Fuel-Cell Fundamentals at Low and Subzero Temperatures

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<u>Solicitation Partners:</u>

United Technologies Research Center

Los Alamos National Laboratory

3M Company

The Pennsylvania State University

Project ID # **FC 026**

May 15, 2013

Overview

Timeline

- Project initiated FY09
  - Start **September 2009**
- 4 year project duration
  - End **September 2013**
- ~85% 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 FY11: $812.5k
- Funding Received in FY12: $1,290k
- Planned Funding for FY13: $1,095k
  - LBNL $510k
  - Partners $585k

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, Ahmet Kusoglu, Clayton Radke, Alastair MacDowell, Alexander Hexemer, Frances Allen
- 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 (directly funded through other DOE projects)
  - **Ion Power**: Stephen Grot (membrane and MEAs)
  - **NIST**: Daniel Hussey, David Jacobson (neutron imaging of water)
  - **The Pennsylvania State University**: Michael Hickner (membrane thin films)
  - **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\Calgary University:** Kunal Kuran (Nafion® thin-film data and samples)
  - **University of Michigan**: Massoud Kaviany (Nafion® MD simulations, ESEM)

Relevance: Objectives

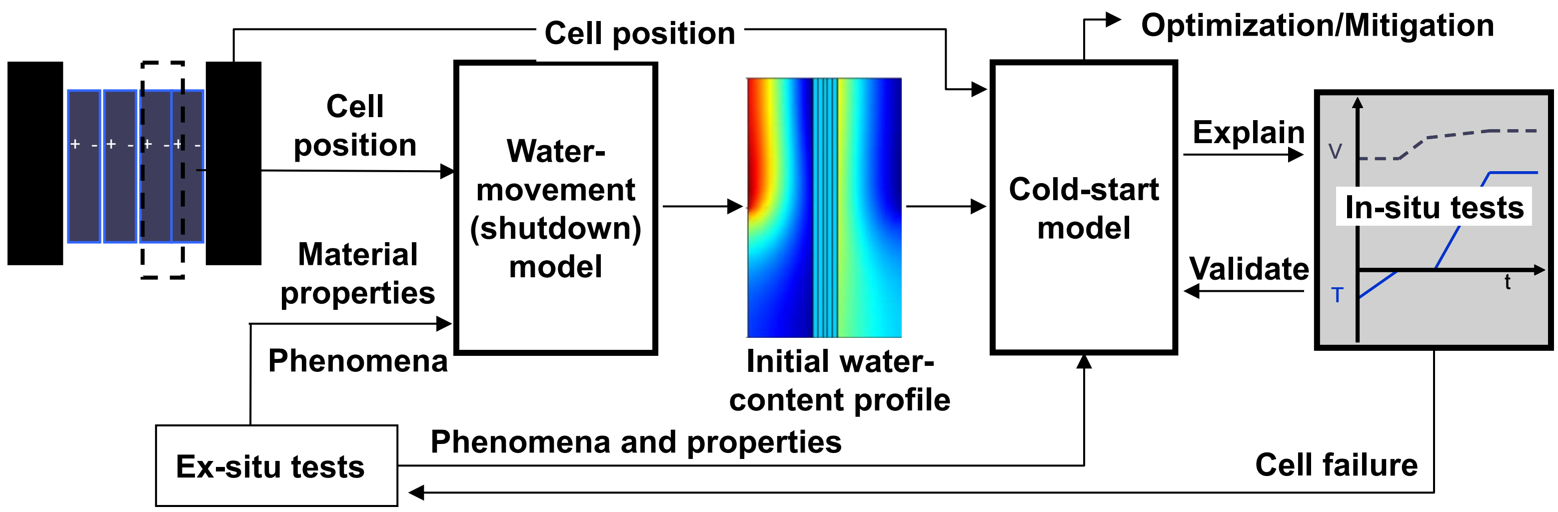
- Fundamental understanding of transport phenomena and water and thermal management at low and subzero temperatures using state-of-the-art materials
  - Examine water management with thin-film catalyst layers (NSTF)
  - Examine water management and key fundamentals in the various fuel cell components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

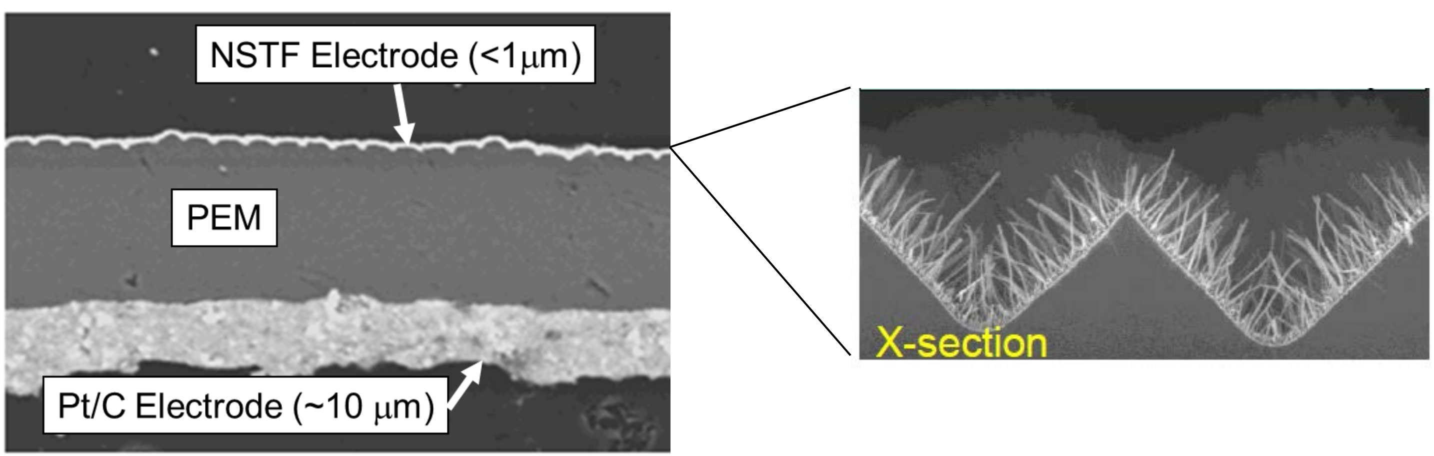


- Multi-scale, multi-physics continuum-based modeling
  - Develop, validate, and refine a series of models for cell performance including cold and cool operation, startup, and shutdown
- Experimentally characterize component, cell, and stack properties and performance
  - Measure critical properties 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		
Catalyst layer	NSTF PtCoMn	Low-loaded traditional	
GDL	MRC	SGL	Freudenberg
MPL	Hydrophobic	None	
Flow field	Quad serpentine		
Bipolar plate	Solid	Hybrid (one WTP)	



Workplan/Organization

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

Task	Lead	Partners	Activities
Task 1. Cold-start model	**LBNL**	PSU	Steady state Startup Simple stack 3-D effects
Task 2. Degradation model	**LBNL, PSU**		Property degradation Mechanical stress
Task 3. Stack and cell characterization	**UTC**	LANL, 3M	Performance evaluation Stack studies Failure analysis
Task 4. Water imaging	**LANL, LBNL**	PSU	Neutron X-ray
Task 5. Model deployment	**LBNL**	PSU	Cold-start optimization Performance loss Failure mitigation
Task 6. Component characterization	**LANL**	LBNL, 3M, PSU	Membrane Catalyst layer 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, single-cell testing, and testing knowledge including conditioning procedures

UTRC

- Cell parametric studies
- Identify failure mechanisms
- Real-world guidance

PSU

- Develop 3-D scaling expressions and mechanical stress model

Other

- Provide unique materials and diagnostics

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Approach: FY13 Project Timeline

Begin	M1	M2	M3	M4	M5	M6	M7,M8,M9	End
10/12	11/12	12/12	02/13	03/13	05/13	06/13	09/12	09/13

Major Milestones/Deliverables

M1: Correlation developed between isothermal start and freeze/thaw with observed catalyst-layer cracking under ESEM and in-situ cell studies. (*completed, NSTF has much greater durability*)

M2: Impact of 3 different GDLs on cell performance with two different cell-compression levels. (*completed*)

M3: Agreement (<10% deviation) between model analogs and real MPLs in terms of breakthrough pressure and capillary-pressure – saturation behavior. (*delayed due to issues of finding appropriate model materials*)

M4: Results of impact of water balance on startup performance for both NSTF and low-loaded traditional MEAs. (*slight delay due to experimental reproducibility that appear to be resolved*)

M5: Report of rainbow short-stack results with different cell diffusion media and baseline MEAs. (*changed to studies using the adiabatic cell based on reviewer and Tech Team feedback*)

M6: Complete low and high resolution imaging of 3M cells and report results to LBNL. (*on track, some high resolution studies already completed*)

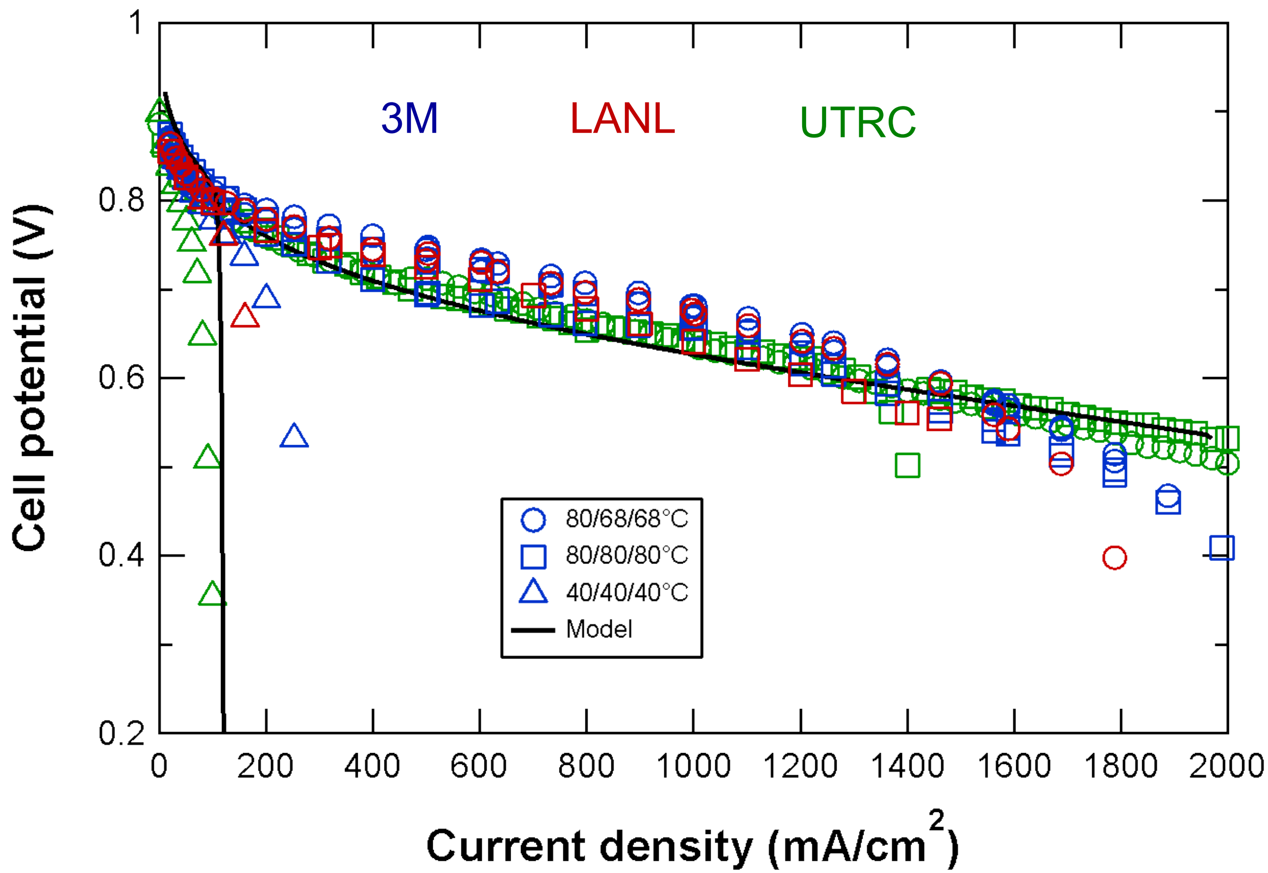
M7: Report on optimum operating conditions and material properties for NSTF catalyst layers operating below 55°C. (*on track, model agreeing with experiments and now looking at parameter space*).

M8: Impact of 3 different NSTF peak heights on cell performance. (*on track, 1 of 3 peak heights completed*)

M9: Model results showing importance of compressive loads and mechanically induced degradation by layer including experimental comparison with ice-front propagation. (*on track, initial mechanical model completed*)

Baseline Performance

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

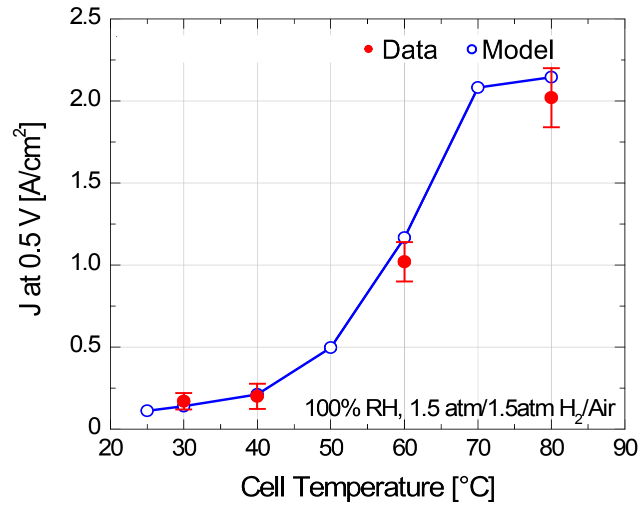


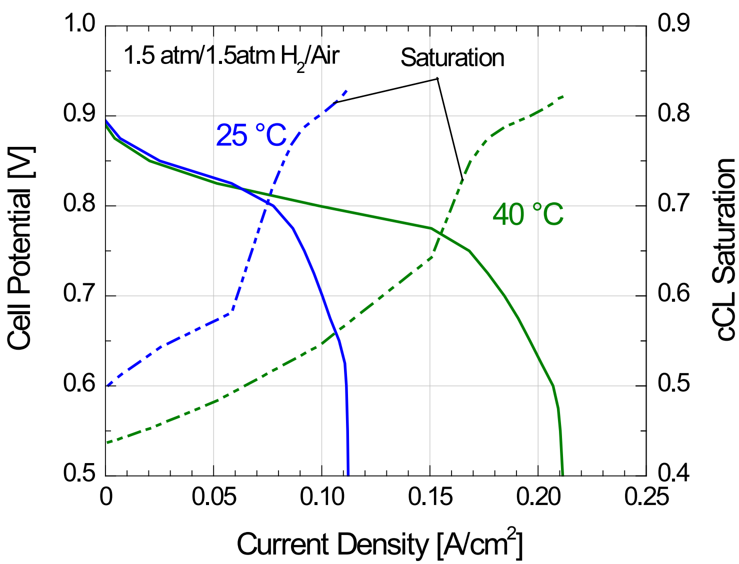
2/2.5 stoichiometry for H_2/Air
150/150 kPa outlet pressures

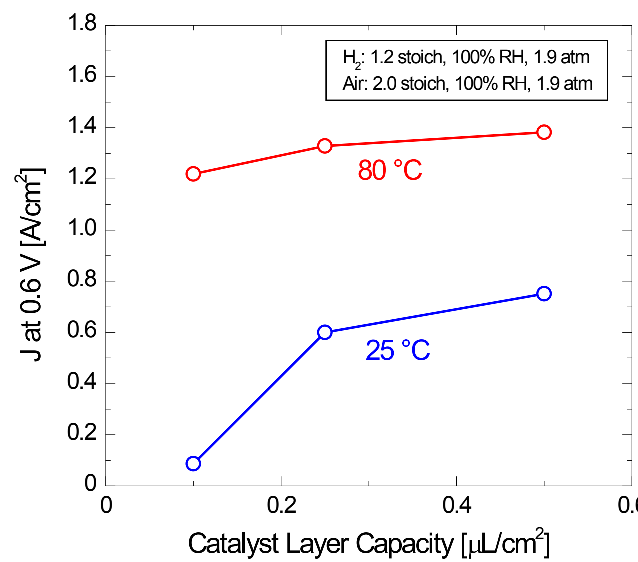
- Performance among the three cell-testing sites is converged
  - Lessons learned
    - Compression and cell assembly/hardware uniformity is critical
    - Need to run and condition NSTF properly

Modeling NSTF

- Use 2-D mathematical model to examine performance with NSTF
  - Good agreement with experimental data
  - Significant reduction in limiting current as temperature drops from 70 to 40°C
    - At higher temperatures the CL temperature is high enough to remove water through vapor phase by phase-change-induced flow
    - Near room temperature, severe CL flooding reduces the limiting current due to low water-capacity of NSTF CL

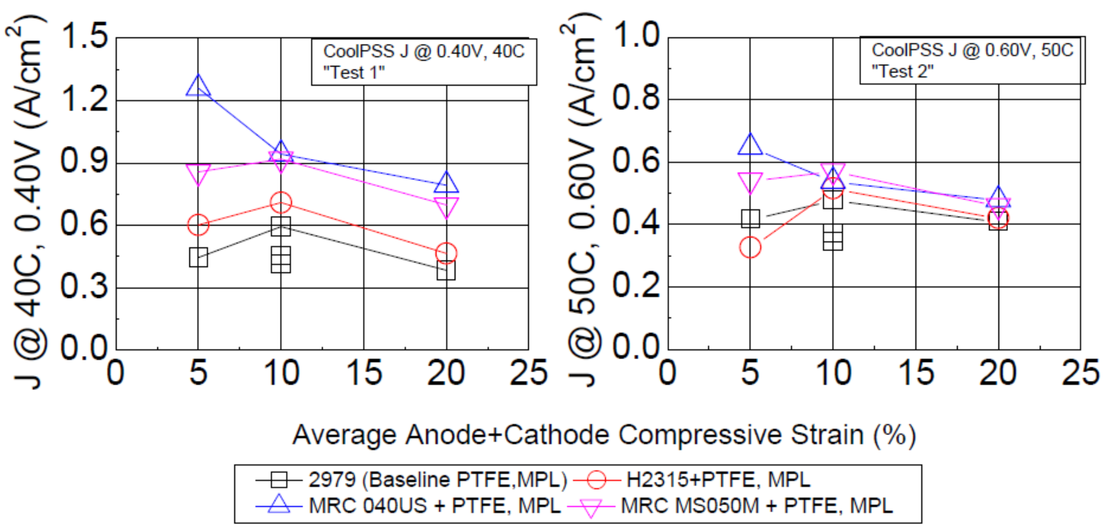


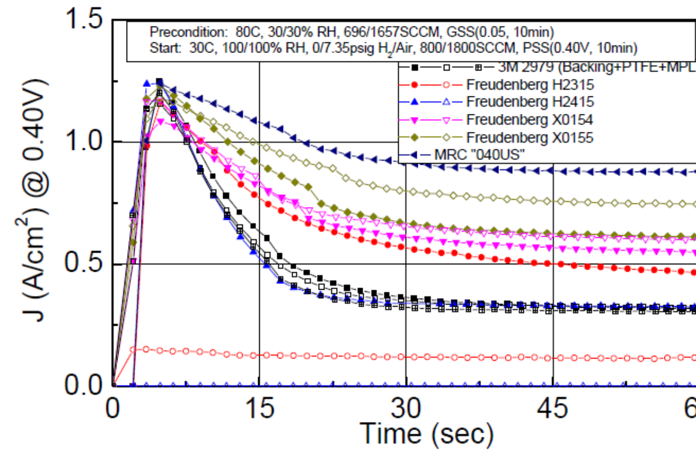




Anode GDL Studies

- Evaluation of 4 anode GDLs (backing+PTFE, MPL) as a function of GDL strain
  - Transient and steady state show better low-temperature performance with MRC 040US
    - MRC 040US resistance remains too high



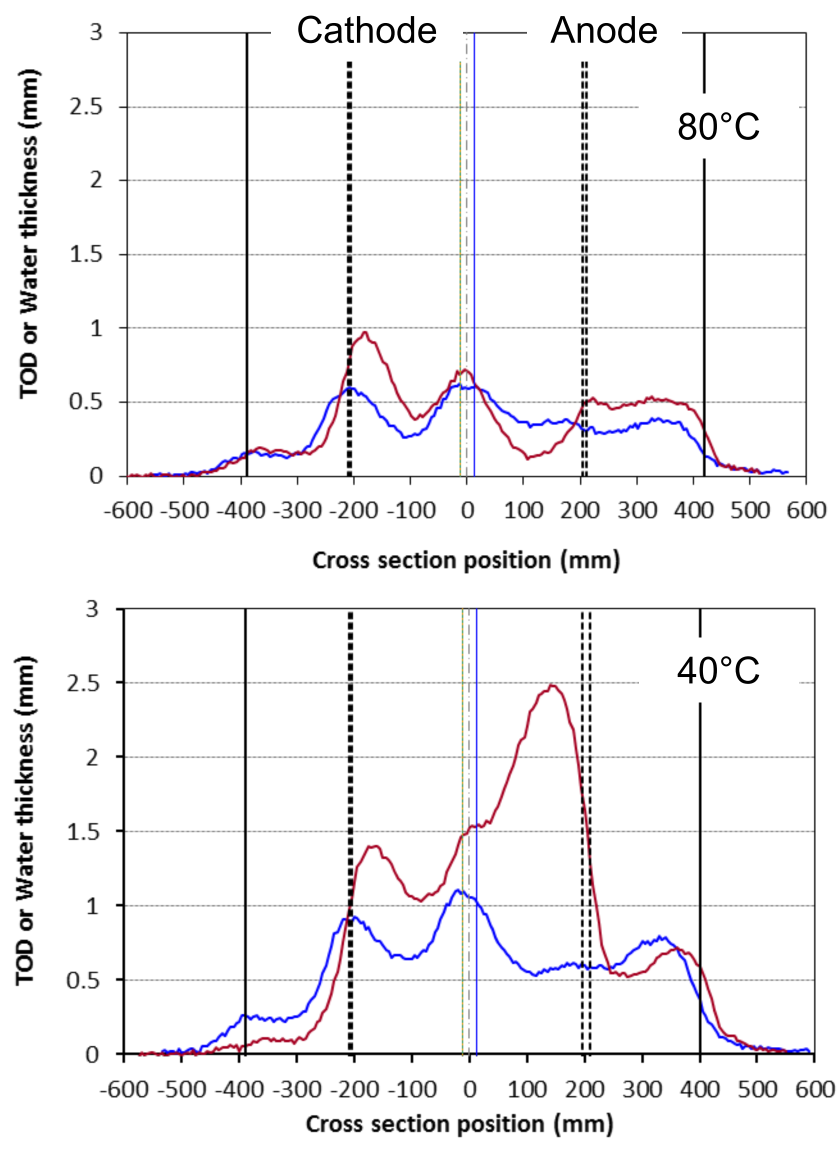


- Response generally decreases as compression increases from 10 to 20%, less consistent results for 5 to 10%

- Drop off of performance as approach 40 to 50°C

Anode GDL Studies

- Use high-resolution neutron imaging to compare water profiles between NSTF with **2979** and **MRC 040US** anode GDLs at 0.3 V
  - Less water at 80°C than 40°C
  - MRC 040US anode GDL consistently has less water in the MEA



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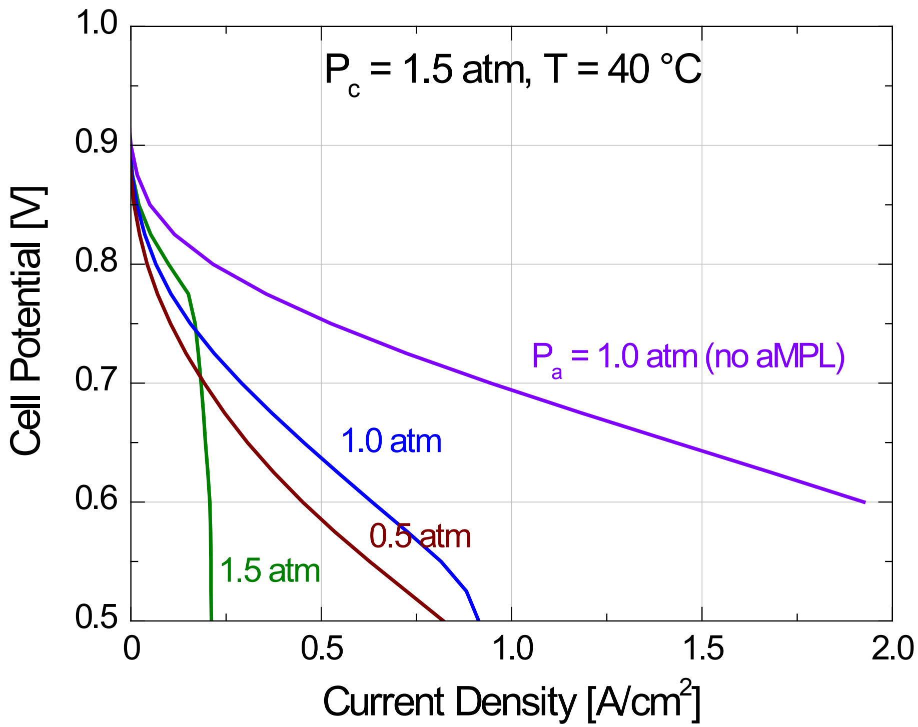
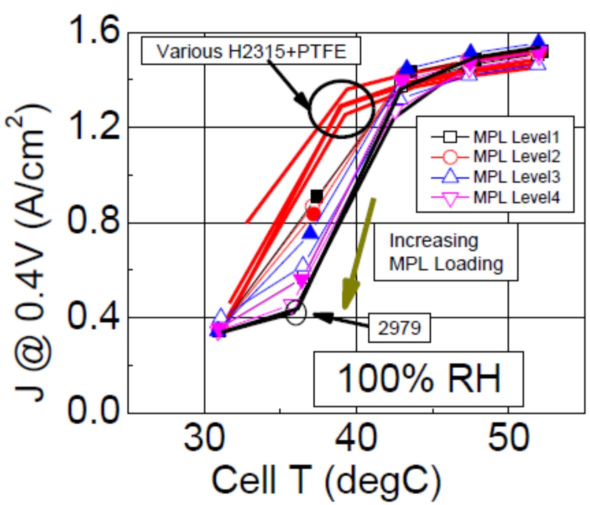
Anode GDL Studies

- NSTF MEA low temperature performance is very sensitive to anode backing
  - Specific material factors responsible currently unknown

Model



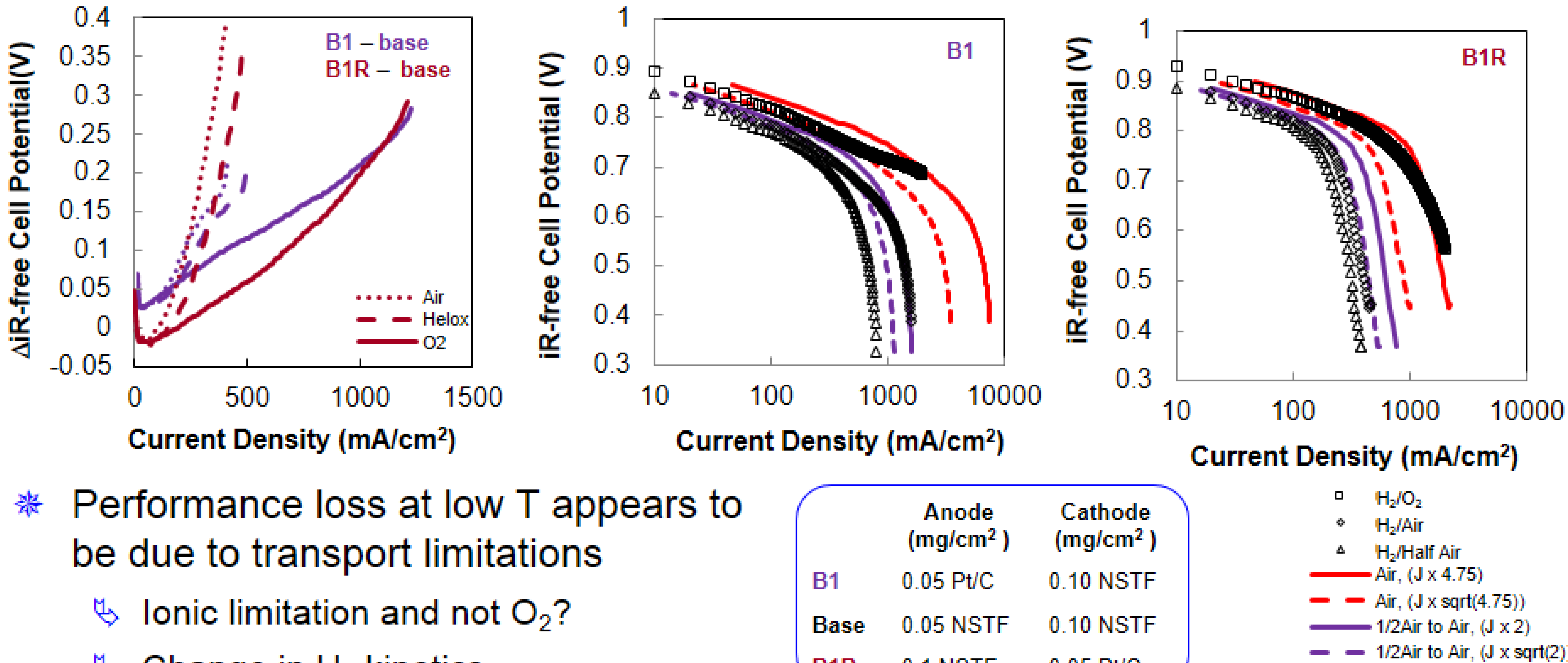
Data



- Model shows the importance of reducing liquid-water transport resistance and enhancing back transport

Oxygen-Gain Analysis

Examine hybrid cells at 35°C with one NSTF and one Pt/C

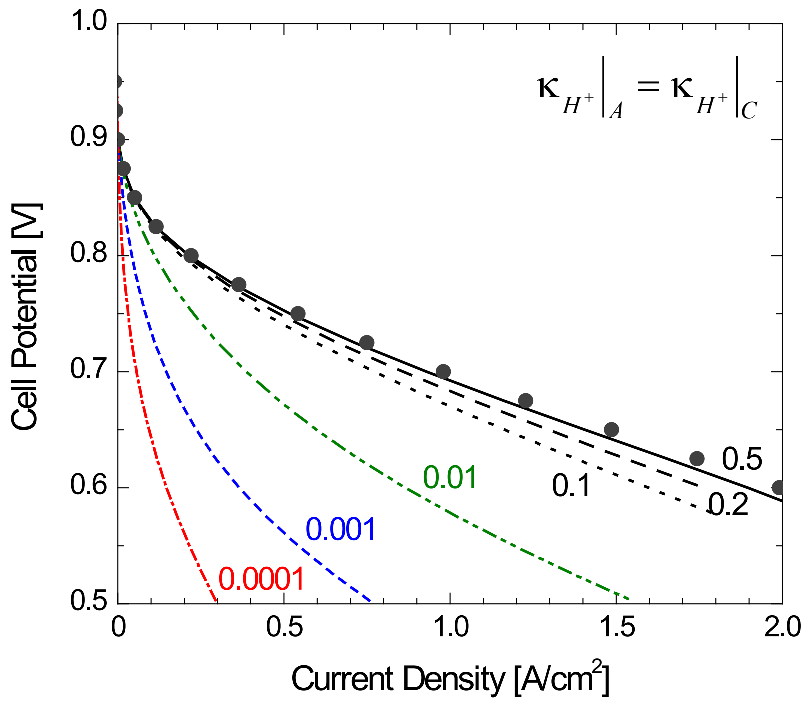


	Anode (mg/cm²)	Cathode (mg/cm²)
B1	0.05 Pt/C	0.10 NSTF
Base	0.05 NSTF	0.10 NSTF
B1R	0.1 NSTF	0.05 Pt/C

- Performance loss at low T appears to be due to transport limitations
  - Ionic limitation and not O_2?
  - Change in H_2 kinetics
  - Anode NSTF
    - Performance a function of oxidant
    - Ohmic limited at moderate current; limiting currents are ~ 1st order
  - Cathode NSTF
    - Different behavior on different oxidants 1st order on O_2, ~ ½ order on air

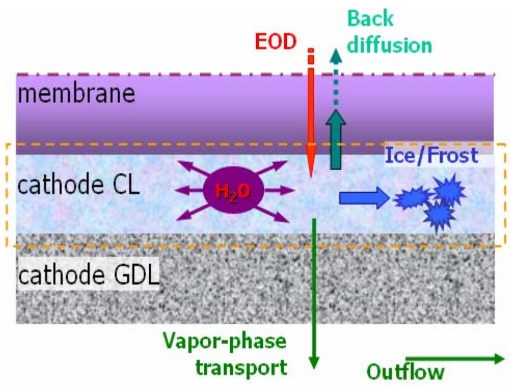
Impact of Proton Conductivity

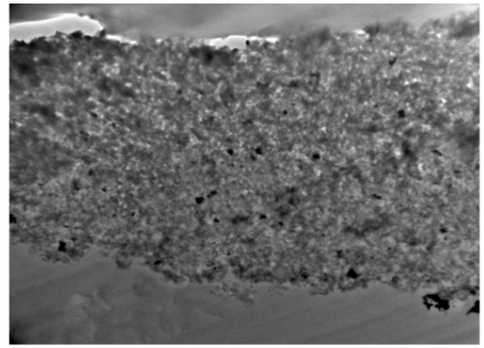
- Parametric study using **model** without aMPL at 40°C
  - NSTF proton conductivity has strong influence on the cell performance when conductivity is below 0.1 S/m



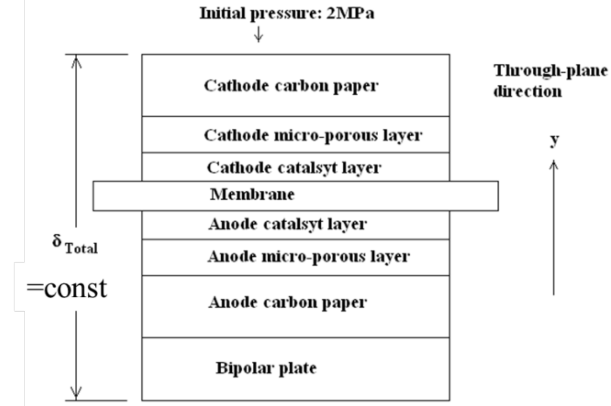
Mechanical Stress Modeling

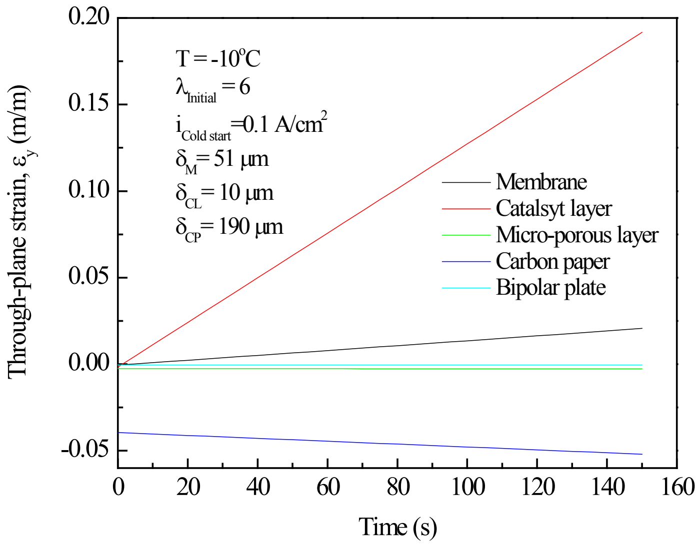
- Stress model of fuel-cell sandwich for purge and cold start

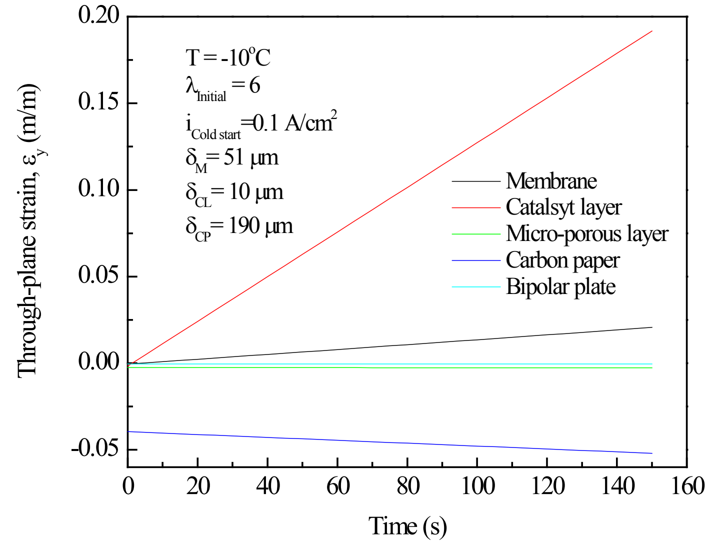




Interfacial delamination after 110 cycles of cold-start at 500 mA/cm²



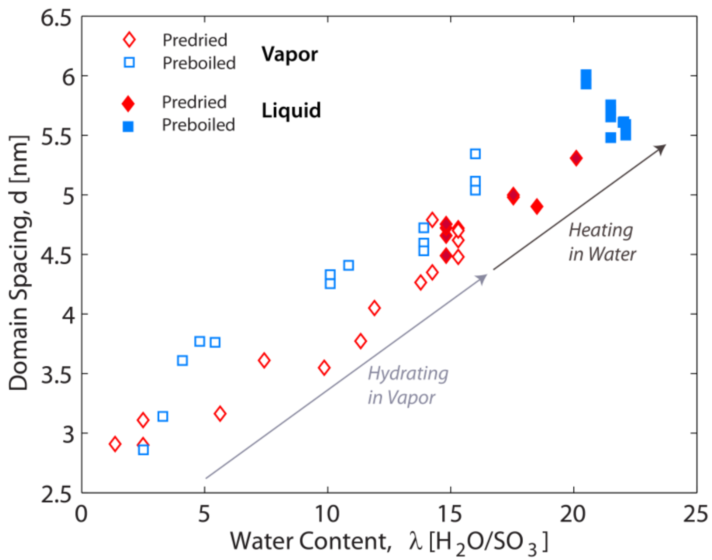


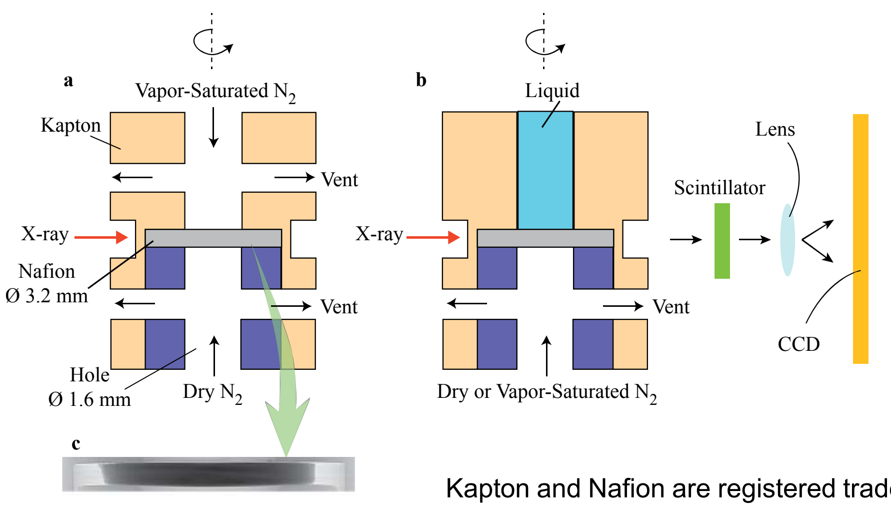


- During cold start, ice production yields very large strain in CL, which could cause CL/mem delamination and CL pore structure collapse
- Cold start from low temperatures leads to large mechanical stress, and high start current density leads to large strain in CL

Membrane Water Profiles

- Understand that pretreatment, crystallinity, and humidity effects are controlled by same chemical/mechanical energy balance
  - Have seen some existence of interfacial phenomena
  - Unknown whether Schroeder's paradox occurs during a gradient
  - The water diffusion coefficient in literature varies, especially its dependence on water content
    - Expect different concavity in water profiles for dynamic versus steady state

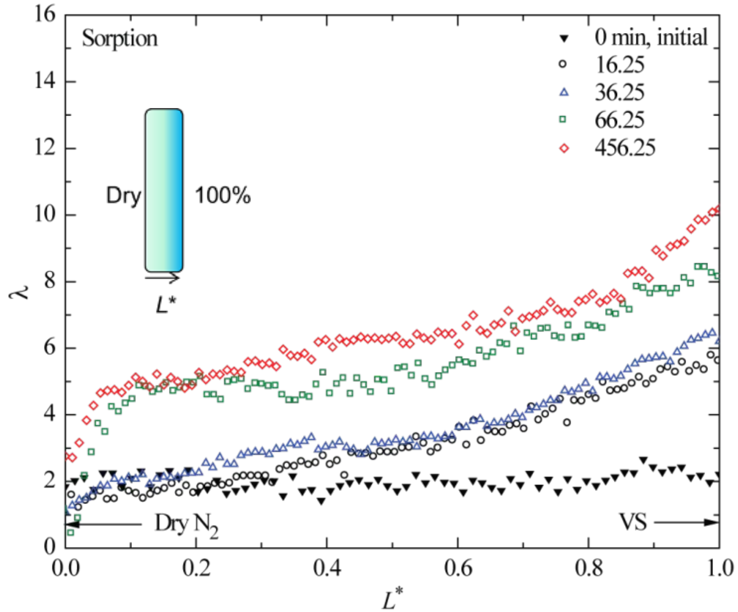




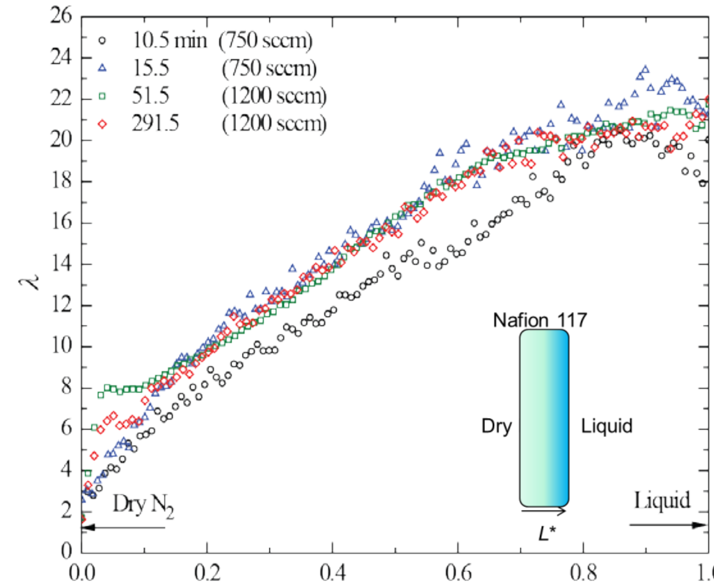
- Measure membrane water profile
  - Use x-ray computed microtomography
    - Good combined temporal (~min) and spatial (~μm) resolution

Membrane Water Profiles

Sorption from Dry to 100% RH



Sorption from Dry to Liquid

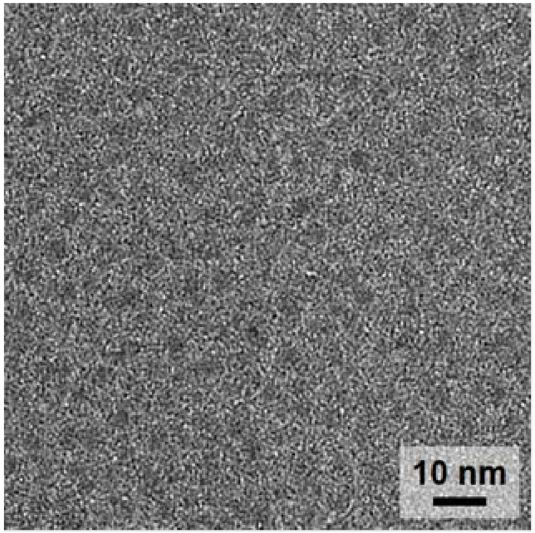


- With saturated vapor/dry, complex transient and steady-state profile
  - Shape changes from concave to convex with time
    - Agrees with different dependence of diffusion coefficient for dynamic and steady state
  - Lower values at boundaries suggest interfacial resistance
- With liquid/dry, rapid approach to steady-state profile
  - Profile is continuous from λ = 22 to 4
    - No liquid interfacial resistance
    - No evidence of sharp transition from liquid to vapor value

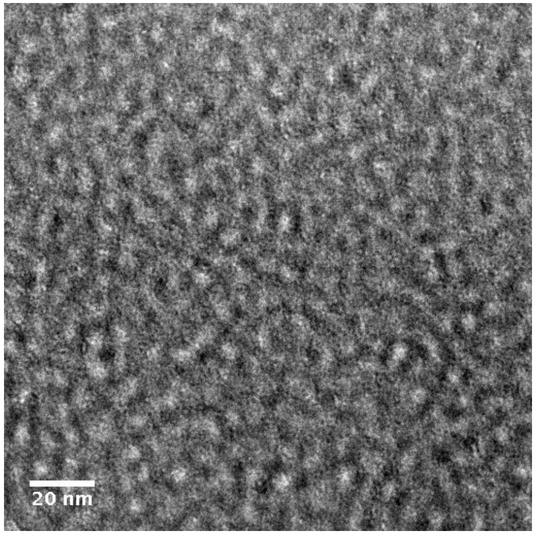
Membrane Morphology

- Examine morphology using SAXS and also TEM

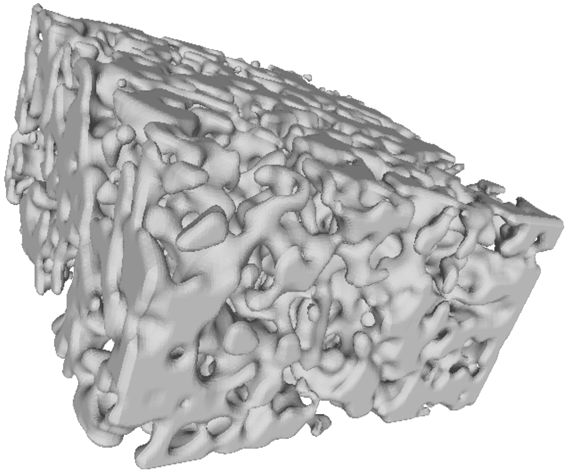
Dry (TEM)



Hydrated (cryoTEM)



Simulated from SAXS



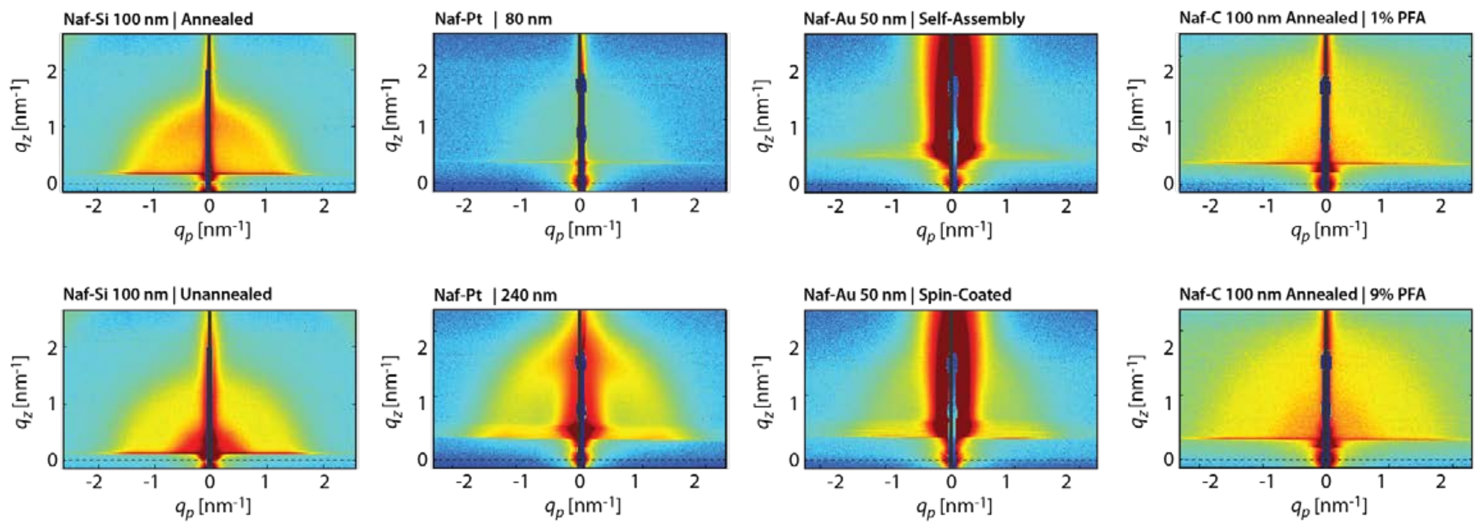
  - Need to determine what the phases are using low-loss EELS
  - Next would be to model transport through the morphology

Thin-Film Morphology

- Thin-film Nafion® shows different morphology
  - Structure depends on interfacial interactions and film thickness
  - Correlating structure with mass uptake and swelling

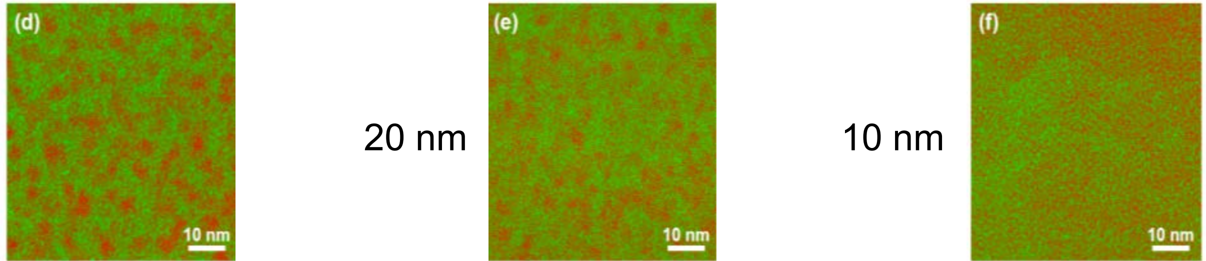
Nafion-Si	Nafion-Pt	Nafion-Au	Nafion-C
Annealing induces crystallinity in films	Thinner films lose phase separation	Sample preparation affects nanostructure	Carbon preparation method has no effect

GISAXS



TEM

100 nm 20 nm 10 nm



PENNSTATE

NIST National Institute of Standards and Technology U.S. Department of Commerce

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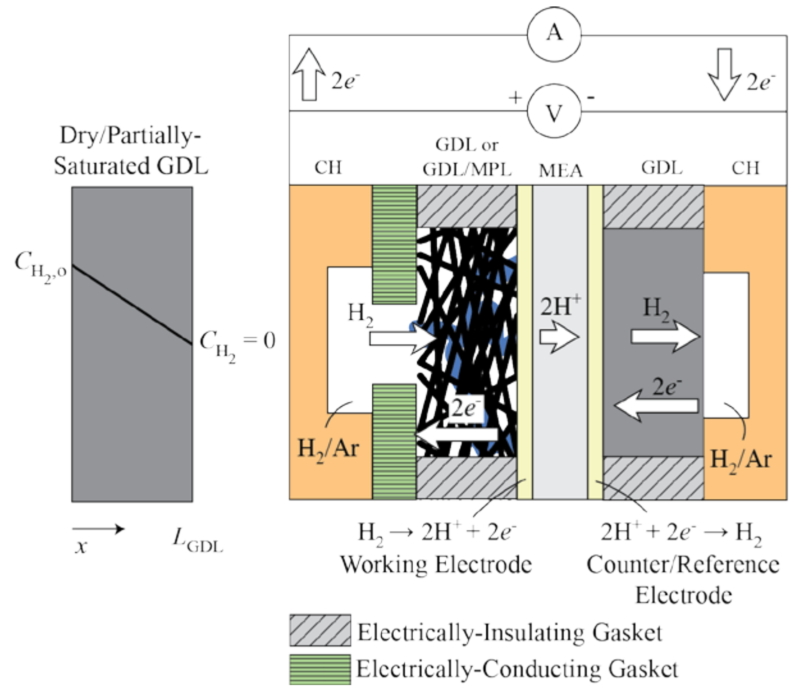
GDL Effective Diffusivity

- Effective diffusivity under saturated conditions is a key transport property that has not been adequately measure
- Designed a hydrogen-pump setup to measure the hydrogen-limiting current for different saturations

$$\langle D_{\text{H2-Ar}} \rangle = \frac{i_o L_{\text{GDL}}}{2\text{F}\, c_{\text{H2,o}}}$$

  - Exploiting the no spontaneous water-rejection properties of GDLs

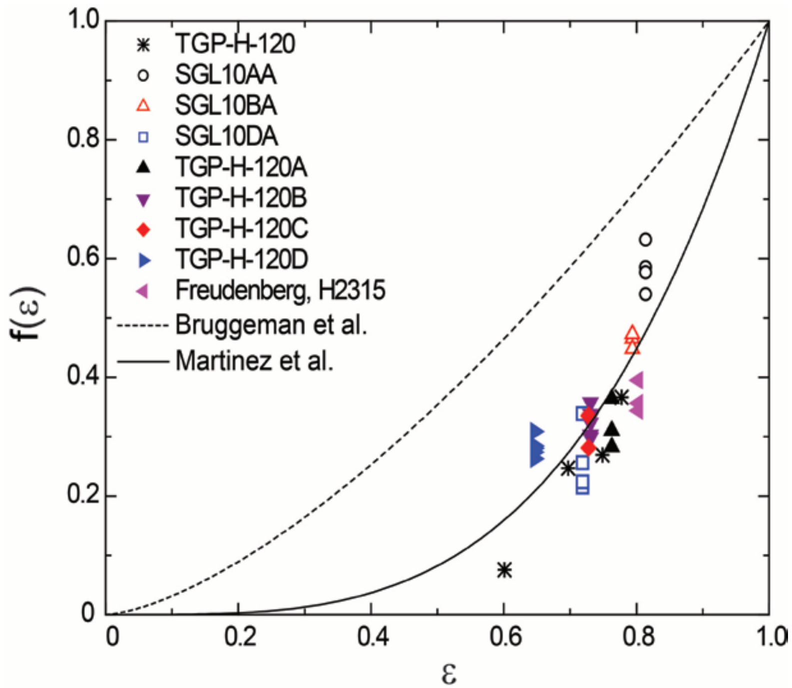


- Effective diffusivity is composed of dry and wet contributions

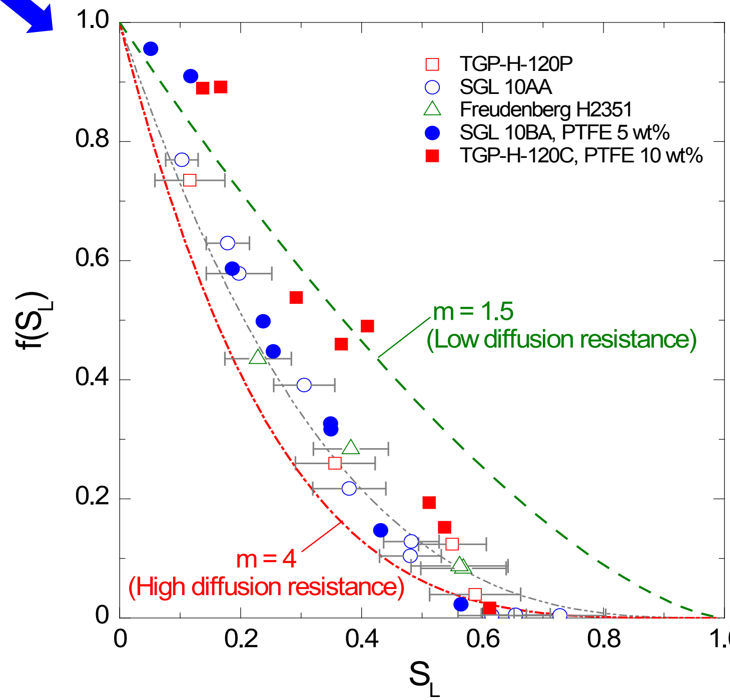
$$\frac{\langle D \rangle}{D} = f(\varepsilon) f(S_L)$$

GDL Effective Diffusivity

$$\frac{\langle D \rangle}{D} = f(\varepsilon) f(S_L)$$



$$f(\varepsilon_0) = \varepsilon_0^{3.6}$$



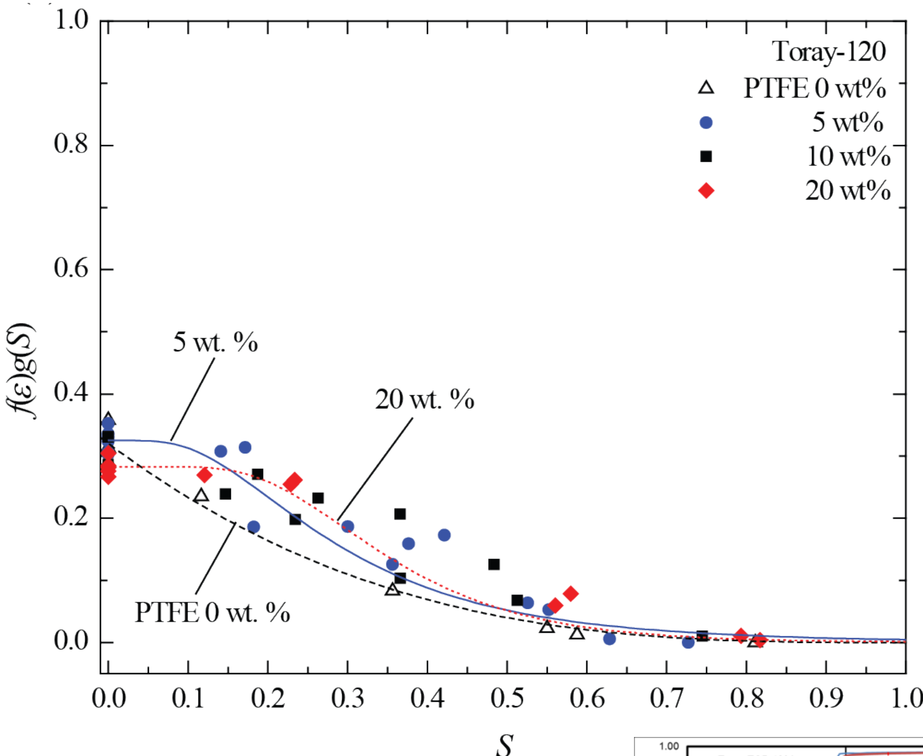
$$f(S_L) = (1 - S_L)^3$$

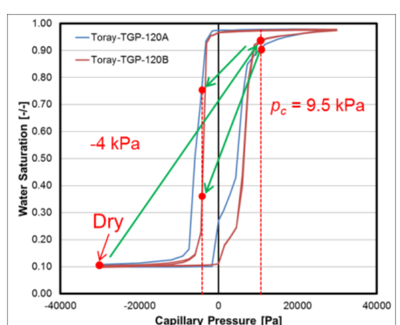
$$f(S_L) = \frac{1}{2}\{1 + \mathrm{erf}[-\frac{\ln(S_L) + a}{b}]\}$$ with PTFE

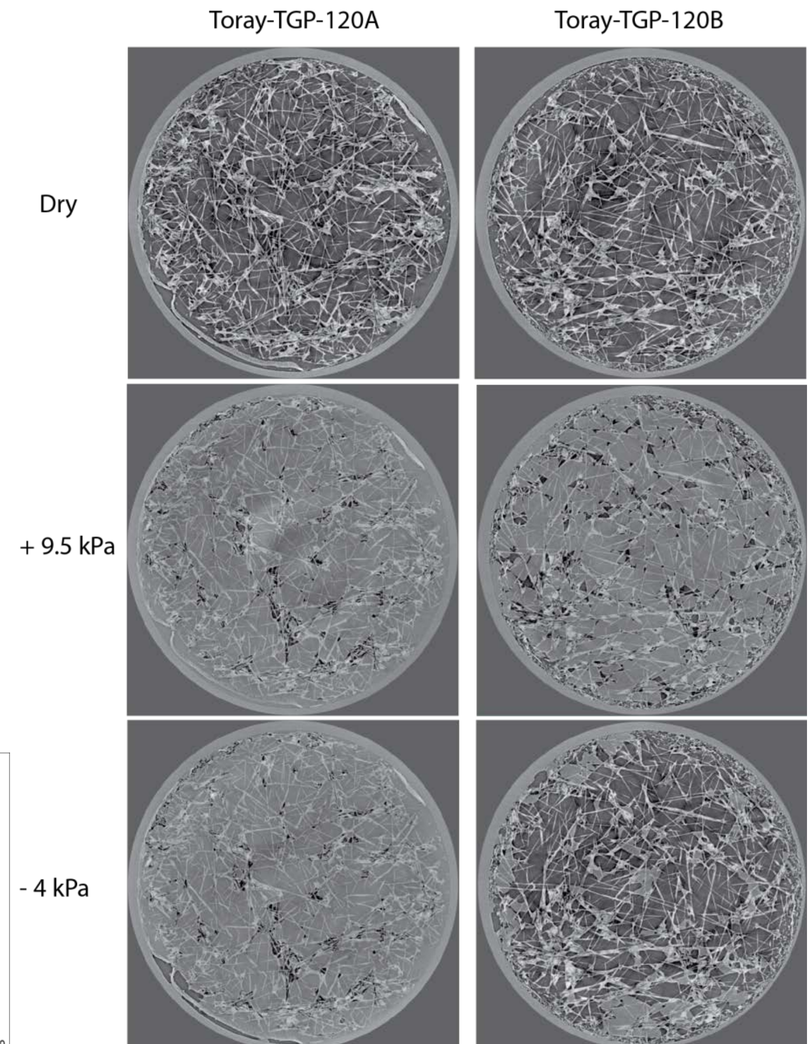
- Much higher tortuosity than expected
- Similar dependences for different papers
  - There is an impact of PTFE

GDL Effective Diffusivity

- PTFE coatings favorably change liquid distribution for diffusivity at $S_L < 0.6$
  - More heterogeneous wetting

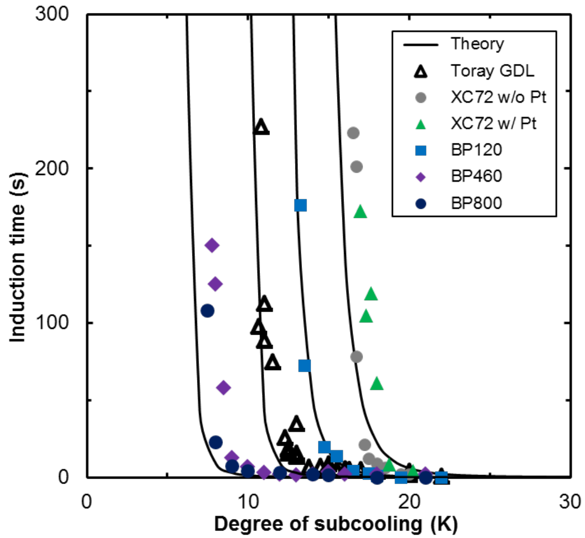


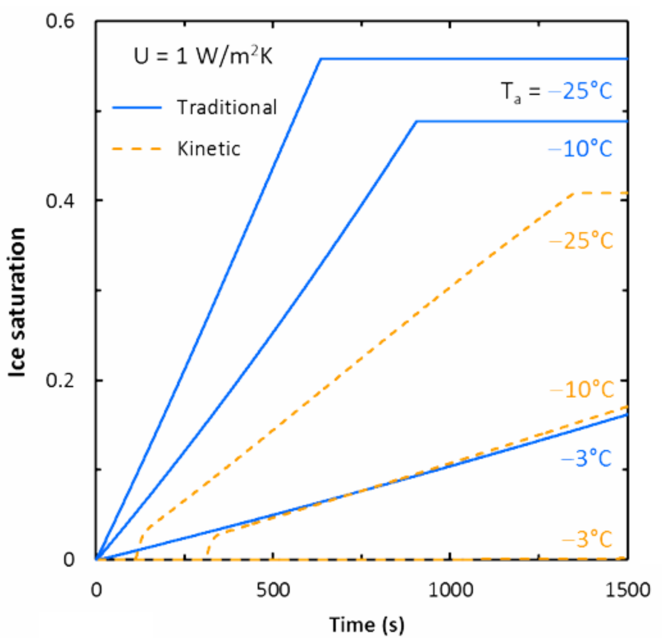




Freezing in Catalyst Layers

- Use dynamic-scanning-calorimetry (DSC) to measure freezing time
  - Cast catalyst layer inside DSC pan
  - Vary catalyst-layer properties
- Water takes longer to freeze in typical catalyst layers than in the gas-diffusion layer
- Use developed rate expression in isothermal freeze model
  - Induction time results in much different performance compared to traditional thermodynamic-based rate expressions
    - Currently correlating to experimental data





Future Work

- Cell Performance
  - UTRC to run cool and cold starts including adiabatic and temperature transients
    - NSTF and low-loaded traditional CLs
    - Run hybrid WTP cells
  - LANL to run NSTF cells including various tests
    - Segmented cell
    - Power transients
    - NIST high and higher resolution imaging
  - 3M to run cells to determine water balance and impact of NSTF structure
- Component characterization
  - Traditional CLs
    - Examine thin-film membrane morphology
  - NSTF CLs
    - Proton migration on platinum
  - GDLs
    - Liquid-water movement out of the GDLs by droplets
    - Measurement of effective diffusivities, thermal conductivities, and relative permeabilities
  - MPLs: how do they work with liquid water?
  - Membrane
    - Interfacial resistance and membrane morphology with different environments
- 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 as a function of CL thickness
  - Optimize schemes and structures to increase low-temperature performance
- Examine failed MEAs and cyclical isothermal cold starts for durability concerns
- Understand and increase the operating window with thin-film catalyst layers

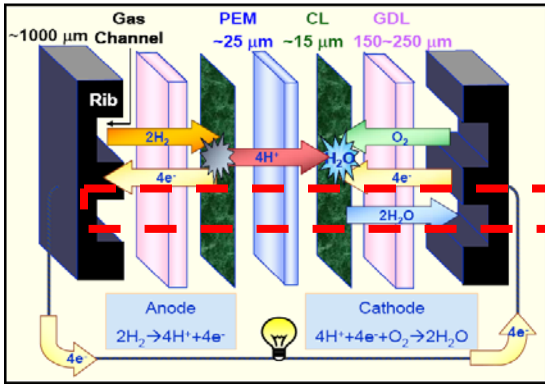
Summary

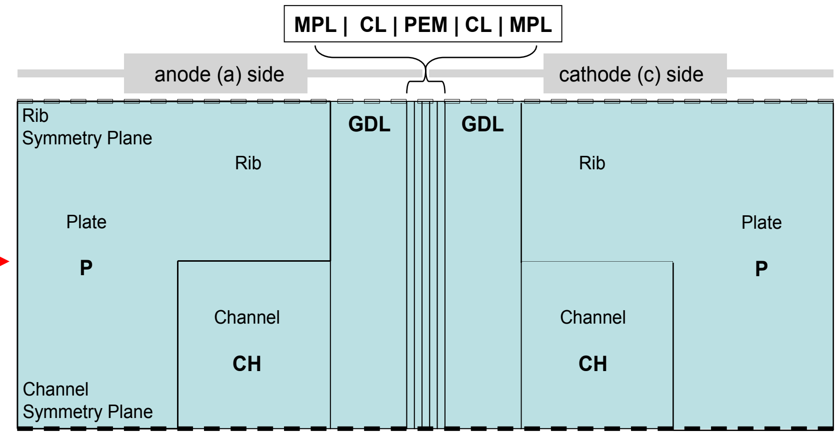
- **Relevance/Objective**:
  - Help enable, optimize, and mitigate failure in state-of-the-art materials through fundamental understanding of operation at low and subzero temperatures
- **Approach/Collaborations**:
  - Use synergistic combination of cell and component diagnostic studies with advanced mathematical modeling at various locations (national laboratories, industry, and academia)
- **Technical Accomplishments**:
  - Combined modeling and experiment to understand low-temperature performance of NSTF
    - Examining impact of different anode GDLs
    - Hybrid cell assemblies to determine limiting layers and phenomena
  - Measured effective diffusivities as a function of saturation for GDLs
    - Shows roughly cubic and not Bruggeman power-law dependence on saturation and porosity
  - Developed mechanical stress model for cold start and ice formation and membrane swelling
  - Investigated membrane morphology and transport, especially as thin films
    - Thin films below 50 nm exhibit different and more resistive properties and is dependent on the interfaces
    - Measured water profiles across the membrane with good temporal and spatial resolutions
- **Future Work**:
  - Understand liquid-water movement, interactions, and freeze in fuel-cell components
  - Benchmark cell performance and durability with different assemblies

Technical Back-Up Slides

Cold-Start Model

Model Geometry





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

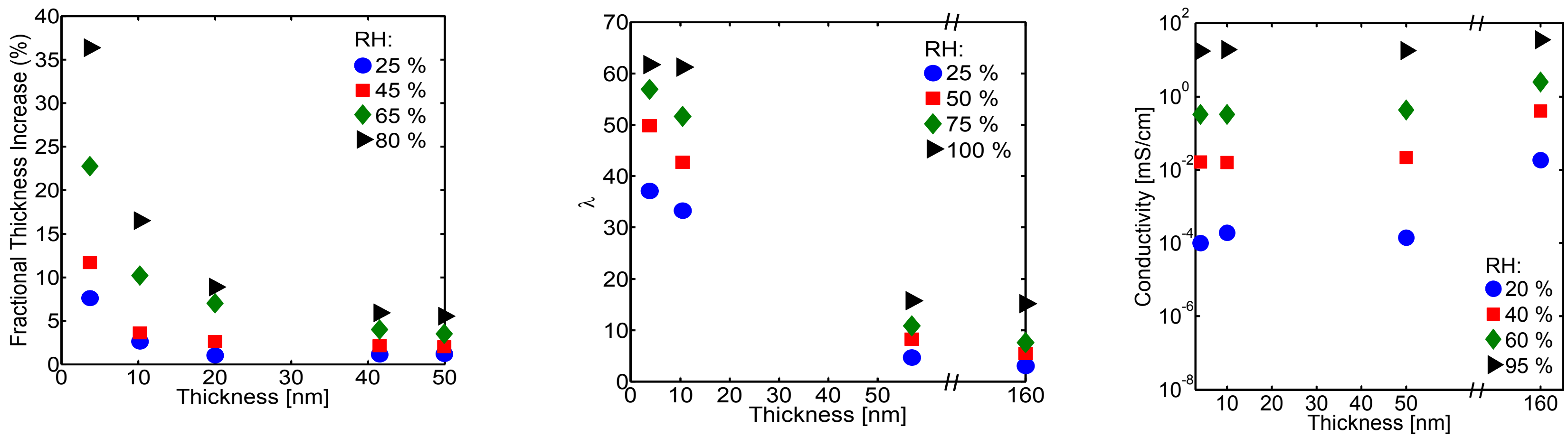
Properties

Function of *T*
and H_2O content

Equations (12): 7 2^{nd}-order PDEs; 5 Algebraic equations

Self-Assembled Nafion® Thin Films

- From both ellipsometry and QCM, the thinner films have more swelling and higher water uptake
- Conductivity decreases due to loss of phase mixing and extreme hydration



3M GDL/Compression Studies

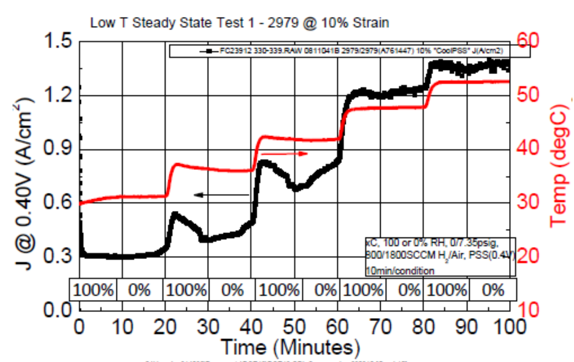
- Anode work consisted of 3 basic series (28 MEAs, 22 constructions)

1. Anode Backing Screening (9 types)
2. Anode Backing/GDL – Compression Effects (4 types @ 3 levels)
3. Periodic Baseline Checks (3 MEAs)

- Most evaluated over wide range of conditions.
  - **Peak Power (80C).**
  - **Temp. Sensitivity Steady State (2 tests)**
  - **Low Temp Cool Start Transient vs. T, RH**

QTY	Anode GDL	Cathode GDL	Comp	Series
1	Freudenberg H1410	3M 2979	10%	Anode Backing Screening
2	Freudenberg H2315	3M 2979	10%	Anode Backing Screening
2	Freudenberg H2415	3M 2979	10%	Anode Backing Screening
1	Freudenberg X0090	3M 2979	10%	Anode Backing Screening
2	Freudenberg X0154	3M 2979	10%	Anode Backing Screening
2	Freudenberg X0155	3M 2979	10%	Anode Backing Screening
1	MRC MS050M	3M 2979	10%	Error
1	MRC 040US	3M 2979	10%	Anode Backing Screening
1	3M 2979	3M 2979	5%	Anode GDL - Compression
1	3M 2979	3M 2979	20%	Anode GDL - Compression
1	Freudenberg H2315+PTFE,MPL	3M 2979	5%	Anode GDL - Compression
1	Freudenberg H2315+PTFE,MPL	3M 2979	10%	Anode GDL - Compression
1	Freudenberg H2315+PTFE,MPL	3M 2979	20%	Anode GDL - Compression
1	MRC 040US	3M 2979	5%	Anode GDL - Compression
0	MRC 040US	3M 2979	10%	Anode GDL - Compression
1	MRC 040US	3M 2979	20%	Anode GDL - Compression
1	MRC 040US+PTFE,MPL	3M 2979	5%	Anode GDL - Compression
1	MRC 040US+PTFE,MPL	3M 2979	10%	Anode GDL - Compression
1	MRC 040US+PTFE,MPL	3M 2979	20%	Anode GDL - Compression
1	MRC MS050M+PTFE,MPL	3M 2979	5%	Anode GDL - Compression
1	MRC MS050M+PTFE,MPL	3M 2979	10%	Anode GDL - Compression
1	MRC MS050M+PTFE,MPL	3M 2979	20%	Anode GDL - Compression
3	3M 2979	3M 2979	10%	Baselines
28				

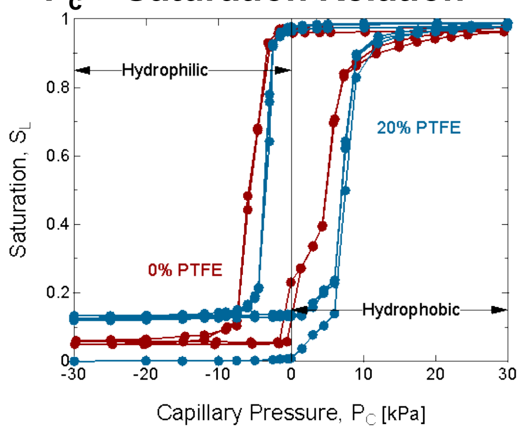
MEA: Roll Good CCM, one lot (Anode: 0.05mgPGM/cm2 PtCoMn/NSTF; Cathode: 0.15mgPGM/cm2 PtCoMn/NSTF; PEM: 3M 825EW 24u). Single cell and test station.



Model Kinetics and Transport Properties

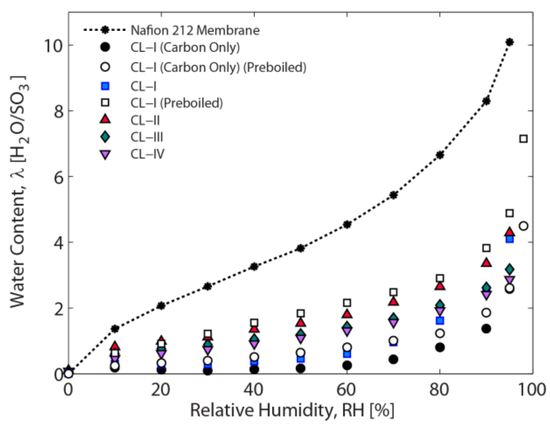
- Kinetic parameters
  - 3M and UTRC (NSTF MEA); Los Alamos (Pt/C MEA)
  - Literature (R.K. Ahluwalia et al., J. Power Sources, 215, 2012)
- Transport properties
  - Measured at LBNL (Pc – saturation relation, ionomer water uptake, effective gas diffusivity, effective thermal conductivity, etc.)
  - Also taken from literature

P_c – Saturation Relation



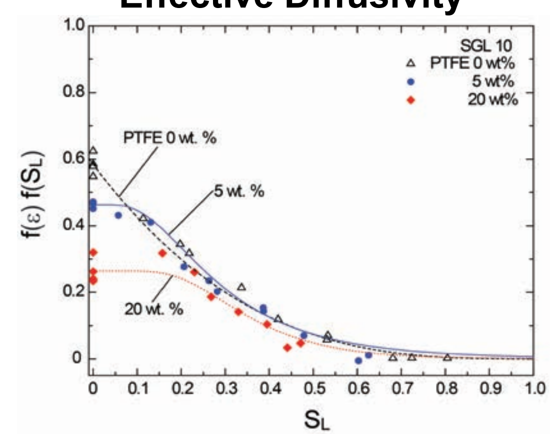
P.K. Das, A. Gripping, A. Kwong, and A.Z.Weber, *JES*, 159, B489-B496, 2012.

Ionomer Water Uptake



A. Kusoglu, A. Kwong, K.T. Clark, H.P. Gunterman, and A.Z. Weber, *JES*, 158, F530-F535, 2012.

Effective Diffusivity



G.S. Hwang and A.Z. Weber, *JES*, 159, F683-F692, 2012.

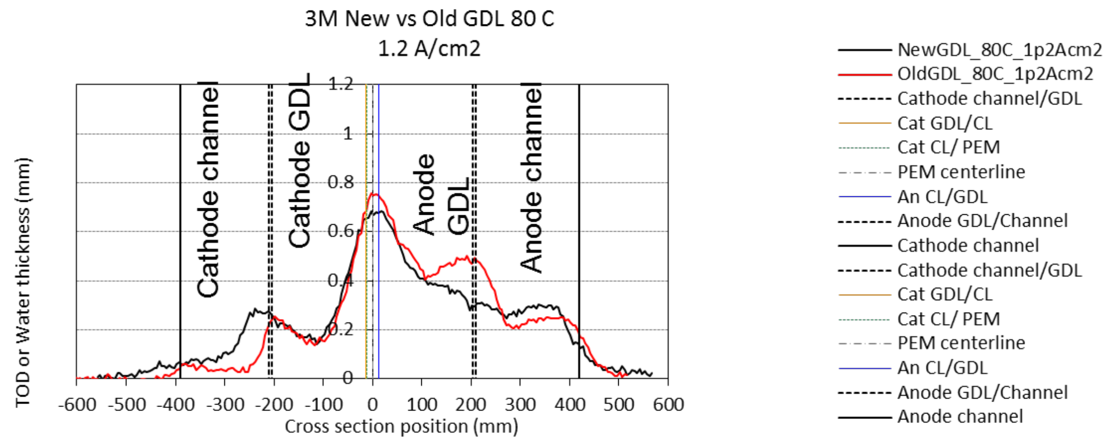
Neutron-Imaging Comparison

- Similar water contents at 80C
  - Need to do tests at 40C

3M cells: NSTF MEA, cathode GDL fixed, vary anode GDL.

2.5 cm2 cell, 100/200 sccm H_2/Air (fixed flows), 10.5 psig backpressure, 80 C (or 40 C), 100% RH

Co-flow, inlets high



Gore MEA: 0.2/0.4 mg Pt/cm2 loading, Pt/C, 710 Membrane (18 microns thick).

VARY cathode GDL (same substrate, vary MPL only), anode GDL fixed.

The GDLs are from SGL Carbon.

2.5 cm2 cell, 100/200 sccm H_2/Air (fixed flows), zero backpressure, 80 C only, 100% RH

Co-flow, inlets high