



DOE Hydrogen Program



UTC Power

A United Technologies Company

2007 DOE Hydrogen Program
*PEM Fuel Cell Freeze Durability and Cold
Start Project*

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Project ID #
FCP5

Timeline

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

Budget

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

Barriers

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

Partners

- United Technologies Research Center (UTRC)

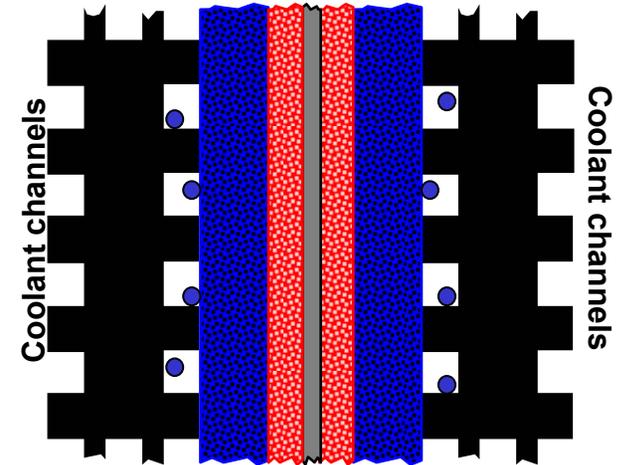
- **Improve cold-start, or Boot-Strap Start, (“BSS”) time by investigating the effects of cell properties and start procedures**
- **Subject a short stack to freeze/thaw cycling between - 40°C and + 20°C to investigate any possible damage mechanisms**
- **Subject single cells and/or short stacks to repeated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

- **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 °C
 - 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

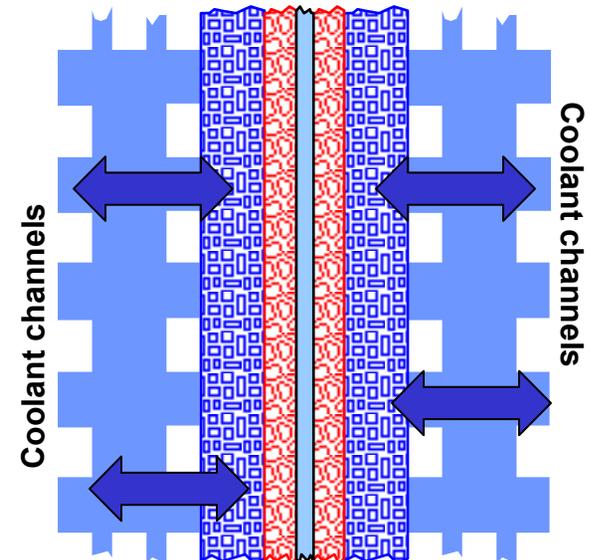


UTC's PEM fuel-cell technology

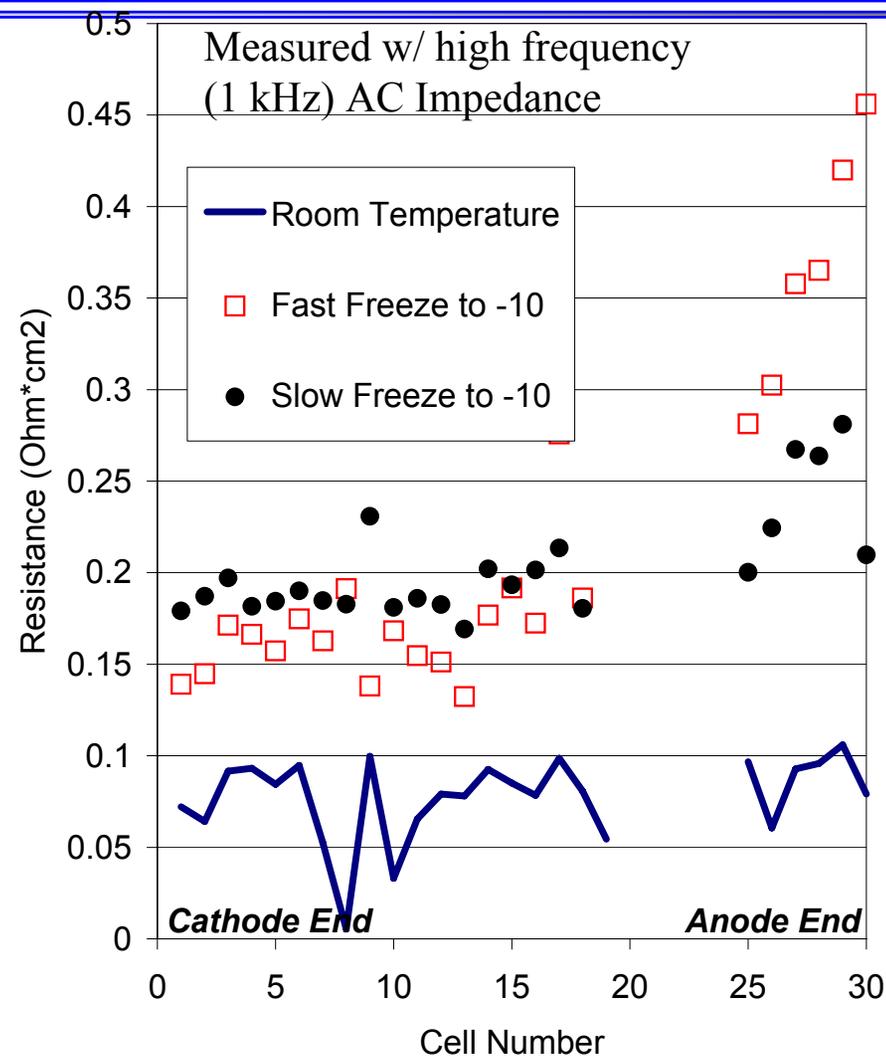
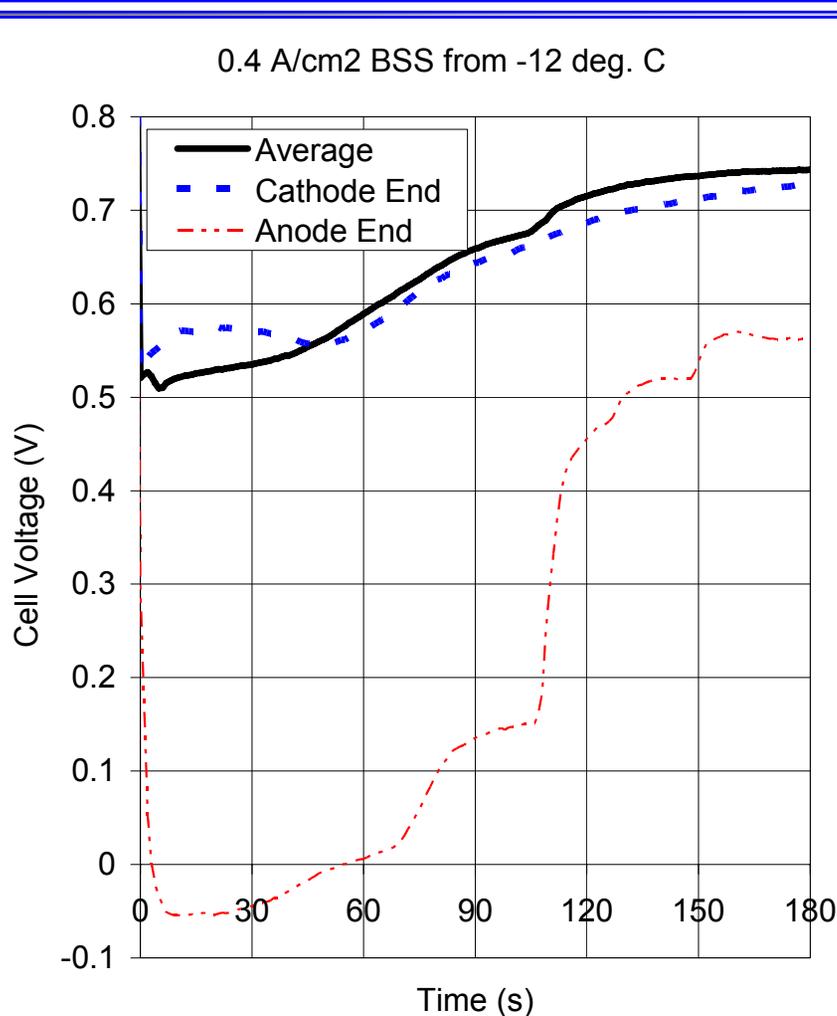
- Traditional, Solid-Plate Cell
 - Water movement is in the channels
 - External water management required
 - Humidification and water recovery
 - Liquid water build-up is unavoidable
 - In the channels and in the GDLs



- **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-cm² per cell)



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

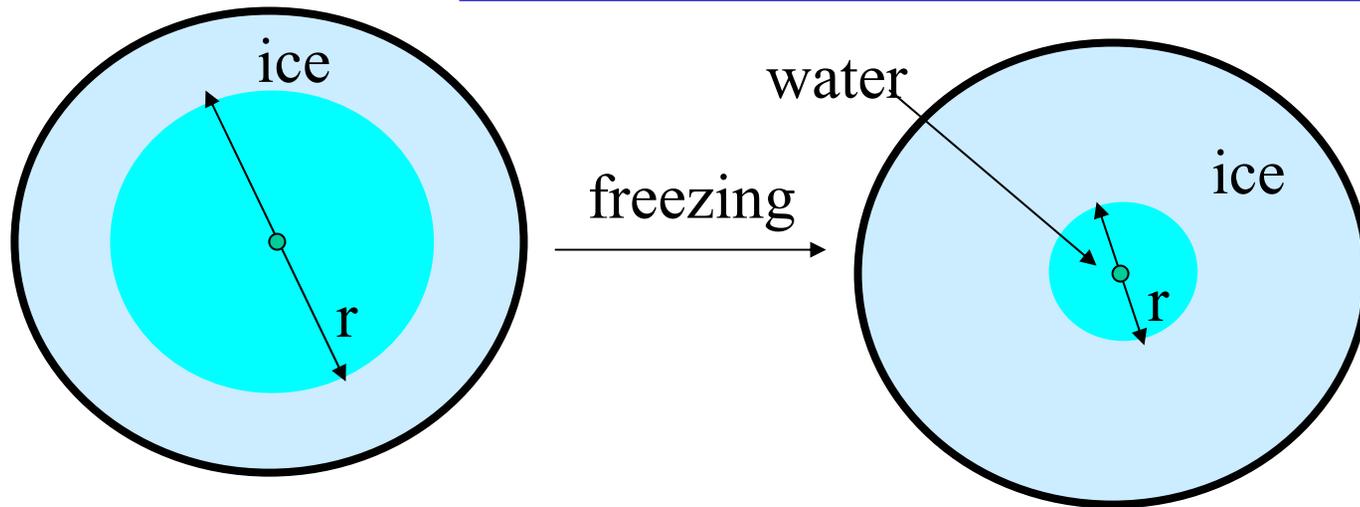
Proposed Performance-Loss Mechanism (1)

Water Movement During Freeze: Frost-Heave Mechanism

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

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

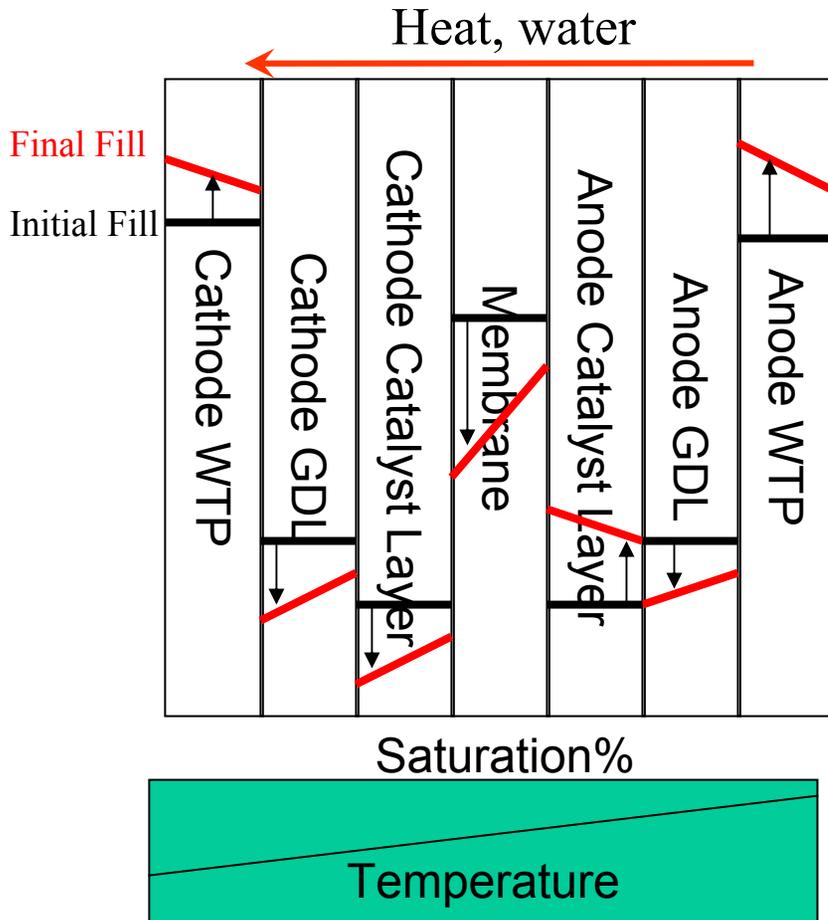
- As water freezes, effectively, the pore radius decreases, drops the liquid pressure, and induces liquid water movement towards the freezing point
- In extreme cases, the excess of ice which is formed may push against the porous media, resulting in “frost heave”



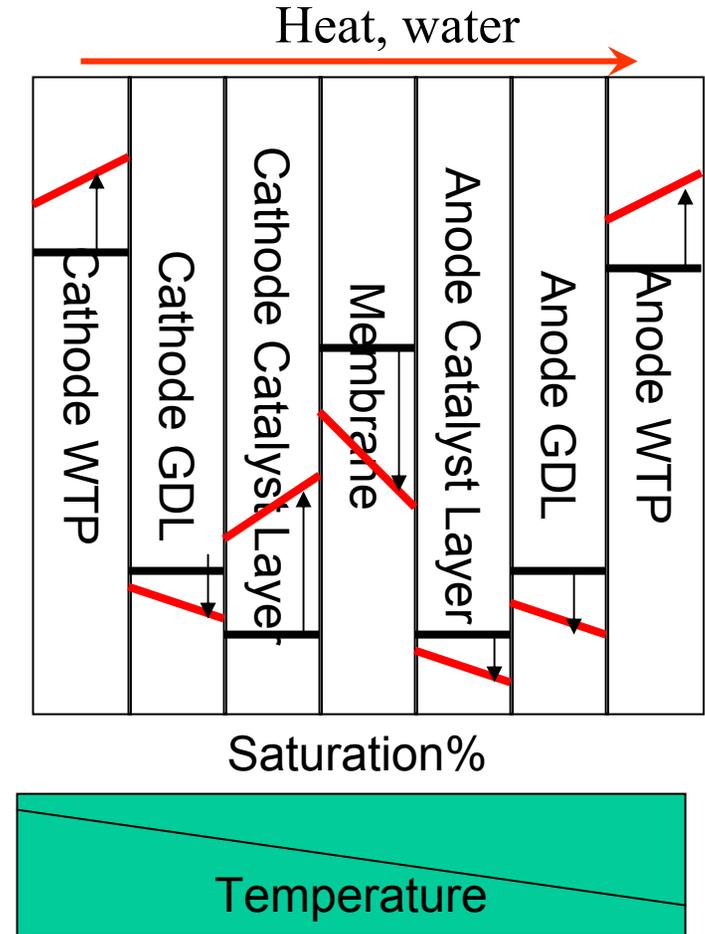
Pore cross-section

Proposed Performance-Loss Mechanism (2)

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

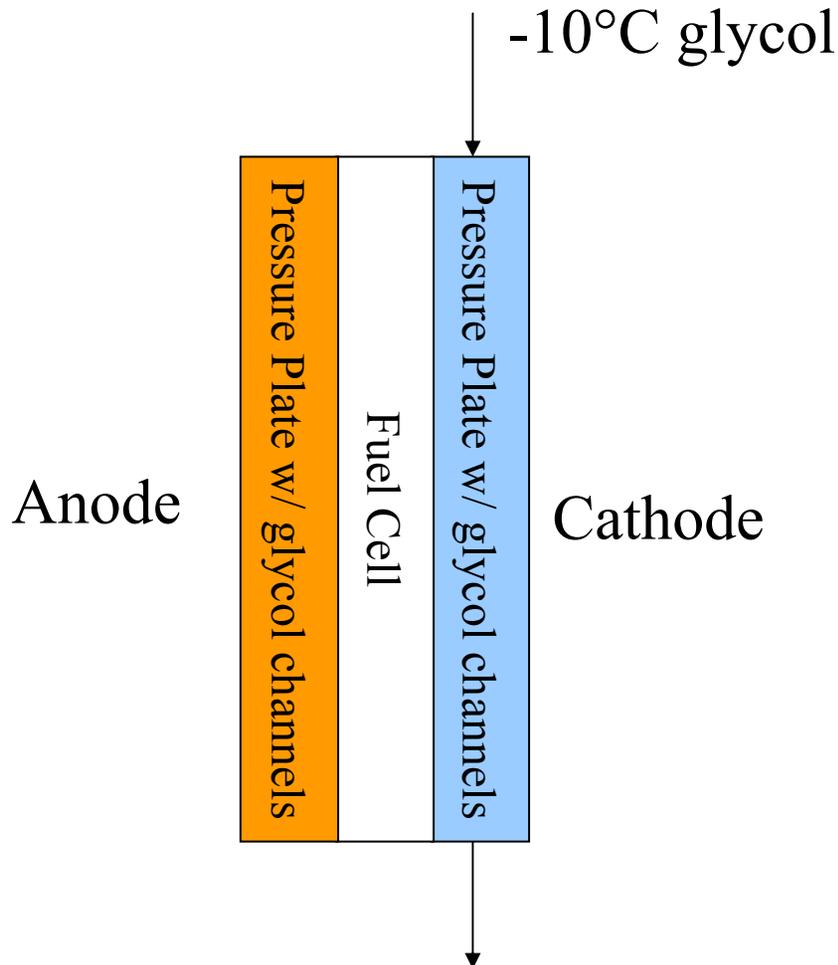


Anode Side:
Water transport towards cold anode side
Cathode catalyst layer water content *increases*

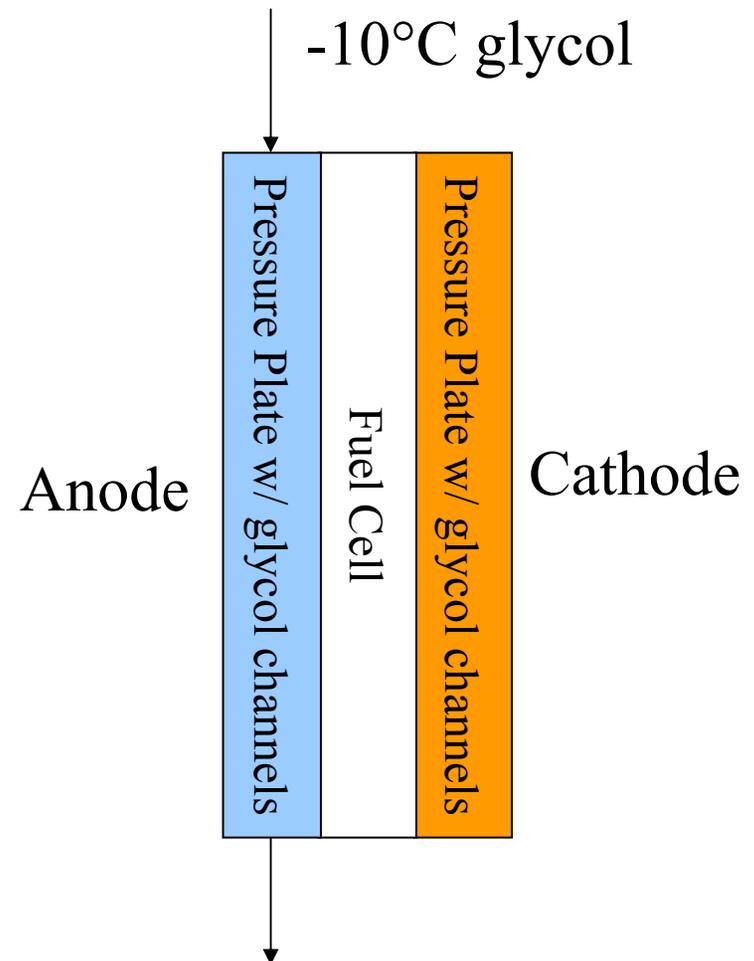


Single-Cell Hardware Configuration: Glycol used to create freeze direction

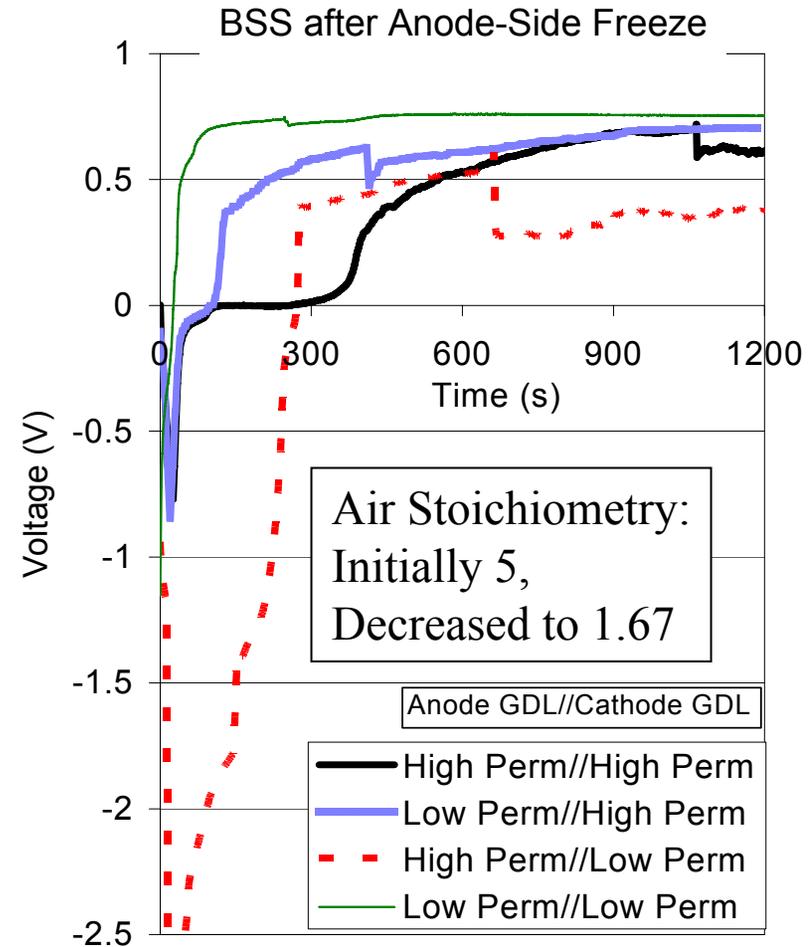
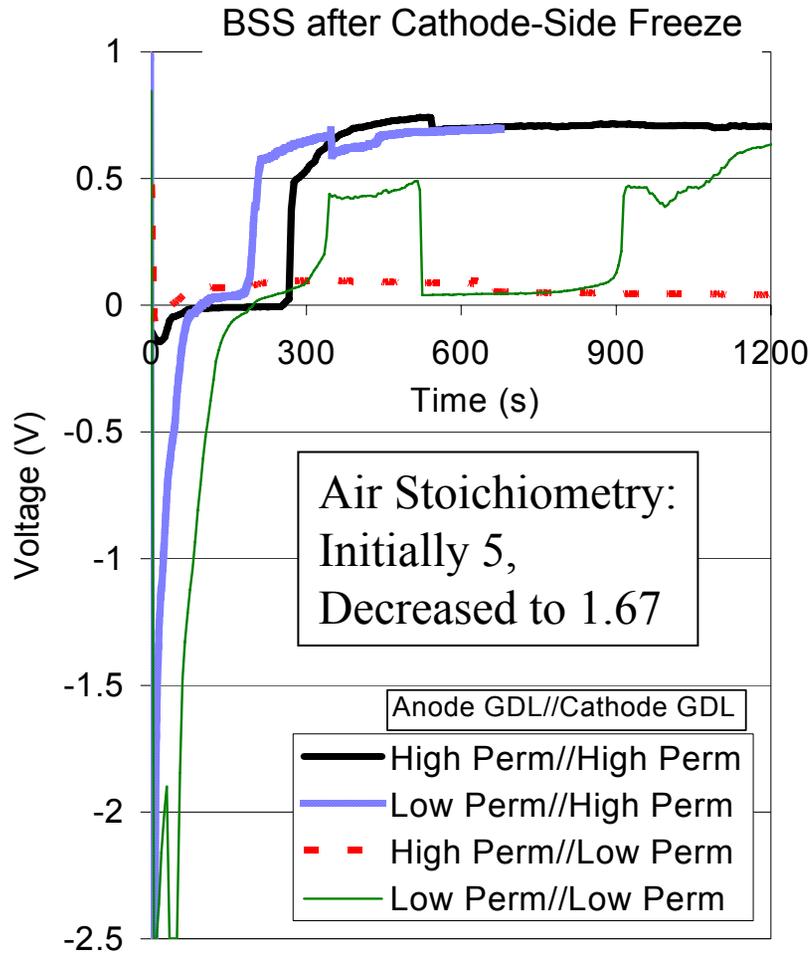
Cathode-Side Freeze



Anode-Side Freeze



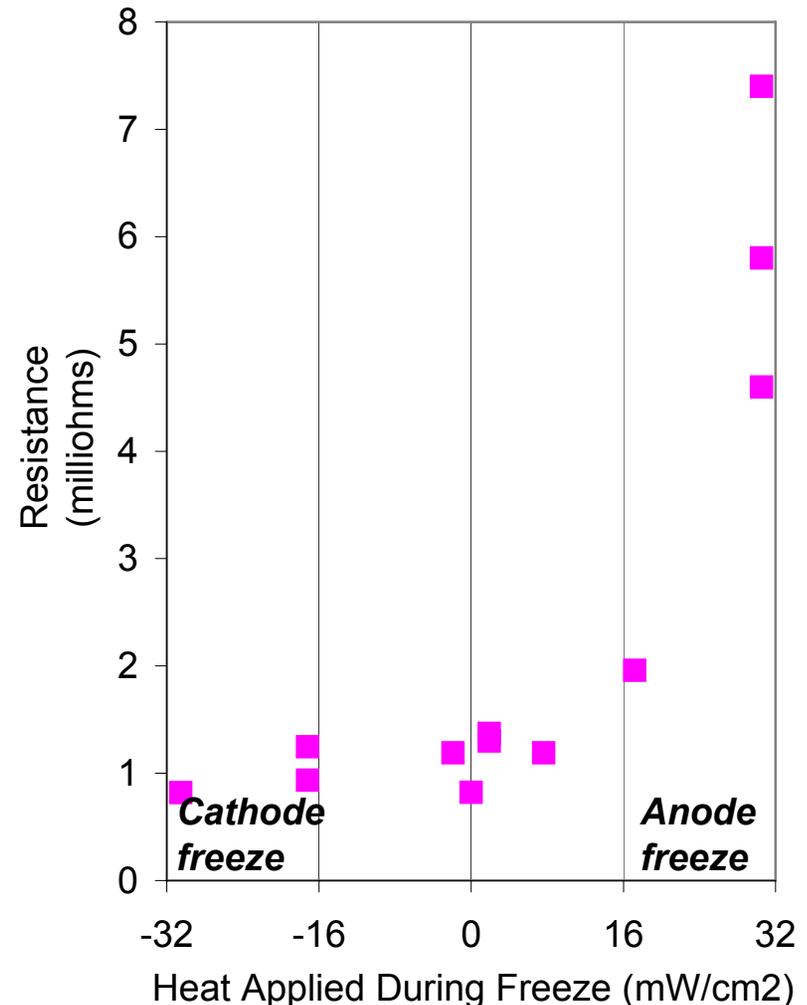
Single-Cell Results: Effect of GDL Permeability



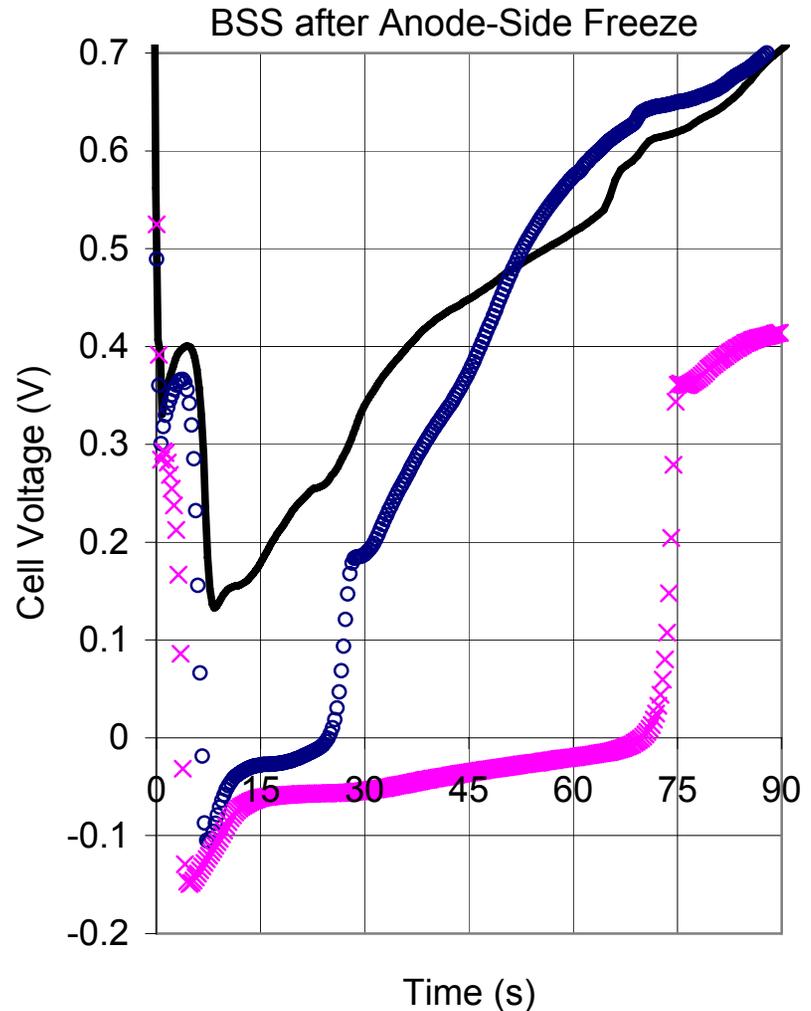
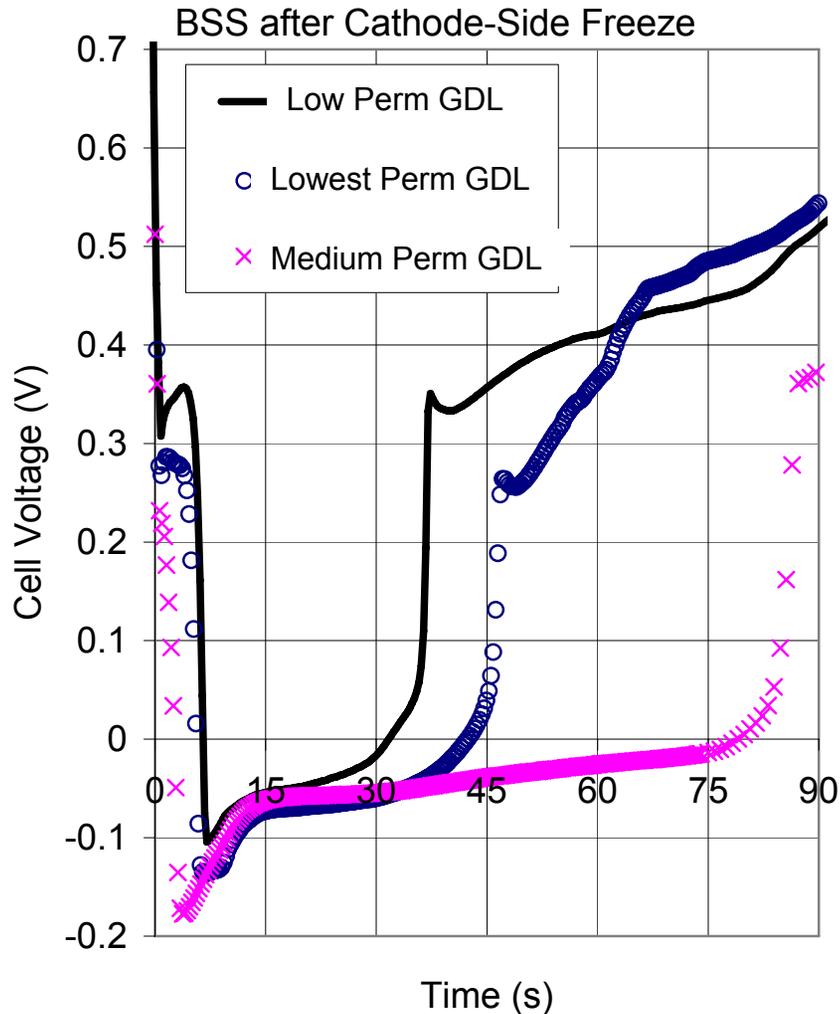
- Cell w/ High Permeability GDL performed better after cathode-side freeze
- Cell w/ Low Permeability GDL performed better after anode-side freeze

“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 H₂O movement during freeze (see slides 7 & 8)

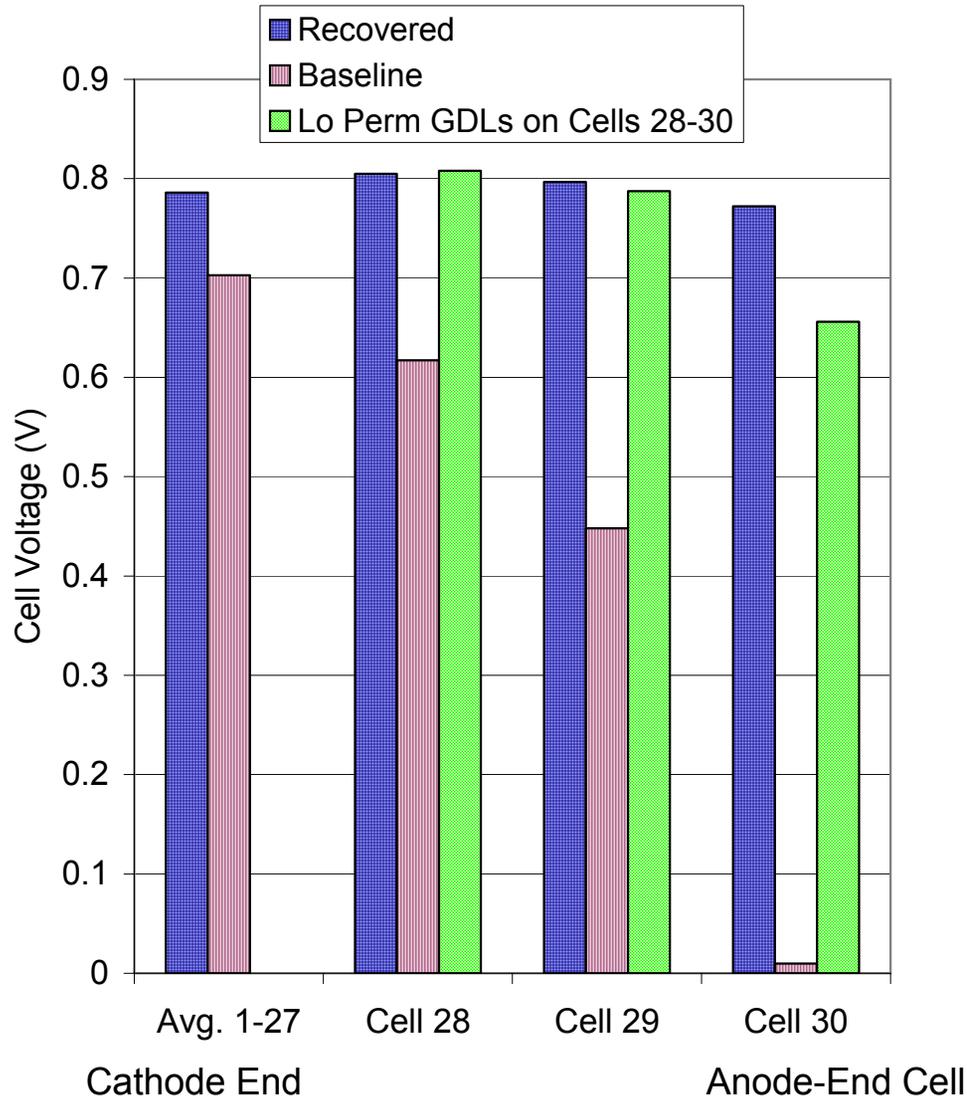


“Adiabatic” Single-Cell Results: 0.6 A/cm² BSS from -30°C



- 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

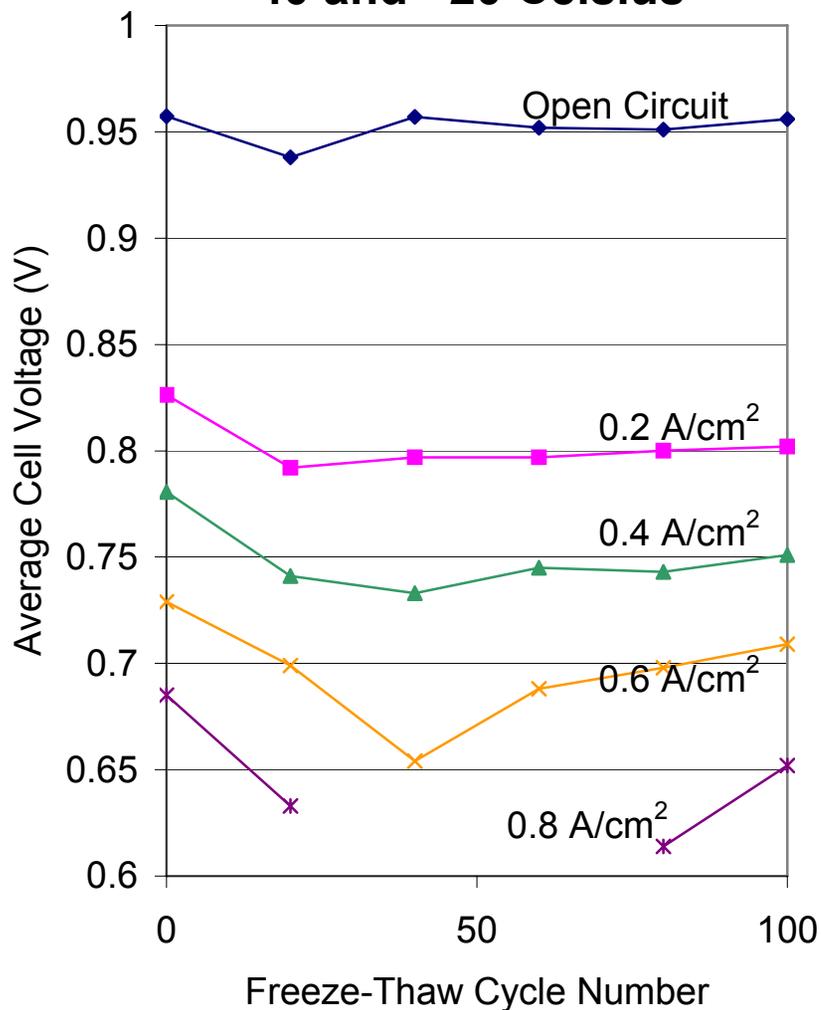


- When all cells had baseline GDL configuration, anode end performed poorly on 0.3 A/cm² BSS.

- Inserting low permeability GDLs on the anode-end cells greatly improved their BSS performance.

-40°C Freeze/Thaw Survivability

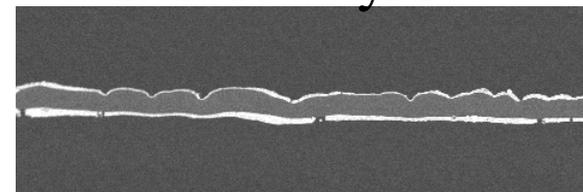
Performance after Freeze-Thaw Cycling -40 and +20 Celsius



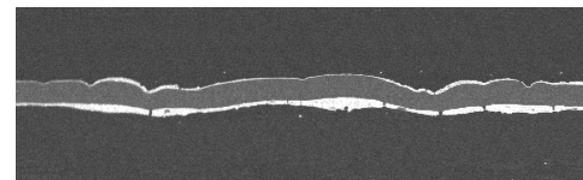
Scanning Electron Micrographs (SEM) of Unitized Electrode Assemblies (UEA)

After 100 cycles

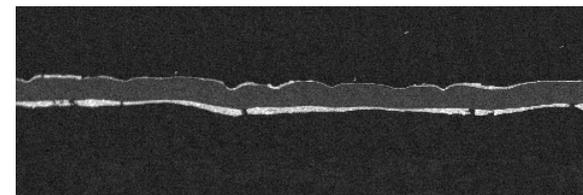
UEA 2
Cathode-end



UEA 10
Middle

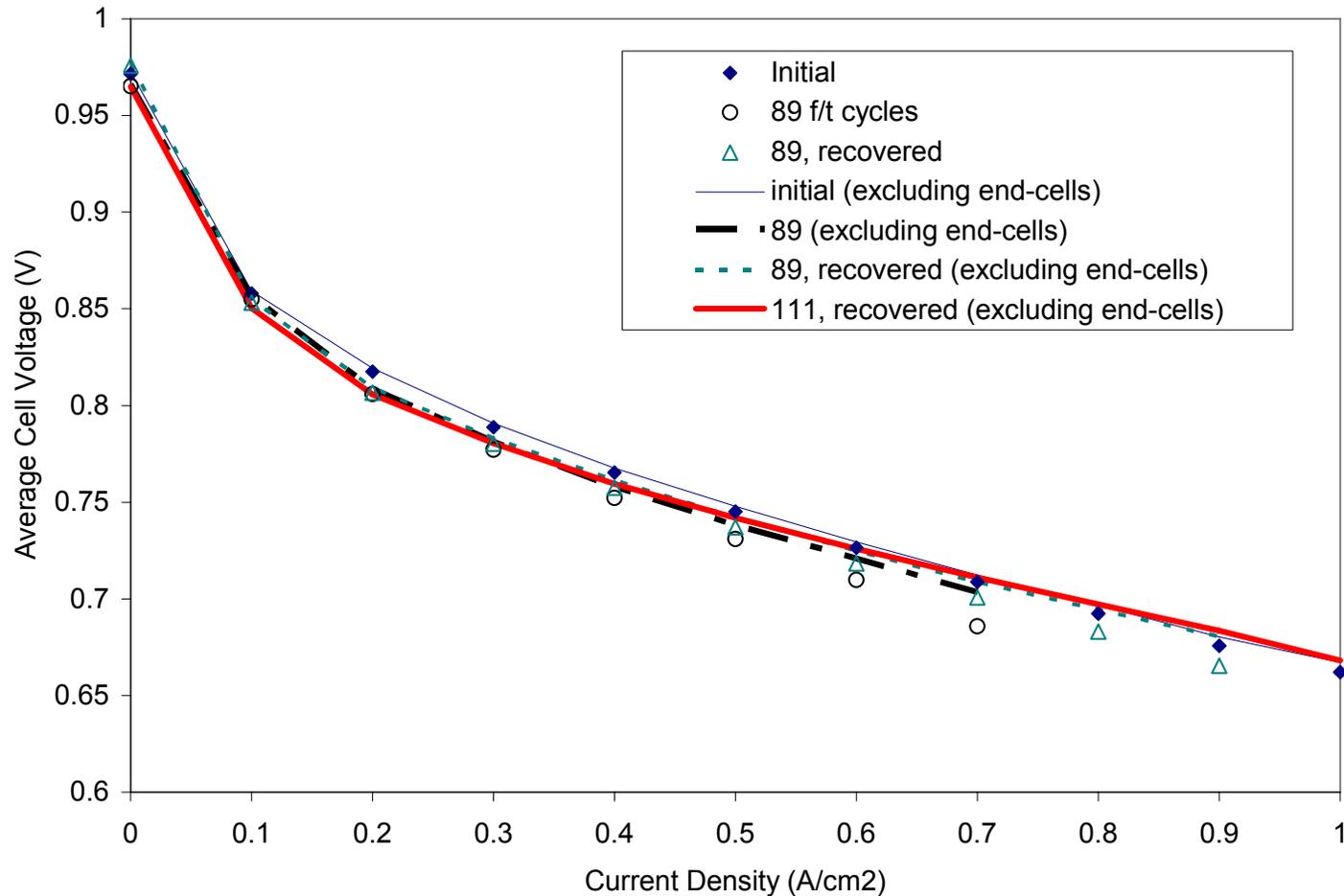


UEA 19
Anode-end



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



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

Progress vs. 2010 DOE Targets

- 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 $+20^{\circ}\text{C}$
 - Achieved: 94% r.p. in 5s from $+23^{\circ}\text{C}$ (single cell)

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

- 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

- Excellent BSS and freeze durability results have been achieved with UTC's microporous-plate cells.
- Freeze-decay mechanism:
 - H₂O moves down thermal gradient across GDL
 - Anode end of stack: More cathode flooding during freeze
- With low permeability GDL:
 - Less H₂O 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