Fuel-Cell Fundamentals at Low and Subzero Temperatures

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Solicitation Partners:

United Technologies Research Center
Los Alamos National Laboratory
3M Company
The Pennsylvania State University

Project ID #
FC 026

June 9, 2010

Overview

Timeline

- Project initiated FY09
  - Start **September 2009**
- 4 year project duration
  - End **September 2013**
- ~15% complete

Budget

- Total project funding

DOE share:	$4,700k
Contractor share:	$445k
TOTAL:	$5145k

- Funding for FY10

LBNL	$675k
Partners	$979k
FY10 Total	$1654k

Barriers

- A. Durability
- C. Performance
- D. Water Transport within the Stack
- E. System Thermal and Water Management
- G. Start-up and Shut-down Time and Energy/Transient Operation

Partners

- Project lead**: Lawrence Berkeley NL**
- Direct collaboration with Industry, National Laboratories and University (see list)
- Other collaborations with material suppliers and those with unique diagnostic or modeling capabilities
- Discussion with related project leads

Collaboration: Organizations/Partners

- Lead
  - **Lawrence Berkeley National Laboratory**: Adam Weber, John Newman, Clayton Radke, Alastair MacDowell
- Subcontractors
  - **Los Alamos National Laboratory**: Rod Borup, Rangachary Mukundan
  - **3M Company**: Mark Debe, Andy Steinbach
  - **United Technology Research Center**: Michael Perry
  - **The Pennsylvania State University**: Chao-Yang Wang
- Other relationships (direct funded through other DOE projects)
  - **Ion Power**: Stephen Grot (Nafion® samples)
  - **SGL Carbon Group**: Peter Wilde (GDL and MPL samples)
  - **NIST**: Daniel Hussey, David Jacobson (neutron imaging of water)
  - **Oak Ridge National Laboratory**: Karren More (GDL imaging)
- Other relationships (no cost)
  - **UTC Power**: Tom Madden (freeze data)
  - **University of Michigan**: Massoud Kaviany (Nafion® molecular-dynamics simulations)

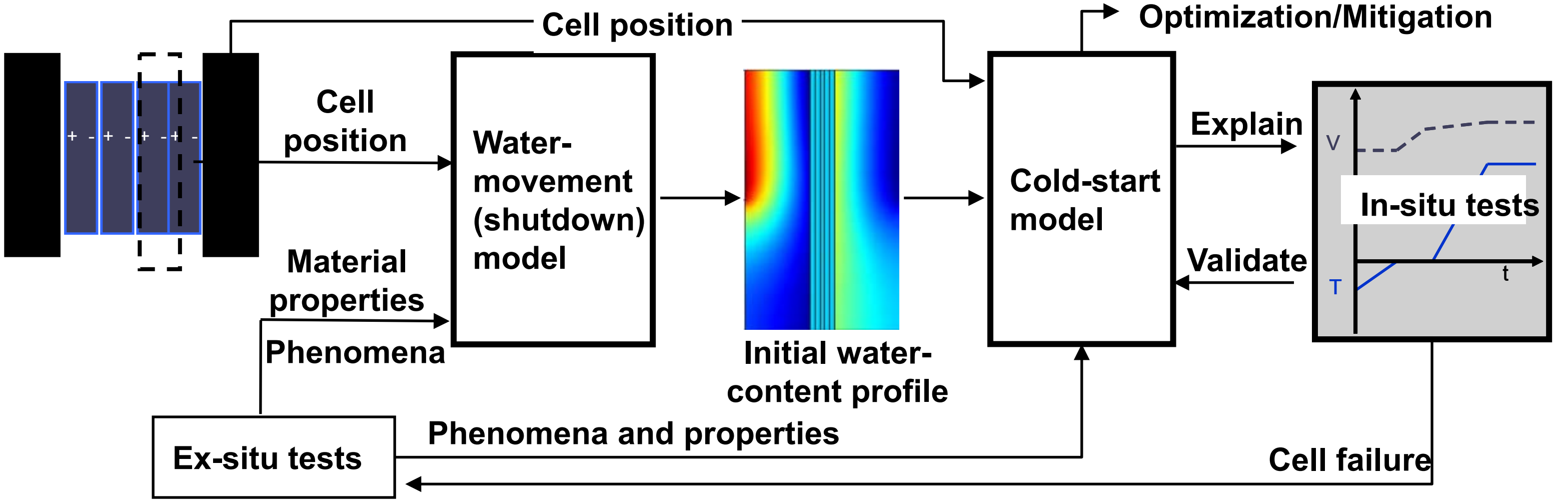
Relevance: Objectives

- Fundamental understanding of transport phenomena and water and thermal management at low and subzero temperatures using state-of-the-art materials
  - Examine water (liquid and ice) management with thin-film catalyst layers (NSTF)
  - Enable optimization strategies to be developed to overcome observed bottlenecks
    - Operational
    - Material
- Elucidate the associated degradation mechanisms due to subzero operation
  - Enable mitigation strategies to be developed

Improved understanding will allow for the DOE targets to be met with regard to cold start, survivability, performance and cost

Approach

- Synergistic effort of modeling and experimental characterization



Cell position

Optimization/Mitigation

Cell position

Material properties

Phenomena

Water-movement (shutdown) model

Initial water-content profile

Cold-start model

Explain

Validate

In-situ tests

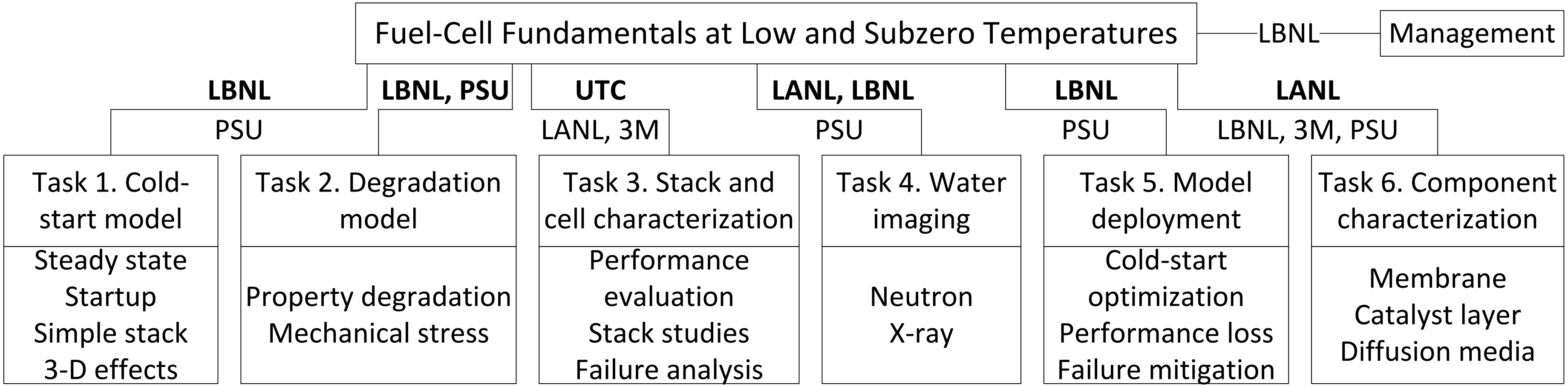
Ex-situ tests

Phenomena and properties

Cell failure

- Multiscale, multiphysics continuum-based modeling
  - Develop, validate, and refine a series of models for cell performance including cold and cool operation, startup, and shutdown
- Experimentally characterize component, cell, and stack properties and performance
  - Measure critical properties including visualizing water and ice distributions
  - Utilize various assemblies and components to elucidate governing phenomena
- Durability and degradation
  - Elucidate and mitigate critical failure mechanisms related to cold and cool operation
  - Experimentally observe and characterize failed cells

Approach: Workplan/Organization



Fuel-Cell Fundamentals at Low and Subzero Temperatures — LBNL — Management

LBNL
PSU
Task 1. Cold-start model
Steady state
Startup
Simple stack
3-D effects

LBNL, PSU
Task 2. Degradation model
Property degradation
Mechanical stress

UTC
LANL, 3M
Task 3. Stack and cell characterization
Performance evaluation
Stack studies
Failure analysis

LANL, LBNL
PSU
Task 4. Water imaging
Neutron
X-ray

LBNL
PSU
Task 5. Model deployment
Cold-start optimization
Performance loss
Failure mitigation

LANL
LBNL, 3M, PSU
Task 6. Component characterization
Membrane
Catalyst layer
Diffusion media

LBNL

- Project management and coordination
- Model development
- GDL and membrane characterization including x-ray tomography

LANL

- Ex-situ component characterization
- Single-cell durability tests
- Neutron imaging

3M

- Material supplier and testing knowledge

UTRC

- Stack and cell parametric studies
- Identify and characterize failure mechanisms
- Real-world guidance

PSU

- Help with x-ray studies and traditional, supported catalyst-layer diagnostics
- Develop 3-D scaling expressions and mechanical stress model

Other

- Provide unique materials and diagnostics

Approach: FY10 Project Timeline

Begin
09/09

M1
03/10

M2
06/10

M3
07/10

M4, M5, M6
09/10

End
09/10

<u>Major Milestones/Deliverables</u>

M1: Baseline cell assembly (material set) defined. *(Delayed, 40% complete)*

M2: Stack data and model agree (< 10% error) with respect to thermal and mass boundary conditions and cell position. *(On-track, 90% complete)*

M3: Complete round-robin baseline cell testing of sub-scale cells under normal and low temperature conditions. *(Delayed, 30% complete)*

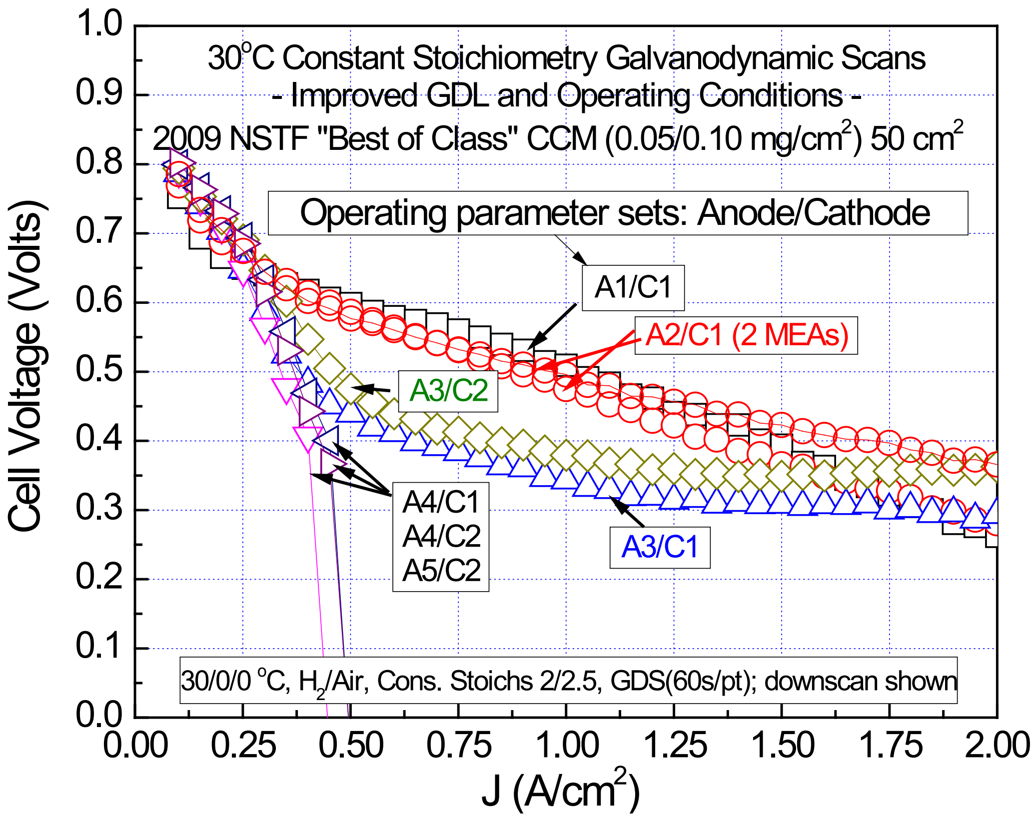
M4: Diagnostic method to quantify ice formation in traditional catalyst layers developed. *(On-track, 80% complete)*

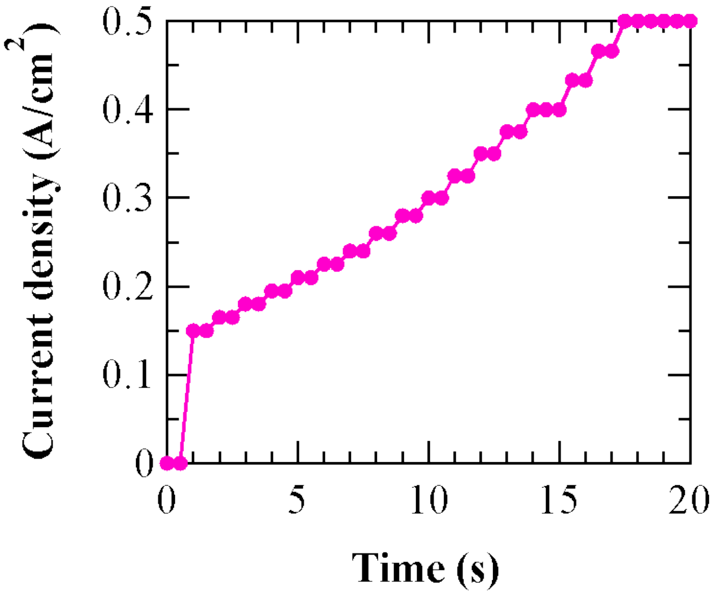
M5: Simulation results showing the 2-D changes in water distribution and phase during shutdown conditions. *(On-track, 80% complete)*

M6: Description and design of experimental setup to measure the kinetics of freeze in GDLs. *(On-track, 30% complete)*

Baseline Performance

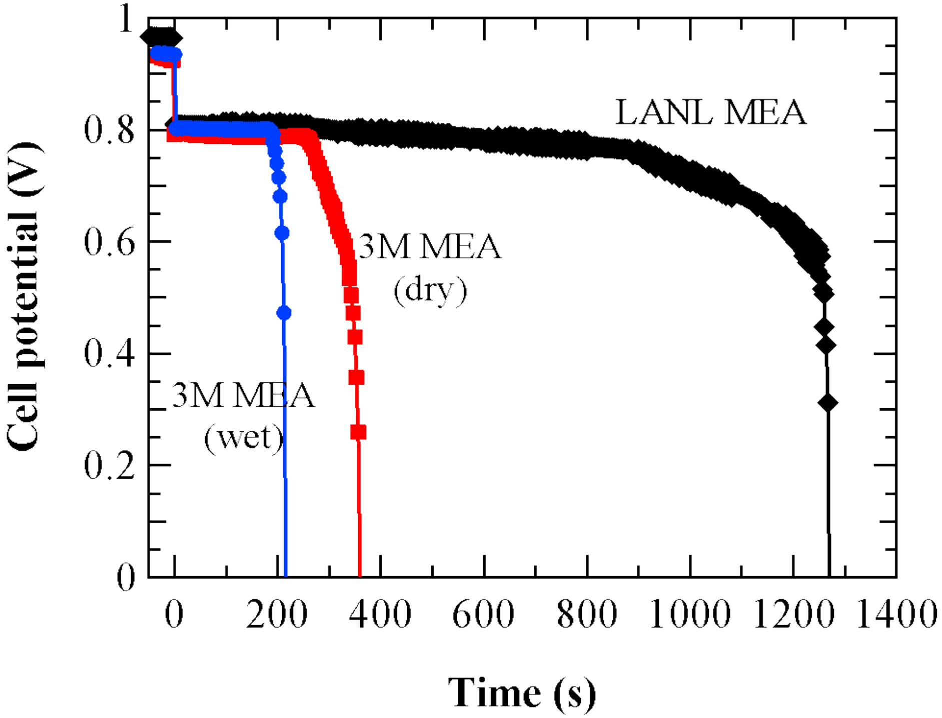
- 3M has demonstrated much improved NSTF single-cell, low temperature performance due to improved GDLs and operating conditions
  - Greatly improved limiting current density
- Even if have poor single-cell performance, stack operation is quite different





  - Successful short-stack startup at 10°C using A4/C1 cells

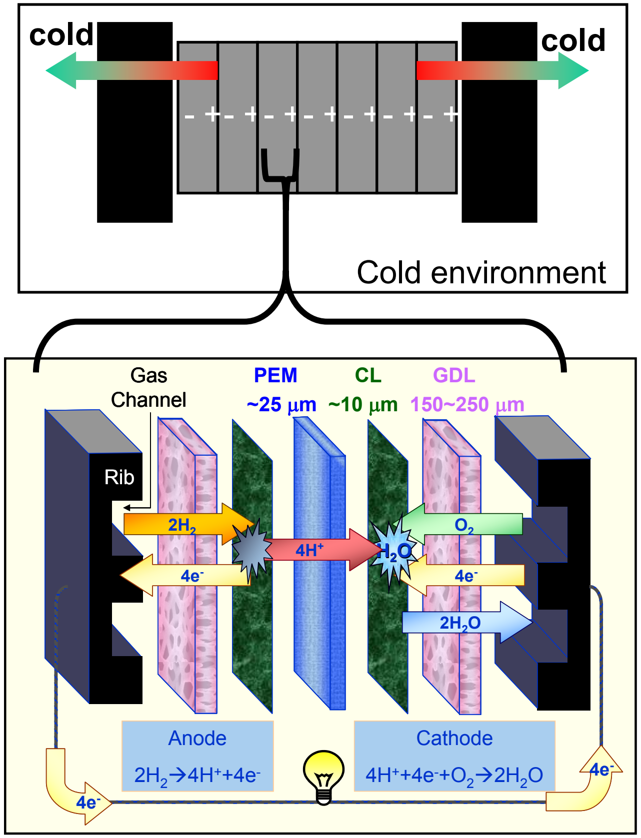
Baseline Performance: Isothermal Start



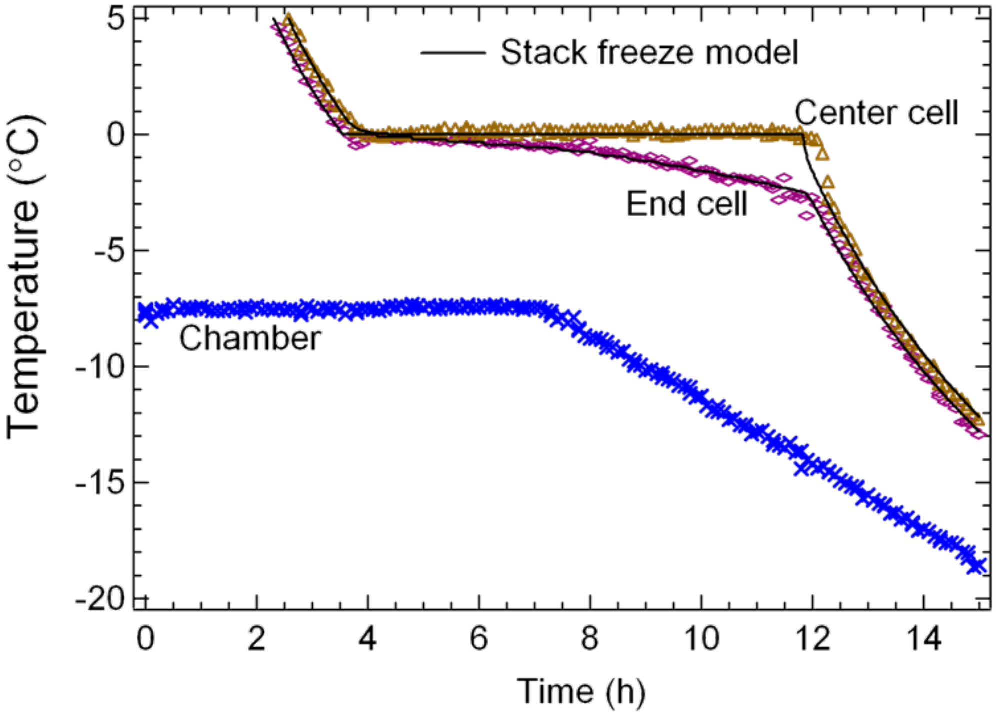
- Comparison of cold start at 10 mA/cm^2, –10°C between NSTF and supported-catalyst cells
  - NSTF shows shorter time to failure
  - Charge passed corresponds to membrane uptake capacity
    - Water transferred to membrane and not out through diffusion medium
- Need more studies, especially examining durability with cycling

Modeling Cell Position

- Utilize simple thermal cooldown model for the stack
  - Calibrate to experimental data
  - Temperature as a function of time becomes simulation boundary condition
  - Can add in thermal mass and behavior of adjacent cells (e.g., current)



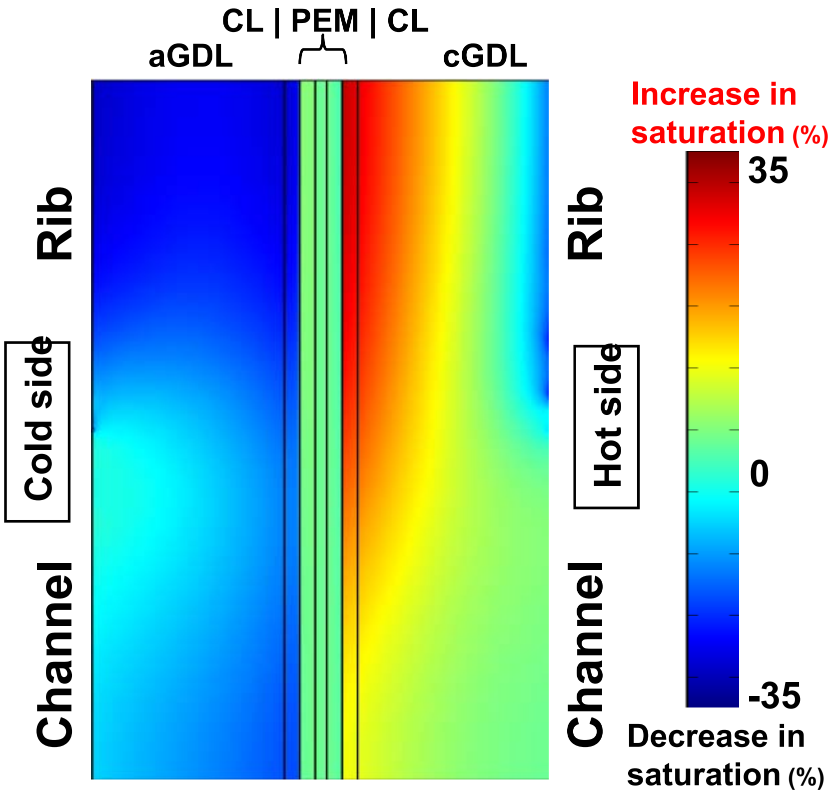
Freeze of a 30-cell stack



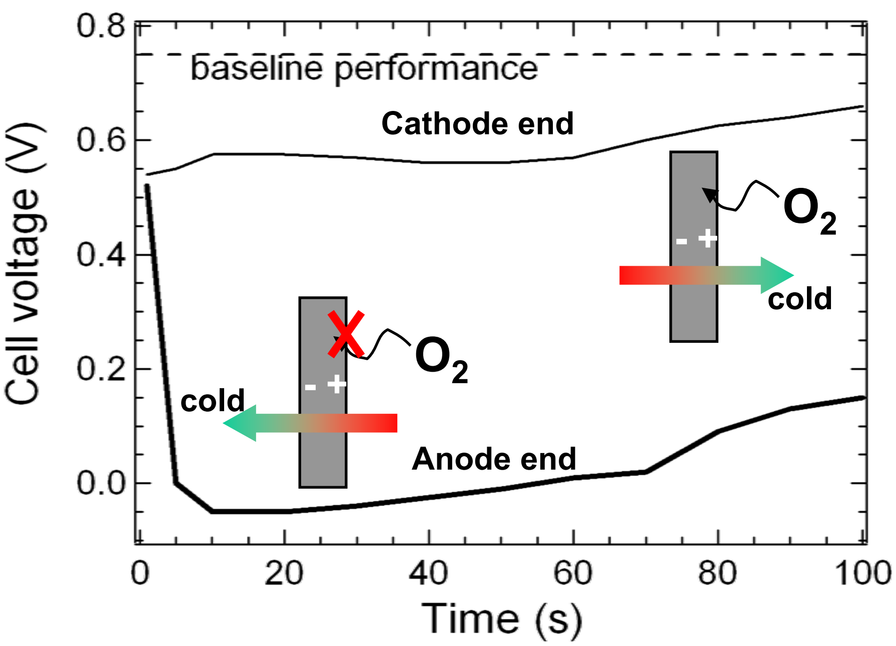
R. J. Balliet, K. E. Thomas-Alyea, J. Newman, ECS Transactions, 16 (2), 285 (2008)

Water Movement: Shutdown

- As cell cools, phase-change-induced (PCI) flow causes water redistribution
  - Depends on shutdown procedure, stack position, and how the cell cools
- Water redistribution can create mass-transport problems on startup



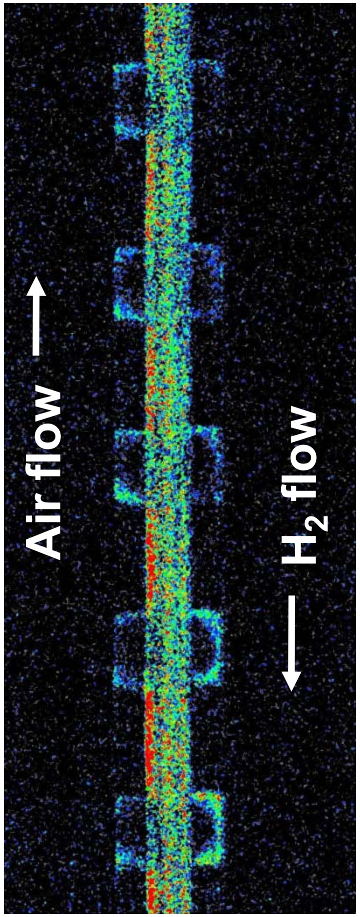
30-cell stack start from –12°C at 0.4 A/cm^2



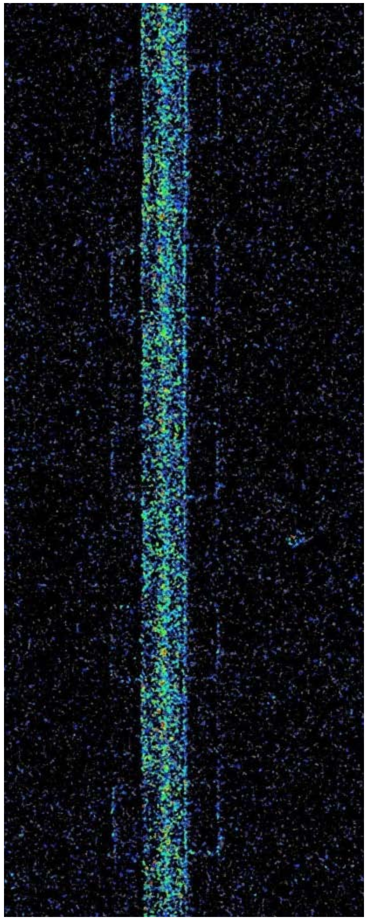
Data: T. W. Patterson, J. O'Neill, and M. L. Perry, Report DE-FG36-06GO86042, DOE (2007)

Water Movement: Shutdown

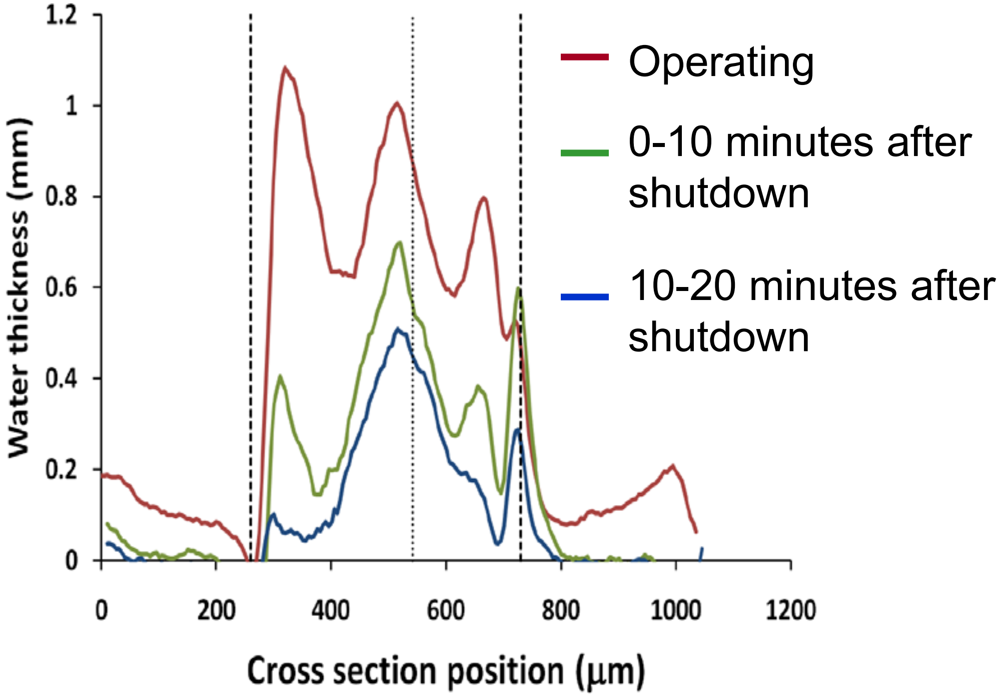
Operating 1 A/cm^2



0-10 minutes after shutdown



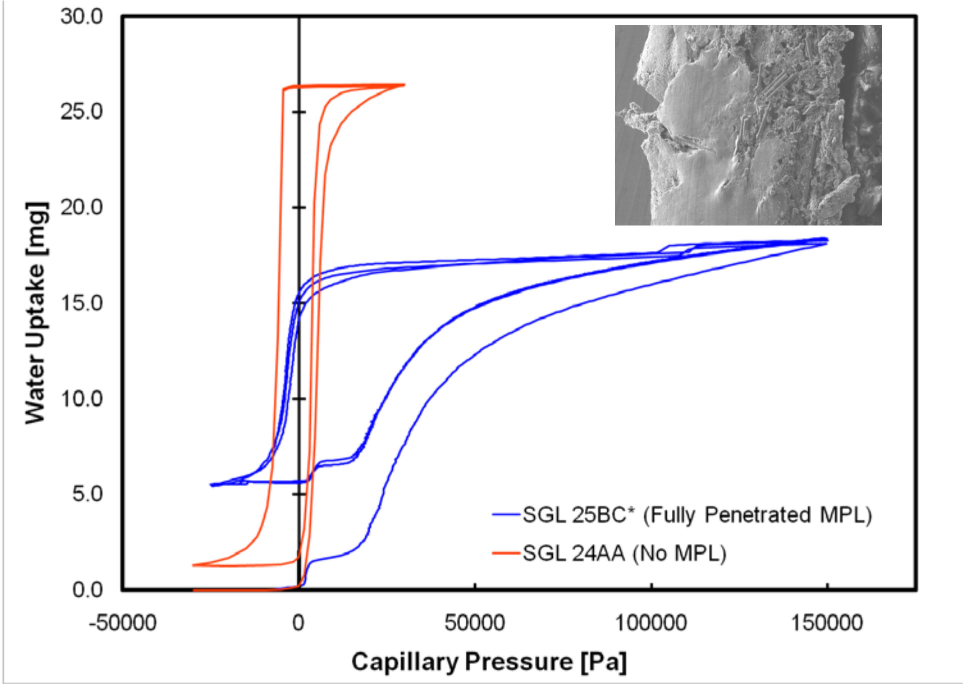
Water profiles

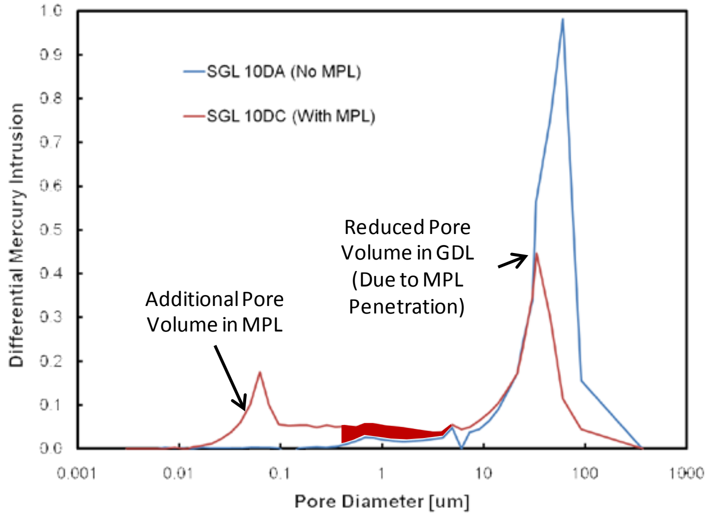


- Redistribution and lowering of water content, even with humidified feeds
  - More water towards MEA
  - Anode DM stays wetter than cathode DM

Cell details:
Gore® 710 MEA, SGL 24BC GDLs
100% RH anode/cathode, 50/100 sccm H_2/air
Anode at 80°C, cathode cooling from 80 to 67°C

MPL Capillary Pressure – Saturation Curves





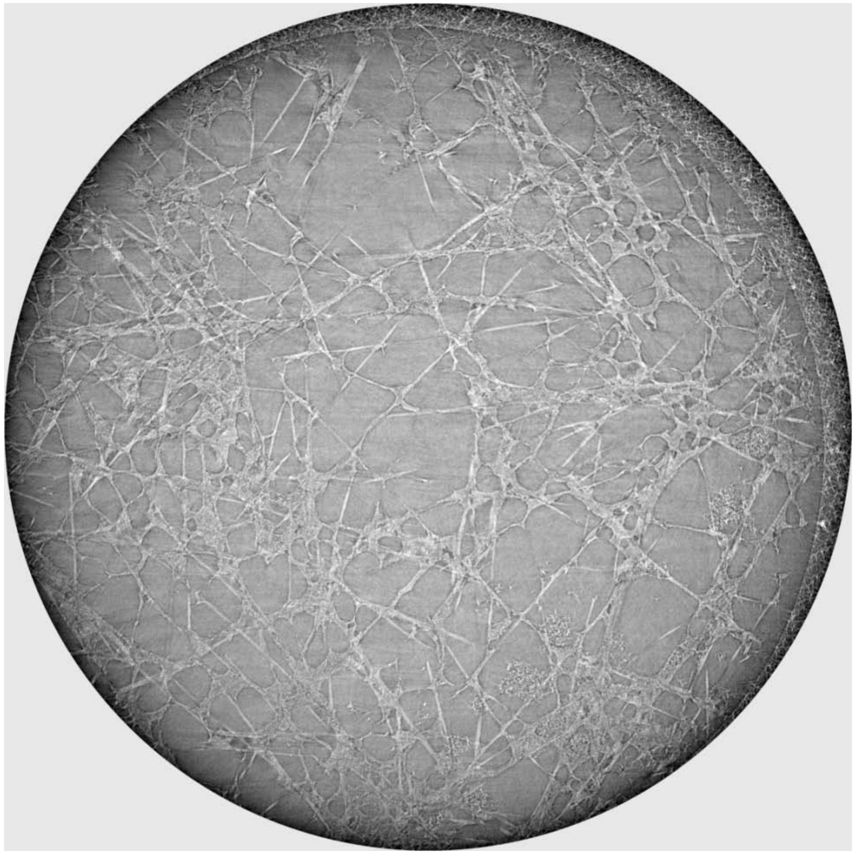
Reduced Pore Volume in GDL (Due to MPL Penetration)

Additional Pore Volume in MPL

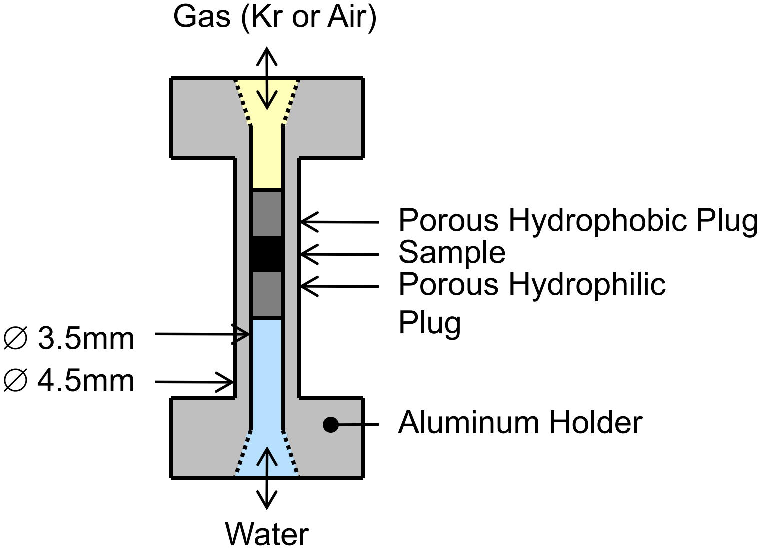
- Custom made samples with fully penetrated MPLs
  - Minimize substrate effects
- Not much water is spontaneously ejected from MPL, similar to GDL behavior
  - Neutral wettability
- Much more hydrophobic signature than GDL
- Complete filling of MPL was not achieved; much higher pressures are required
  - 2 atm (current limit) will fill down to ~ 300 nm hydrophobic pores

Visualizing Water Distributions

- Designed setup to examine water distribution during capillary pressure – saturation measurements using x-ray microtomography at ALS

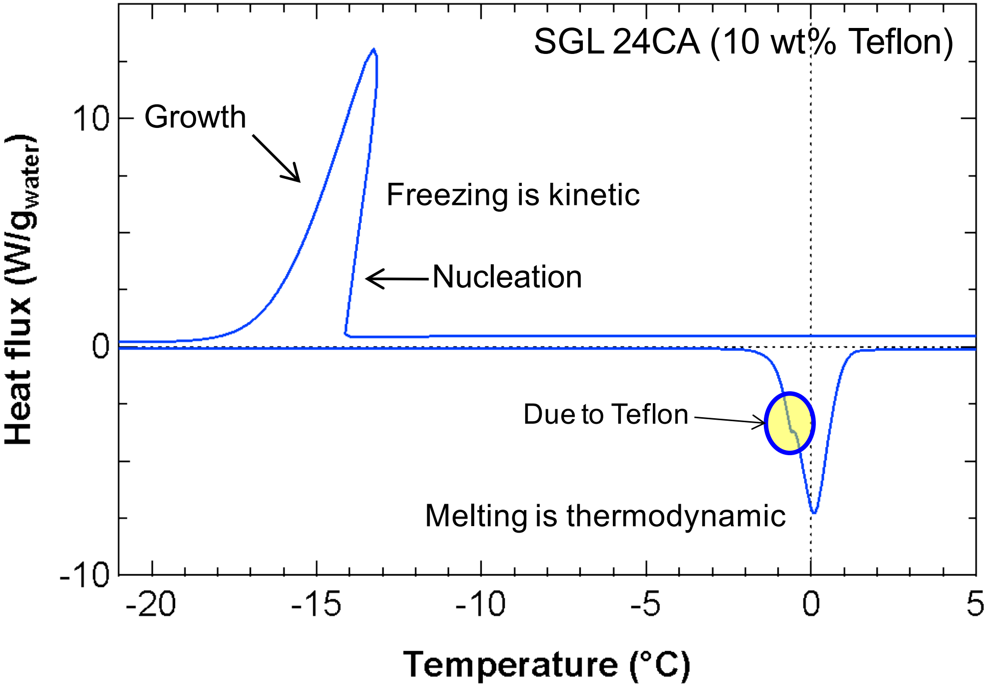


- Sub-micron spatial resolution with relatively good temporal resolution
- Issues remain of cell leakage and image segmentation



Freezing Fundamentals

- Use Dynamic Scanning Calorimetry (DSC) to determine water freeze rate in GDLs
  - Vacuum fill GDL and then place in DSC, run at 5 °C/min for several cycles
- Can model the freeze curve using nucleation and growth theory with overall heat balance
  - From nucleation theory:



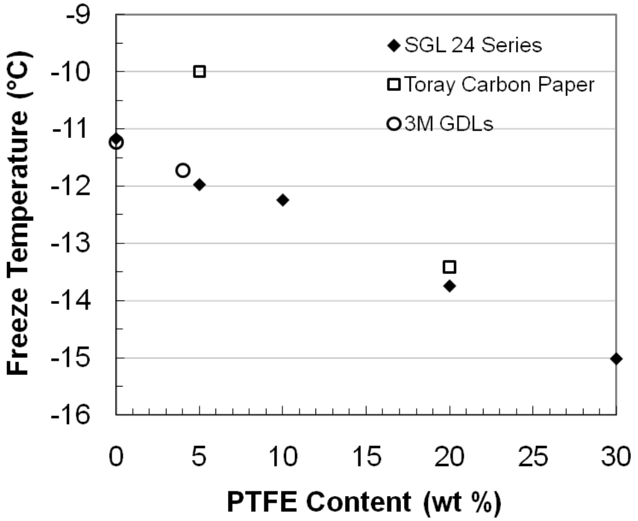
$$\frac{d\varepsilon_{\text{ice}}}{dt} = k(T)\left(1-\varepsilon_{\text{ice}}(t)\right) \qquad k(T) = \frac{k_b T}{3\pi\eta}\exp\left(\frac{-\Delta G^*(T) f(\theta)}{k_b T}\right) \qquad \Delta G^*(T) = \frac{16\pi\sigma^3}{3\Delta H_f^2}\frac{T_0^2}{(T-T_0)^2}$$

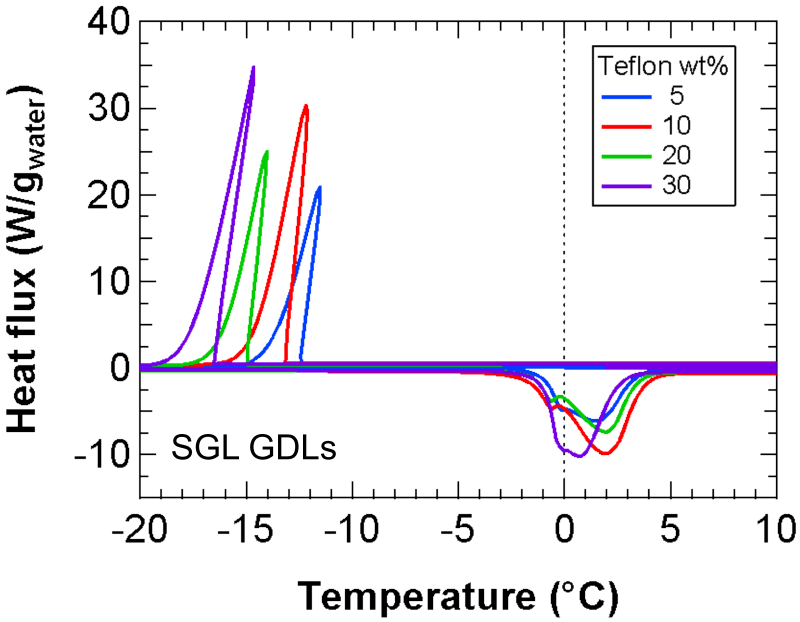
    - ☞ Nucleation gives expected curve properties/values but growth expression is unknown
  - Need more sophisticated model
  - Simple rate expressions (e.g., linear or constant) cannot fit the curve shape or data

DSC - Effect of Teflon® Addition

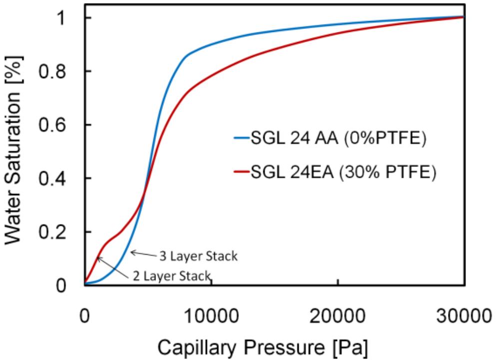
- As add Teflon®, freeze peak shifts
  - Linear decrease in freezing temperature
    - Depends on microstructure?
  - Relative change can be predicted from nucleation theory when accounting for varying surface energy in $k(T)$

$$\cos\theta = f_T \cos\theta_T + (1 - f_T)\cos\theta_c$$





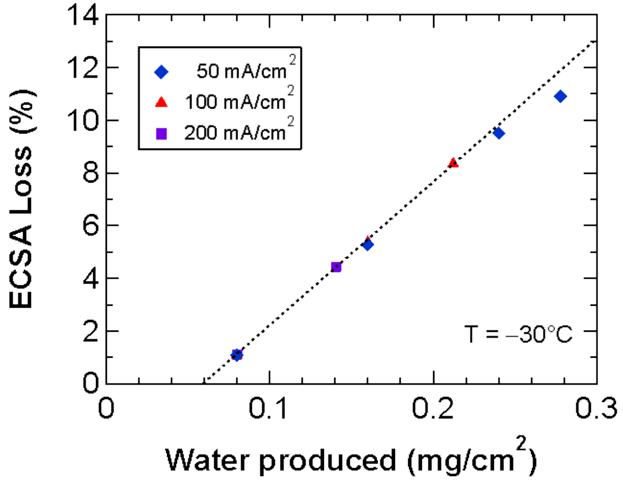
- As add Teflon®, second, lower temperature peak forms and grows in melting peak
  - Suggests some small microporosity
    - Agrees with capillary-pressure measurements

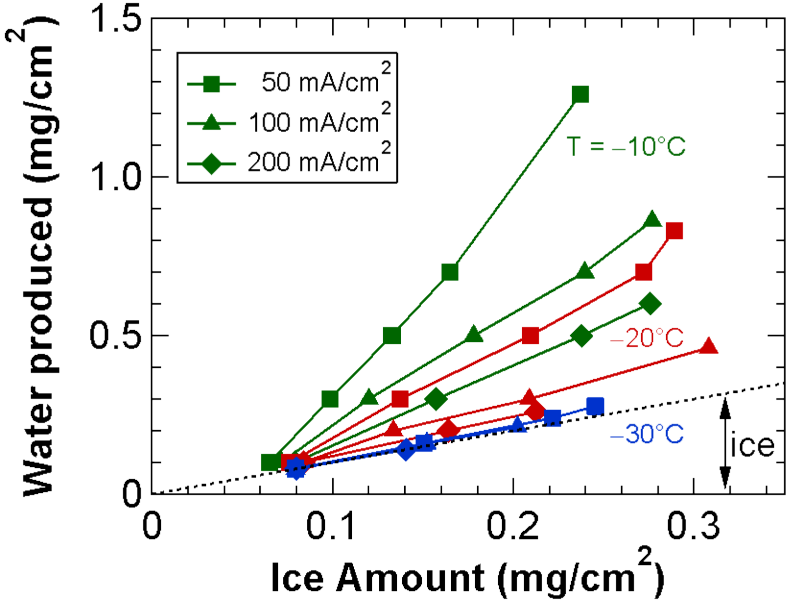


Determining Catalyst-Layer Ice

- Determine ice amount in supported catalyst layer by subzero cyclic voltammetry after isothermal starts
- Total ice amount should be proportional to ECSA loss at very low temperature and high current density
  - Water immediately freezes at reaction site

$$m_{H2O,CL}\,(\mathrm{mg/cm^2}) = 0.059 + 0.018\Delta ECA\,(\%)$$





- After have correlation, use it to understand how much water is reaction-site-blocking ice in catalyst layer
  - Substantial amount of water moves out of catalyst layer
    - Occurs more at higher temperatures and lower current densities
  - Water probably moves to the membrane so initial hydration and storage capacity are key

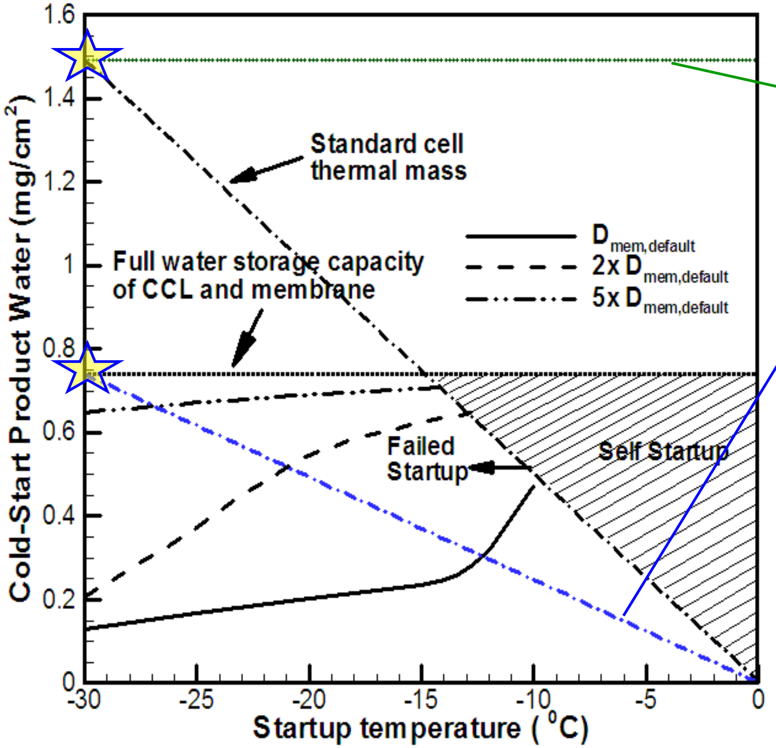
Design Map for Cold Start

- Simple approach of examining transport and storage capacity needed for successful cold start

$$(mc_p)T_o \le (E_h - V_{cell})It = \frac{2F(E_h - V_{cell})}{M_{H2O}}\left(W_{cap,CL} + W_{cap,m}\right)$$

$$\frac{W_{cap,CL}+W_{cap,m}}{mc_pT_o} \ge 0.106 \quad \text{[mg/J]} \Rightarrow \boxed{\frac{\delta_m \Delta\lambda_m}{mc_pT_o} \ge 32.7}$$

where δ_m is in μm and $(mC_p)_{cell}$ is in J/cm²K



Double water-storage capacity (double membrane thickness)

One-half cell thermal mass (of standard value)

necessary conditions for self startup of a PEFC with 1μm thick CL from –30°C

Future Work

- Cell performance
  - Round-robin testing and definition of the baseline assembly
  - Testing of non-baseline assemblies
  - Isothermal and adiabatic starts including cycling studies for tracking durability
- Component characterization
  - Consolidate/measure membrane properties at subzero conditions
  - Diffusion media
    - Neutron imaging of shutdown and water redistribution
    - Capillary pressure – saturation relationships
      - Impact of flowrate, temperature, injection sites (MPL analogs), materials
      - X-ray tomography for the water distribution
    - Measure effective gas diffusion coefficient and relative permeability versus saturation
    - Measure and model freeze rate and ice-front propagation as a function of saturation
- Modeling of shutdown, cold start, and isothermal start
- Stack studies for temperature distribution and performance characterization
- Understand and increase the operating window with thin-film catalyst layers

Summary

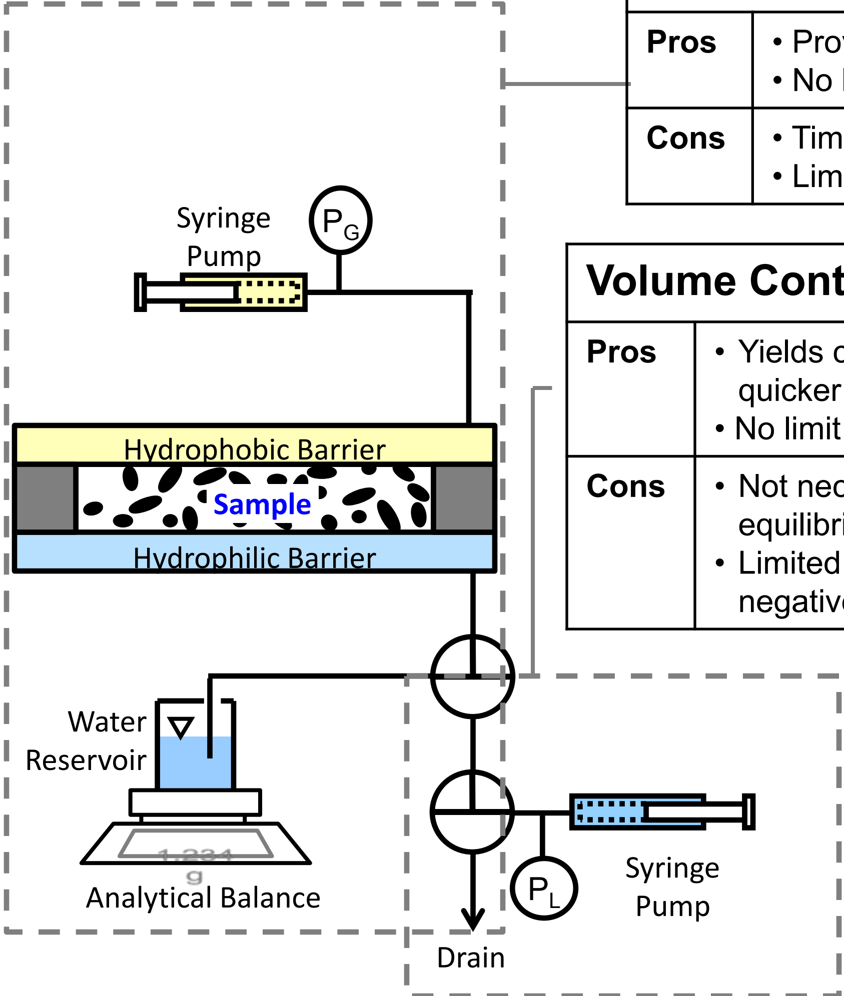
- **Relevance/Objective**:
  - Help to enable, optimize, and mitigate failure in state-of-the-art materials through fundamental understanding of operation at low and subzero temperatures
- **Approach/Collaborations**:
  - Use synergistic combination of cell, stack, and component diagnostic studies with advanced mathematical modeling at various locations (national laboratories, industry, and academia)
- **Technical Accomplishments**:
  - Preliminary baseline cell studies including isothermal starts
  - Development of novel experimental diagnostics for CL ice, GDL freeze, and GDL liquid-related properties
  - Modeling of water movement during shutdown including cell-position effects
- **Future Work**:
  - Fundamental understanding of liquid-water movement, interactions, and freeze in fuel-cell components
  - Benchmarking cell and stack performance and durability with different assemblies

Supplemental Slides

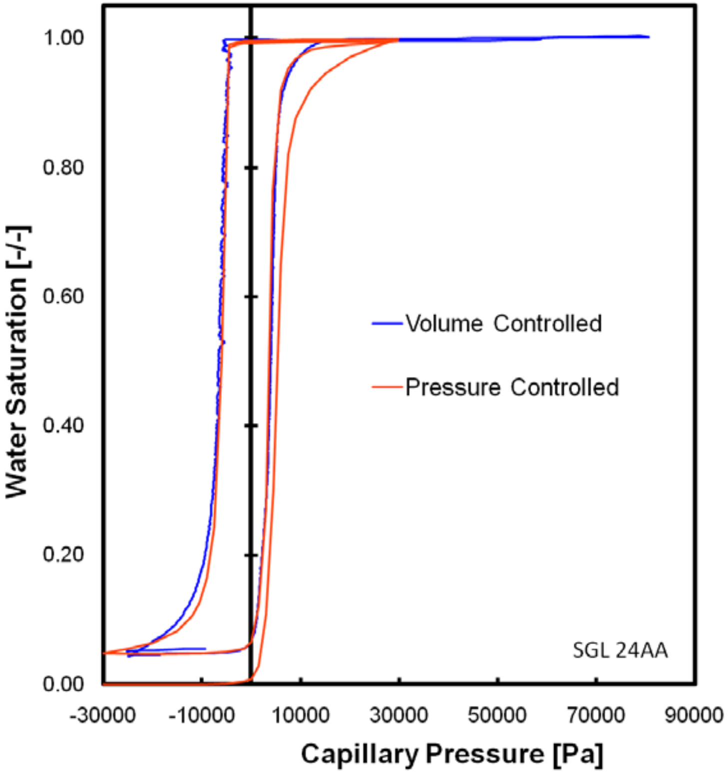
Understanding Layer Wetting Properties

- One key property is the capillary pressure – saturation relationship
  - Designed apparatus to measure this accurately for various FC components

Pressure Controlled	
Pros	• Provides true equilibrium P_C-S_W curves • No limit on negative P_C
Cons	• Time consuming • Limited to < 1 atm positive P_C



Volume Controlled	
Pros	• Yields curves somewhat quicker • No limit on positive P_C
Cons	• Not necessarily true equilibrium curves • Limited to < 1 atm negative P_C



Cell Assemblies

- Utilize various assemblies to elucidate governing and controlling phenomena

Material	Baseline	Alternative 1	Alternative 2
Membrane	3M 850 EW	Gore	3M variable thickness
Catalyst layer	NSTF PtCoMn	Supported carbon	NSTF advanced
GDL	Hydrophobized	SGL	MRC
MPL	Hydrophobic	Very hydrophobic	Mixed property
Flow field	Quad serpentine	Parallel channel	Single channel
Bipolar plate	Solid	WTP	Hybrid (one WTP)

Governing Water Equations

Energy balance

$$\overline{\rho C}_{P}\frac{\partial T}{\partial t}+\nabla\bullet(-\bar{k}_{\mathrm{T}}\nabla T)=\Delta\hat{H}_{\mathrm{f}}R_{\mathrm{f}}$$

Darcy’s law & material balance for water

$$\rho_{\mathrm{L}}\frac{\partial\varepsilon_{\mathrm{L}}}{\partial t}+\nabla\bullet(-\frac{\rho_{\mathrm{L}}k}{\eta_{\mathrm{L}}}\nabla p_{\mathrm{L}})=-R_{\mathrm{f}}$$

Rate of freeze

$$R_{\mathrm{f}}=\rho_{\mathrm{i}}\frac{\partial\varepsilon_{\mathrm{i}}}{\partial t}$$

$$R_{\mathrm{f}}=k_{\mathrm{f}}(\varepsilon_{\mathrm{L}}-\varepsilon_{\mathrm{L}}^{*})$$

Sum of volume fractions

$$\varepsilon_{\mathrm{G}}+\varepsilon_{\mathrm{L}}+\varepsilon_{\mathrm{i}}+\varepsilon_{\mathrm{pm}}=1$$

transport & kinetics

Volume-fraction/capillary-pressure

$$\varepsilon_{\mathrm{L}}=\varepsilon_{\mathrm{L}}(p_{\mathrm{L}}-p_{G})=\varepsilon_{\mathrm{L}}(p_{\mathrm{C}})$$

Volume-fraction/temperature (below 0°C)

$$\varepsilon_{\mathrm{L}}^{*}=\varepsilon_{\mathrm{L}}^{*}(T)$$

Relative perm./capillary-pressure

$$k_{\mathrm{r}}=k_{\mathrm{r}}(p_{\mathrm{c}})$$

characteristic relationships

Neglect

Vapor-phase transport (low *T*)

Convective heat transfer (Pe <<1)

Phases (3)

L liquid

i ice

G gas

Unknowns (8)

T, p_{L}

$\varepsilon_{\mathrm{G}}, \varepsilon_{\mathrm{i}}, \varepsilon_{\mathrm{L}}, \varepsilon_{\mathrm{L}}^{*}$

$R_{\mathrm{f}}, k_{\mathrm{r}}$

Multiphase Flow Model

Key assumptions

- Hydrophilic and hydrophobic pore-size distributions (PSDs)
- PSDs can be unimodal or bimodal
- Modes follow a log-normal distribution
- Neglects temperature, hysteresis effects

$\varepsilon_L(p_C)$

$$r_c = -\frac{2\gamma_{GL}\cos\theta_{c,L}}{p_c} \Rightarrow S_h = \sum_k \frac{f_{r,k}}{2}\left[1+\vartheta_h \operatorname{erf}\left(\frac{\ln r_c - \ln r_{0,k}}{s_k\sqrt{2}}\right)\right] \Rightarrow S_L = \frac{\varepsilon_L}{\varepsilon_0}$$

$$\Downarrow$$

$k_r(p_c)$

$$k_r = \frac{S_e^2}{2}\sum_k f_{r,k}\left[1+\vartheta_h \operatorname{erf}\left(\frac{\ln r_c - \ln r_{0,k}}{s_k\sqrt{2}} - s_k\sqrt{2}\right)\right]$$

$$S_e = \frac{S_L - S_L^0}{1 - S_L^0}$$

effective saturation

$$S_L^0 = -5.3202\varepsilon_0^5 + 17.062\varepsilon_0^4 - 21.706\varepsilon_0^3 + 13.692\varepsilon_0^2 - 4.816\varepsilon_0 + 0.9989$$

residual saturation

$\varepsilon_L^*(T)$

$$r_c^* = \frac{-2\gamma_{iL}T_m\cos\theta_{c,i}}{\rho_i\Delta\hat{H}_f(T_m - T)} \Rightarrow S_h^* = \sum_k \frac{f_{r,k}}{2}\left[1+\vartheta_h \operatorname{erf}\left(\frac{\ln r_c^* - \ln r_{0,k}}{s_k\sqrt{2}}\right)\right] \Rightarrow S_L^* = \frac{\varepsilon_L^*}{\varepsilon_0}$$

Nomenclature

indices

h	philic (HI) or phobic (HO)
k	phase or distribution (1 or 2)

PSD characteristics

$f_{r,k}$	fraction in distribution *k*
$r_{0,k}$	characteristic radius
s_k	characteristic spread
$\theta_{c,L}$	contact angle, liquid
$\theta_{c,i}$	contact angle, ice

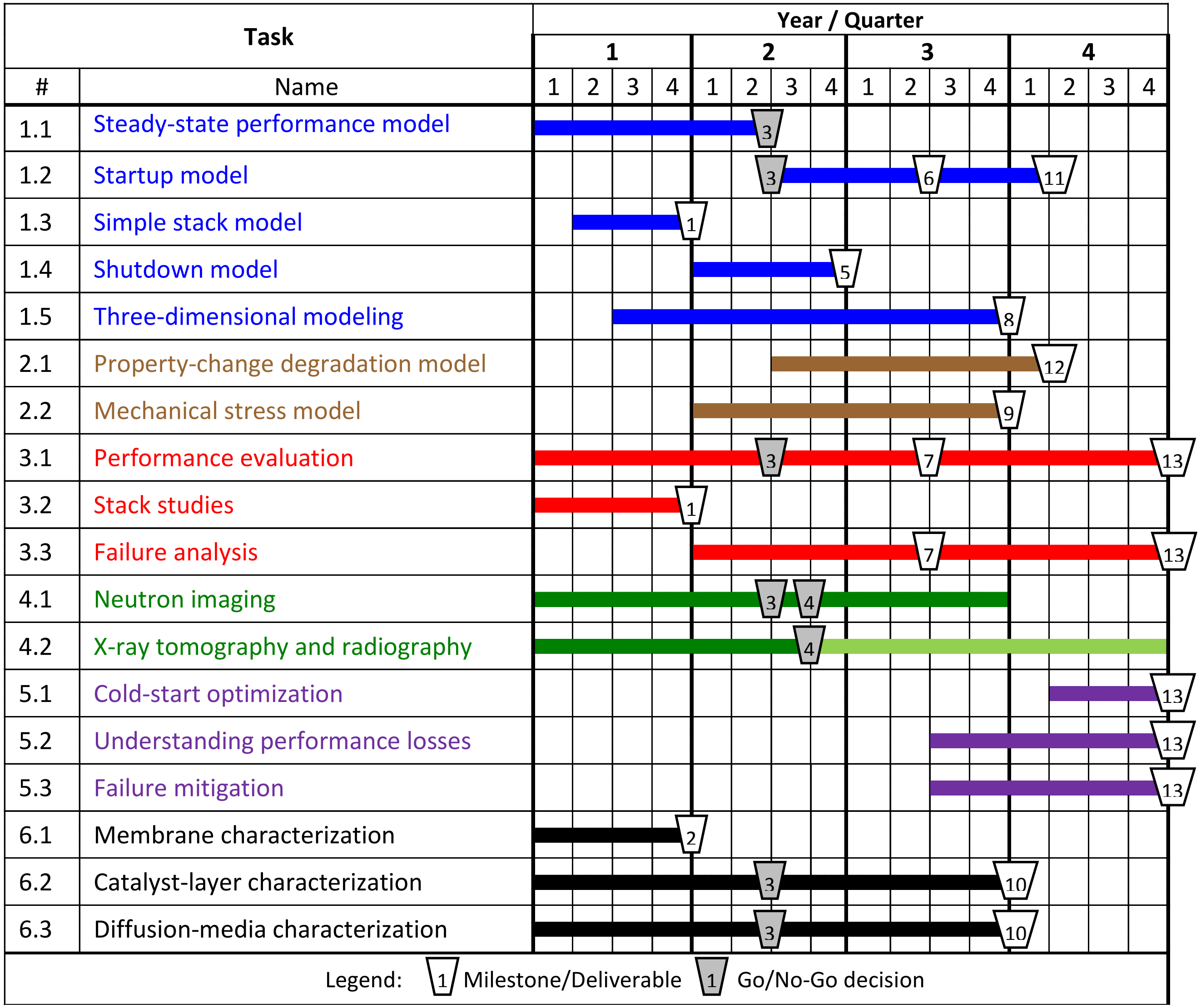
other

$\Delta\hat{H}_f$	specific heat of fusion
T_m	melting point of bulk water
ϑ_h	equal to 1 for HI, -1 for HO
γ_{kL}	surface energy, *k* = G or i
ρ_k	density of phase k

Adapted from: A. Z. Weber, R. M. Darling, and J. Newman, *J. Electrochem. Soc.*, **151**, A1715 (2004).

Project Timeline

- Main tasks
  - Performance modeling
  - Durability modeling
  - Cell and stack characterization
  - Imaging
  - Mitigation and optimization
  - Component characterization



Task #	Name
1.1	Steady-state performance model
1.2	Startup model
1.3	Simple stack model
1.4	Shutdown model
1.5	Three-dimensional modeling
2.1	Property-change degradation model
2.2	Mechanical stress model
3.1	Performance evaluation
3.2	Stack studies
3.3	Failure analysis
4.1	Neutron imaging
4.2	X-ray tomography and radiography
5.1	Cold-start optimization
5.2	Understanding performance losses
5.3	Failure mitigation
6.1	Membrane characterization
6.2	Catalyst-layer characterization
6.3	Diffusion-media characterization

Legend: 1 Milestone/Deliverable 1 Go/No-Go decision