Fundamental issues in subzero PEMFC startup and operation

Jeremy P. Meyers

February 1, 2005

DOE Freeze Workshop

UTC Fuel Cells
A United Technologies Company

Outline of presentation

- Motivation
- Stack performance
- Technology gaps
- Recommendations

Outline of presentation

- **Motivation**
- Stack performance
- Technology gaps
- Recommendations

THE LOW TEMPERATURE CHALLENGE

Status

- DOE has identified cold start as key requirement
- Automotive requirements not met
  - many announcements but little data
  - private discussions indicate capability is low

- In excess of 100 inventions (patents & applications) worldwide
  - little published in the open literature
  - little activity at universities and research labs

- Progress toward fundamental understanding is slow and gap between between present capability and vehicle requirements is large

…Hyundai and UTC Fuel Cells to work jointly to develop a freeze-capable fuel cell power plant and integrate it into a Hyundai sport utility vehicle platform.

"it is not an easy problem to solve" Toyota web site

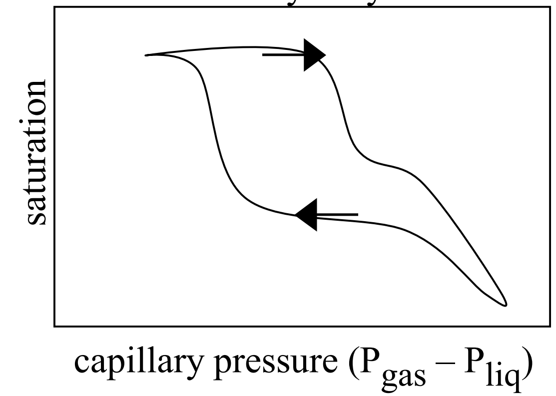
"the FCX successfully started after being parked outside overnight in temperatures as low as -11ºC (+12ºF). Test drives conducted immediately afterward demonstrated the vehicle's excellent cold weather driving performance." February 27, 2004 Honda press release

Scientists and engineers at GM's Global Alternative Propulsion Center recently demonstrated repeated freeze and quick start-up performance of GM fuel cell stacks down to -20°C., *Autoworld.com*

Water-balance considerations

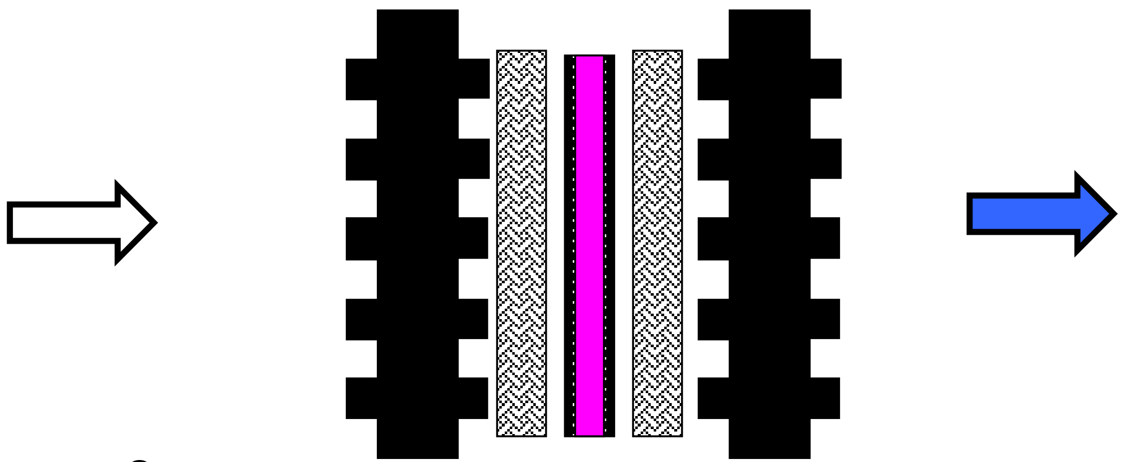
- Can freeze issue be avoided altogether by drying out the stack?
- Probably not.
  - Literature suggests that Nafion's hydrophobic "skin" becomes hydrophilic upon exposure to liquid water; drying out will require considerable rewetting to regain performance.

Sketch of hysteresis in catalyst layer



  - Simple water balances suggest that prohibitive external heating would be required to avoid formation of liquid water.

Water balance calculations

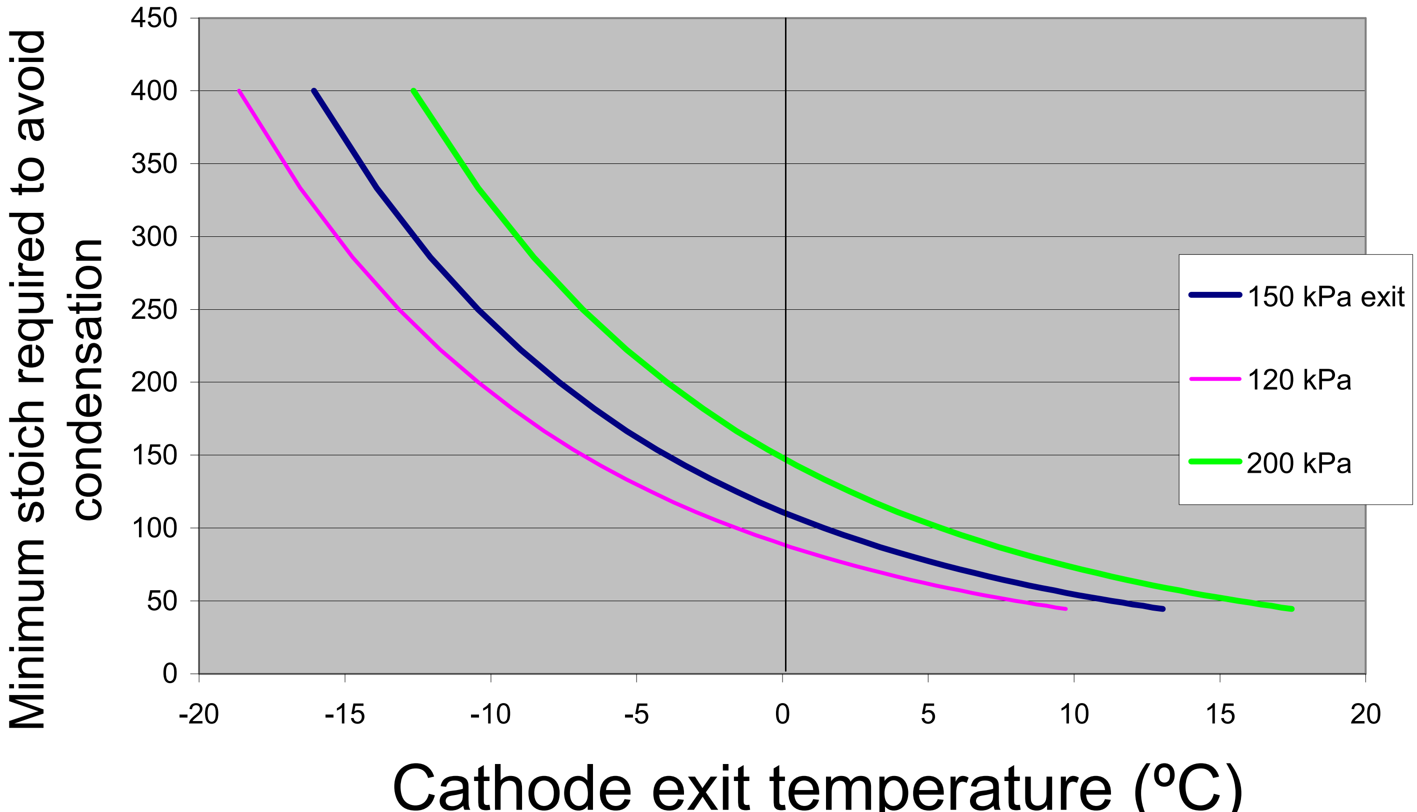


$\cancelto{0}{\text{Water in}}$ + Water generated = Water removed

$$\frac{iA}{2F} < \frac{iA}{4F}\,\frac{p_{H2O}}{p_{tot}-p_{H2O}}\left[S\left(p_{N2}^{air}/p_{O2}^{air}+1\right)-1\right]$$

Water management in cold temperatures

Even with dry membranes, need to handle liquid water/ice under cold conditions



Must remove product water by vapor or liquid transport; low carrying capacity in vapor phase because of very low saturation pressures in cold temperatures.

UTC Fuel Cells
A United Technologies Company

Outline of presentation

- Motivation
- **Stack performance**
- Technology gaps
- Recommendations

Freeze

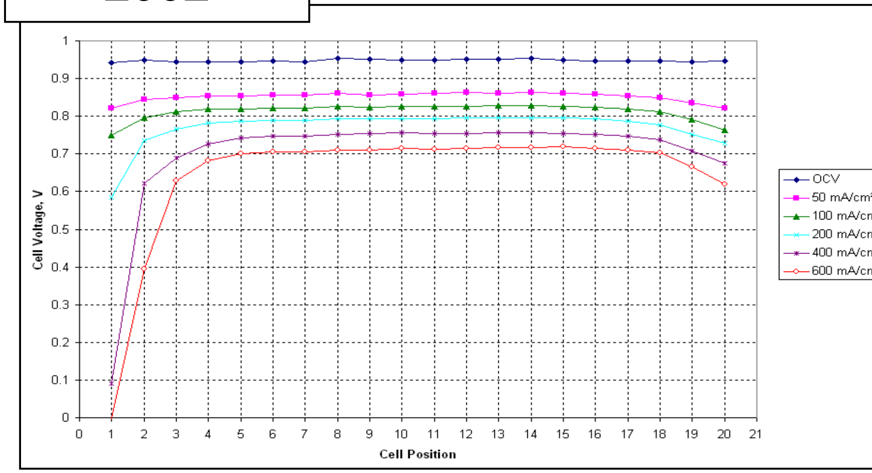
Startup cycles on 20-cell stacks;

No external heating of reactants or stack.

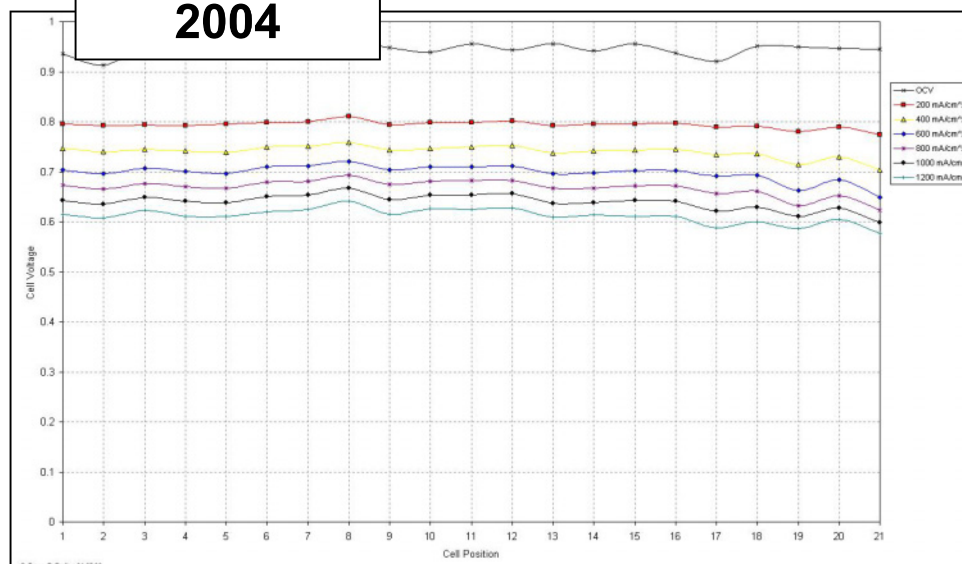
Performance decay observed in initial tests; causes investigated to develop corrective actions.

- Before: Cells on one end performed poorly after startup
- Action:
  - Investigation of water movement and cell performance response
  - Change in stack design and startup procedures
- Now:
  - Cell performance is uniform after startup
  - No recovery procedure required

2002



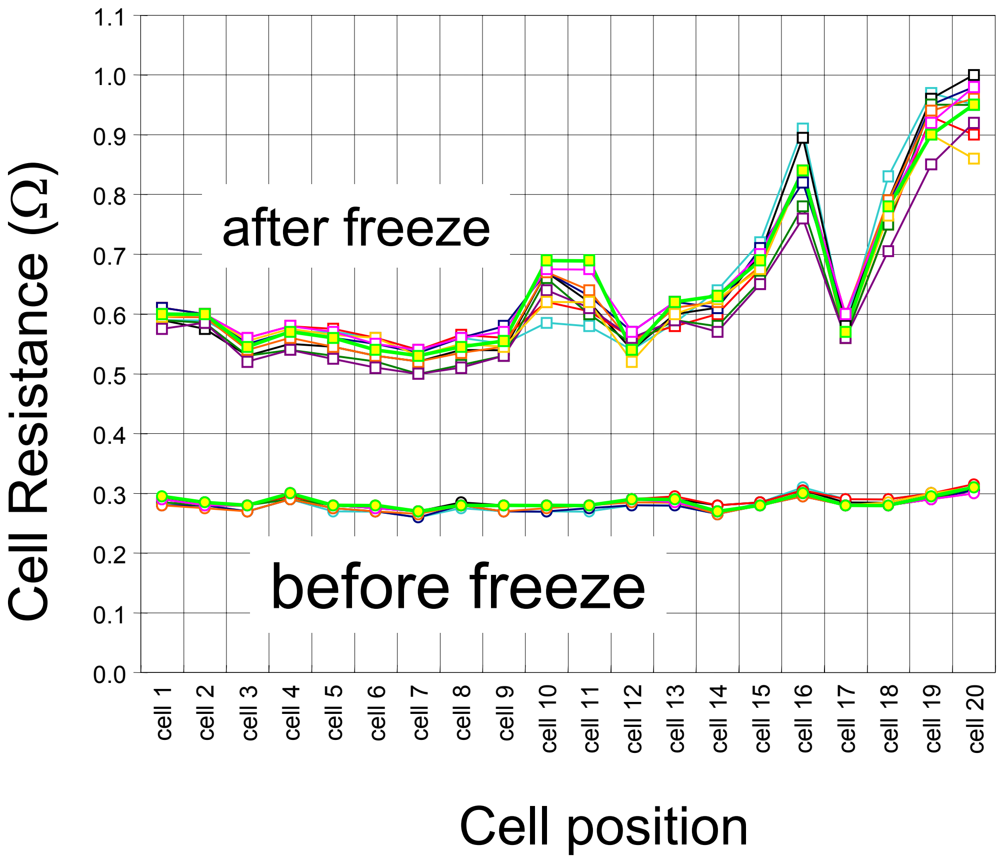
2004



UTC Fuel Cells

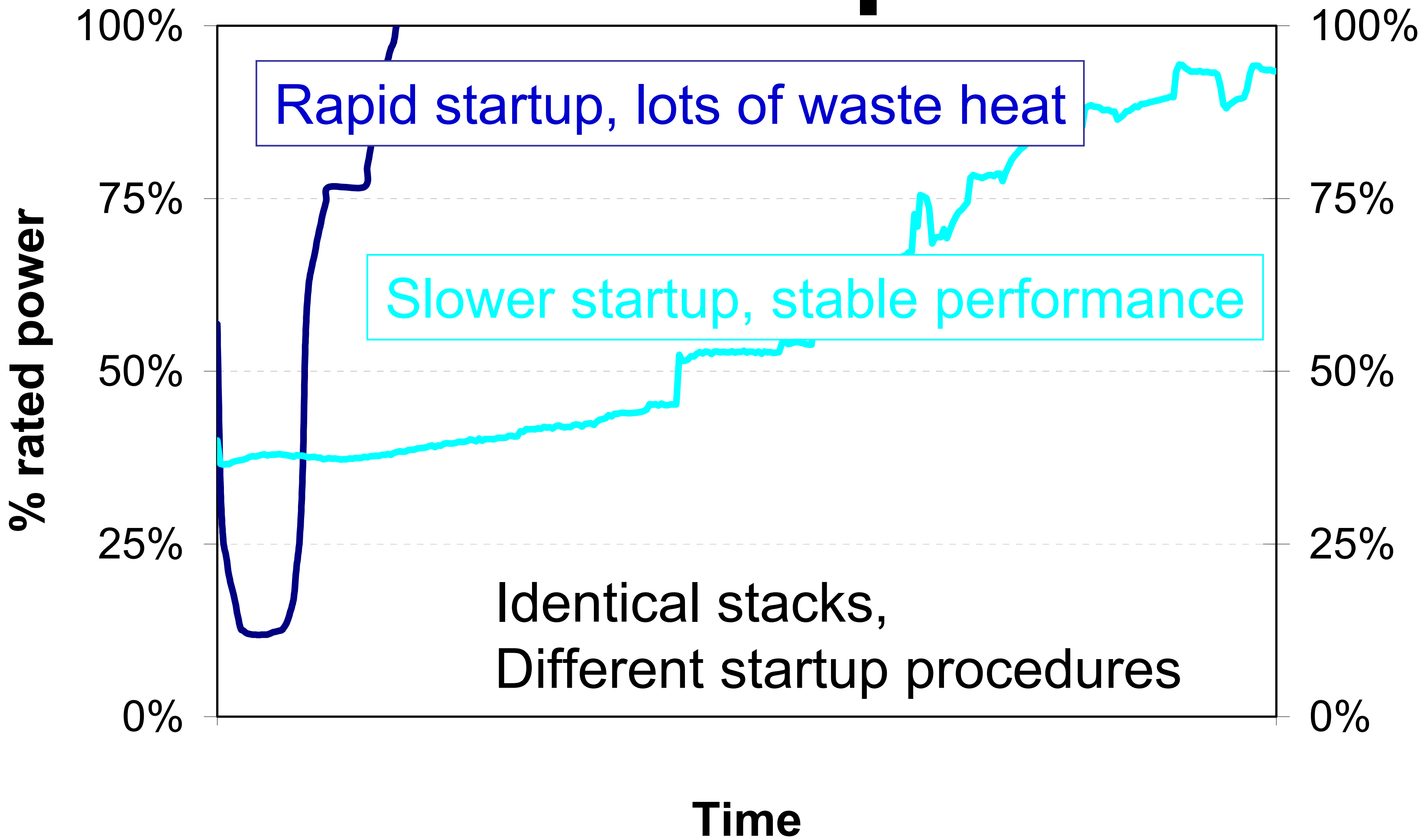
A United Technologies Company

Water redistribution can affect cell resistance



UTC Fuel Cells
A United Technologies Company

Startup



Must optimize over competing demands of system operation, stack waste heat generation, water balance

UTC Fuel Cells
A United Technologies Company

Outline of presentation

- Motivation
- Stack performance
- **Technology gaps**
- Recommendations

Technology gaps

T (°C)	Requirements	Technology gaps	Program element
> 0 °C	90,000 starts	-Electrode stability -Catalyst dissolution	N/A
-10 °C	200 starts 1-2 seconds	-Water movement during freeze/thaw process -Mitigating recoverable decay	Modeling temperature-induced water movement, fully characterizing porous media and ionomer
-20 °C	100 starts 1-2 seconds	-Increasing rate of startup -Mitigating recoverable decay -Optimizing electrode	-Neutron imaging of water distribution
-30 °C	50 starts 3-4 seconds	-Membrane and catalyst failure, state of water in ionomer, multiple phase transitions	-Reaction kinetics, catalyst layer optimization, membrane properties
-40 °C	Survive, Start w/ assist	-Membrane and catalyst failure, state of water in ionomer, multiple phase transitions	Ionic conductivity in frozen state.

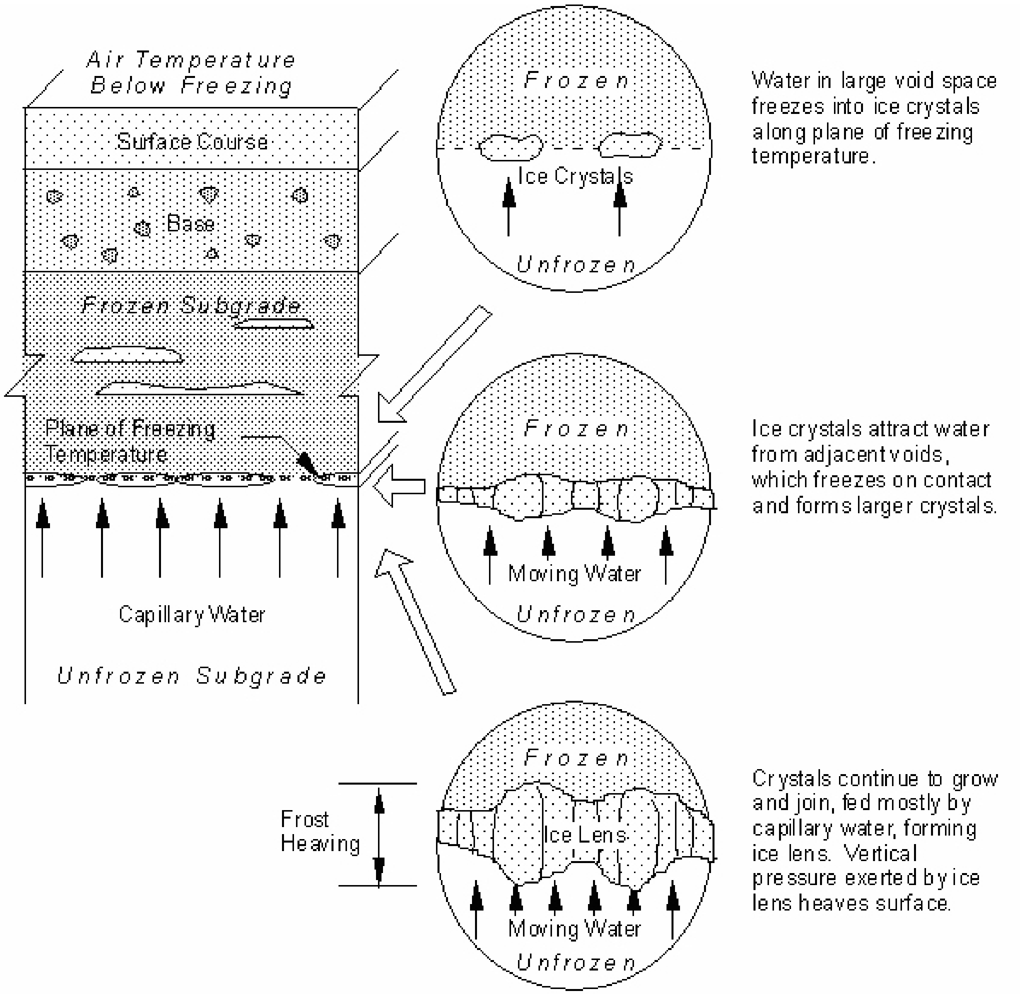
Outline of presentation

- Motivation
- Stack performance
- **Technology gaps**
- Recommendations

Outline of presentation

- Motivation
- Stack performance
- **Technology gaps**
  - **Water movement**
- Recommendations

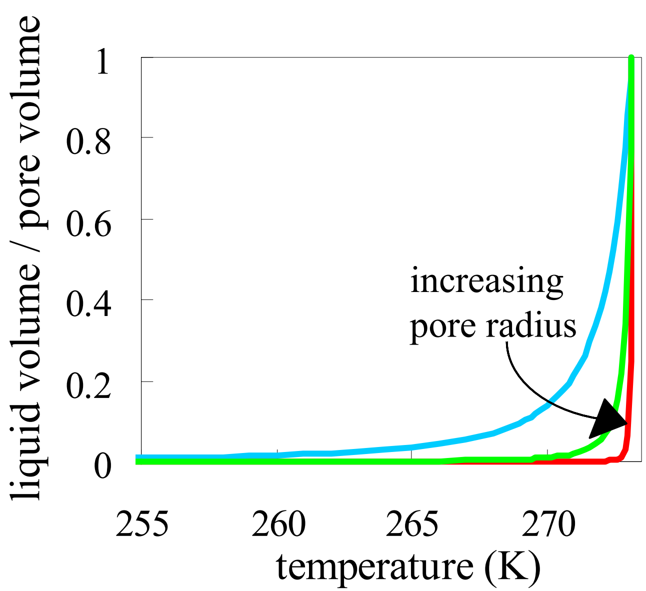
Water movement under thermal gradient near frozen conditions

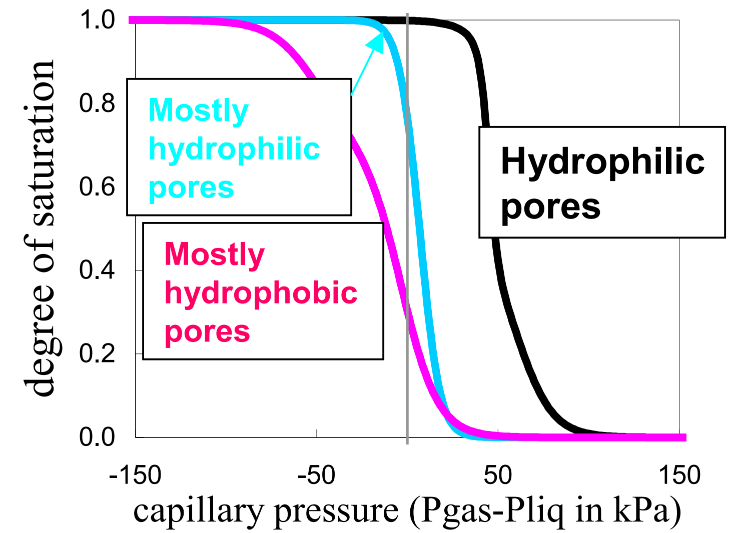


Phenomenon known in geology literature as "frost heave"

UTC Fuel Cells
A United Technologies Company

Properties of porous media





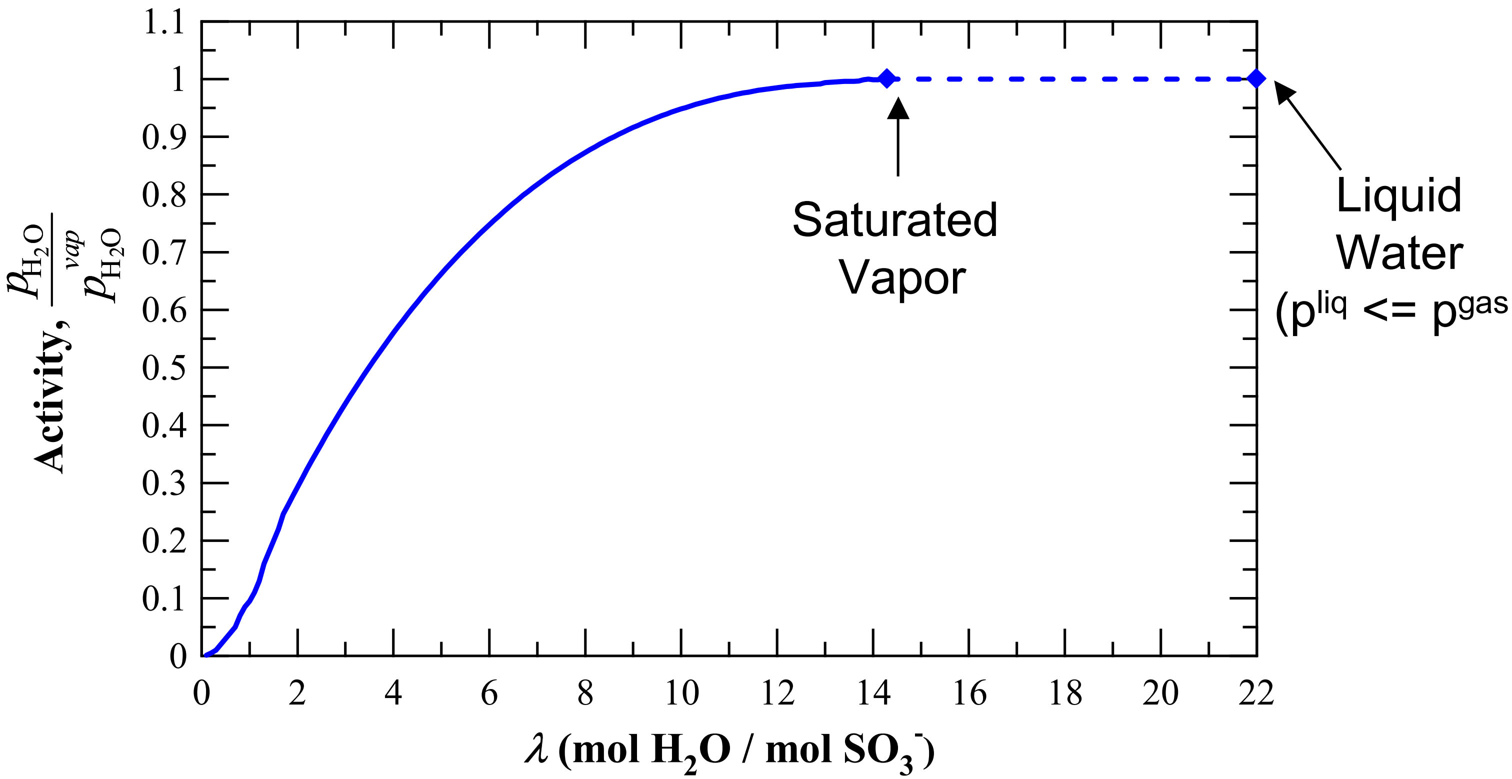
<u>Freezing-point depression:</u>

liquid water exists over range of temperature below bulk freezing

<u>Fill level of porous media:</u>

Liquid pressure depends on water content (saturation)

Membrane water uptake

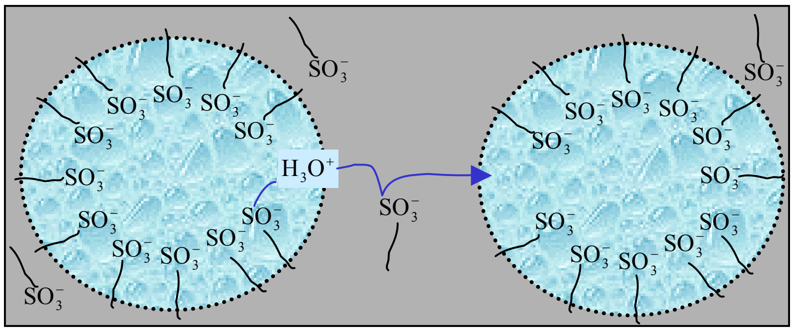


- Schroeder's paradox: Different membrane water uptake at the same chemical potential
- Need a model and methodology to handle Schroeder's paradox in fuel-cell simulations

UTC Fuel Cells
A United Technologies Company

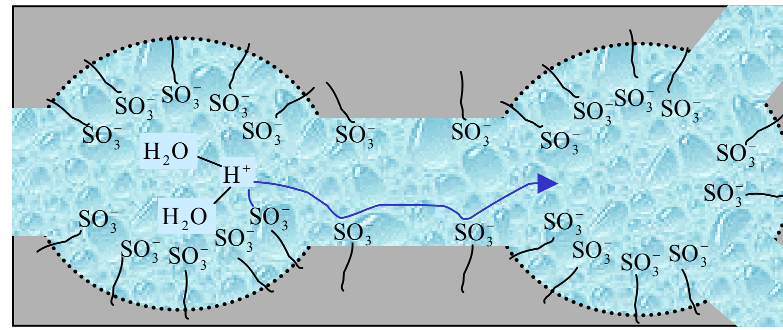
Transport Mechanisms

Vapor-equilibrated mode



- Treat as a single-phase homogenous system
- Use chemical potential gradient as the driving force for water flow
- λ is determined by the chemical potential of water

Liquid-equilibrated mode

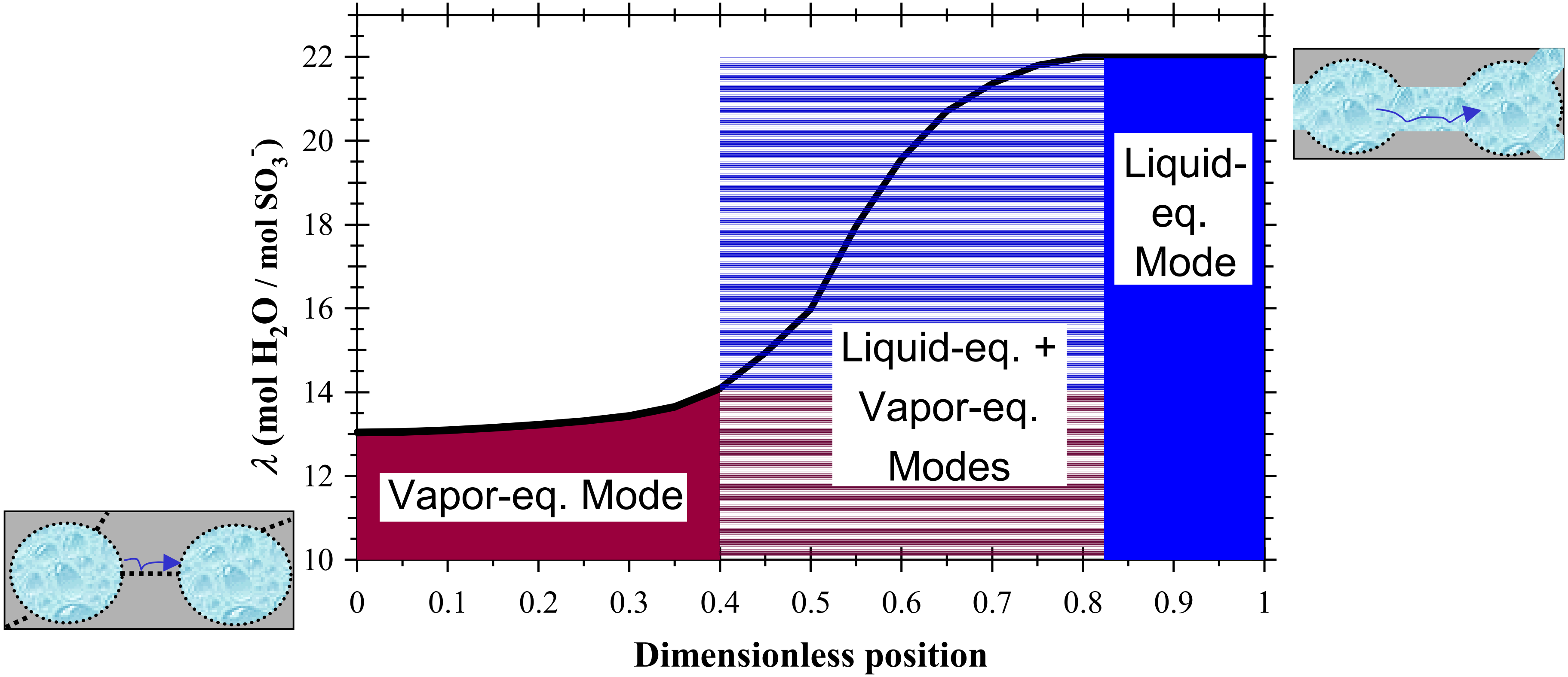


- Treat as a two-phase porous medium
- Use hydraulic pressure gradient as the driving force for water flow
- λ is set at the observed filled channel value of 22

From "A Physical Model of Transport in Polymer-Electrolyte Membranes," Adam Weber and John Newman, 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah.

UTC Fuel Cells
A United Technologies Company

Model Implementation



- Modes operate in parallel with one overall net water flux
  - Switched by the fraction of expanded channels
    - Depends on liquid pressure needed to infiltrate and expand the channels
- Permits modeling of Schroeder's paradox

UTC Fuel Cells
A United Technologies Company

From "A Physical Model of Transport in Polymer-Electrolyte Membranes," Adam Weber and John Newman, 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah.

Water movement in Nafion

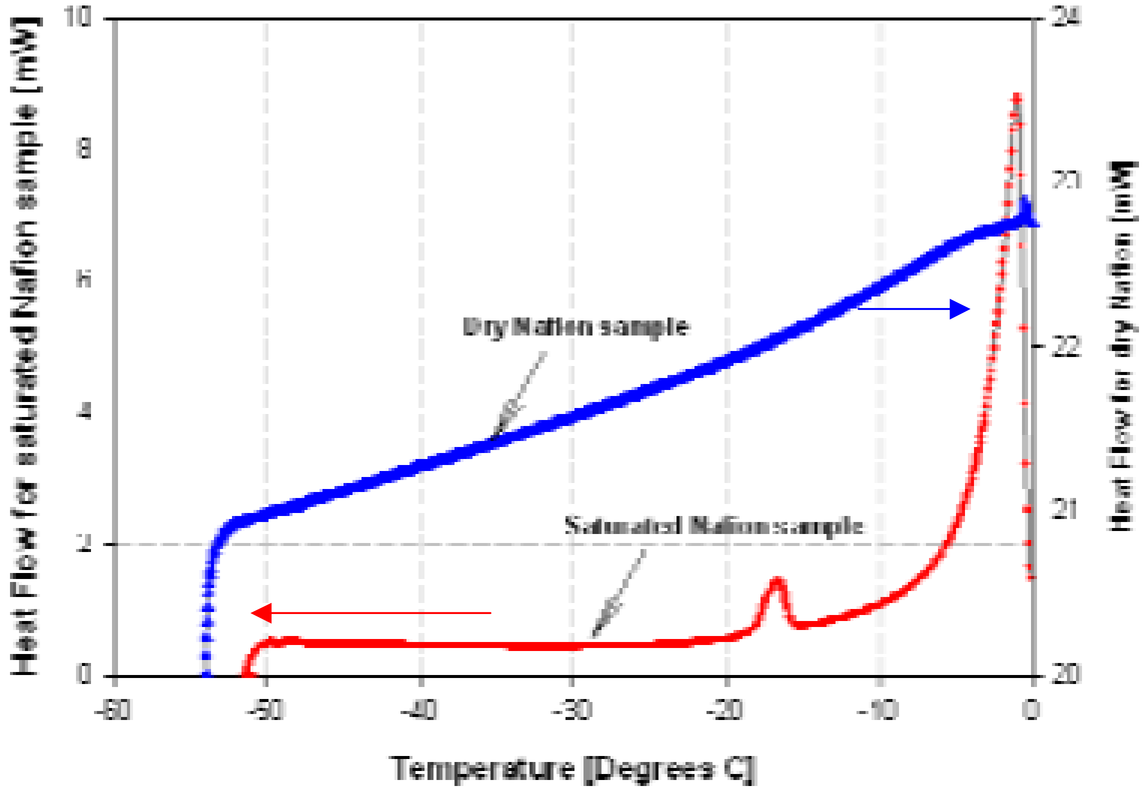
- To obtain quantitative predictions, need experimental data for the following:
  - effect of liquid pressure on water content of ionomer
  - permeability of Nafion below 0 °C
  - freezing-point depression of fuel-cell components

Outline of presentation

- Motivation
- Stack performance
- **Technology gaps**
  - Water movement
  - **Morphological changes**
- Recommendations

State of water in Nafion

Dynamic scanning calorimetry



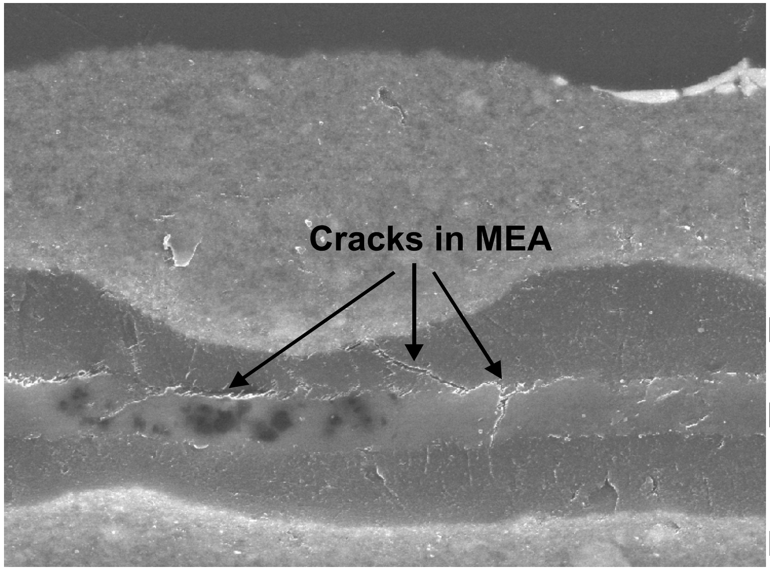
From "Behavior of Ionic Polymer-Metal Composites Under Subzero Temperature Conditions," J.W. Paquette and K.J. Kim, *Proceedings of IMECE'03*, 2003 ASME International Mechanical Engineering Congress, Washington, DC, November 2003.

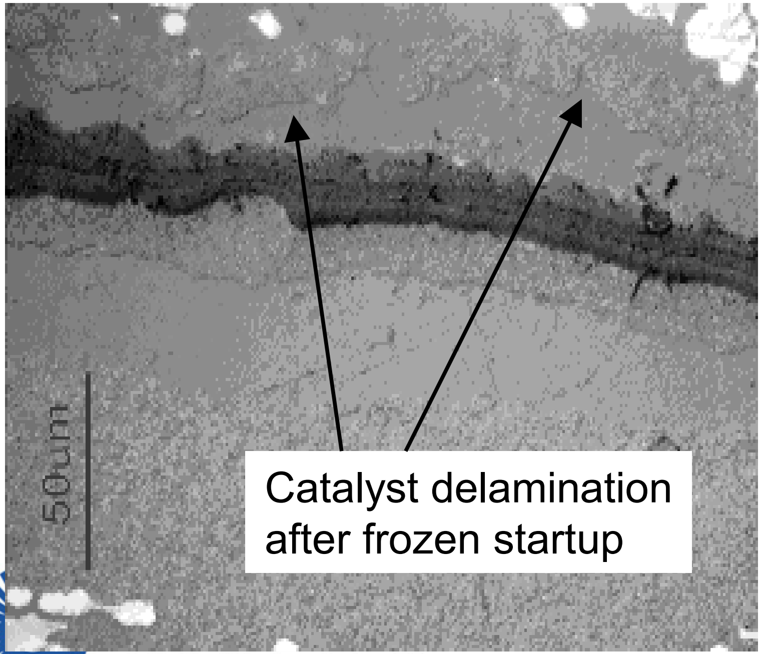
Freeze/Thaw Cyclic Decay

UTC Fuel Cells
A United Technologies Company

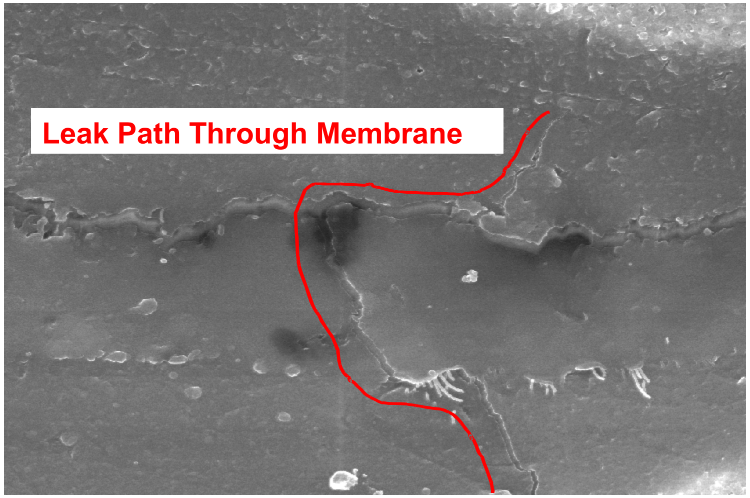
- Cracks have been observed along and through membranes due to –20°C exposure
- More severe cases show large H_2 crossover currents
- Some catalyst delamination observed on end cells

Commercial Pt/Pt MEA After 20 F/T Cycles





Cracks Develop Through Membrane Support As a Result of F/T Cycling to –20 °C



Outline of presentation

- Motivation
- Stack performance
- Technology gaps
- **Recommendations**

Research topics in subfreezing PEM

- State of water vs. T, degree of saturation in PEM fuel cell components
  - Membrane, catalyst layer, GDL's
- Morphological changes and localized stresses in fuel cell components associated with phase transition
- Water movement under temperature gradients and multiphase transport in porous media under very low temperature conditions
- Kinetics of phase change
- Tailoring materials and components to enhance freeze tolerance
- Stack design and operation to improve subfreezing operation and robustness