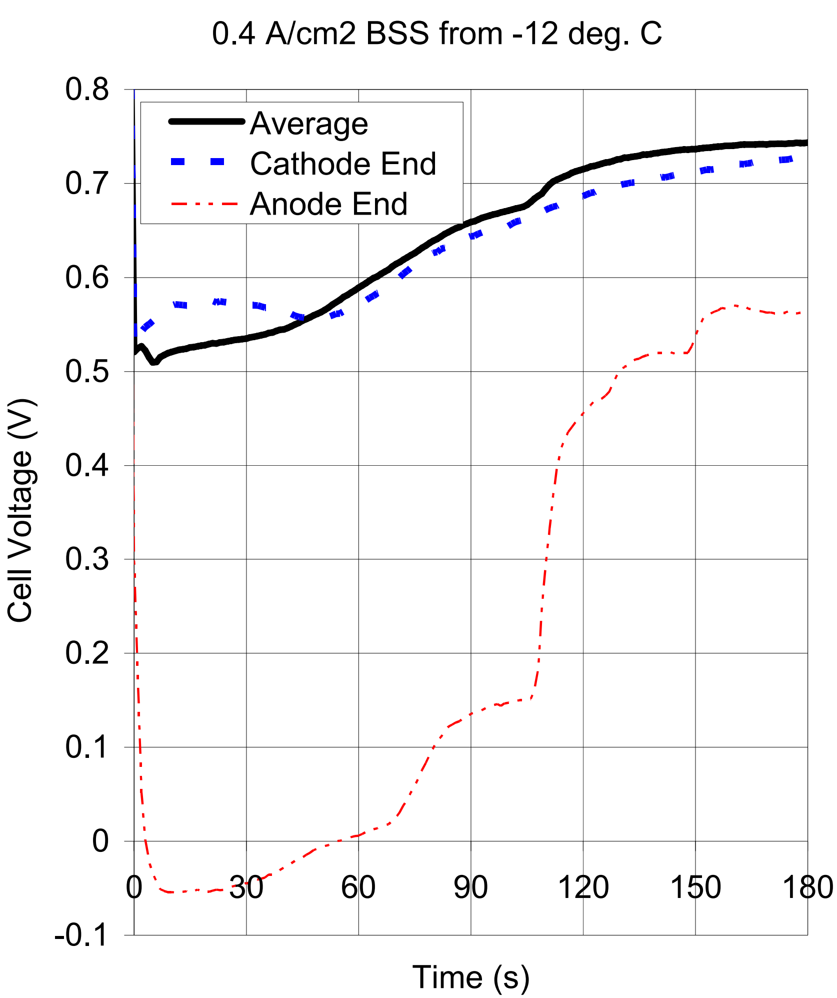
- Traditional, Solid-Plate Cell
  - Water movement is in the channels
  - External water management required
    - Humidification and water recovery
  - Liquid water build-up is unavoidable
    - In the channels and in the GDLs

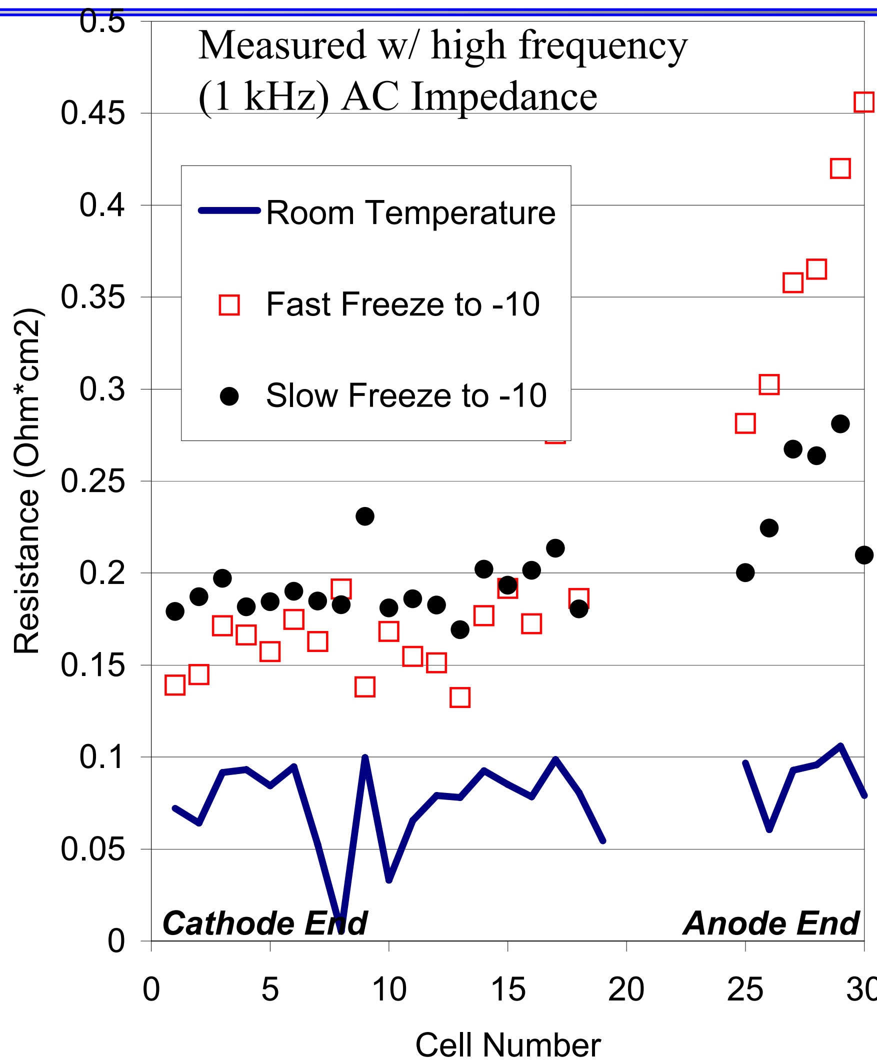


- ***UTC's* Microporous-Plate Cell**
  - Water movement is through the plate
  - Provides humidification and removal of excess liquid water
  - Single-phase flow in the channels
    - Low pressure drop
    - No local flooding/starvation



Baseline Performance:
30-cell Stack (320-cm^2 per cell)





- Poor BSS performance and high frozen resistance on anode end of stack.
- Anode-end resistance is affected by rate of freeze.

Proposed Performance-Loss Mechanism *(1)*

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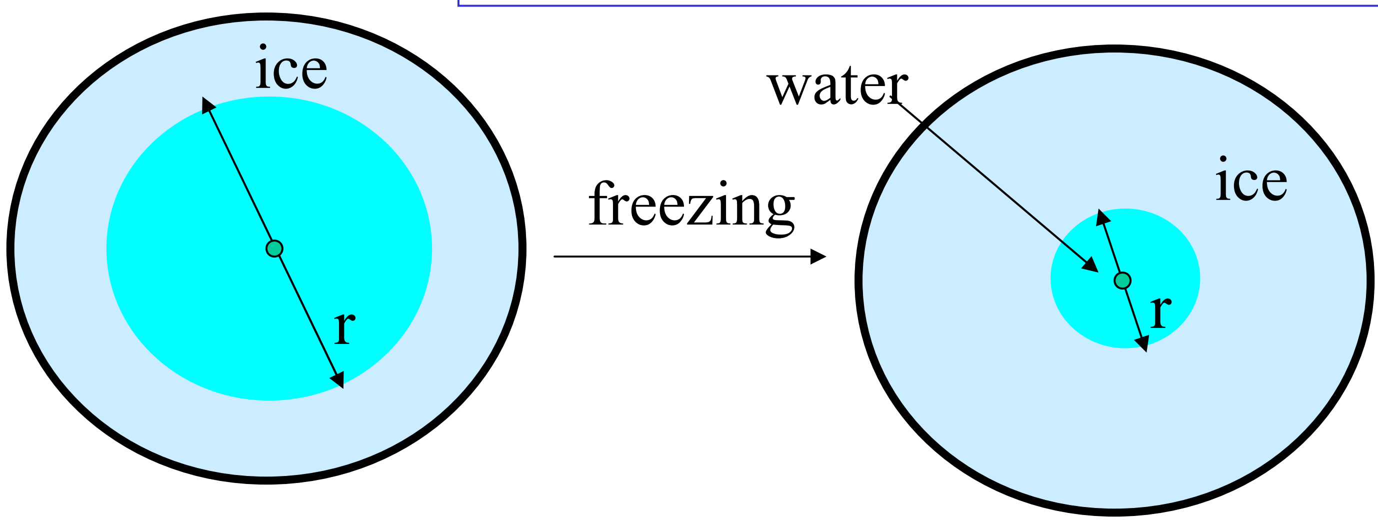
Water Movement During Freeze: Frost-Heave Mechanism

$$P_c = \frac{2\gamma \cos\theta}{r}$$

$$P_{liq} = P_{gas} - \frac{2\gamma \cos\theta}{r}$$

- As water freezes, effectively, the pore radius decreases, drops the liquid pressure, and induces liquid water movement towards the freezing point
- In extreme cases, the excess of ice which is formed may push against the porous media, resulting in "frost heave"



Pore cross-section

Proposed Performance-Loss Mechanism *(2)*

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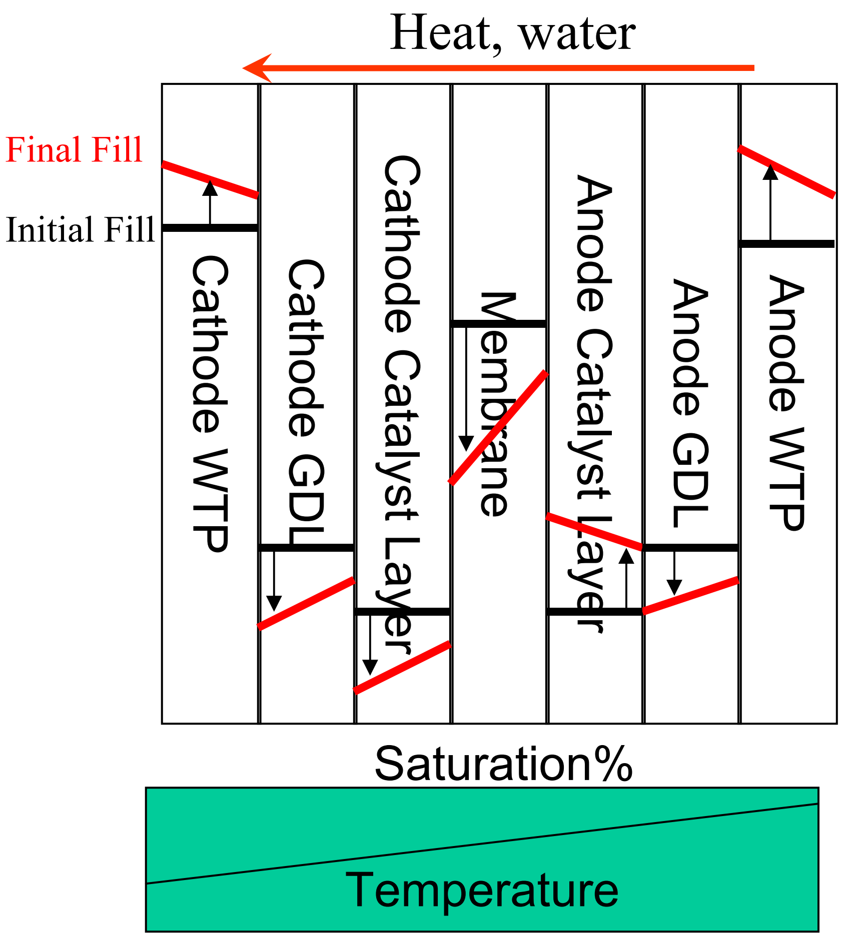
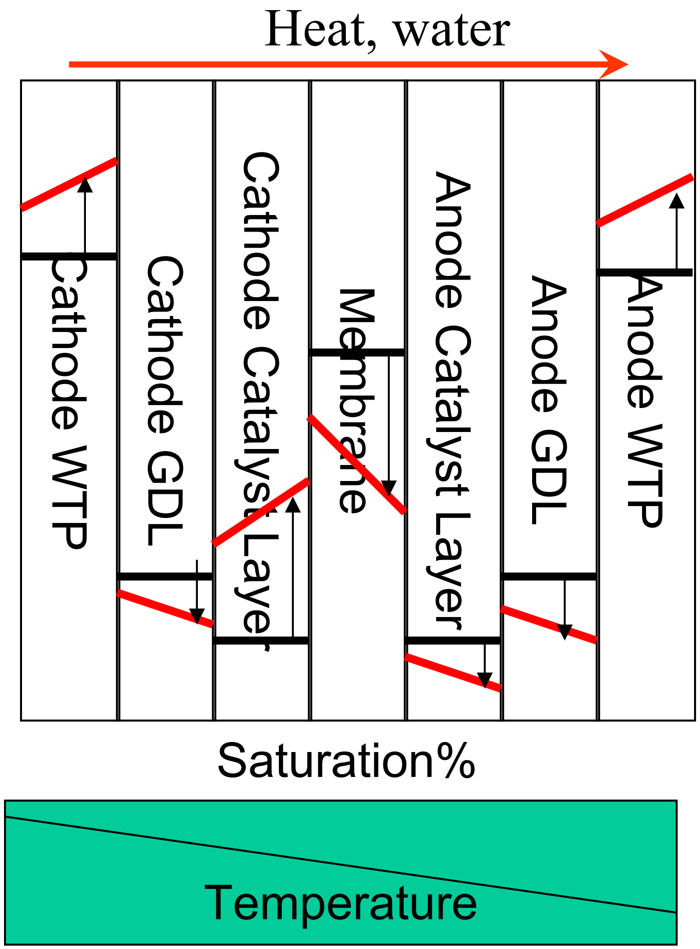
Cathode Side:
Water transport towards cold cathode side
Cathode catalyst layer water content *decreases*

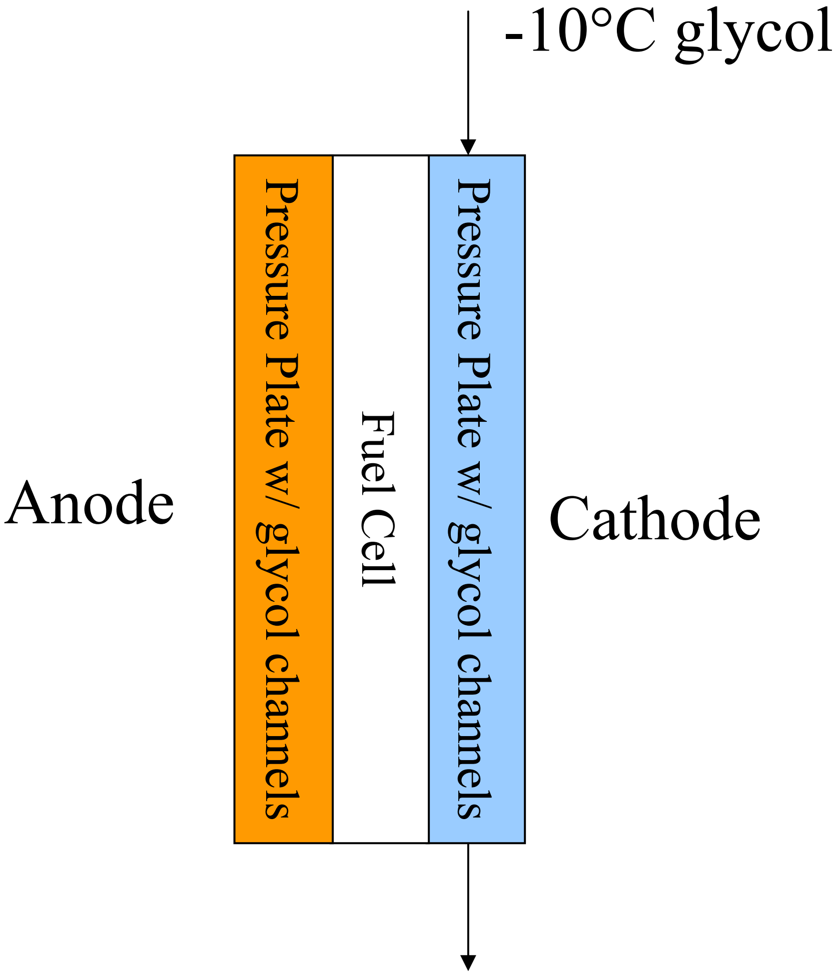


Anode Side:
Water transport towards cold anode side
Cathode catalyst layer water content *increases*

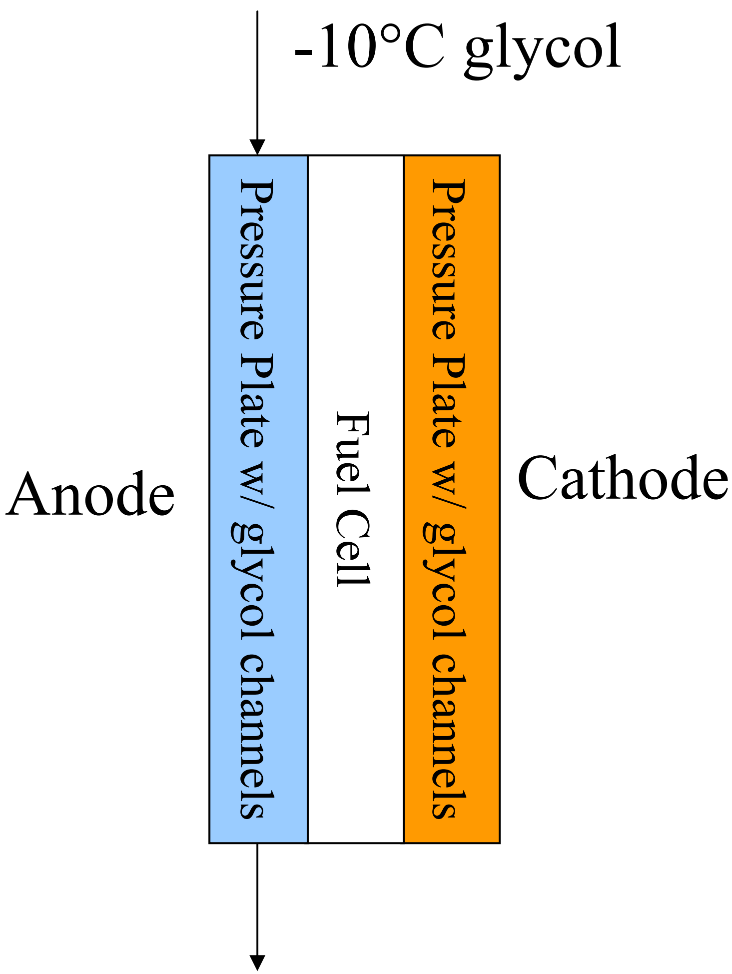


Single-Cell Hardware Configuration: Glycol used to create freeze direction

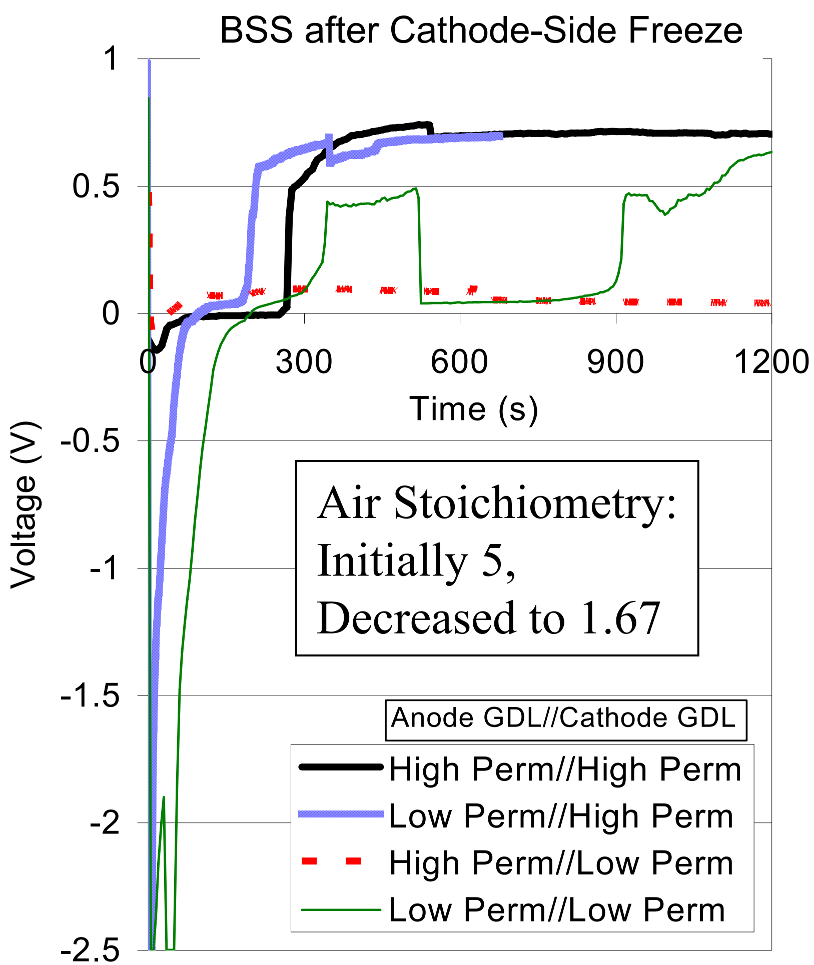
Cathode-Side Freeze

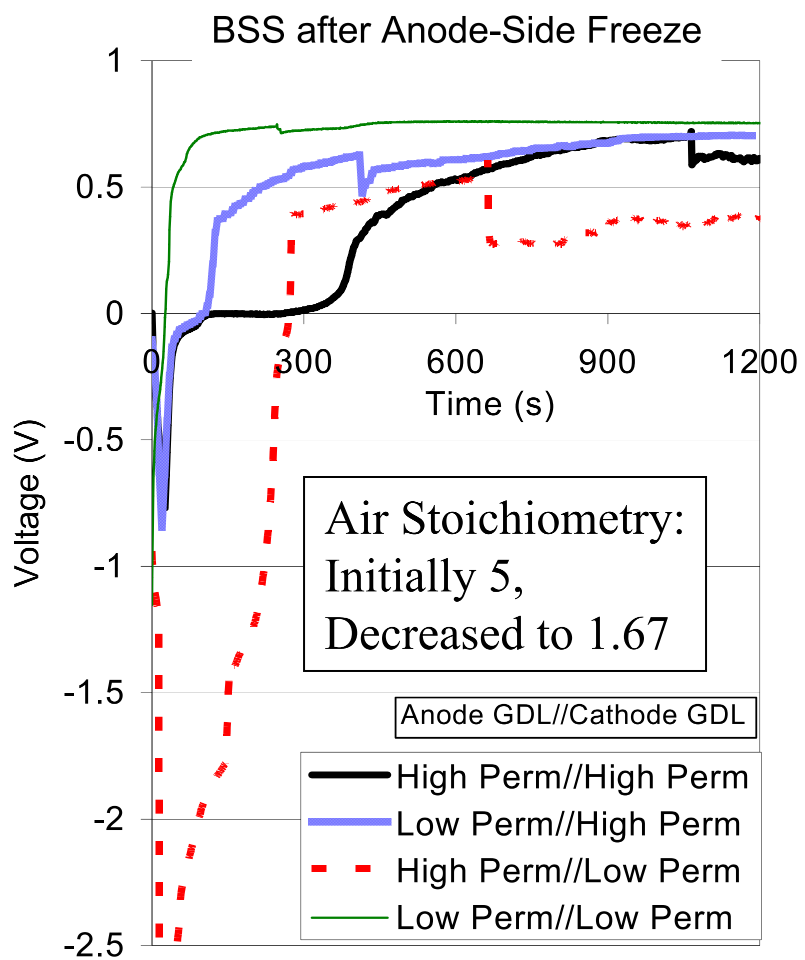


Anode-Side Freeze



Single-Cell Results: Effect of GDL Permeability

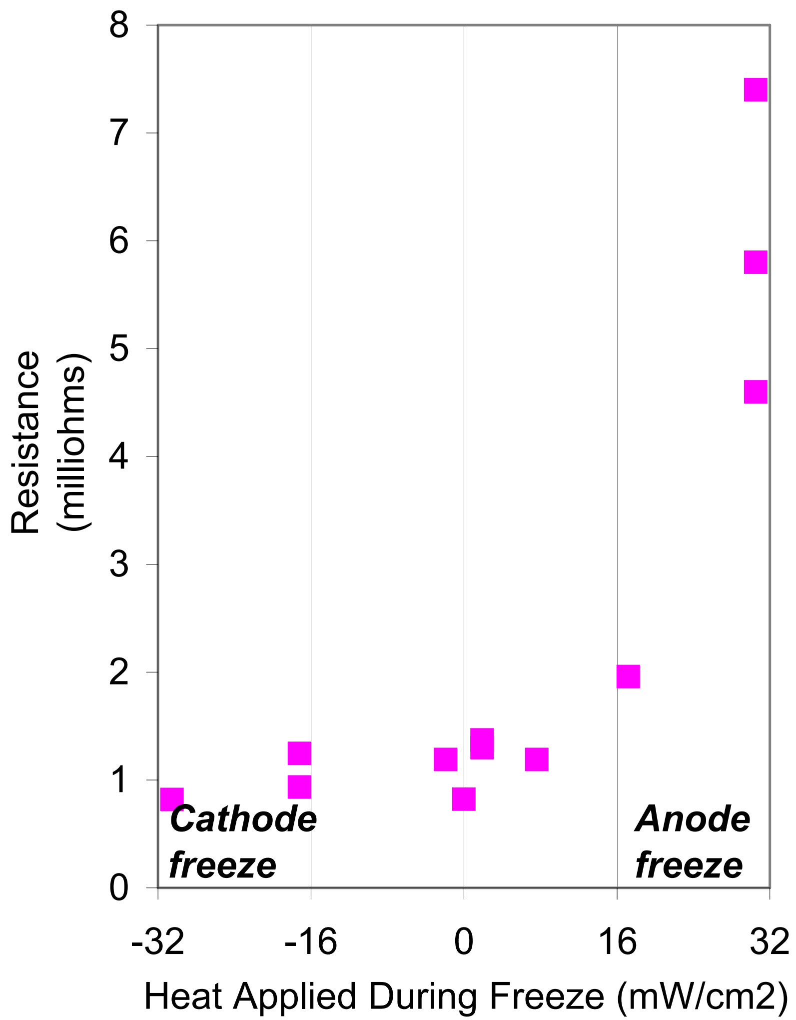




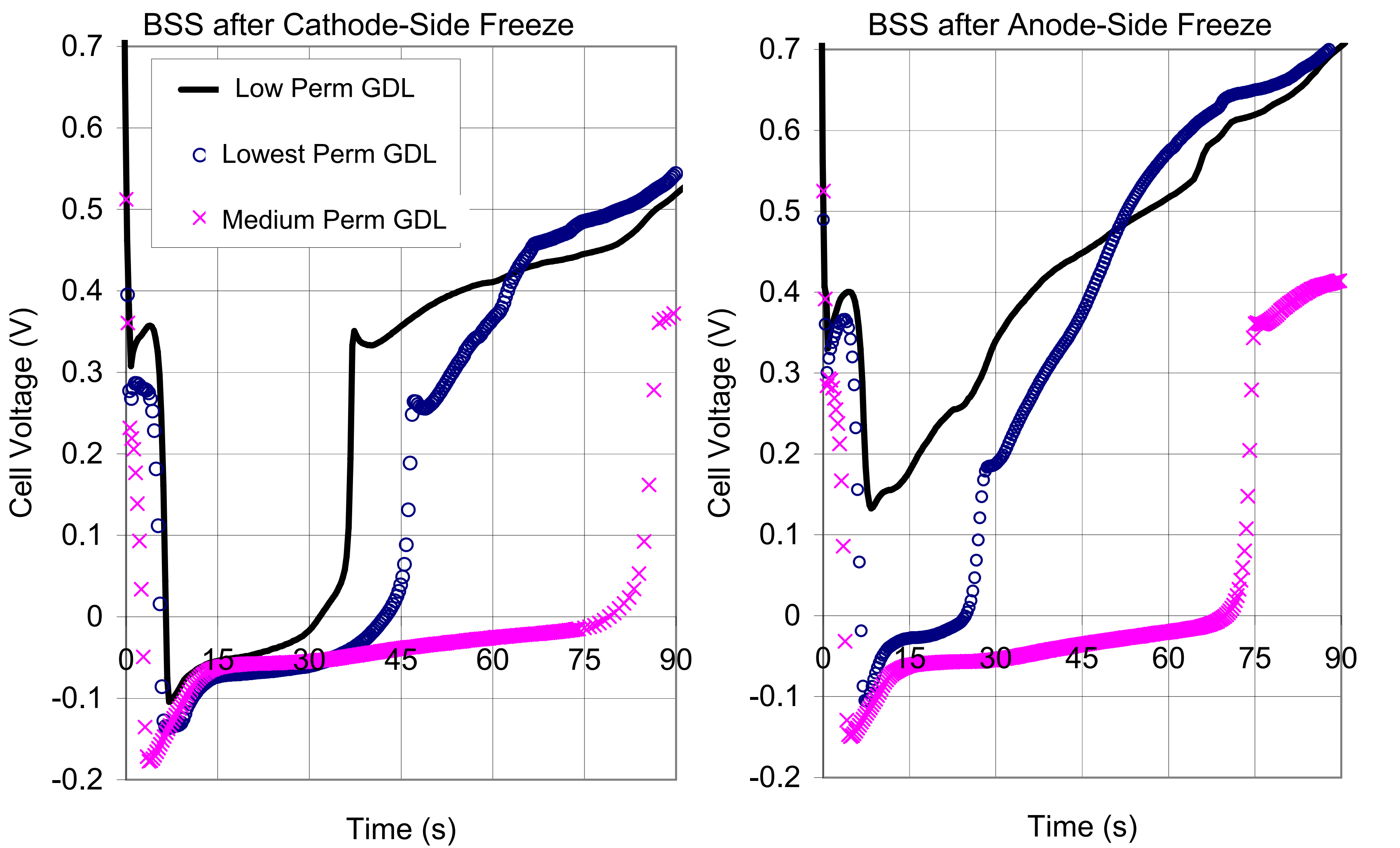
- Cell w/ High Permeability GDL performed better after cathode-side freeze
- Cell w/ Low Permeability GDL performed better after anode-side freeze

"Adiabatic" Single-Cell Hardware: Heat used to create freeze direction

- Heating pads on each side mimic stack heat
  - Cell in freezer, no glycol
  - Heating one side during freeze simulates freeze direction
  - Freezing rates more realistic to those experienced in stacks
  - Variable heat on each side during startup, pegged to current density
- Pyropel© insulation between cell and pressure plates and high-density Pyropel© manifolds
- Resistance is very high after anode freeze, due to H_2O movement during freeze (see slides 7 & 8)

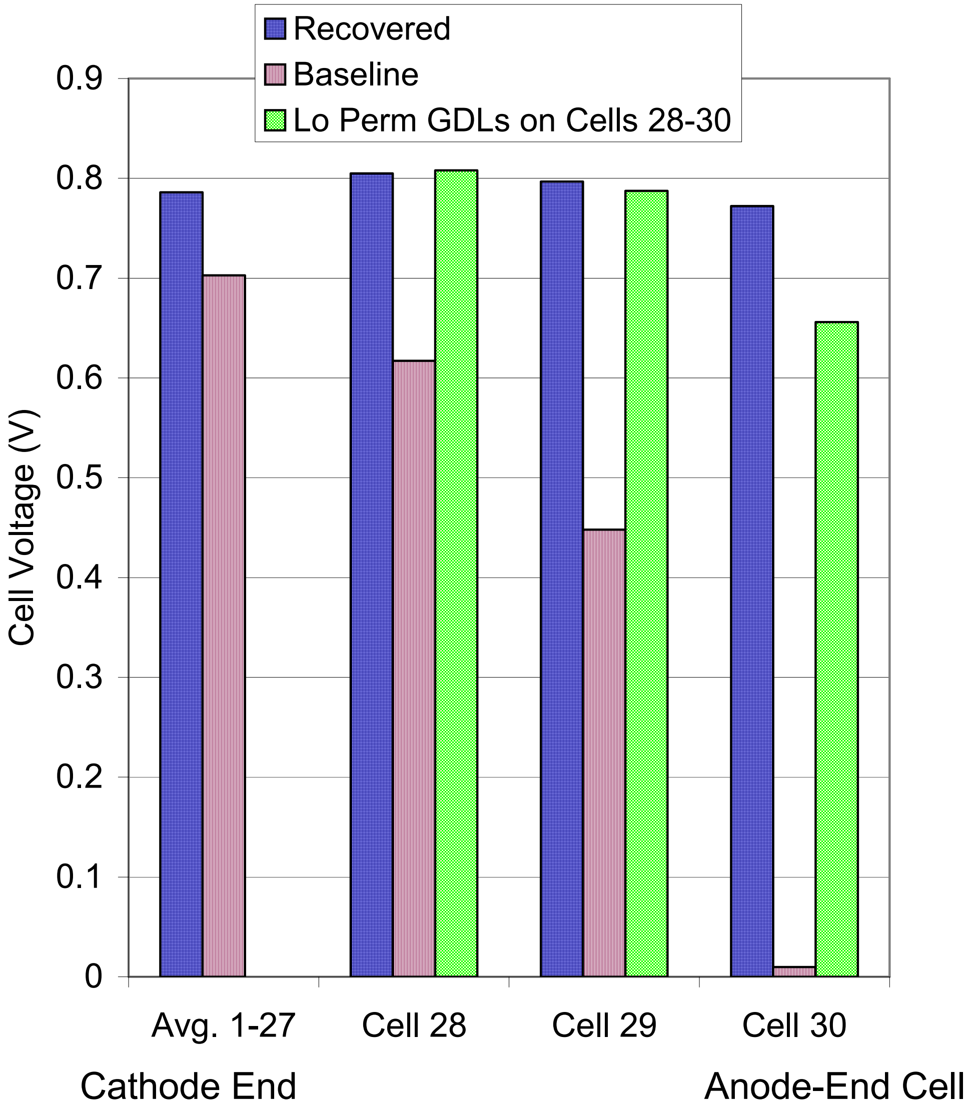


"Adiabatic" Single-Cell Results: 0.6 A/cm² BSS from -30°C



- Cell w/ Low Perm GDL maintained positive voltage at 0.6A/cm² after anode freeze to -30°C
- There appears to be an optimum permeability. Results are dependent on rate of freeze.

Effect of GDL on Short-Stack BSS



- When all cells had baseline GDL configuration, anode end performed poorly on 0.3 A/cm^2 BSS.
- Inserting low permeability GDLs on the anode-end cells greatly improved their BSS performance.

-40°C Freeze/Thaw Survivability

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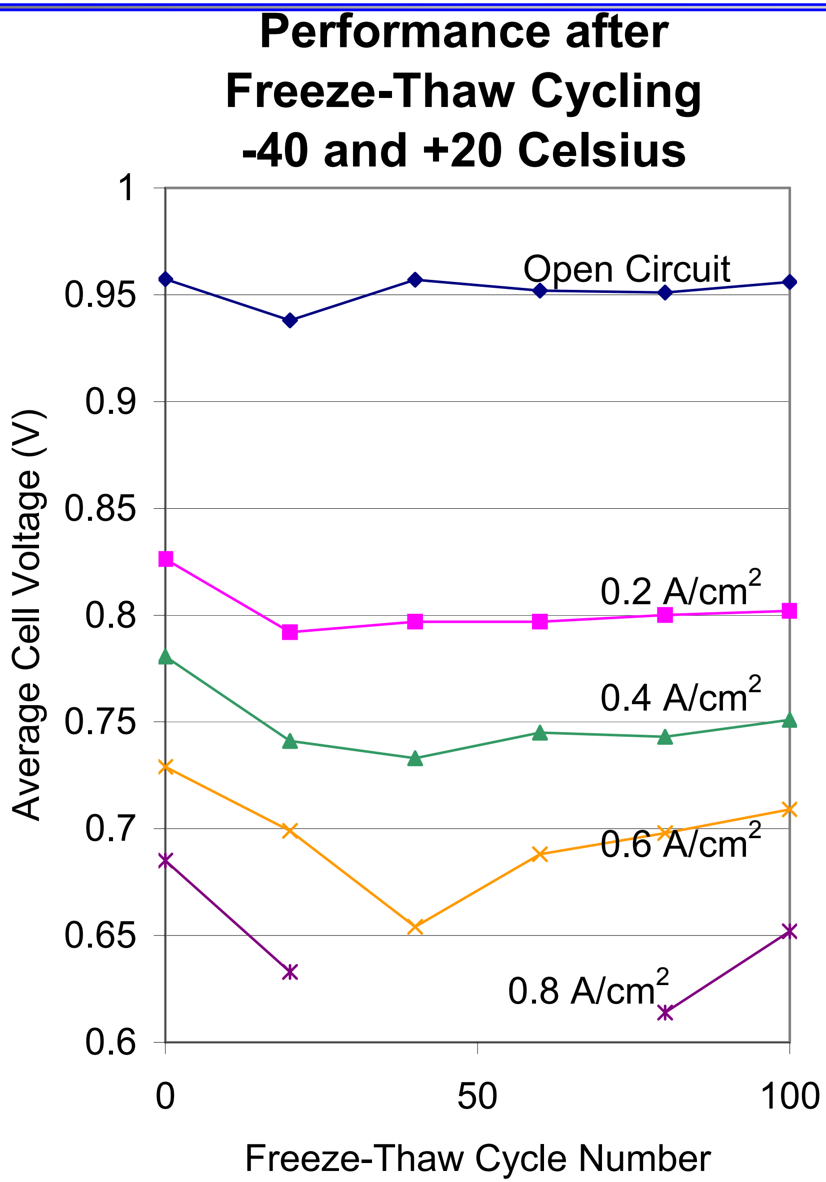
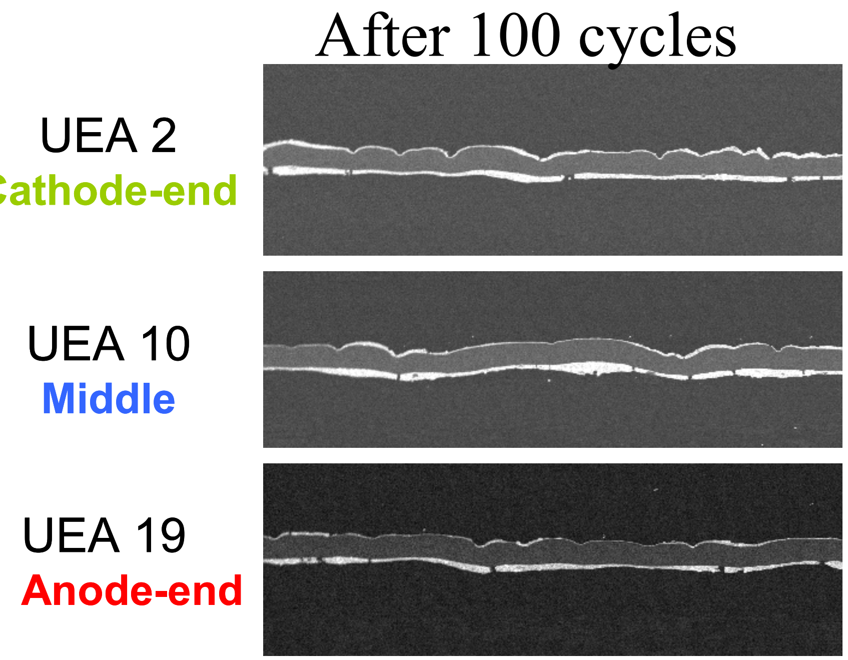


Scanning Electron Micrographs (SEM) of Unitized Electrode Assemblies (UEA)



No changes observed in 20-cell stack after 100 freeze-thaw cycles to -40°C. SEM images same as as-received.

-40°C Freeze/Thaw Survivability: Second 20-Cell Short Stack

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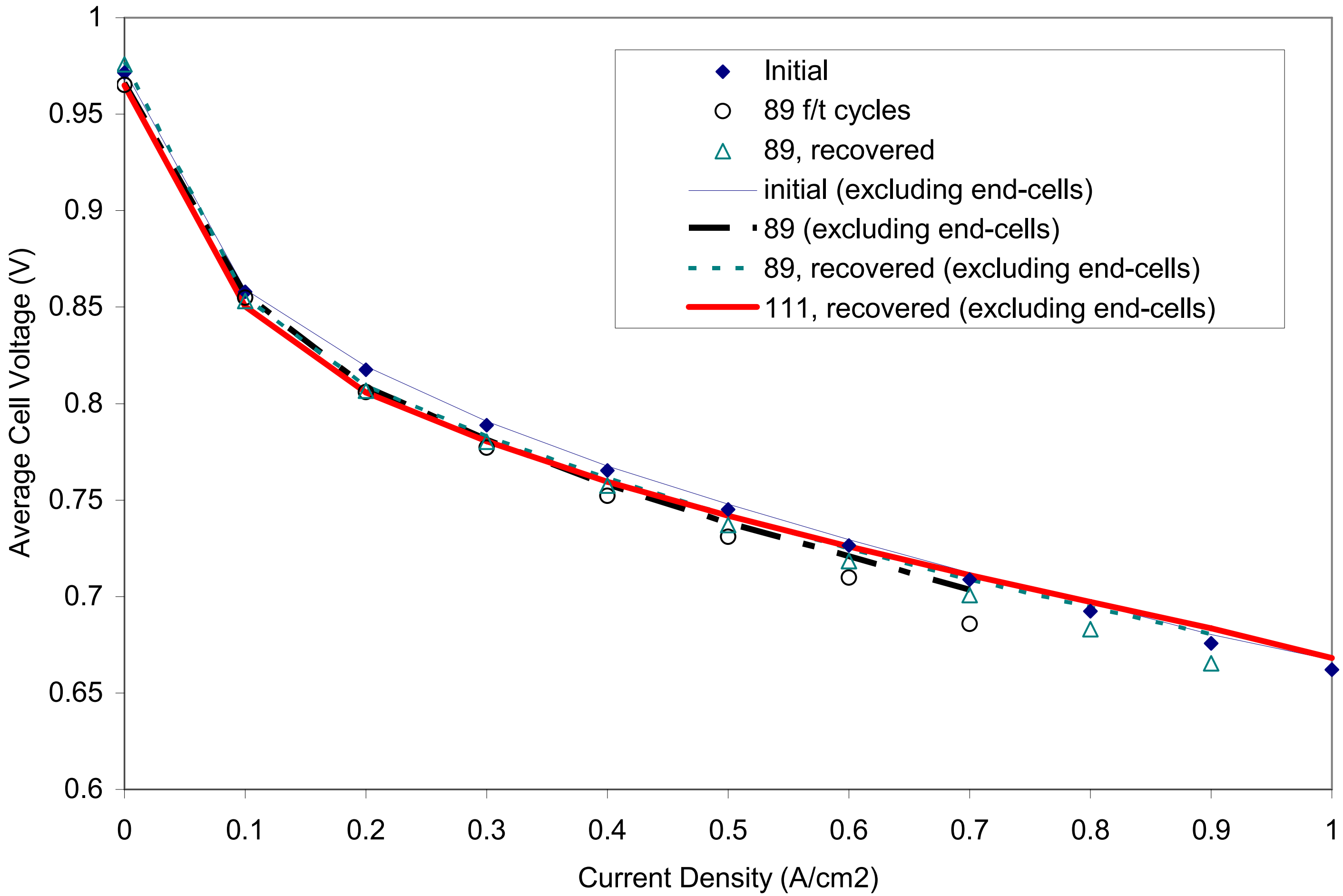

- **Excluding end-cells, negligible performance loss after 111 freeze/thaw cycles.**
- **Mostly recoverable decay observed on end-cells**.

Progress *vs.* 2010 DOE Targets

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- DOE Target: BSS from -40°C
  - Achieved: BSS from -35°C with Short Stack
    - With no air-side purge required on shutdown
    - Short fuel-side purge for system components (*e.g.,* fuel regulator)
  - Achieved: -40°C Freeze/Thaw Survivability
- DOE Target: 50% rated power in 30s from -20°C
  - Baseline Short Stack: 33% r.p.* in 30s from -12°C
  - Single Cell w/ Low Perm GDL:
    - 65% r.p. in 30s from -10°C (anode freeze & cathode freeze)
    - 47% r.p. in 30s from -29°C (anode freeze)
    - 33% r.p. in 30s from -29°C (cathode freeze)
- DOE Target: 50% rated power in 5s from +20°C
  - Achieved: 94% r.p. in 5s from +23°C (single cell)

* UTC's rated power is 0.65 W/cm^2

Future Work

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- DOE-funded program completed on 4/30/2007
- Freeze work continues at UTC Power & UTRC
  - Both stack and system-level work ongoing
  - Additional optimization of cell design and materials required to achieve faster cold-start times
  - Further system simplifications to improve robustness
- Results strongly depend on water management:
  - Amount of water present in cell on shutdown
  - Water movement during freeze
  - Water production, movement, and removal on start

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Summary

- Excellent BSS and freeze durability results have been achieved with UTC's microporous-plate cells.
- Freeze-decay mechanism:
  - H_2O moves down thermal gradient across GDL
  - Anode end of stack: More cathode flooding during freeze
- With low permeability GDL:
  - Less H_2O movement during freeze than baseline cells
  - Excellent performance after both anode- and cathode-side freeze
- Notable short-stack results:
  - Cold starts (BSS) successfully conducted down to -35°C
    - No purging of stack on shutdown required
  - 111 freeze/thaw cycles to -40°C with negligible performance loss