# Fuel-Cell Fundamentals at Low and Subzero Temperatures


**Adam Z. Weber**
Lawrence Berkeley National Laboratory


Solicitation Partners:

United Technologies Research Center

Los Alamos National Laboratory

3M Company

The Pennsylvania State University

Project ID #
**FC 026**

May 17, 2012

# Overview

## Timeline

- Project initiated FY09
  - Start **September 2009**
- 4 year project duration
  - End **September 2013**
- ~60% complete

## Barriers

- A. Durability
- C. Performance
  - Cell Issues
  - Stack Water Management
  - System Thermal and Water Management
  - System Start-up and Shut-down Time and Energy/Transient Operation

## Budget

- Total Project Funding: $5,145k
  - DOE share: $ 4,700k
  - Contractor share: $ 445k
- Funding Received in FY10: $742.5k
- Funding Received in FY11: $812.5k
- Planned Funding for FY12: $1,290k
  - LBNL $670k
  - Partners $620k

## 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, Alexander Hexemer, Frances Allen
- Subcontractors
  - **Los Alamos National Laboratory**: Rod Borup, Rangachary Mukundan
  - **3M Company**: Mark Debe, Andy Steinbach, Steve Hamrock
  - **United Technology Research Center**: Michael Perry, Rachid Zaffou
  - **The Pennsylvania State University**: Chao-Yang Wang
- Other relationships (directly funded through other DOE projects)
  - **Ion Power**: Stephen Grot (Nafion® samples)
  - **SGL Carbon Group**: Ruediger-Bernd Schweiss (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)
  - **UC Berkeley/JCAP**: Rachel Segalman (Nafion® scattering and other studies)
  - **General Motors**: Craig Gittleman (Nafion® conductivity data)
  - **Queens University:** Kunal Kuran (Nafion® thin-film data and samples)
  - **University of Michigan**: Massoud Kaviany (Nafion® MD simulations, ESEM)

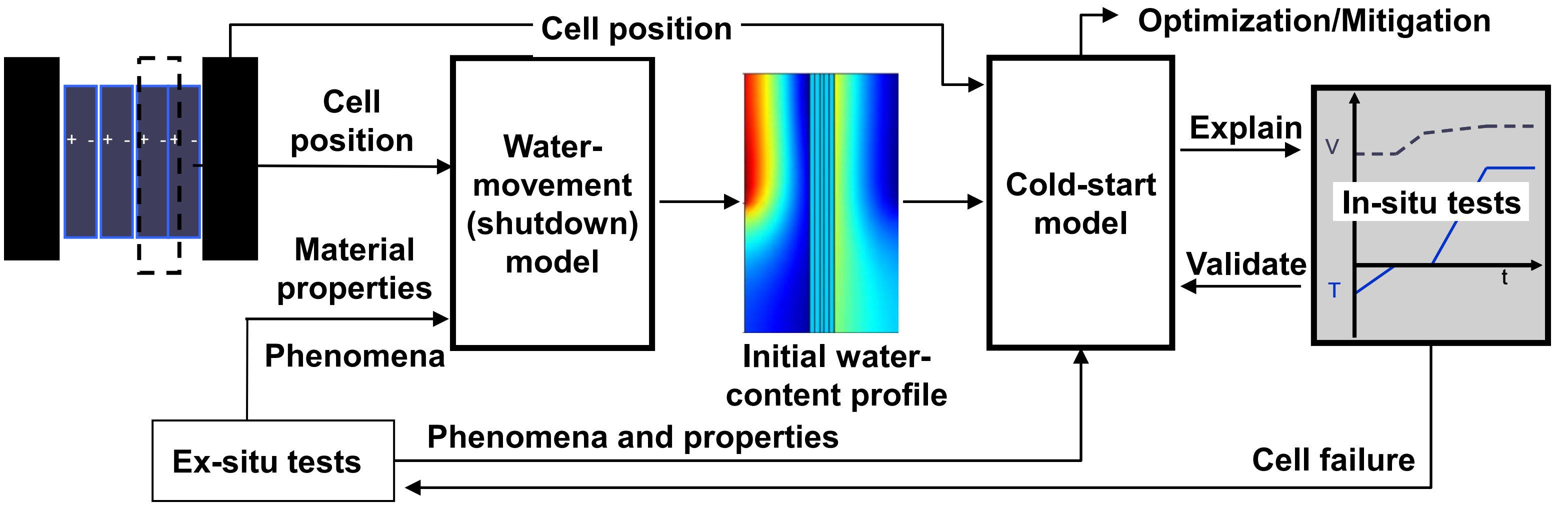
# Relevance: Objectives

- Fundamental understanding of transport phenomena and water and thermal management at low and subzero temperatures using state-of-the-art materials
  - Examine water management with thin-film catalyst layers (NSTF)
  - Examine water management and key fundamentals in the various fuel cell components
  - 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

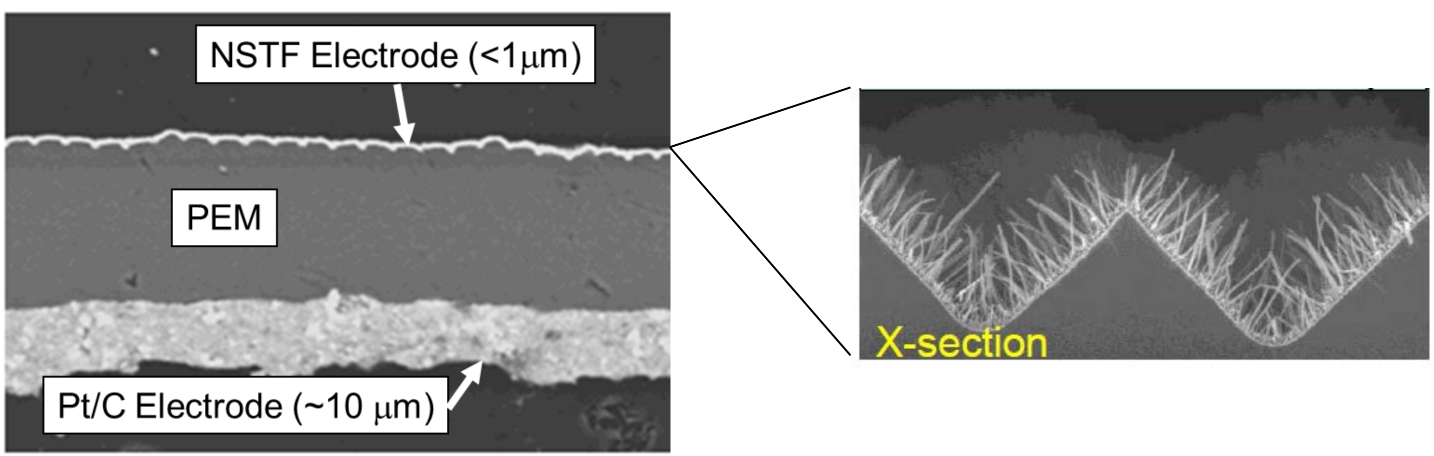



- Multi-scale, multi-physics continuum-based modeling
  - Develop, validate, and refine a series of models for cell performance including cold and cool operation, startup, and shutdown
- Experimentally characterize component, cell, and stack properties and performance
  - Measure critical properties 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: Cell Assemblies

- Utilize various assemblies to elucidate governing and controlling phenomena

| Material | Baseline | Alternative 1 | Alternative 2 |
| --- | --- | --- | --- |
| **Membrane** | 3M 850 EW | 3M reinforced | |
| **Catalyst layer** | NSTF PtCoMn | NSTF $Pt_3Ni_7$ | Low-loaded traditional |
| **GDL** | MRC | SGL | Freudenberg |
| **MPL** | Hydrophobic | None | |
| **Flow field** | Quad serpentine | Parallel channel | |
| **Bipolar plate** | Solid | Hybrid (one WTP) | |



# Workplan/Organization

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

| Task1. Cold - Start Model | Task 2. Degradation Model | Task 3 . Stack and Cell Characterization | Task4. Water Imaging | Task 5. Model Deployment | Task 6. Component Characterization |
|---|---|---|---|---|---|
| **LBNL** | **LBNL, PSU** | **UTC** | **LANL, LBNL** | **LBNL** | **LANL** |
| PSU | | LANL, 3M | PSU | PSU | LBNL, 3M, PSU |
| • Steady state<br>• Startup<br>• Simple stack 3-D effects | • Property degradation<br>• Mechanical stress | • Performance evaluation<br>• Stack studies<br>• Failure analysis | • Neutron<br>• X - ray | • Cold-start optimization<br>• Performance loss<br>• Failure mitigation | • Membrane<br>• Catalyst layer<br>• Diffusion media |

## LBNL

- Project management and coordination
- Model development
- GDL and membrane characterization

## LANL

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

## 3M

- Material supplier and testing knowledge including NSTF conditioning procedures

## UTRC

- Stack and cell parametric studies
- Identify and characterize failure mechanisms

## 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: FY12 Project Timeline

| Begin | M1 | M2,M3 | M4 | M5 | M6,M7,M8 | End |
|---|---|---|---|---|---|---|
| 10/11 | 1/12 | 03/12 | 06/12 | 08/12 | 09/12 | 09/12 |

**Major Milestones/Deliverables**

M1: Go/No-Go for use of X-ray tomography to visualize ice. The decision will be made based on the ability to distinguish ice, liquid, and air within the tomographic images with thresholds of 80% deviation between phases. *(completed…no-go; did not meet threshold resolution to distinguish ice)*

M2: Report on the conditions for successful start up at cool and cold temperatures as a function of catalyst-layer thickness and diffusion-media permeability. *(model convergence issues)*

M3: Cell constructed for IR thermography. *(retasked for DSC instead of IR; IR does not have adequate spatial or temperature resolution into the material)*

M4: Effective gas-phase diffusivities obtained for 3 different fuel-cell materials. *(experimental cell designed and built)*

M5: Report explaining the impact of anode hydrogen pressure and diffusion-media properties on fuel-cell performance. *(cells currently being tested with different diffusion media)*

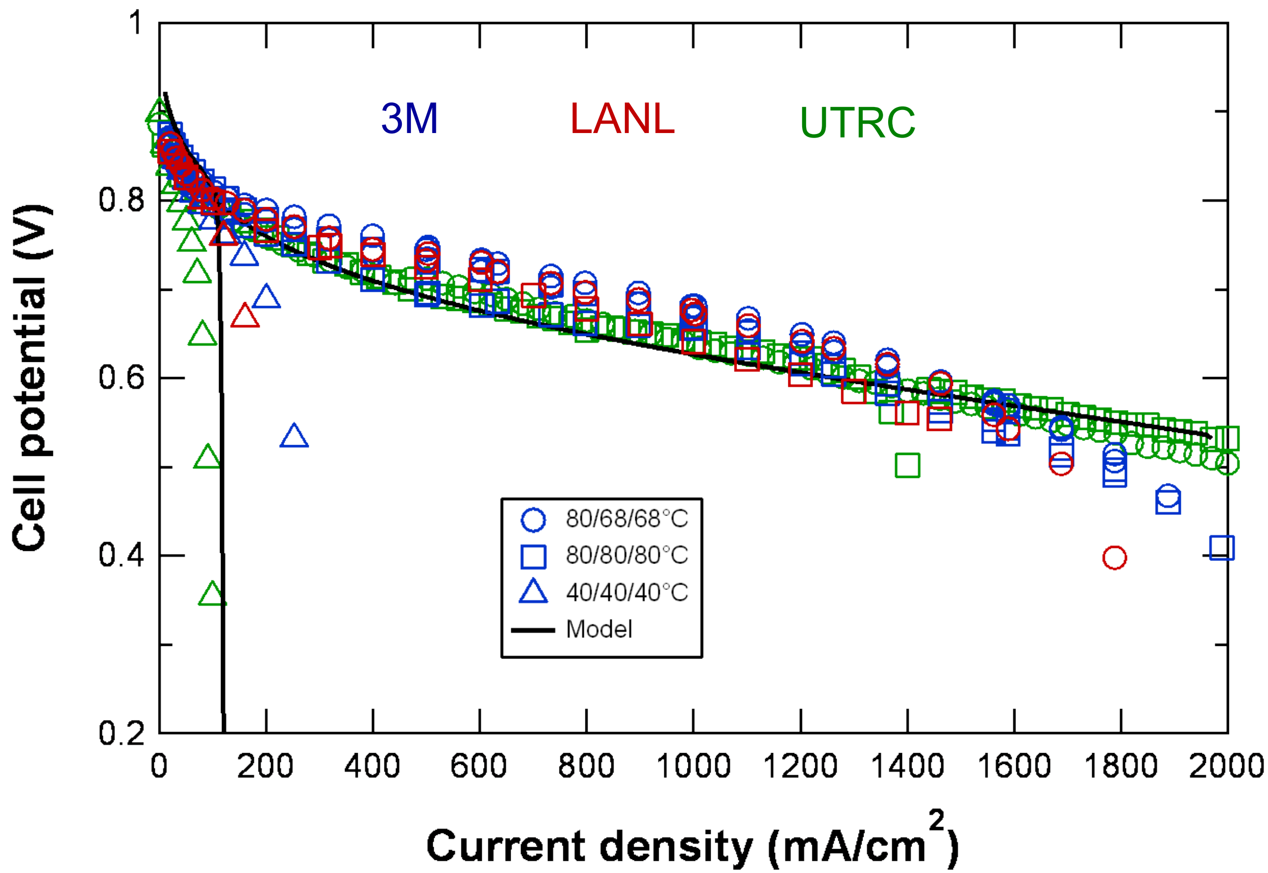
M6: Report on the limiting phenomena during adiabatic and isothermal cold and cool starts using both NSTF and low-loaded traditional MEAs. *(low-loaded are almost complete; NSTF are now being tested)*

M7: Rainbow short-stack fabricated with different cell diffusion media. *(cell components being identified)*

M8: Impact of at least 3 different diffusion media on the performance and durability of NSTF baseline MEA cells after isothermal-cold-start cycling. *(cells currently being conditioned and isothermal-start cycled)*

# Baseline Performance

- Baseline system is 3M NSTF "2009 best of class" MEA including 2009 GDLs



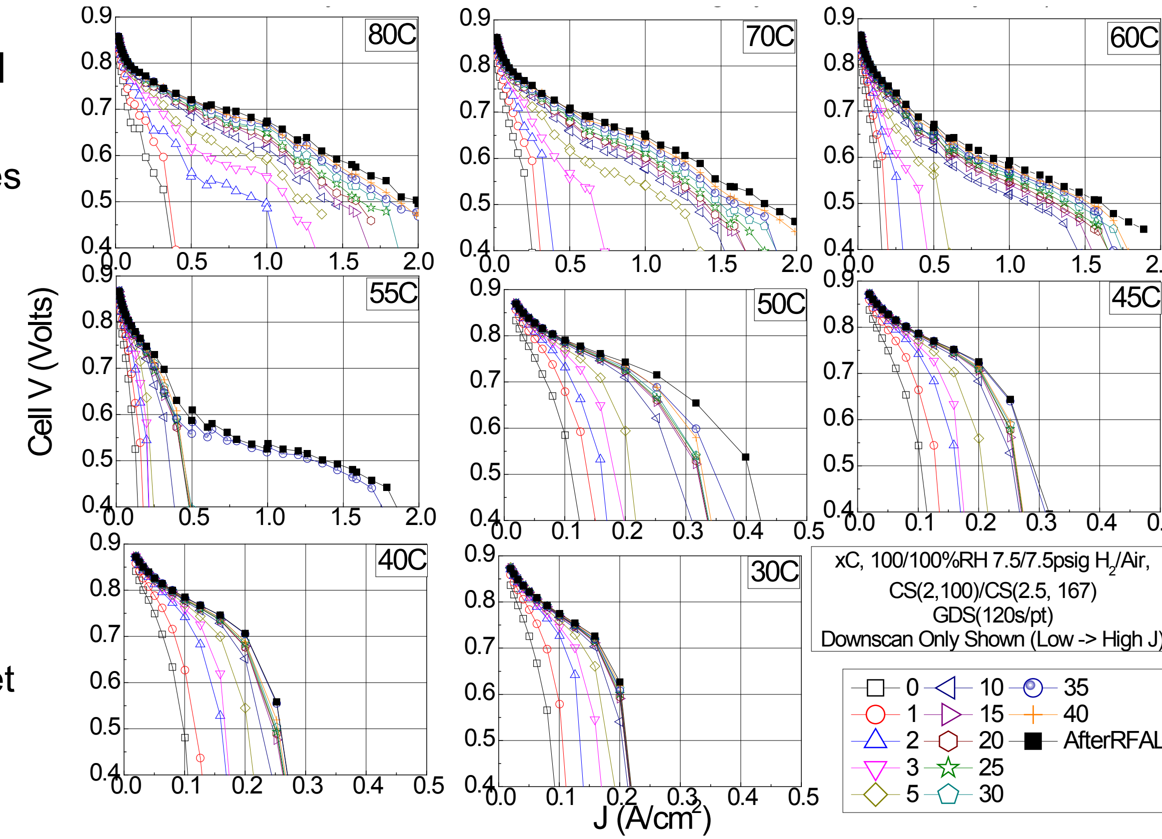

2/2.5 stoichiometry for $H_2$/Air
150/150 kPa outlet pressures

- Performance among the three cell-testing sites is converged
  - Lessons learned
    - Compression and cell assembly/hardware uniformity is critical
    - Need to run and condition NSTF properly

# Thermal-Cycle Conditioning

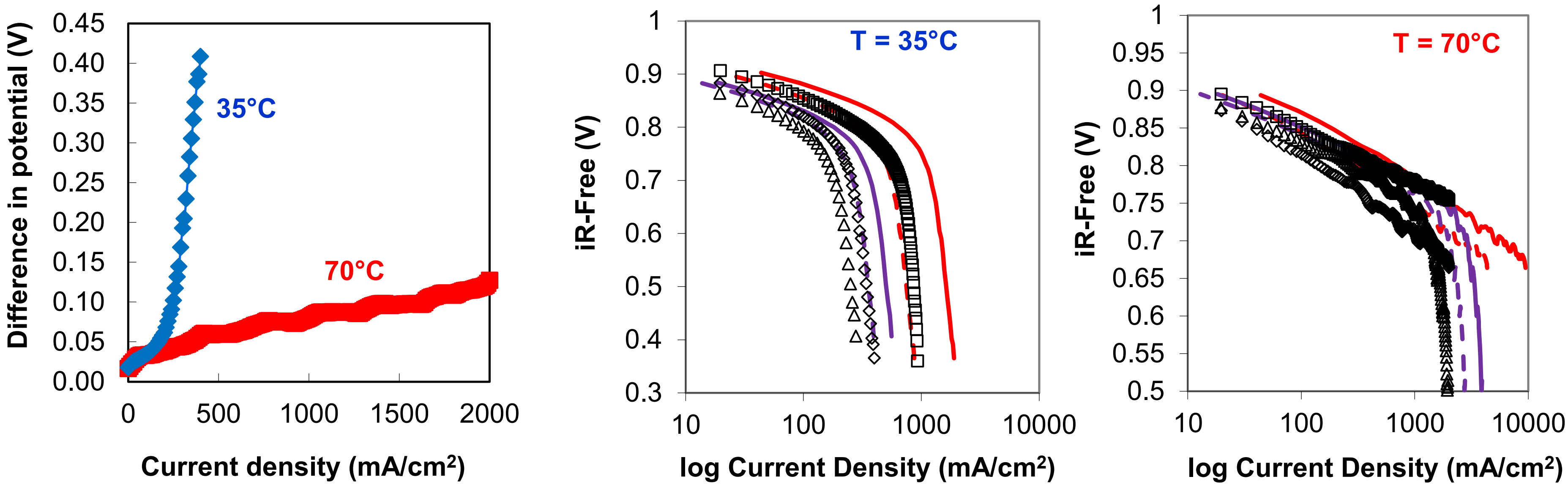
*Thermal cycle: Fixed-flow pol. curves at 70°C (40 min), OCV cool down by liquid-water injection (40 min), repeat*

- With conditioning cycles
  - Limiting current increased 2 to 10x
    - At 30°C, need ~20 cycles
    - At >40°C, need ~40 cycles
      - 70 to 80°C shows major differences after 25 cycles
  - Sensitivity to "over"-humidification decreased
    - Performance difference at 80°C between 100% inlet RH and 100% outlet RH (calculated) decreased substantially after 25 cycles
- Removes MEA contaminants and wets materials



# Oxygen-Gain Analysis

*Determine limitations by examining polarization curves*




- Oxygen gain shows external transport limitations at low temperatures

| Case | Tafel slope | $O_2$ order | Oxygen gain |
|---|---|---|---|
| Kinetic | single | 1 | normal |
| Diffusion | double | 1 | double |
| Ohmic (ionic) | double | 1/2 | normal |

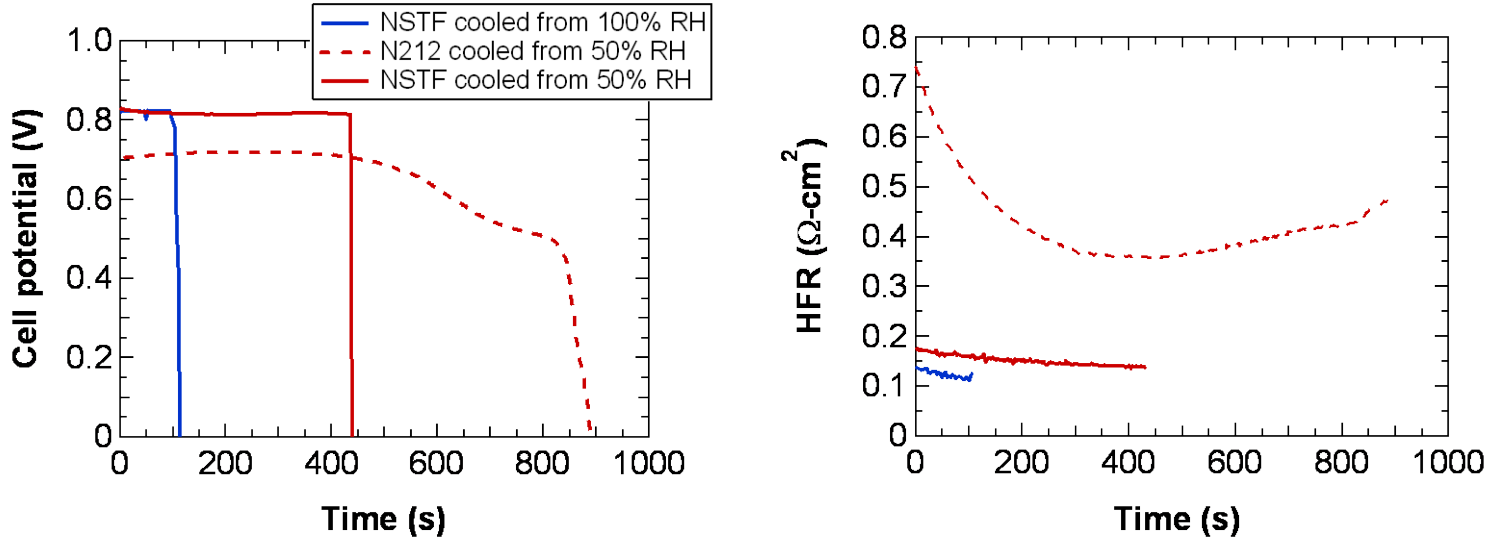
0.05mg PtCoMn/cm2 on H2/O2
0.05mg PtCoMn/cm2 on H2/Air
0.05mg PtCoMn/cm2 on H2/Half Air
Air, (J x 4.75)
Air, (J x sqrt(4.75))
1/2Air to Air, (J x 2)
1/2Air to Air, (J x sqrt(2))

- Analysis of polarization curves suggests ohmic limitations at lower temperatures
  - Higher temperature performance not limited in this fashion
  - Different ionic-transport mechanism with different activation energy?

M. Perry, R. Balliet and R. Darling, "Experimental Diagnostics and Durability Testing Protocols," in *Modern Topics in Polymer Electrolyte Fuel Cell Degradation*, M. Mench, E. Kumbur, and T. Veziroglu, Editors; Elsevier, Denmark (Sept. 2011).

# Isothermal Cold Start

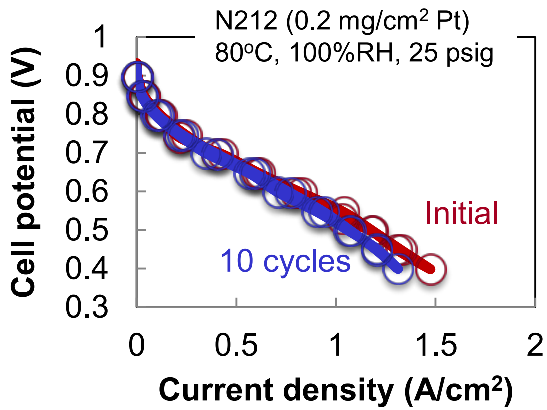
- Isothermal operation at –10°C, 0.02 A/cm$^2$

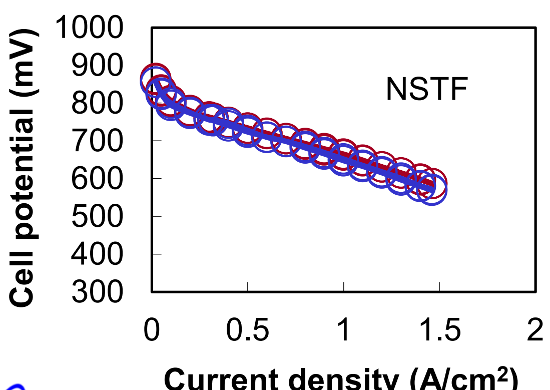



- NSTF MEA has 2 to 9 C/cm$^2$ ice/water-storage capacity depending on initial conditions
  - Most of this water is expected to be in the ~20 μm thick membrane
  - Indicates some water-storage capacity outside of membrane at –10°C operation
- Compared to Nafion® 212 with dispersed Pt electrodes
  - NSTF shows less water-holding capacity
  - NSTF exhibits lower membrane resistance and better performance at –10°C
- Total ice/capacity of cell is increased if
  - Starting membrane HFR is high when cell started at –10°C
  - There is less water in the other components of the MEA/GDL

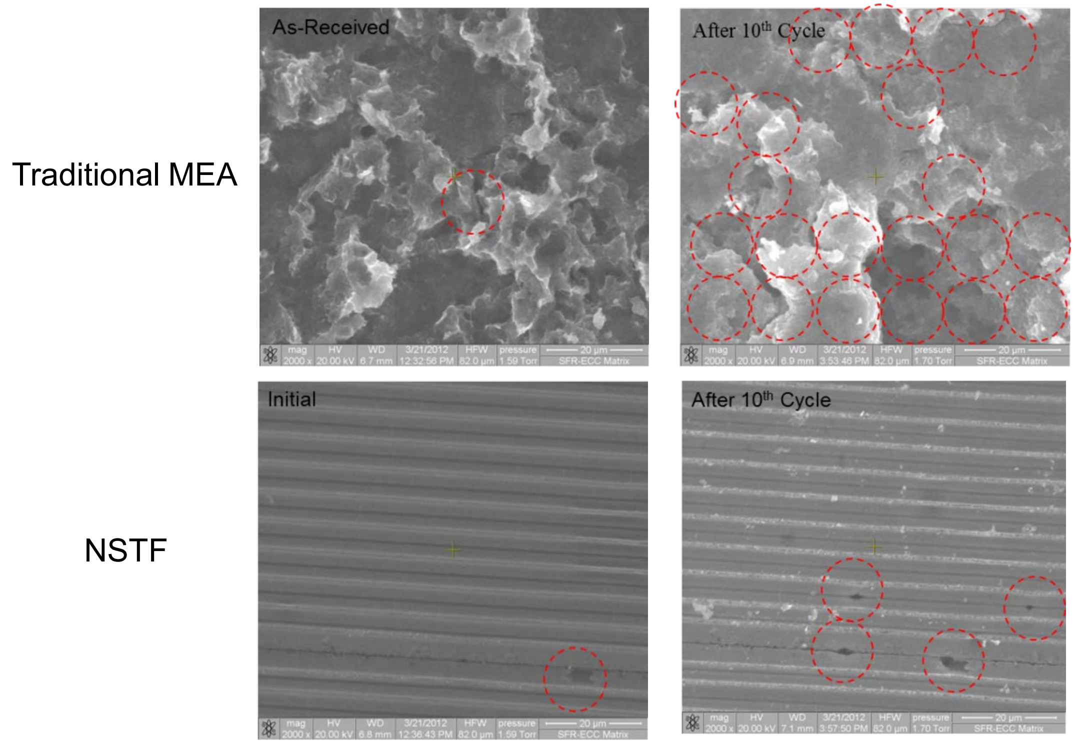
# Catalyst-Layer Freeze Durability

- No significant degradation for NSTF after isothermal starts
  - 10 cycles of isothermal starts at –10°C
  - Loss of ECSA and performance loss for traditional MEAs
    - Possibly related to ice formation and cracking of the CL



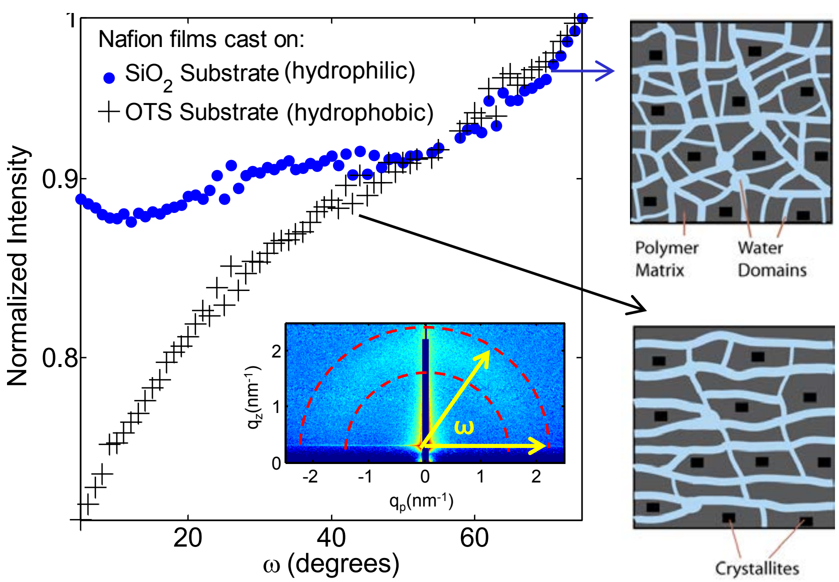




- Cycling from liquid to ice (–10°C) in environmental SEM
  - Significant cracks develop in traditional MEA but not in NSTF

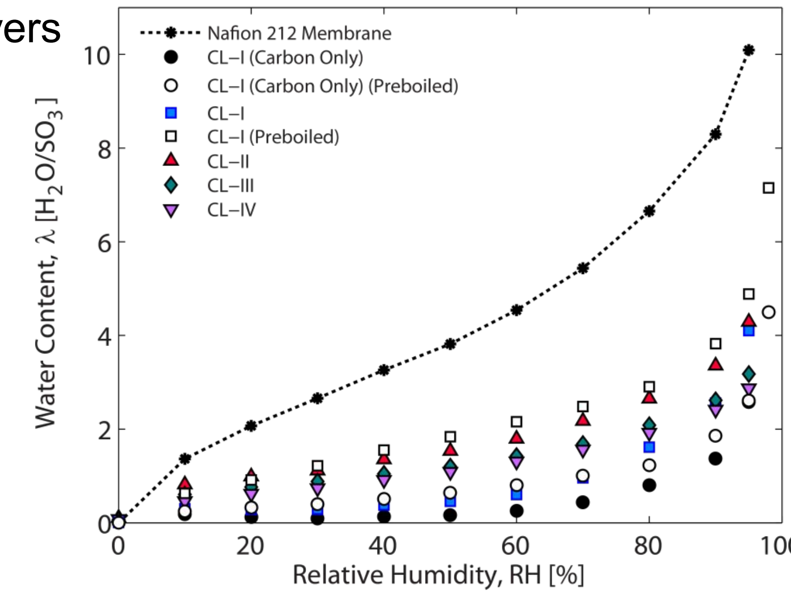


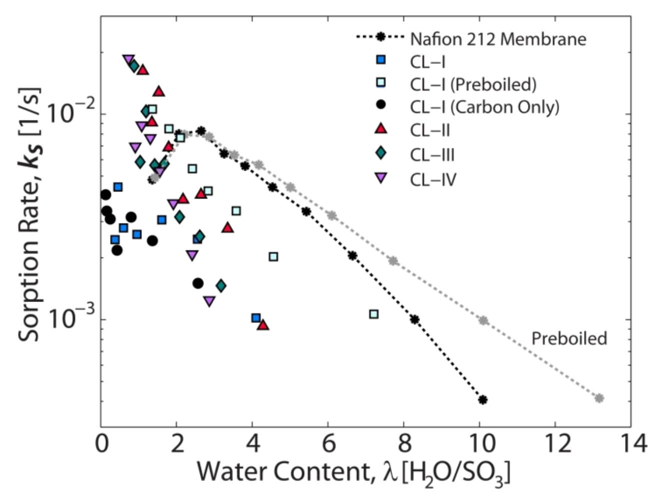
# Catalyst-Layer Water Uptake

- Known that catalyst-layer ionomer absorbs less water and is impacted by Pt
  - Many different commercial and home-made layers
- Investigated morphology of ionomer thin films as surrogate cases using GISAXS



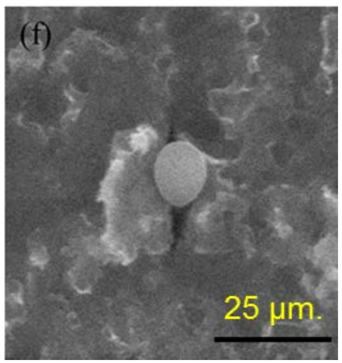

  - Morphology impacted by environment and substrate interactions
- Sorption rates same order of magnitude as bulk film although films are much thinner
  - Similar to pure interfacial resistance



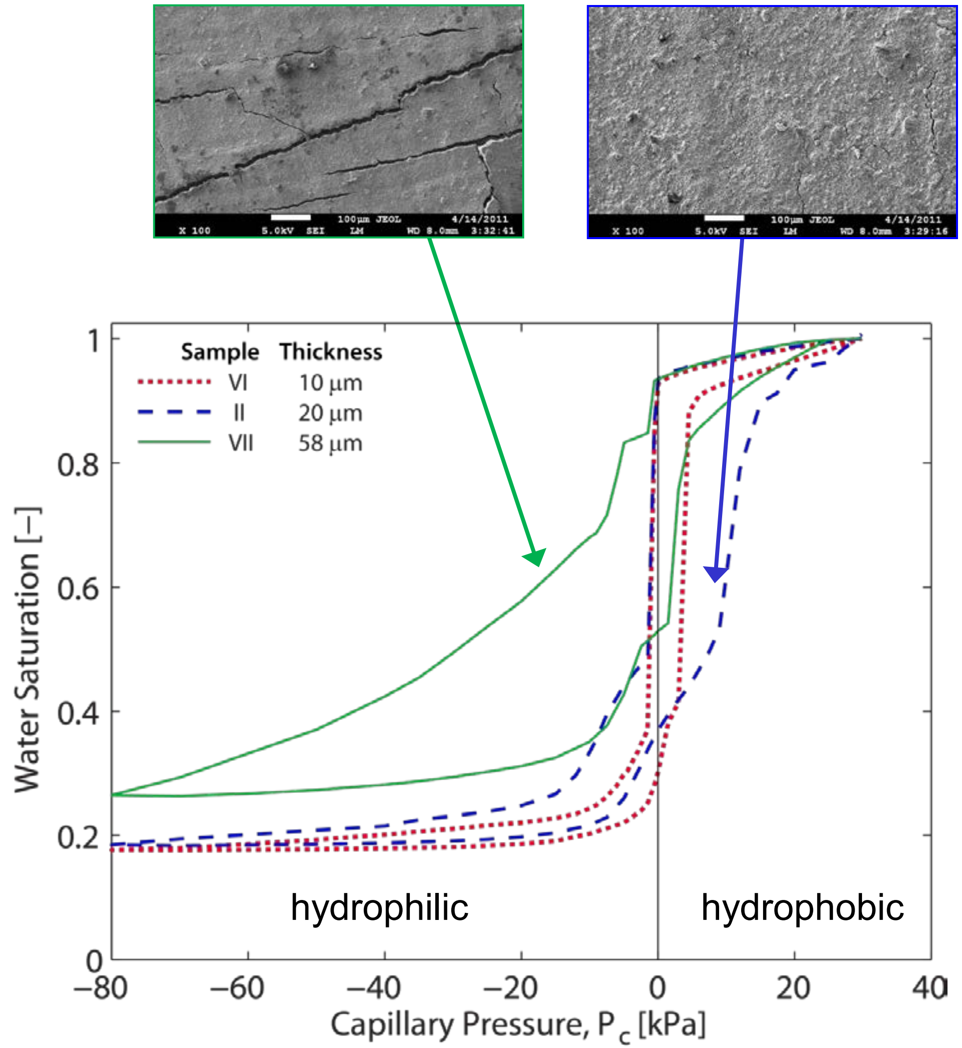
# Catalyst-Layer Water Uptake

- Measured capillary pressure – saturation relationship for traditional catalyst layers
  - Cracked samples are more hydrophilic
    - Caused by the way water wets
      - Environmental SEM



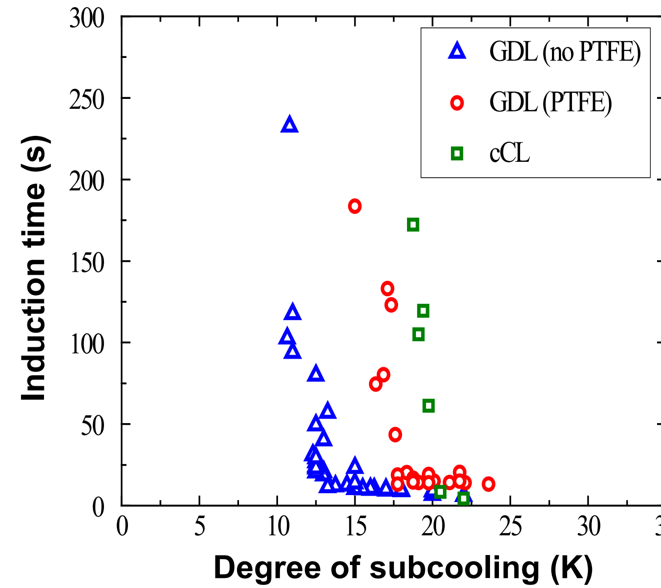

UNIVERSITY OF MICHIGAN

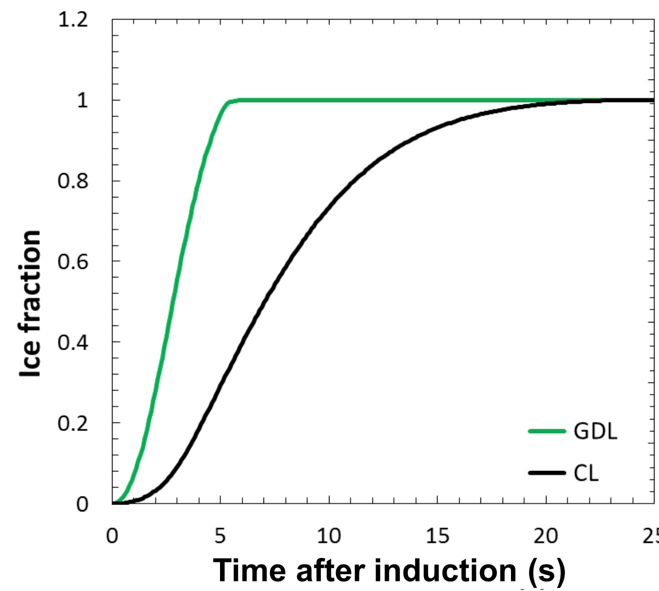
  - All samples are somewhat hydrophilic
    - More than any other component
    - Spontaneous imbibition at 0 capillary pressure
  - No significant temperature impact



# Freezing in Catalyst Layers

- Use dynamic-scanning-calorimetry (DSC) to measure freezing time
  - Cast catalyst layer inside DSC pan
- For induction time expect Poisson distribution due to nucleation theory
- Water takes longer to freeze in the catalyst layer than in the gas-diffusion layer
  - Induction of critical nuclease is longer
  - Crystallization is longer
  - Probably due to smaller pores and membrane interactions
    - Nucleation on a sphere
    - Heat transport from interface
- Currently developing a rate expression and ascertaining its impact



# Membrane Water-Uptake Model

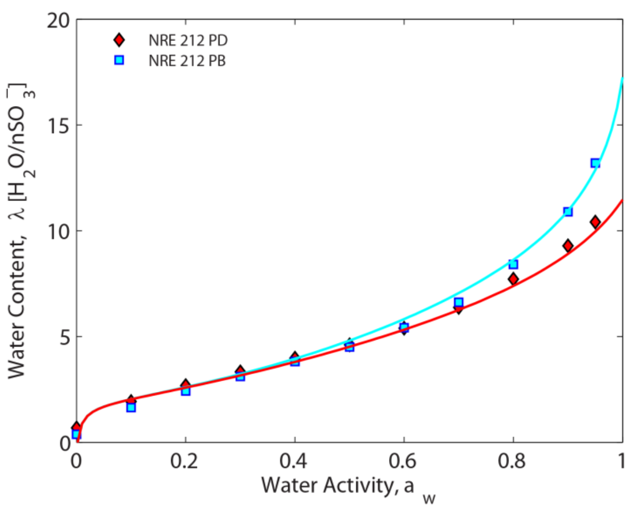
- Use a modeling framework assuming balance between mechanical and chemical energies
  - Swelling equilibrium

$$\mu_w^{ext} = \mu_w^p = RT \ln a_p + \bar{V}_w P$$

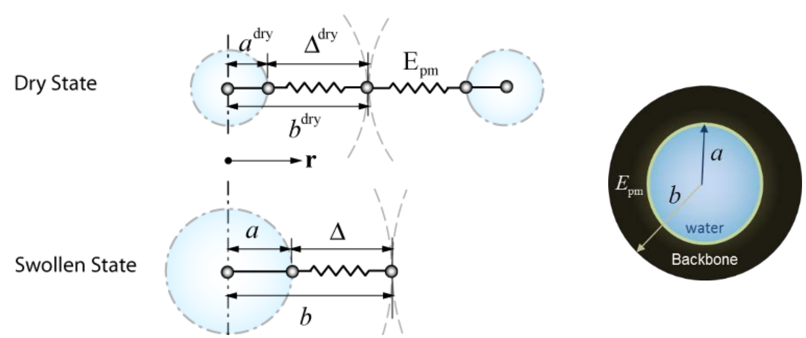
  - Flory-Huggins theory

$$\ln a_w = \ln \phi_w + \left(1 - \frac{1}{\bar{V}_p / \bar{V}_w}\right)\phi_p + \underbrace{\chi}_{\text{Interaction Energy}} \phi_p^2 + \frac{1}{RT}\underbrace{P_s}_{\text{Swelling Pressure}}$$

  - Agrees with water-uptake isotherms



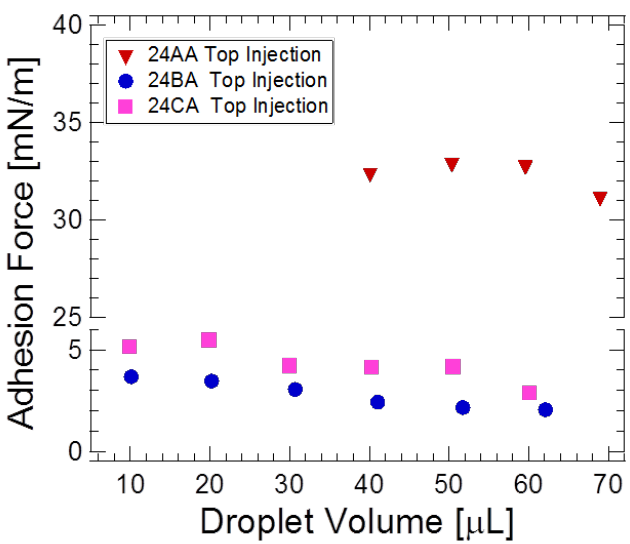

- Swelling quasi-equilibrium
  - Membrane absorbs water
    - Entropic effects
    - Enthalpic interactions
  - Polymer matrix limits expansion
    - Micro-deformation of matrix
    - External loads
    - Pretreatment effects
  - Swelling pressure
  - Informed by SAXS
    - Humidity, compression, annealing, pretreatment



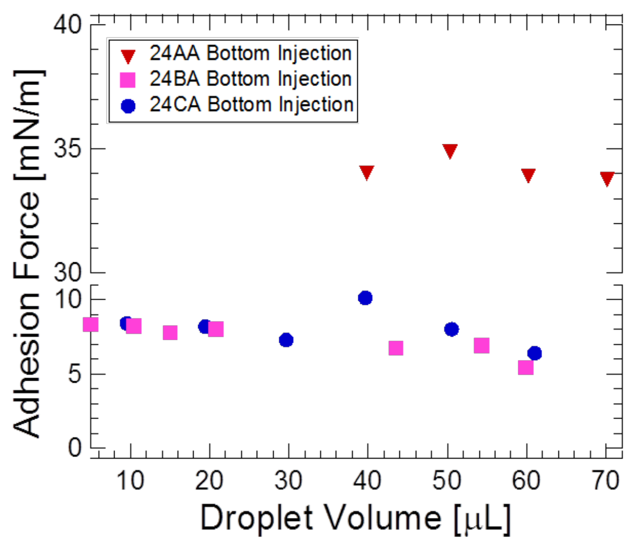
# Droplet Adhesion Force

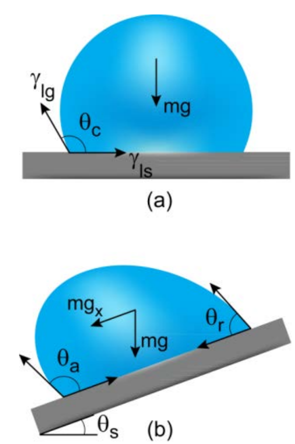
- GDL/channel boundary condition is critical for understanding liquid-water removal
  - Force balance or dynamic movement requires knowing the adhesion force
- Previous use of a static contact angle or its hysteresis is not adequate
- Measure the adhesion force directly
  - Use sliding-angle technique of watching at what tilt angle the droplet moves
    - Correlate the adhesion and gravity forces
    - Measure with both injection through bottom and placement on top

**Top injection**




**Bottom injection**




- Bottom injection results in larger adhesion force

# Future Work

- Cell Performance
  - Testing of non-baseline assemblies
    - Examine low-temperature behavior and conditioning for NSTF $Pt_3Ni_7$
    - Impact of anode GDLs
  - Adiabatic starts including NSTF and low-loaded traditional MEAs
  - Temperature and power transients including segmented-cell and neutron-imaging analysis
- Component Characterization
  - Catalyst Layers
    - More data on water-related properties including ionomer morphology, freeze, water uptake, and gas diffusion
  - Diffusion Media
    - Measure effective gas-diffusion coefficient as a function of saturation
    - How MPLs work with liquid water
    - How does liquid water get out of the GDL (boundary condition)
  - Membrane
    - Structure/function relationships, especially with reinforced membranes and impact of environment
- Modeling
  - Use data from all partners and understand the anode GDL and water-out-the-anode scheme for NSTF
  - Develop transient model and examine CL water capacity versus water removal fluxes or resistances as a function of catalyst layer thickness
  - Mechanical stress model and its impacts on performance
- Examine failed MEAs and cyclical isothermal cold starts for durability concerns
- Rainbow stack studies for temperature distribution and performance characterization
- Understand and increase the operating window with thin-film catalyst layers

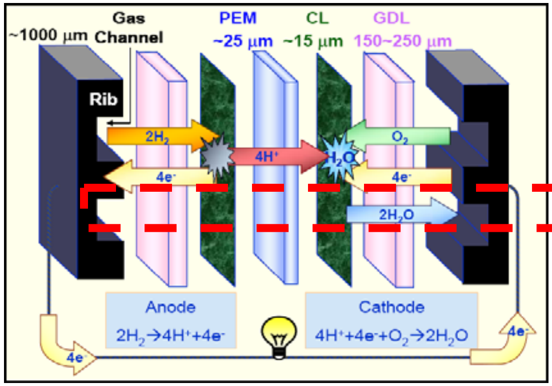
# Summary

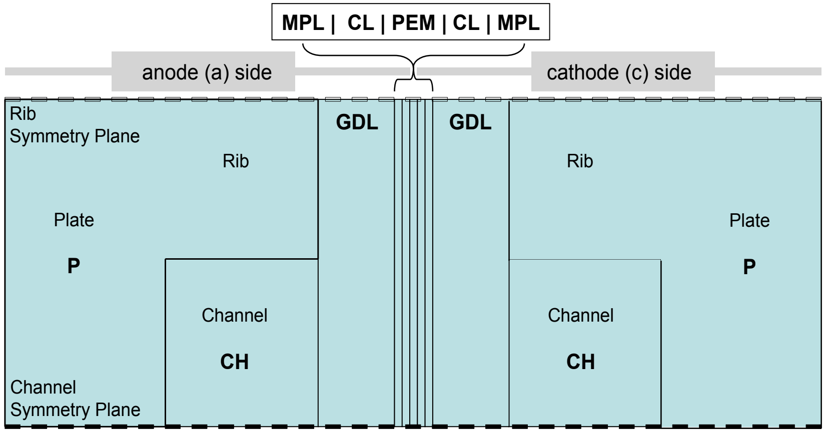
- **Relevance/Objective:**
  - Help enable, optimize, and mitigate failure in state-of-the-art materials through fundamental understanding of operation at low and subzero temperatures
- **Approach/Collaborations:**
  - Use synergistic combination of cell, stack, and component diagnostic studies with advanced mathematical modeling at various locations (national laboratories, industry, and academia)
- **Technical Accomplishments:**
  - Site baseline data converged and systematic cell testing initiated
    - Validating the model and exploring critical parameters
  - Measured adhesion forces accurately and representatively for droplets on GDL surface
  - Isothermal data demonstrate low ice capacity of NSTF but superb durability
  - In-depth examination of membrane structure/function relationships
  - Examined water uptake in traditional catalyst layers
    - Low uptake in ionomer due to interfacial character and morphology
    - Slow freeze kinetics
    - Some hydrophilicity which depends strongly on existence of cracks
- **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

# 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

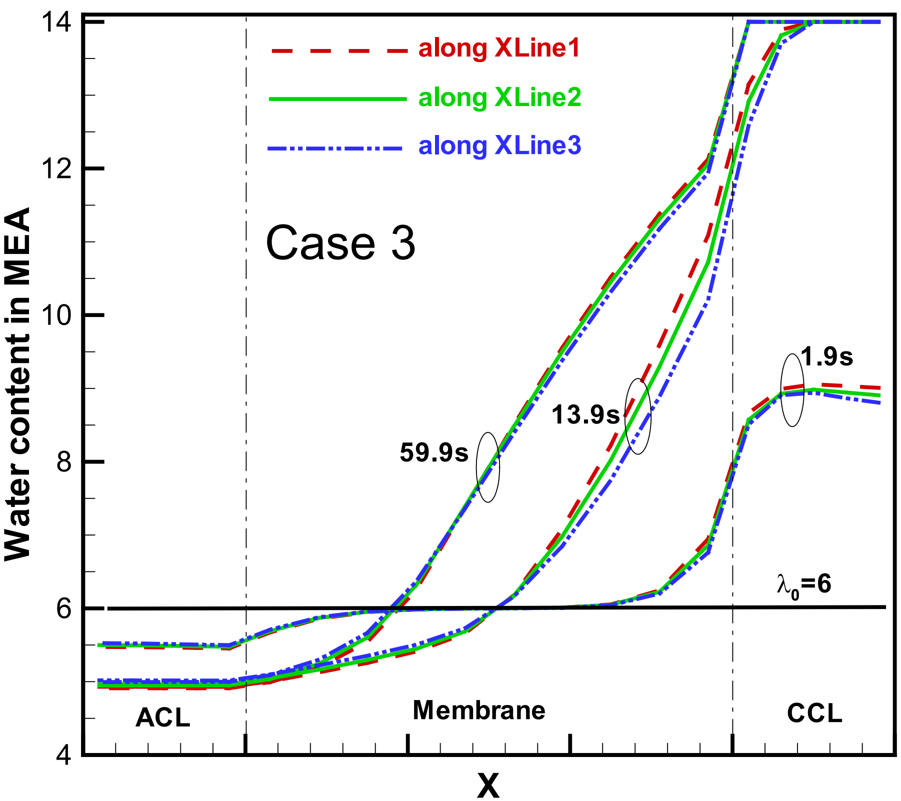
**Properties**

Function of $T$
and $H_2O$ content

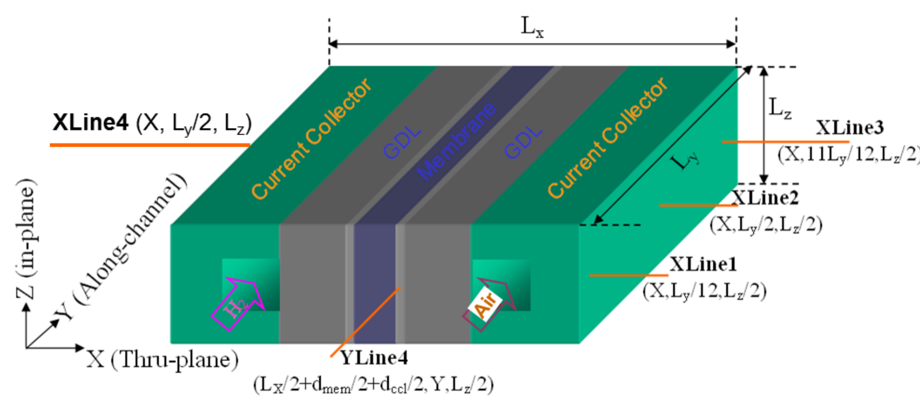
**Equations (14):** 8 $2^{nd}$-order PDEs; 6 Algebraic equations

# Required Model Dimensionality

- Simulation results of water content
  - Not much variation in the 3rd dimensions
    - 2D (XZ) model is sufficient




| | Temperature (°C) | Initial water content in PEM and CLs ($\lambda_0$) | Initial ice fraction in CLs and GDLs ($s_0$) |
|---|---|---|---|
| Case 1 | -20 | 6.0 | 0.0 |
| Case 2 | -40 | 6.0 | 0.0 |
| Case 3 | -20 | 6.0 | 0.15 |
| Case 4 | -20 | 6.0 | $f_2(Y)$ |
| Case 5 | -20 | $f_1(Y)$ | 0.0 |



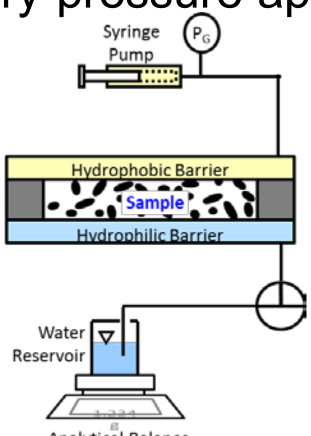

- Under most challenging conditions of cold start, 1D (thru-plane) or 2D modeling is sufficient to understand fundamentals and develop innovative methods.

# Catalyst Layer Studies

- Unique thicker CL samples tested

| Sample | Description | Carbon to ionomer ratio | Platinum Loading [mg/cm²] | Ionomer wt-fraction | Sample Thickness [μm] | Comments on Surface |
|---|---|---|---|---|---|---|
| I | House Made | 5:2 | 1.5 to 1.9 | 0.28 | 25 to 30 | Cracked |
| I CO | House Made Carbon only | 2:1 | 0 | 0.33 | 25 to 30 | Cracked |
| II | Ion Power | 1:1 | 0.15 | 0.44 | 20 | Smooth |
| III | Ion Power | 3:5 | 0.14 | 0.50 | 25 | Smooth |
| IV | Ion Power | 4:5 | 0.11 | 0.57 | 25 | Smooth |
| VI | Ion Power | 1:1 | 0.12 | 0.44 | 10 | Smooth |
| VII | Ion Power | 1:1 | 0.27 | 0.44 | 58 | Cracked |

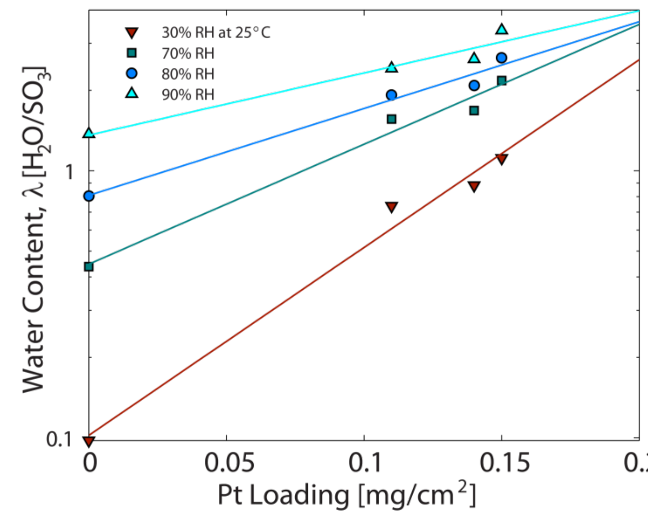
- Capillary-pressure apparatus

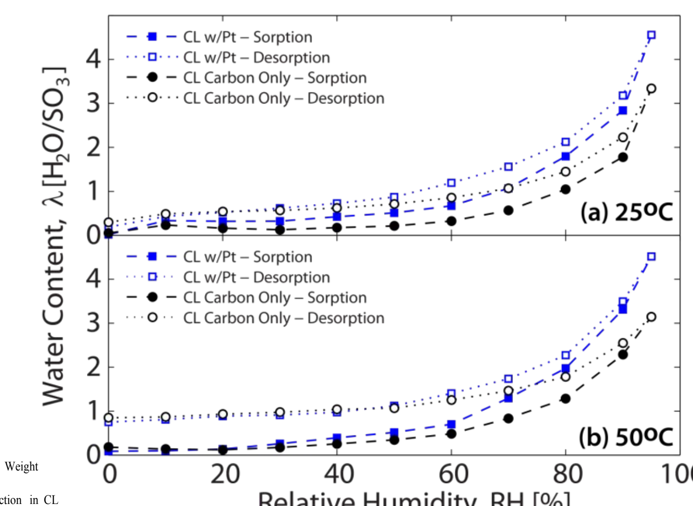



$$\lambda = \frac{n(H_2O)}{SO_3\ \ Group} = \frac{M_w/\overline{M}_w}{M_i/EW} = \frac{M_w/\overline{M}_w}{M_{CL}}\frac{EW}{f_i}$$

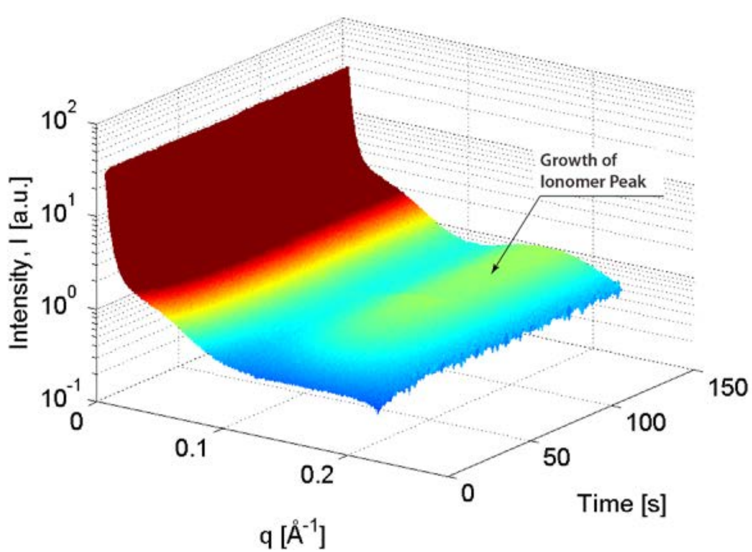
← Equivalent Weight
← Ionomer Fraction in CL

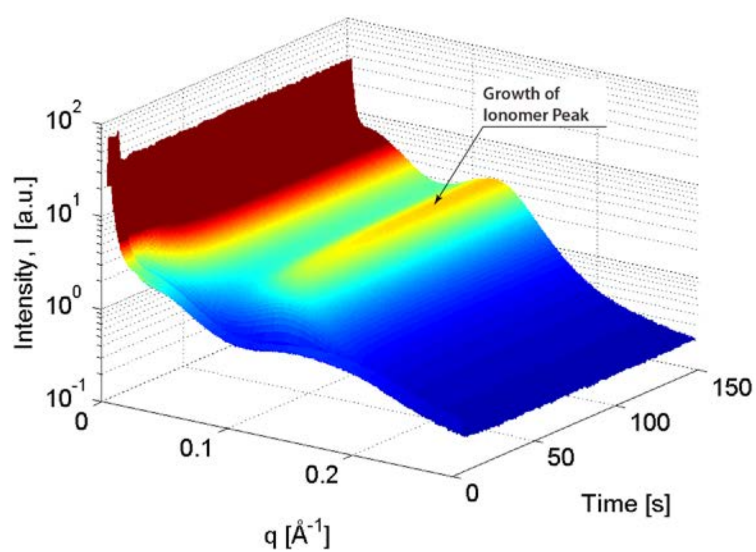
- Impact of Pt is power law for ionomer water uptake



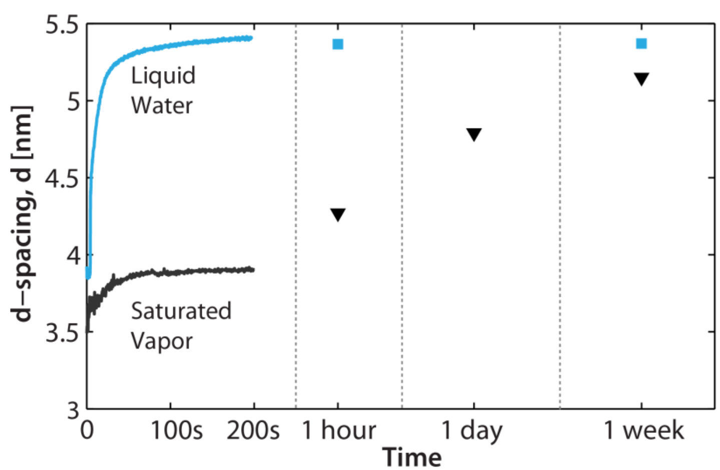



# Dynamic SAXS of Water Uptake in Nafion®




- Interactions with liquid or vapor create different morphologies
  - Interface seems to control kinetics
  - Liquid changes within seconds
  - Vapor takes much longer
    - On the order of days



# Effect of Compression on Domain Spacing

- In-plane d-spacing at various humidities
  - Compression affects nanostructure, especially for hydrated membranes
  - Domain spacing increases in the plane with thickness pressure (high RH)