# 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**

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# Overview

## Timeline

- Project initiated FY09
  - Start **September 2009**
- 4 year project duration
  - End **September 2013**
- ~30% complete

## Budget

- Total project funding
  - DOE share: $4,700k
  - Contractor share: $445k
  - TOTAL: $5145k
- Funding for FY11
  - LBNL $570k
  - Partners $453k
  - FY10 Total $1023k

## 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, Rachid Zaffou
  - **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**: Robert Darling (freeze data)
  - **University of Michigan**: Massoud Kaviany (Nafion® MD simulations, ESEM)

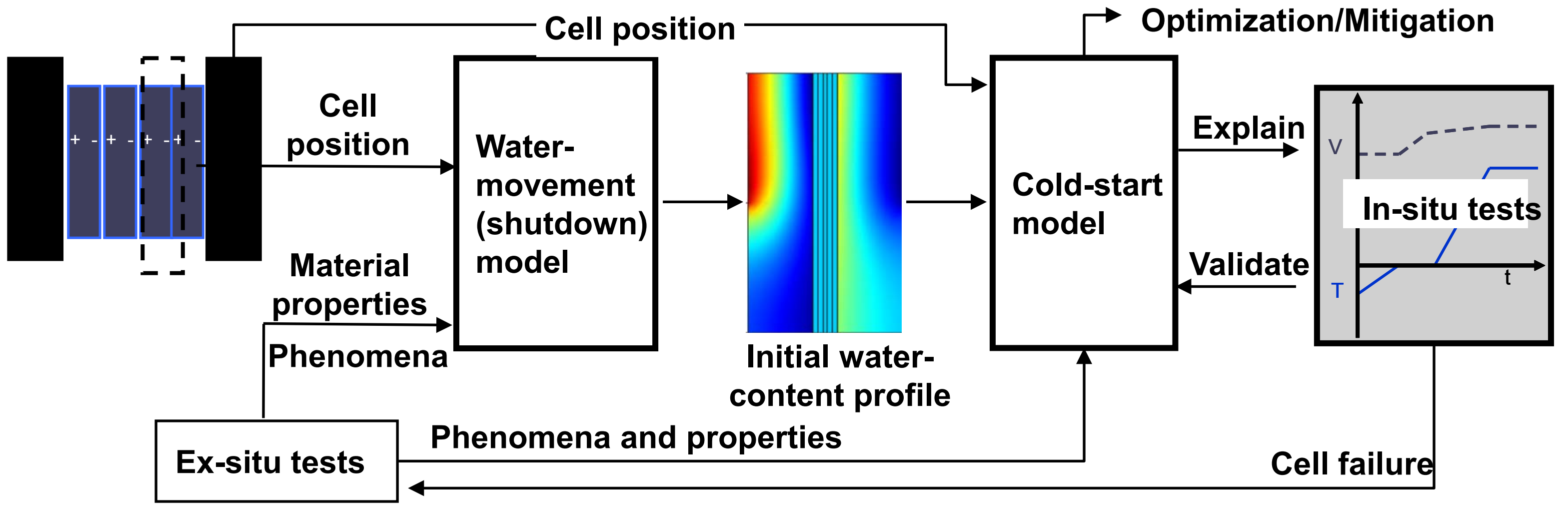
# Relevance: Objectives

- Detailed 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 traditional and 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**

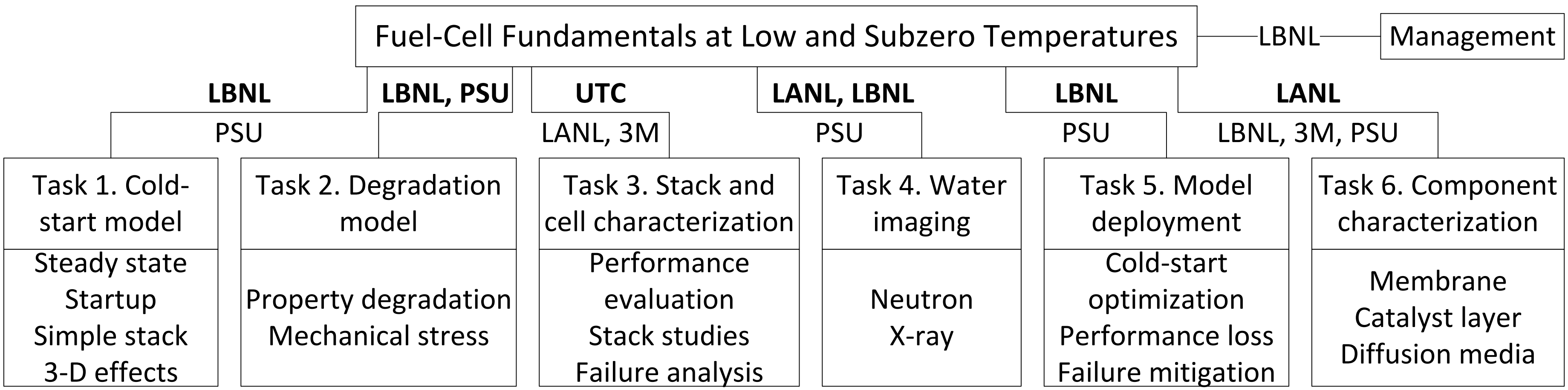
# Approach

- Synergistic effort of modeling and experimental characterization




- 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




## LBNL

- Project management and coordination
- Model development
- Ex-situ component characterization

## 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 traditional, supported catalyst-layer diagnostics
- Develop 3-D scaling expressions

## Other

- Provide unique materials and diagnostics

# Approach: FY11 Project Timeline

| Begin | M1, M2,M3 | M4 | M5 | M6, M7 | End |
|---|---|---|---|---|---|
| 09/10 | 03/11 | 04/11 | 06/11 | 09/11 | 09/11 |

<u>Major Milestones/Deliverables</u>

M1: Steady-state model with NSTF converges. *(completed)*

M2: Complete baseline testing of sub-scale cells under normal and low temperature conditions, as well as starts from frozen state from various participants. *(delayed, 70% complete)*

M3: Data/model agreement (< 10%) for isothermal starts at different temperatures and current densities. *(delayed, 80% complete)*

M4: Device for capillary pressure – saturation curve measurement at the ALS fabricated and tested with results for different GDLs obtained. *(on-track, 80% complete)*

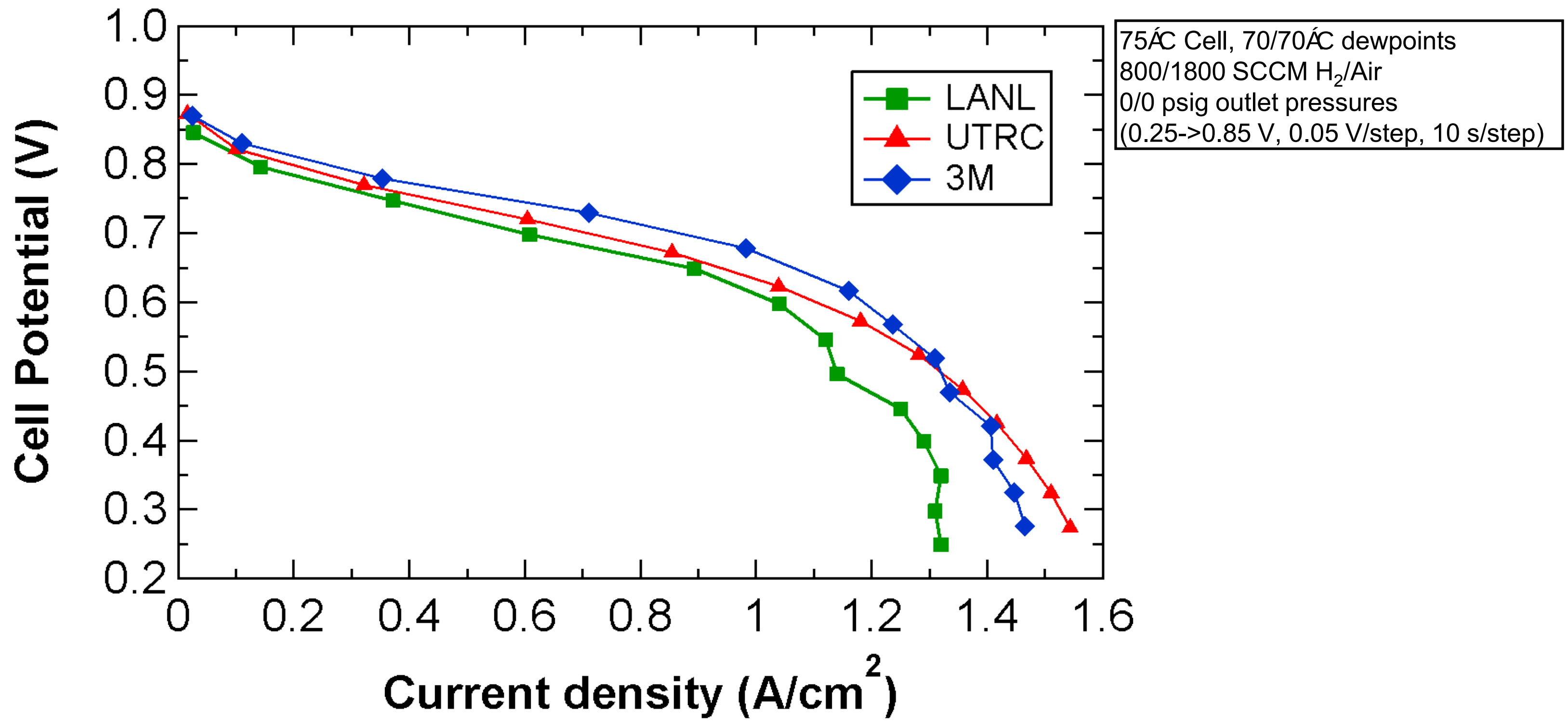
M5: Validated macroscopic model showing effect of compression on water content developed. *(complete)*

M6: Correlation between GDL material properties and kinetic freeze rates established. (on-track, *70% complete)*

M7: Scaling expressions for 3-D (flow-channel) effects determined. *(on-track, 15% complete)*

# Baseline Performance

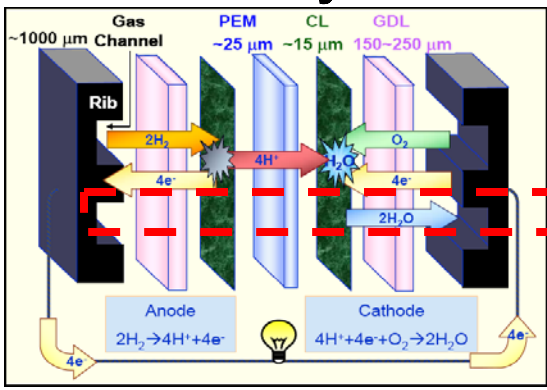
- Baseline system is 3M NSTF “2009 best of class” MEA
  - Not yet with improved anode GDLs reported last year

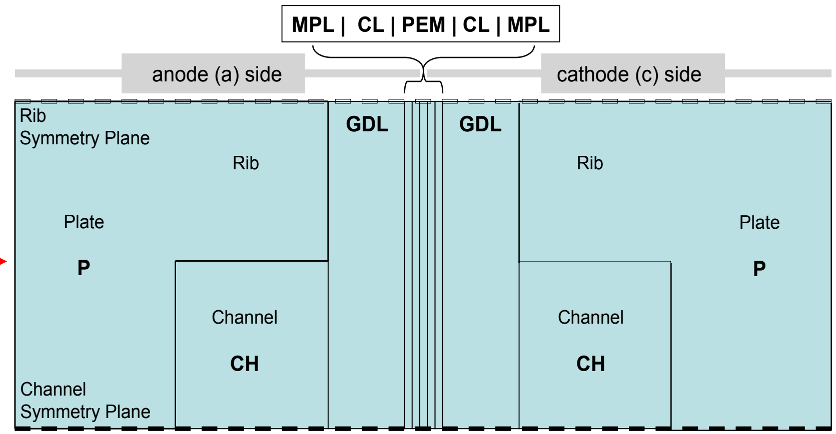



- Performance among the three sites is converging
  - Compression uniformity and cell assembly/hardware uniformity
  - Running NSTF is different and has required test-stand modifications and a learning curve on the conditioning procedure

# Cold-Start Model

## Model Geometry




*For NSTF, model CL as an interface*

## Model physics

**Thermodynamics**

Standard cell potential
Equilibrium $H_2O$ content
membrane, liquid, vapor, ice

**Kinetics**

Butler-Volmer for HOR, ORR
$H_2O$ phase change between
ionomer, vapor
liquid, vapor

**Transport**

Stefan-Maxwell diffusion
for gas-phase components
Darcy's law for liquid, gas phases
Ohm's law for $e^-$ current
Modified Ohm's law for $H^+$ current
$H_2O$ transport by proton drag
$H_2O$ diffusion in membrane

**Conserved quantities**

Mass; Charge; Energy

**Constitutive relations**

Faraday's law
Ideal-gas law

**Properties**

Function of $T$
and $H_2O$ content

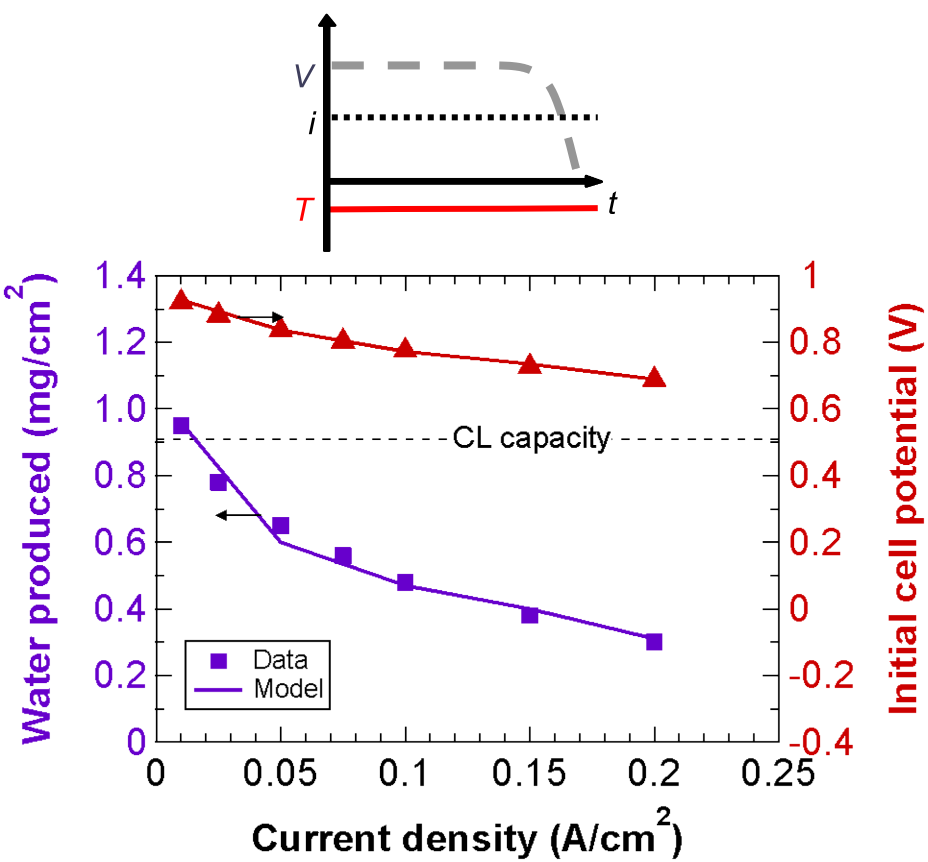
**Equations (14):** 8 $2^{nd}$-order PDEs; 6 Algebraic equations

**Unknowns (14):** $T$ $\omega_{H2}$ or $\omega_{O2}$ , $\omega_{N2}$ , $\omega_{H2O}$ $S_L$ , $S_I$ , $S_G$ $p_L$ , $p_I$ , $p_G$ $\Phi_1$ , $\Phi_2$ $\mu_0$ , $\varepsilon_0$

# Model Validation

- Model has been validated with cold-start data using traditional catalyst layers

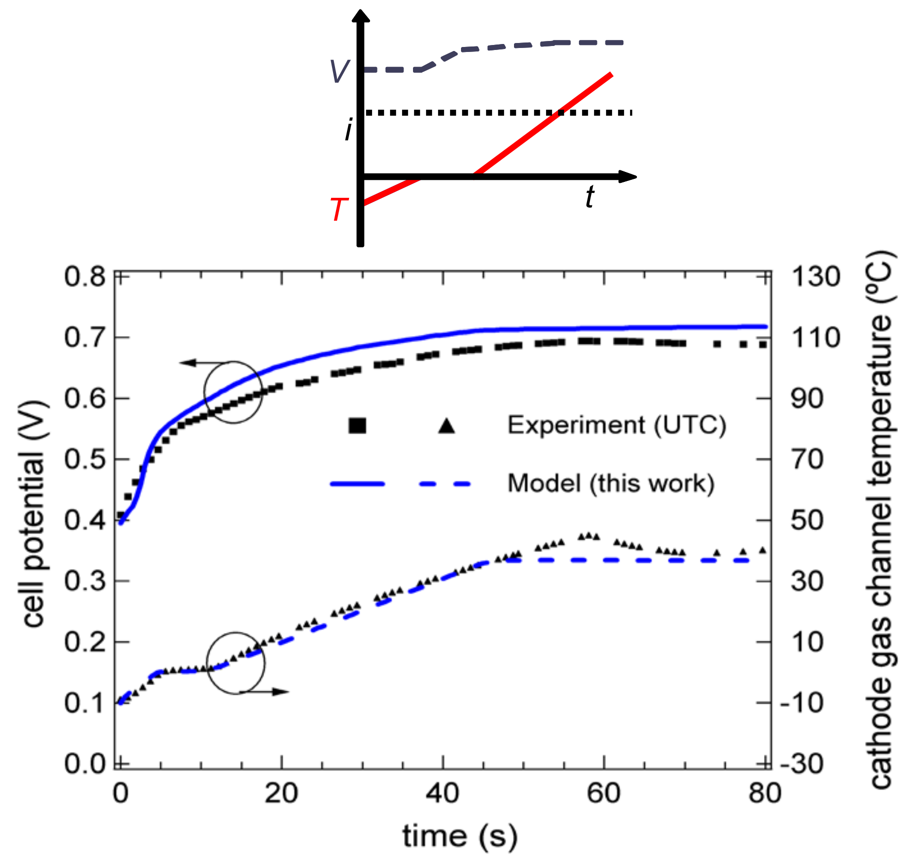
## Isothermal




–20 °C; preconditioning: 97 % RH at 30ÅC; $H_2/O_2$

E. L. Thompson, J. Jorne, W. B. Gu, and H. A. Gasteiger, *JES*, **155**, B625 (2008).

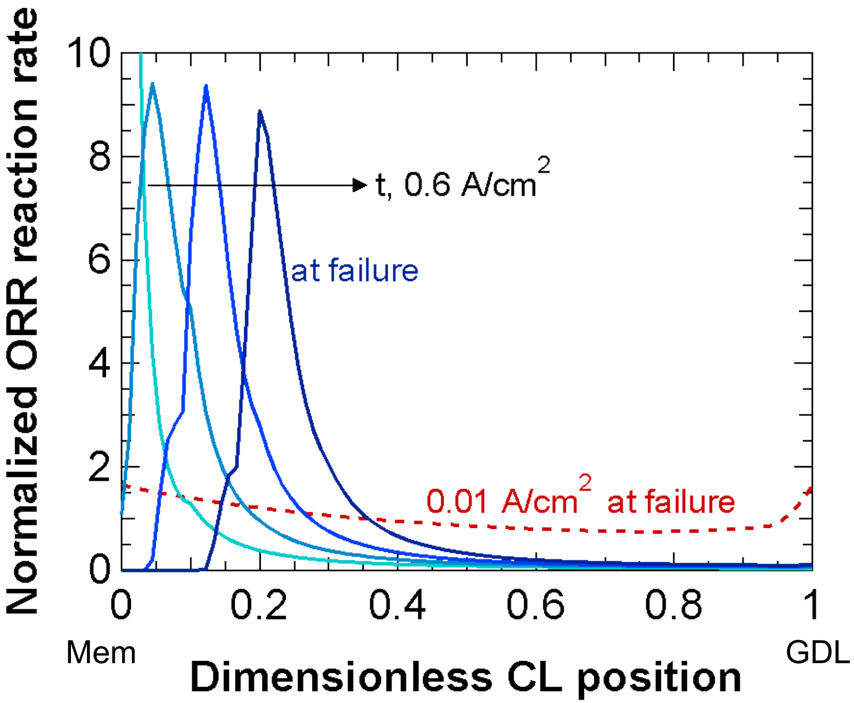
## Nonisothermal

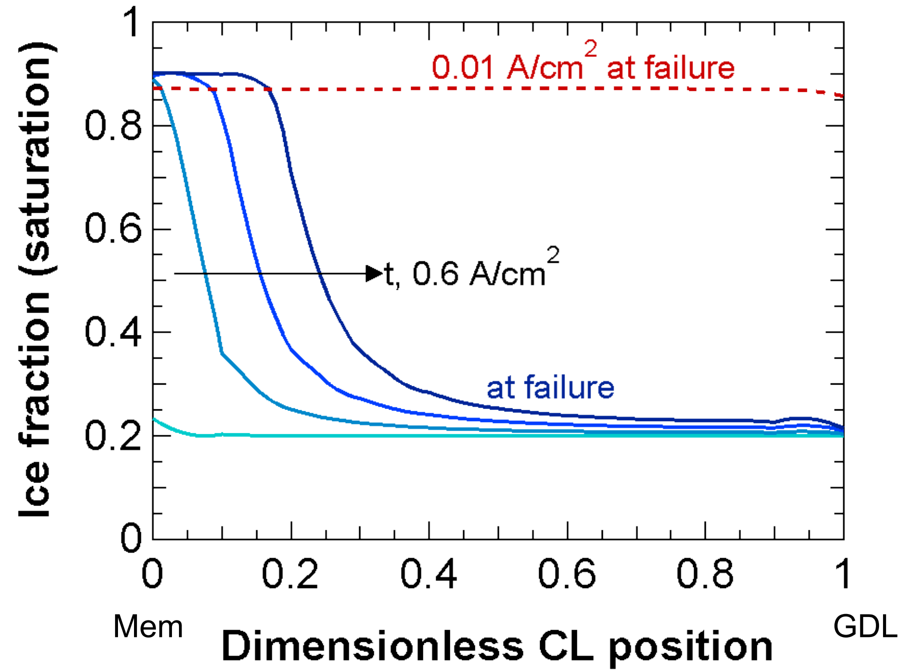



$H_2$/Air; 0.6 A/cm$^2$ ; Initial temperature: –10ÅC

B. Paravastu of UTC Power, personal communication, November 10, 2010.

# Isothermal Cold-Start Simulations



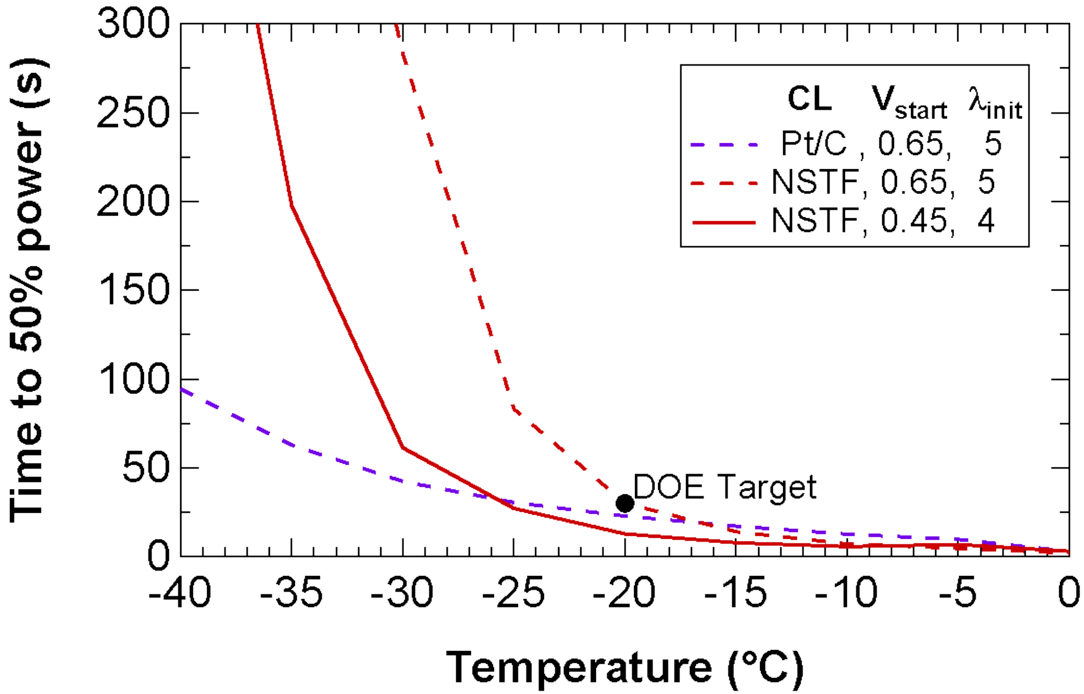

- At high current densities, get ohmically and not mass-transfer limited
  - Protons, not oxygen, can limit performance
    - Not a true limiting current

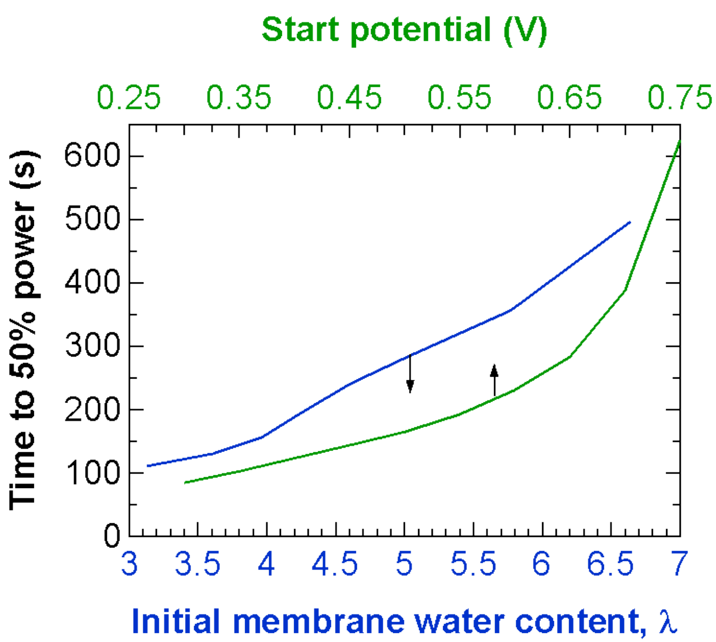
- Durability concerns at high-current-density starts due to rapid build up of ice

# Nonisothermal (NSTF) Cold-Start Simulations

- NSTF has no capacity to store water during cold start
  - Impacts start-up time
  - Overcome this by starting drier and harder

Nonisothermal
$T_{init}$: -30 C
Potentiostatic
Gases (a/c): $H_2$/Air
Gas pressures, a/c (bar): 1/1

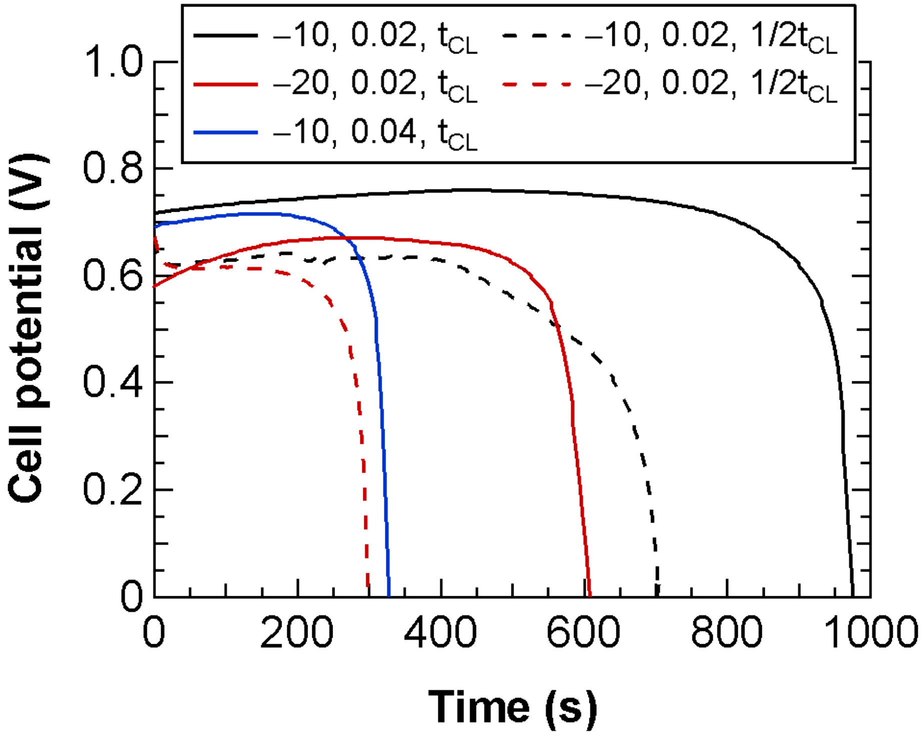


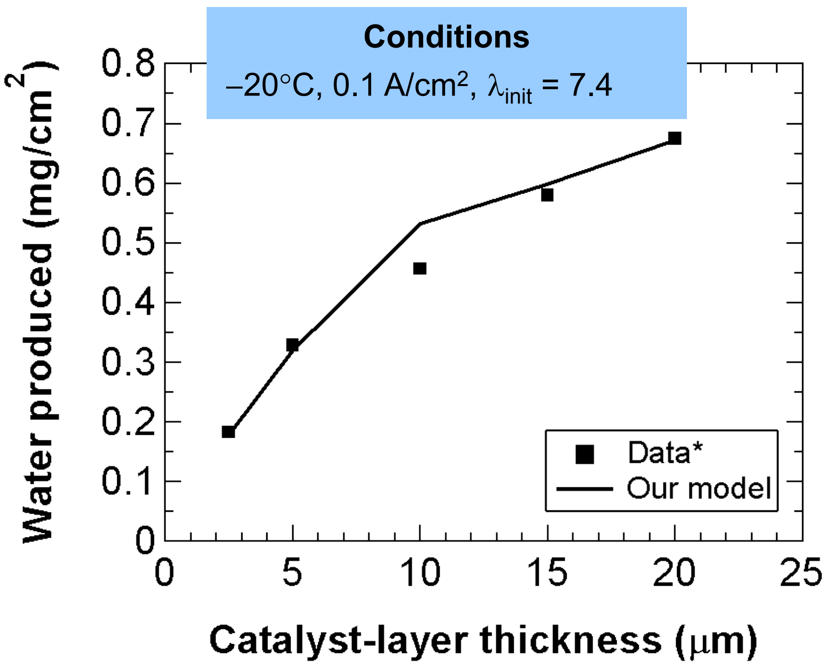




- Need to look into tradeoff between water generation and removal rates

# Isothermal Cold-Start Data

- Use traditional catalyst layers
  - Know that lower temperatures and higher current densities are worse for cold start…but what about CL design?



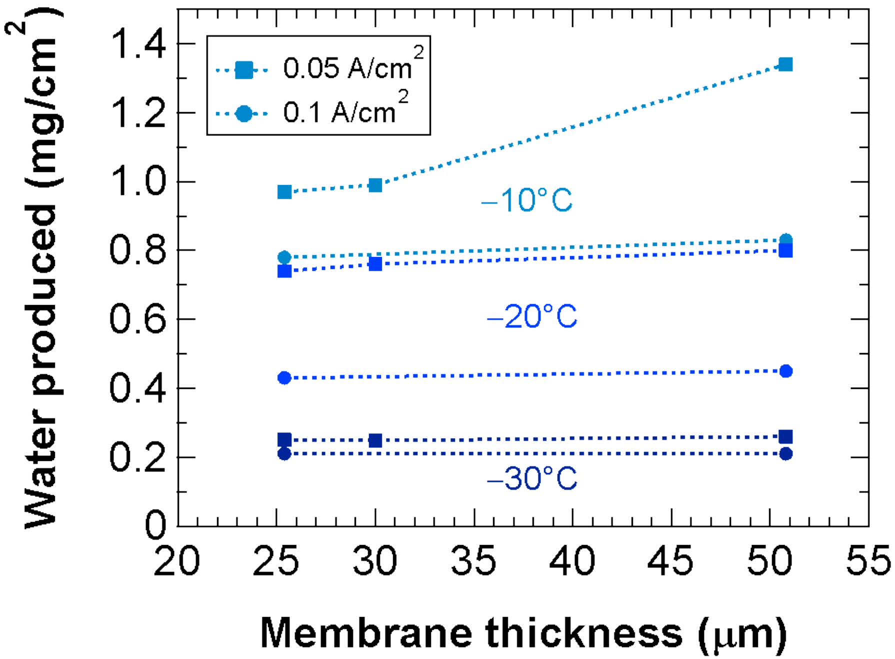




*A. Nandy, F. M. Jiang, S. H. Ge, C. Y. Wang, and K. S. Chen, *JES*, **157**, B726 (2010)

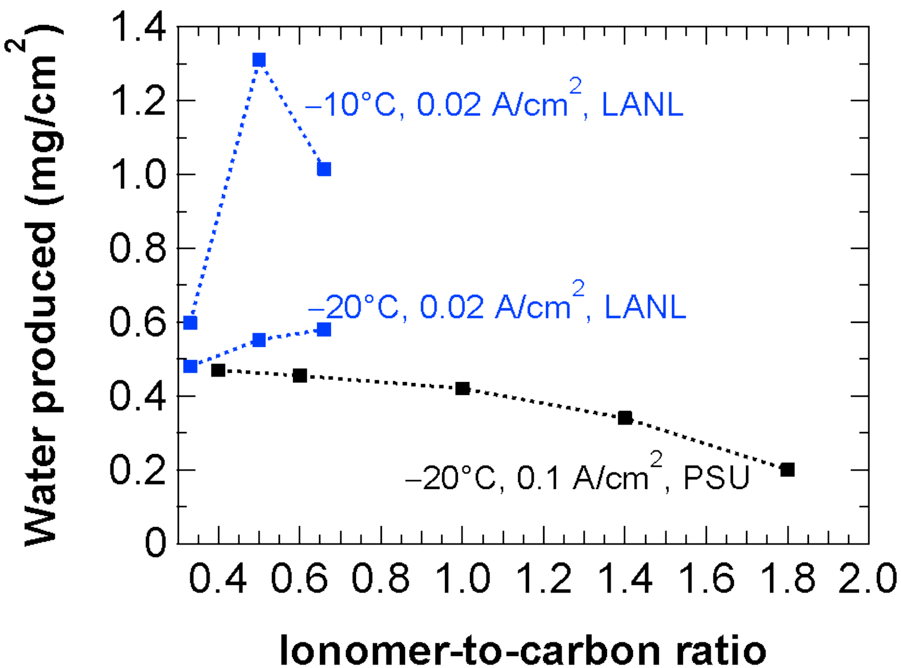
  - Catalyst layer thickness can increase storage capacity which helps isothermal-start performance, especially at lower temperatures, until get ohmically limited

# Isothermal Cold-Start Data

- Membrane thickness




- Ionomer-to-carbon ratio

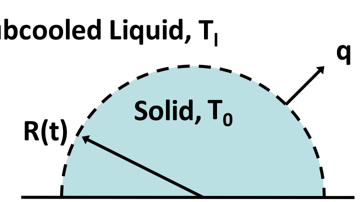


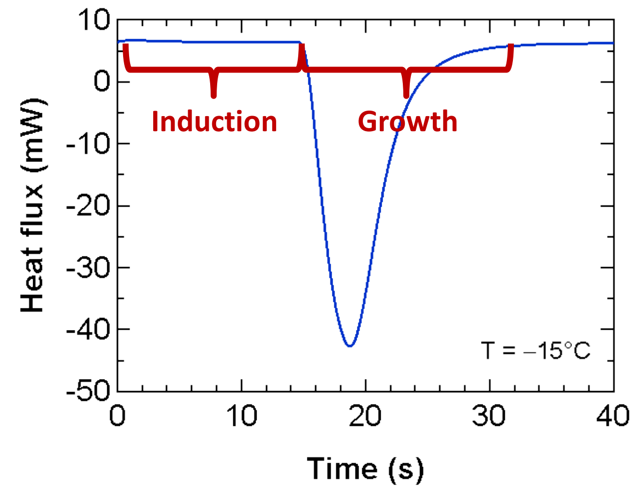

- Thicker membrane offers more capacity for water absorption
- Impact decreases at lower temperatures due to slow water diffusion/absorption

- Interplay between layer porosity and ionomer conductivity and storage capacity
  - High I/C: porosity (storage) limited
  - Low I/C: conductivity limited

# Freezing Fundamentals

- Freezing is controlled by kinetics with induction (nucleation) and growth phases
- Use isothermal DSC to determine rate equation for GDL materials
- Induction
  - Derive from classical nucleation theory and statistical set of experimental data (see next slide)
- Growth
  - Governed by heat transfer
    - Removal of heat of freezing from freezing front through the liquid is limiting (low Stefan number)

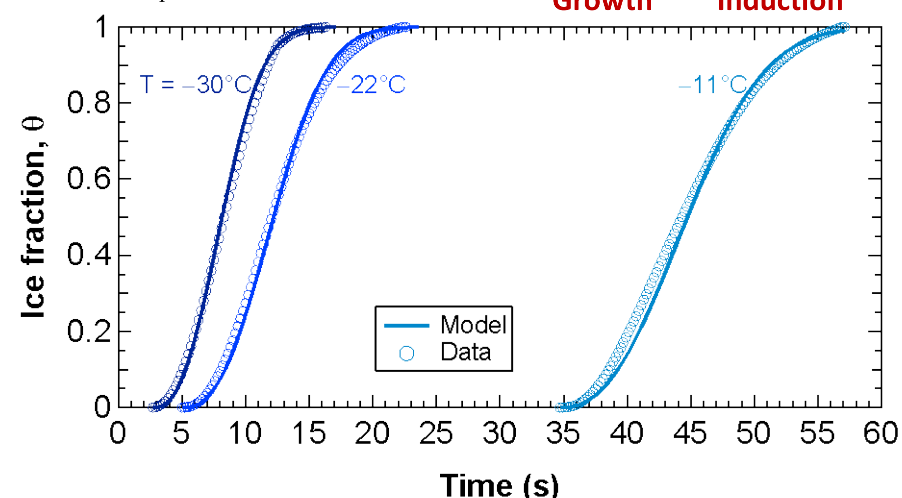



$$\theta = \frac{\text{mass ice}}{\text{mass liquid water}}$$

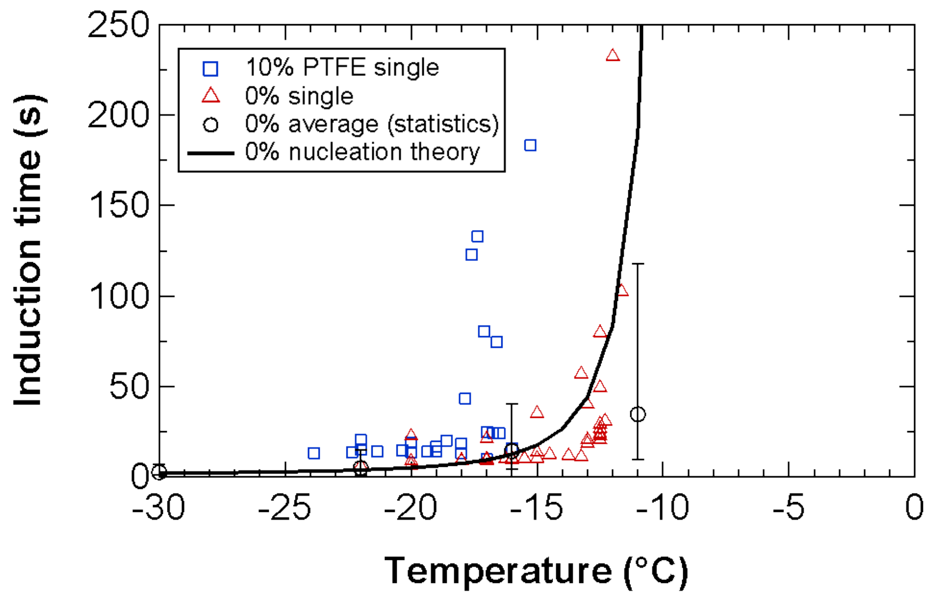
$$\theta = 1 - \exp\left[\frac{-32\pi}{15}\eta_0^3 \alpha_l^{3/2} J (t-\tau)^{5/2}\right]$$

Growth    Induction

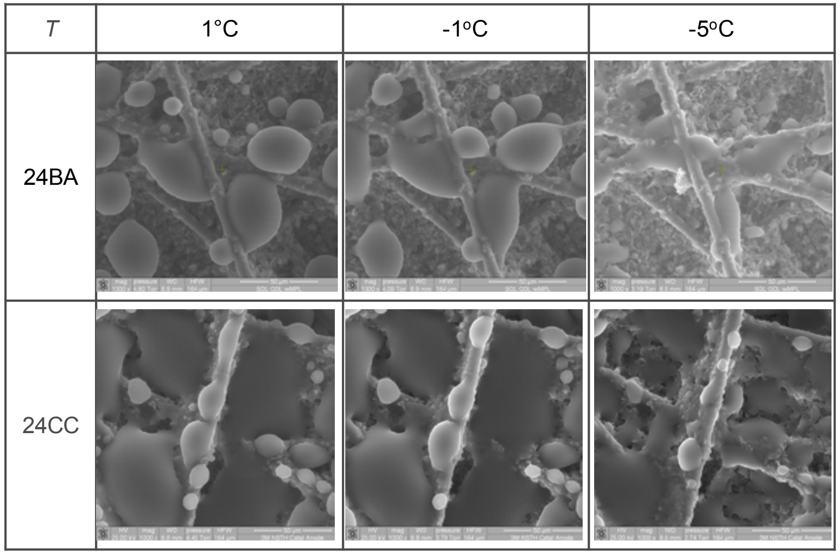


# Freeze Induction Time

- For induction time, analyze data using classical nucleation theory
  - Poisson distribution at each temperature
  - Assume heterogeneous nucleation



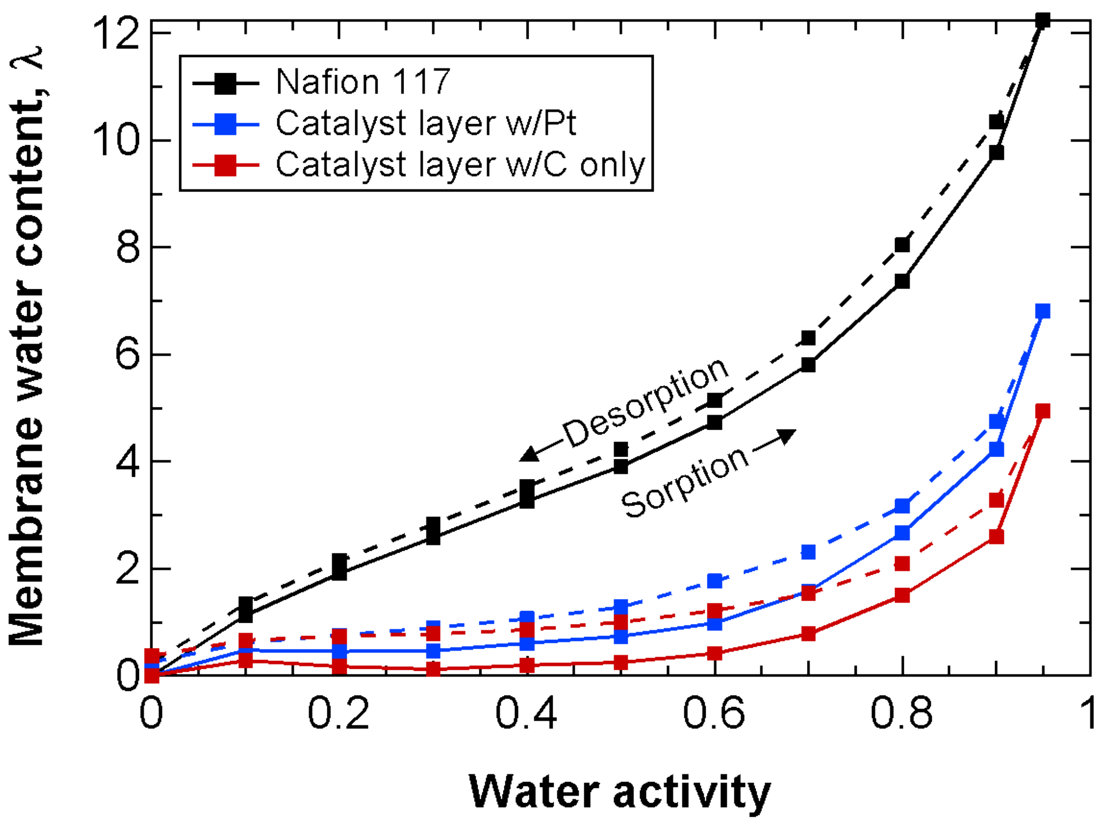

- Water does not freeze in GDLs until subcooled temperatures
  - More hydrophobicity increases the degree of subcooling
  - Environmental SEM confirms subcooling
    - SGL GDLs, top is less hydrophobic
  - NMR also confirms subcooling



# Catalyst-Layer Water Uptake

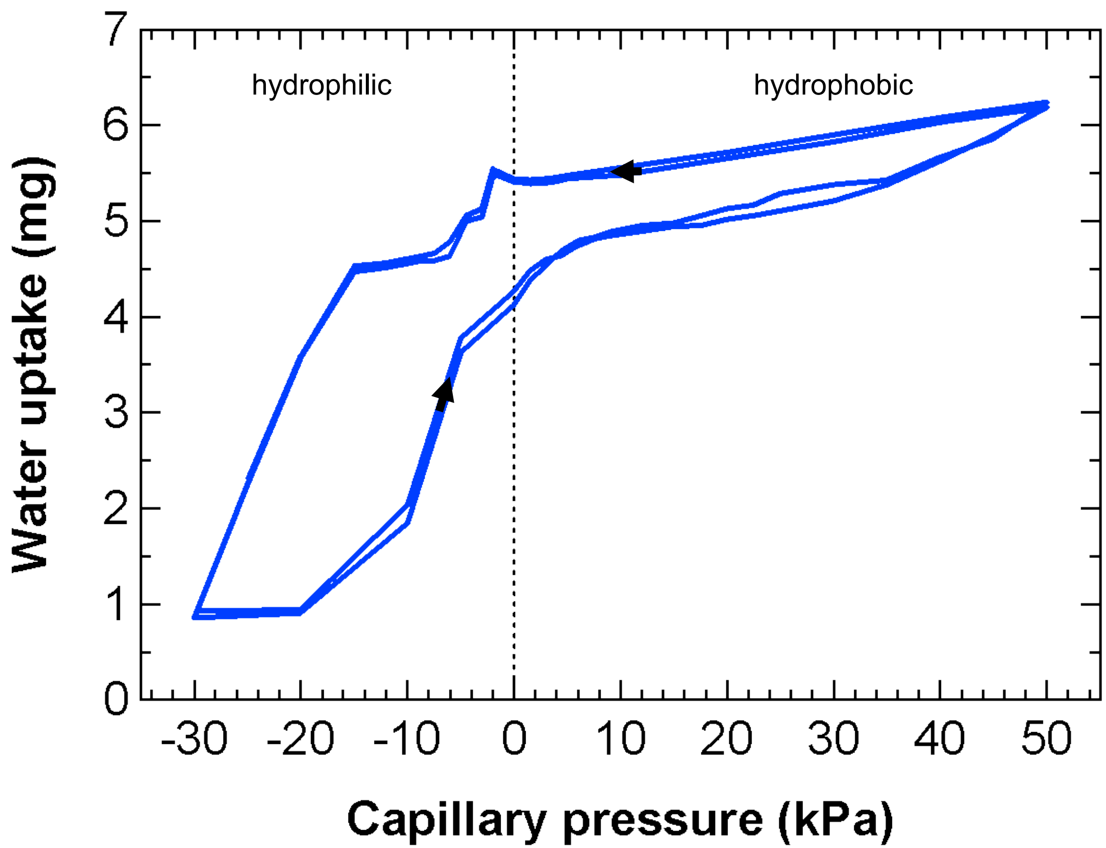
- Painted thick catalyst layers onto PTFE membranes (I/C = 0.4, 40 μm)
- Measured water uptake in dynamic vapor sorption: $\lambda_{catalyst} = \frac{M_{catalyst} - M_{catalyst}^{dry}}{f_{ionomer}\left(1-\varepsilon\right)M_{catalyst}^{dry}} \frac{EW}{18}$

- Water uptake is below that of bulk Nafion®
  - Delayed swelling and domain filling?
- Pt seems to increase water uptake
  - Do not expect capillary condensation except maybe at highest activity
  - Implies Pt/Nafion® interaction



# Catalyst-Layer Water Uptake

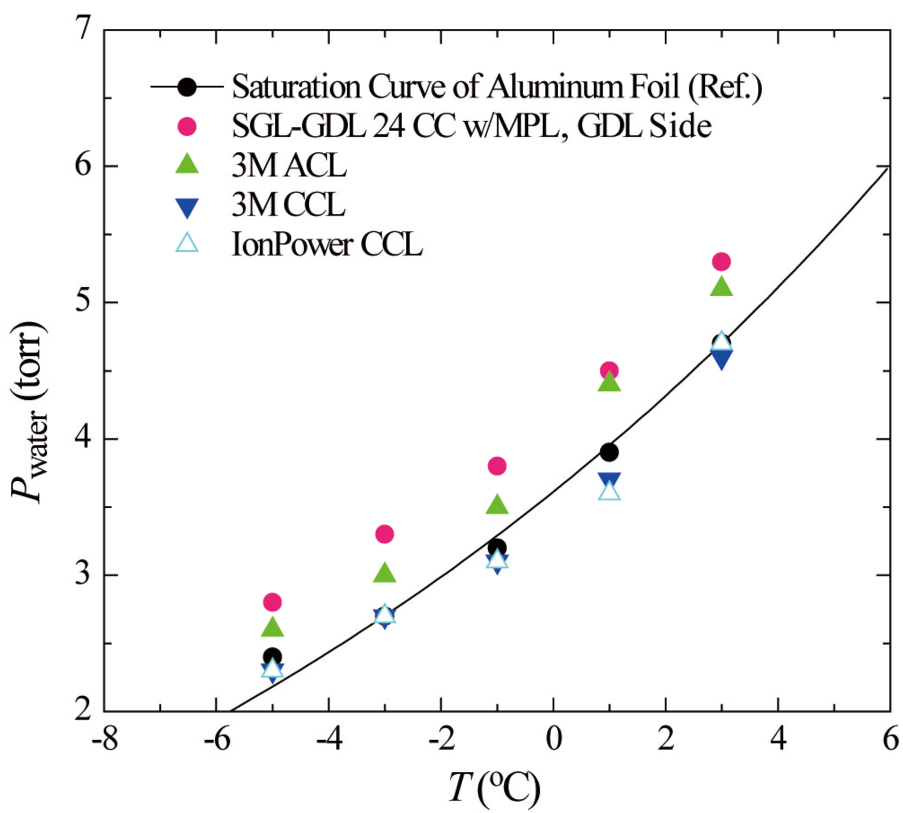
- Painted thick catalyst layers onto PTFE membranes (I/C = 0.4, 40 μm)
- Measured capillary pressure – saturation relationship using pressure control

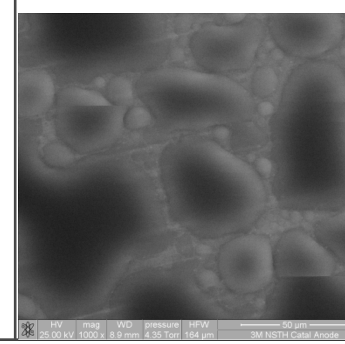
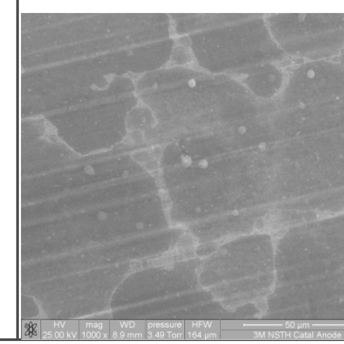



- Appears to be mainly (~2/3) hydrophilic with some smaller hydrophobic pores
- Sample with carbon only (no Pt) appears somewhat less hydrophilic (not shown)

# Catalyst-Layer Surface Water

- ESEM agrees with mainly hydrophilic behavior for both traditional, Pt/C, and NSTF catalyst layers
  - Expect to freeze much closer to 0°C unless pore-effects dominate




| $T_{actual}$ | 1°C | -1°C |
|---|---|---|
| NSTF |  |  |

# Future Work

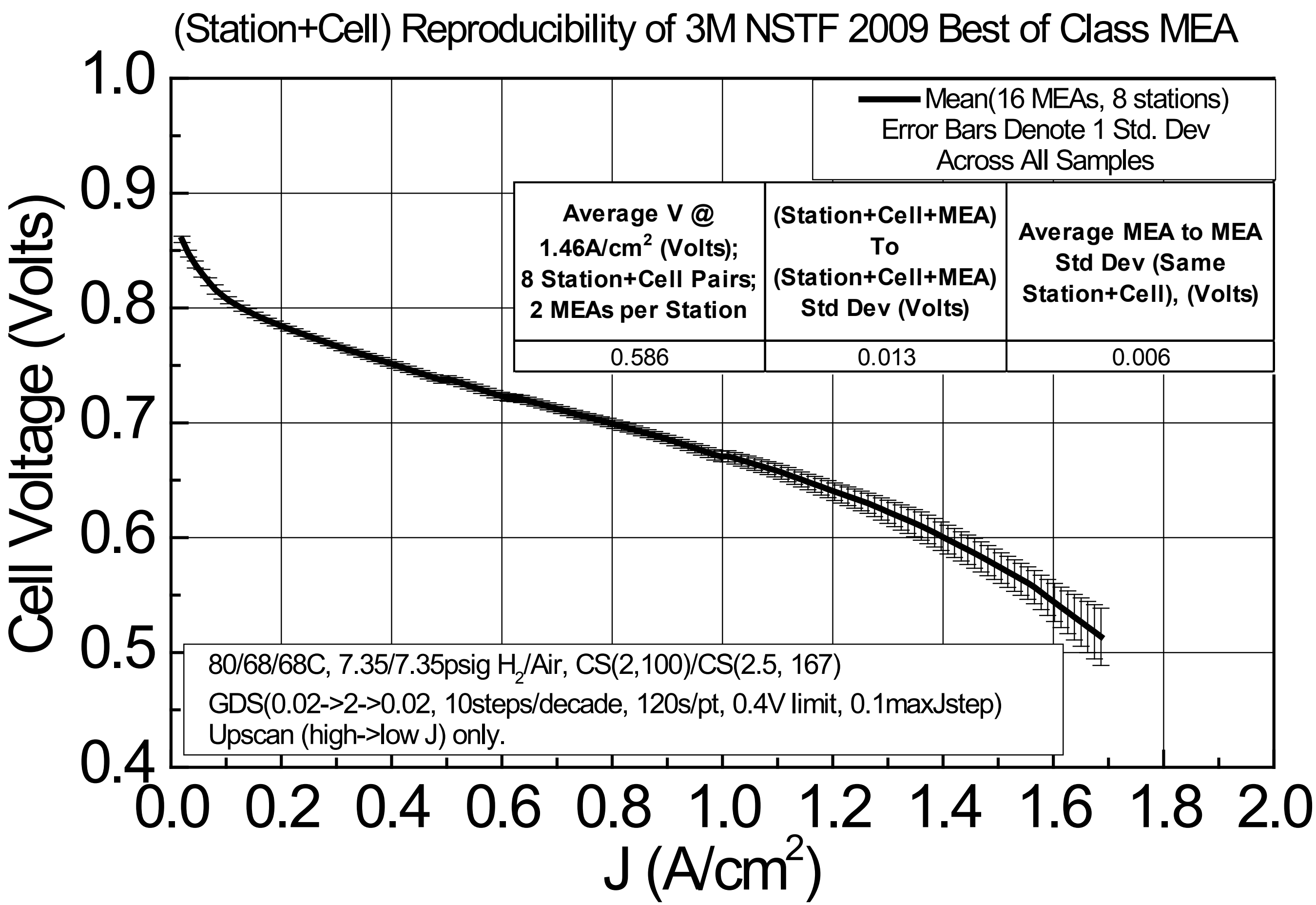
- Cell performance
  - Testing of non-baseline assemblies
  - Isothermal and adiabatic starts including cycling studies for tracking durability
  - Provide model-validation data
- Component characterization
  - Catalyst layers
    - More data on water-related properties
    - Examine ice generation and form using IR thermography and X-ray tomography
  - Diffusion media
    - Capillary pressure – saturation relationships
      - Impact of flowrate, temperature, injection sites (MPL analogs), materials
    - Measure effective gas-diffusion coefficient as a function of saturation
- Modeling of cold start
  - Examine interplay between water storage and movement for transient and startup
  - Develop 3-D to 2-D downscaling correlations
  - Model the low-anode-pressure and alternative-GDL results that 3M has obtained
- 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**:
  - Site baseline data converging so that systematic cell testing can begin soon
  - Developed and initially validated 2-D, cold-start model
  - Isothermal data and modeling demonstrate impact of catalyst-layer properties and membrane thickness on cold start
  - Determined kinetic rates and freezing phenomena inside GDLs
    - Subcooling due to nucleation induction times
  - Analyzed water uptake in traditional, supported catalyst layers
- **Future Work**:
  - Understand liquid-water movement, interactions, and freeze in fuel-cell components
  - Benchmark cell and stack performance and durability with different assemblies

# Technical Back-Up Slides

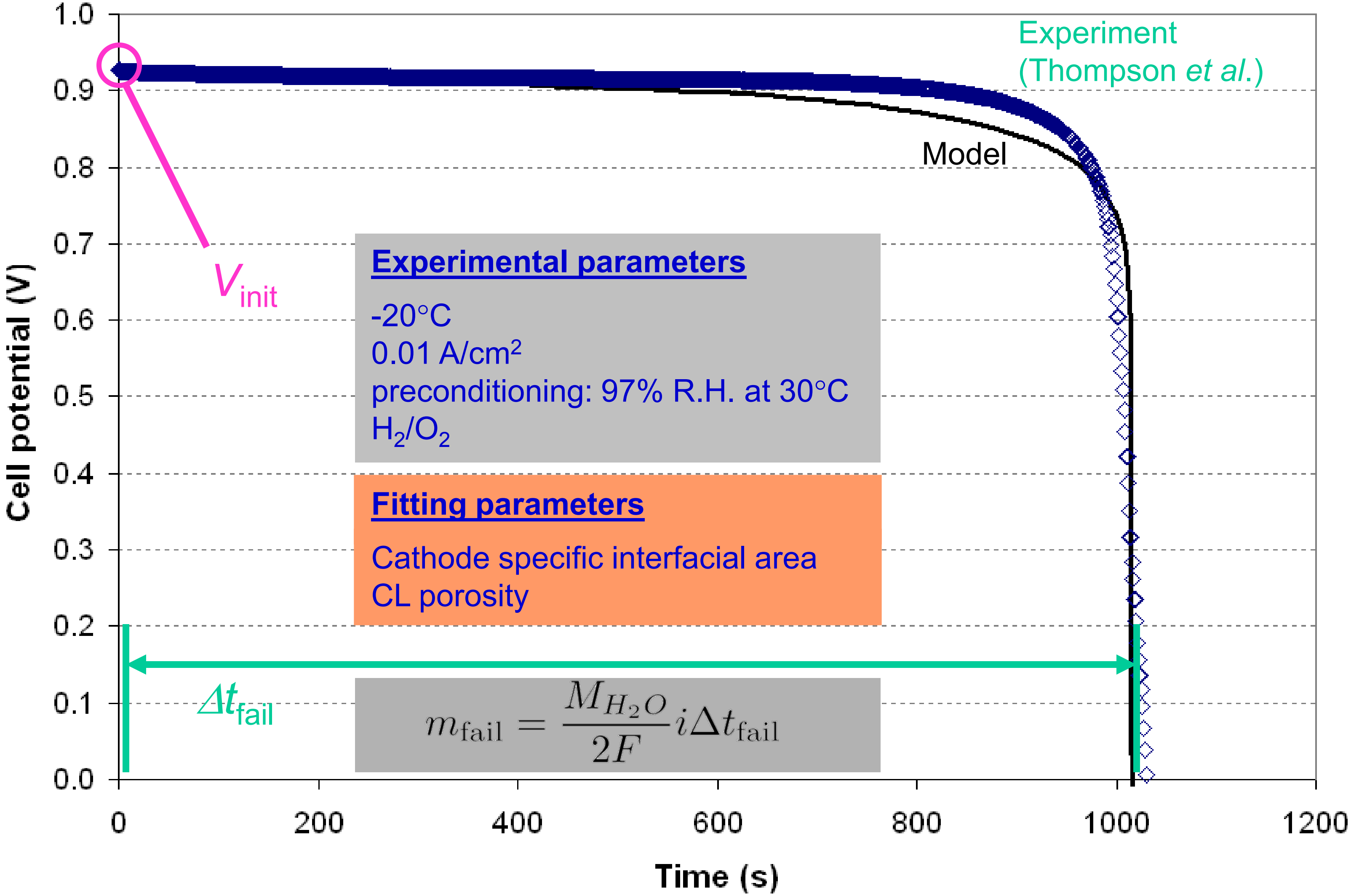
# Expected NSTF Variability




- 16 identical NSTF 2009 Best of Class MEAs across 8 station+cell pairs show good performance reproducibility
  - Many sources of possible variability – stations, cells, MEA fabrication, cell assembly, ...
- MEA to MEA and cell assembly variability (same station+cell) is approximately half the total variability at 1.46 $A/cm^2$

# Modeling Isothermal Cold Start

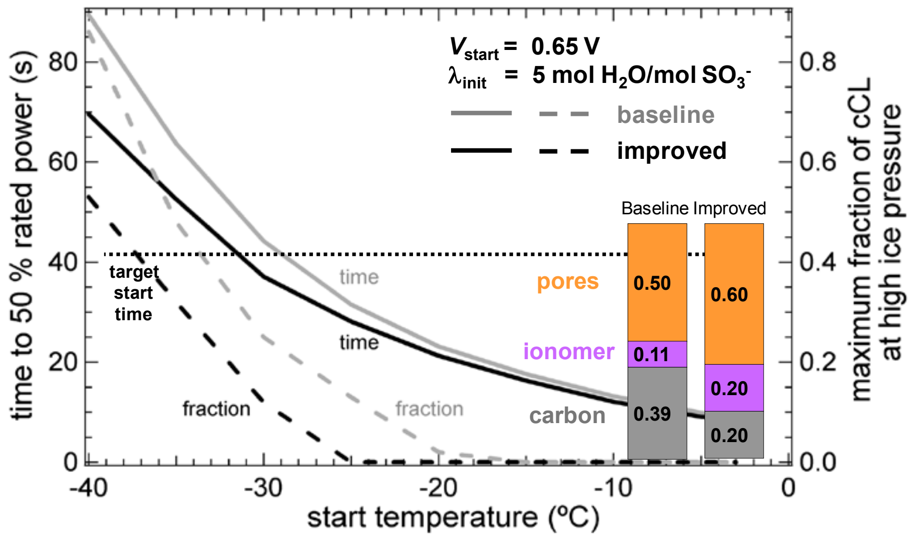
- Key characteristics of isothermal starts can be used to verify the model

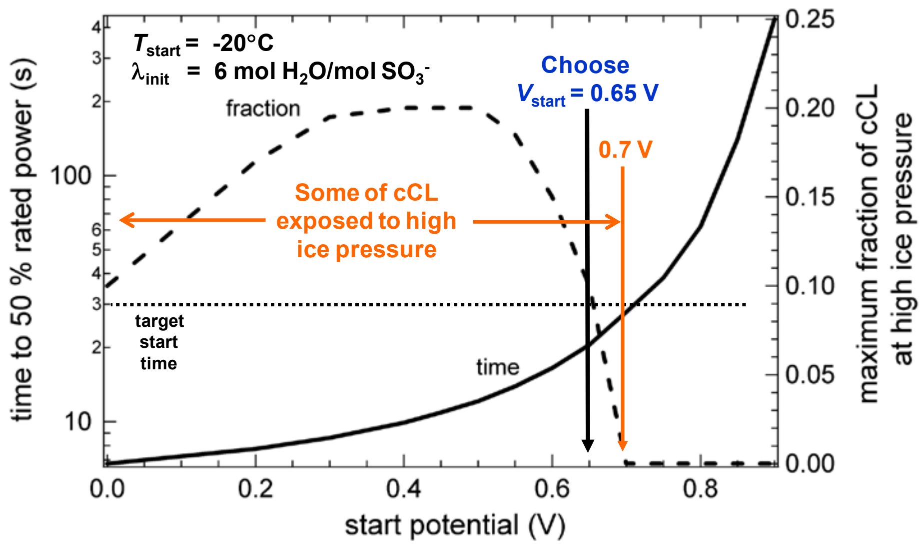


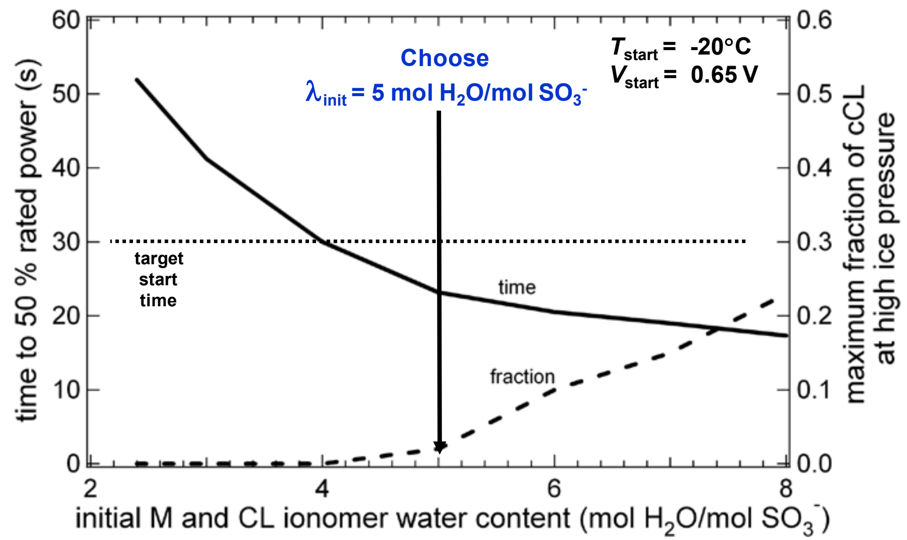

E. L. Thompson, J. Jorne, W. B. Gu, and H. A. Gasteiger, *JES*, **155**, B625 (2008).

# Nonisothermal Cold-Start Simulations

- Use model to examine start time and durability (ice pressure)
  - Increasing CL porosity and ionomer content reduces start time and ice pressure
    - Tradeoff of water capacity, gas diffusion, and effective conductivities
    - Agrees with isothermal start data
  - Examine start potential and initial water content
    - Tradeoff between time and ice pressure

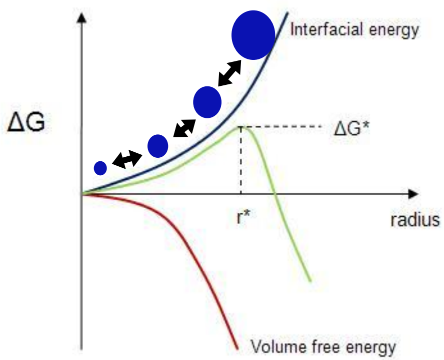


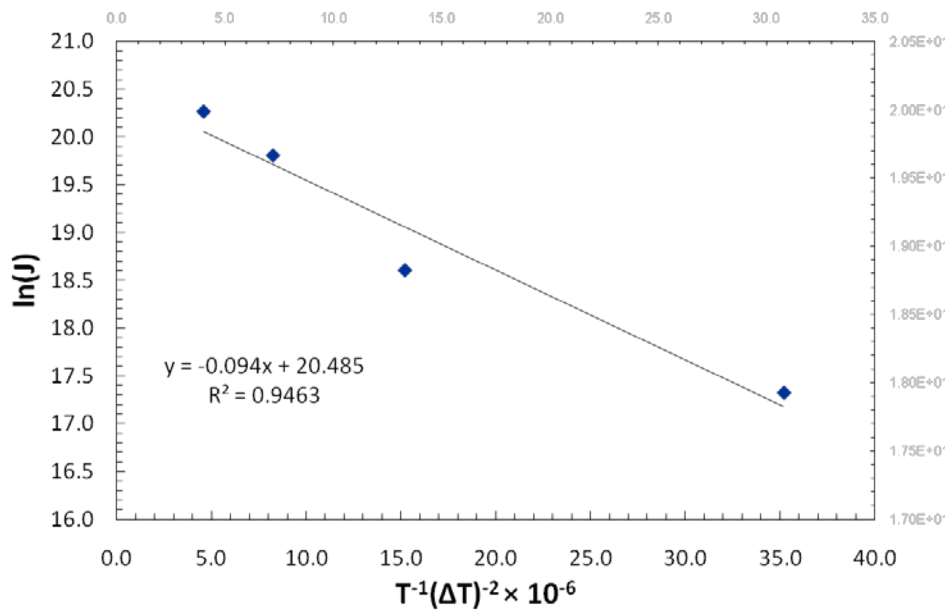
# Nucleation/Induction

## Free energy of freezing



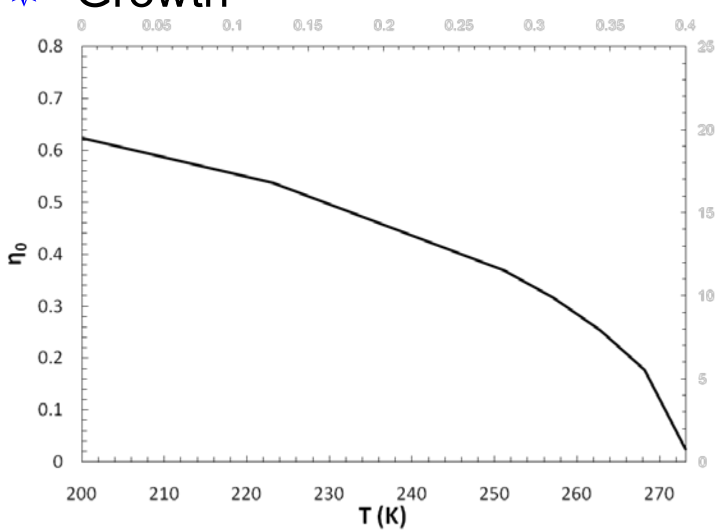

## Classical nucleation theory

$$J = J_0 \exp\left[\frac{-\Delta G^*_{\text{hom}} f(\varphi)}{k_b}\right] \quad \Delta G^*_{\text{hom}} = \frac{16\pi\gamma_{sl}^3 T_0^2 \hat{v}_s^2}{3\Delta\hat{H}_f^2 (T_0 - T)^2} \quad f(\varphi) = \frac{1}{4}(2\cos\varphi)(1-\cos\varphi)^2 \quad \tau = \frac{1}{JV}$$




$$J = 7.9\times10^8 \exp\left(\frac{-9.4\times10^4}{T(\Delta T)^2}\right)\frac{\text{nuclei}}{\text{m}^3 s}$$

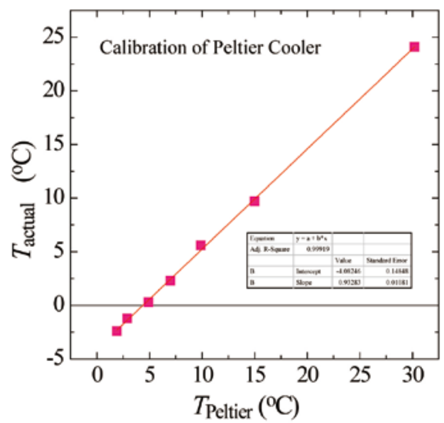
## Growth

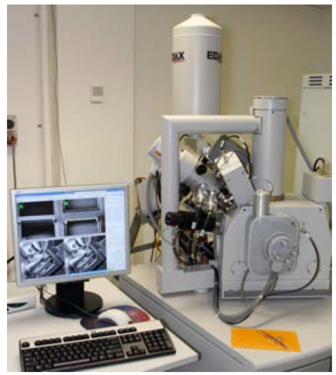



$$R(t) = 2\eta_0\sqrt{\alpha_l t} \quad \text{where} \quad \eta_0^2 \exp(\eta_0^2)\left[\exp(-\eta_0^2) - \sqrt{\pi}\,\eta_0 \operatorname{erf}(\eta_0)\right] = \frac{c_{p,l}\Delta T}{2\Delta\hat{H}_f} = \frac{1}{2} Ste$$

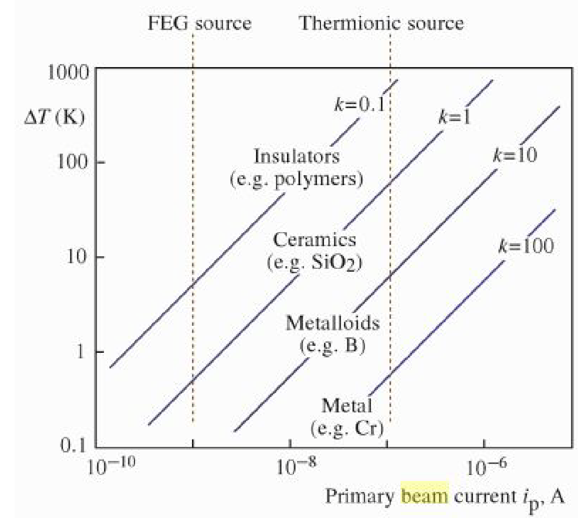
# ESEM

- Calibration

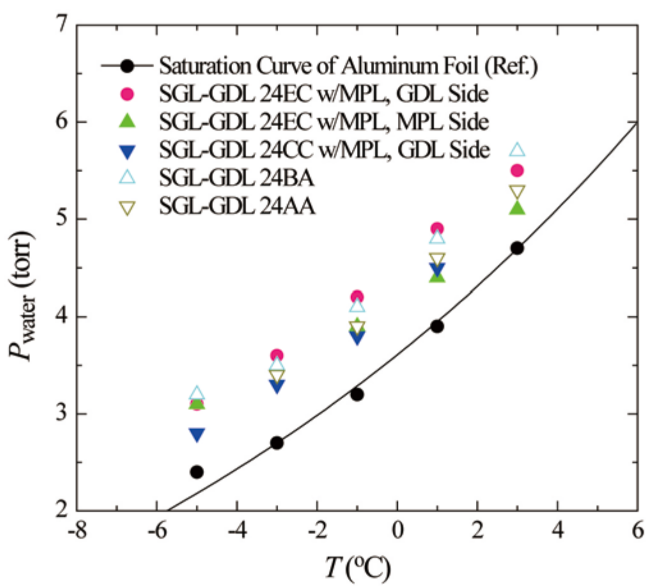


- Beam heating expect to be < 0.5°C




- GDL phase diagram




- Protocol