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**
- ~85% complete

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

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

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)

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Relevance: Objectives

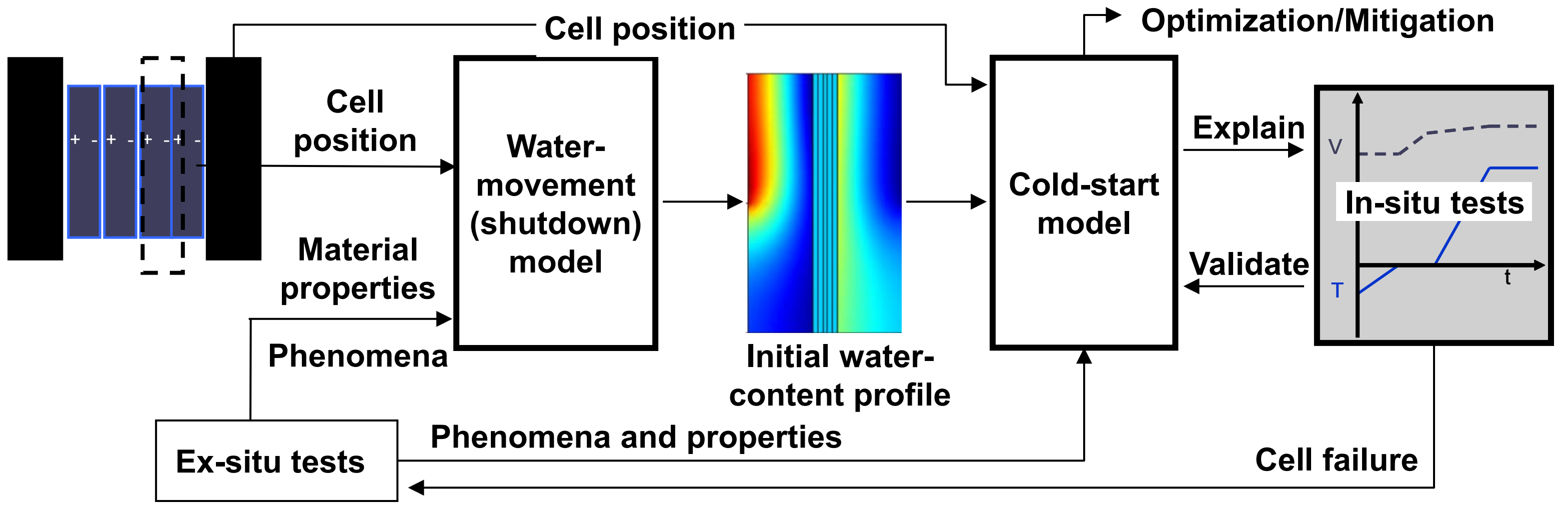
- Fundamental understanding of transport phenomena and water and thermal management at low and subzero temperatures using state-of-the-art materials
  - Examine water management with thin-film catalyst layers (NSTF)
  - Examine water management and key fundamentals in the various fuel cell components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

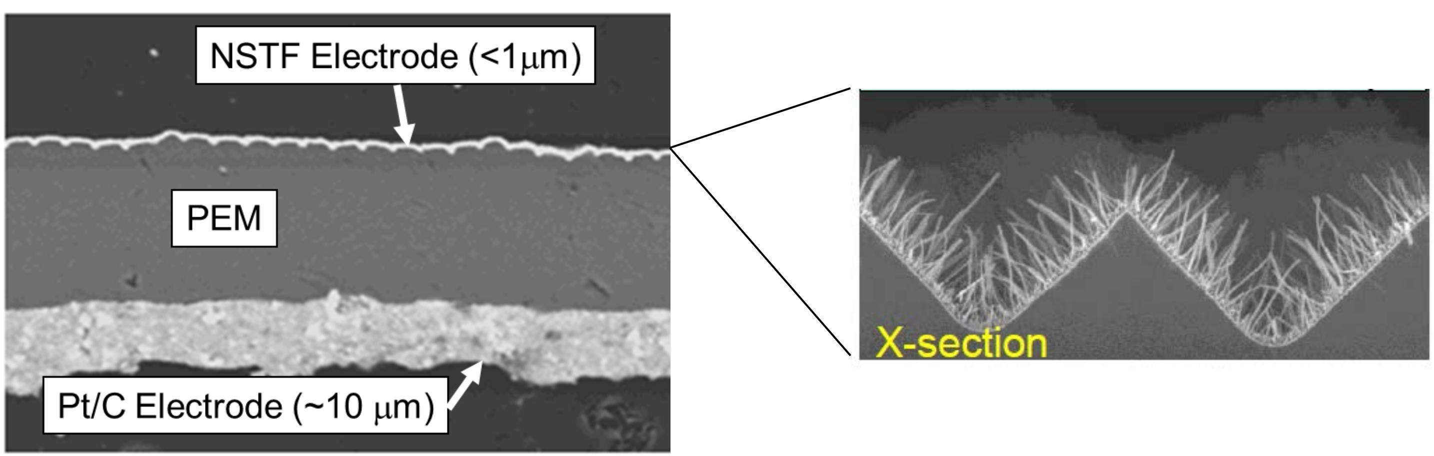


- Multi-scale, multi-physics continuum-based modeling
  - Develop, validate, and refine a series of models for cell performance including cold and cool operation, startup, and shutdown
- Experimentally characterize component, cell, and stack properties and performance
  - Measure critical properties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

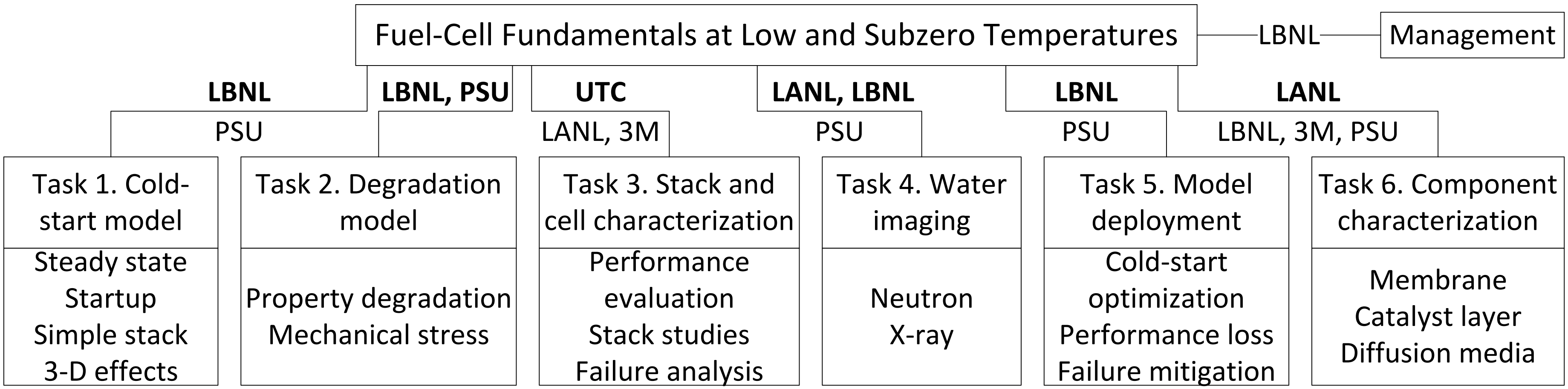
Approach: Cell Assemblies

- 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



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

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

<u>Major Milestones/Deliverables</u>

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*)

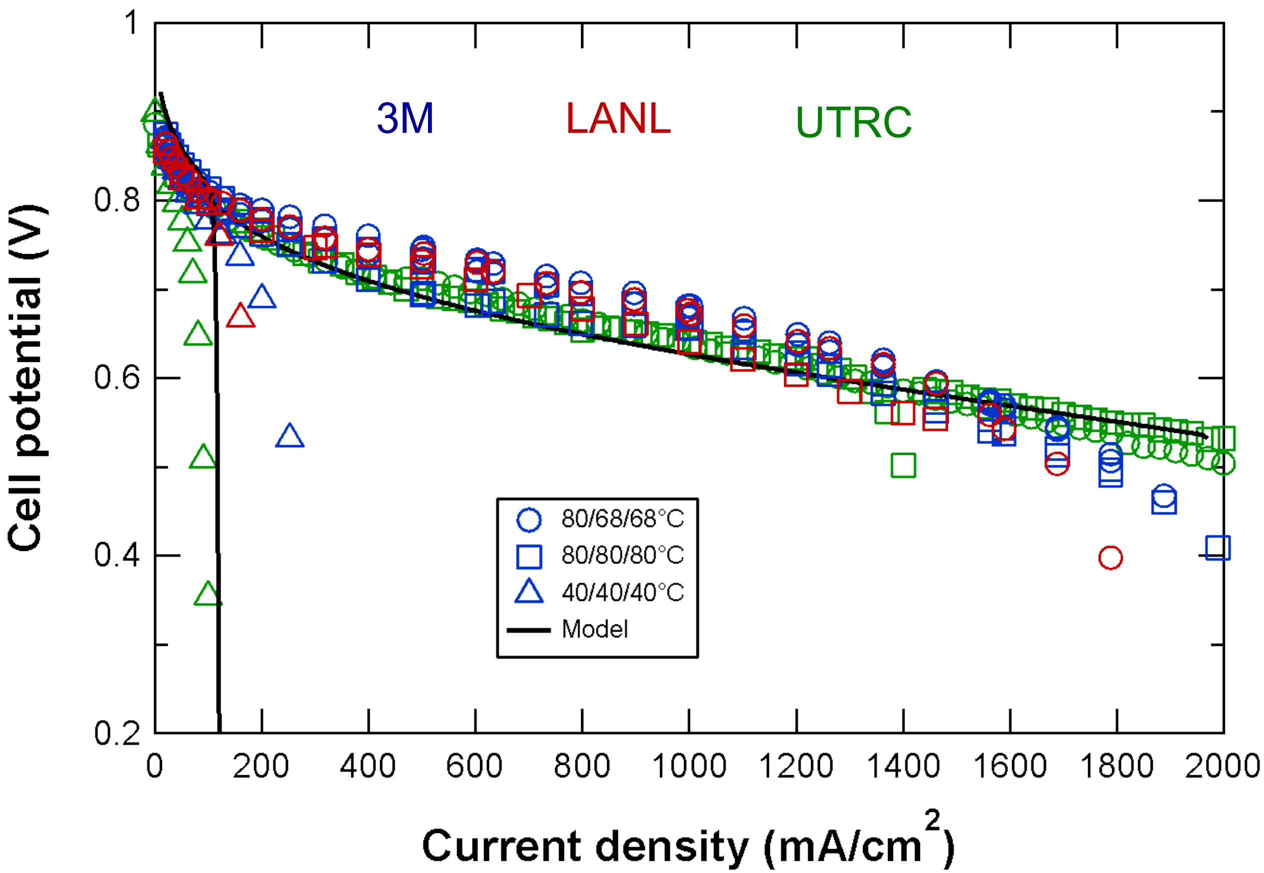
M7: Report on optimum operating conditions and material properties for NSTF catalyst layers operating below 55°C. (*on track, model agreeing with experiments and now looking at parameter space*).

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

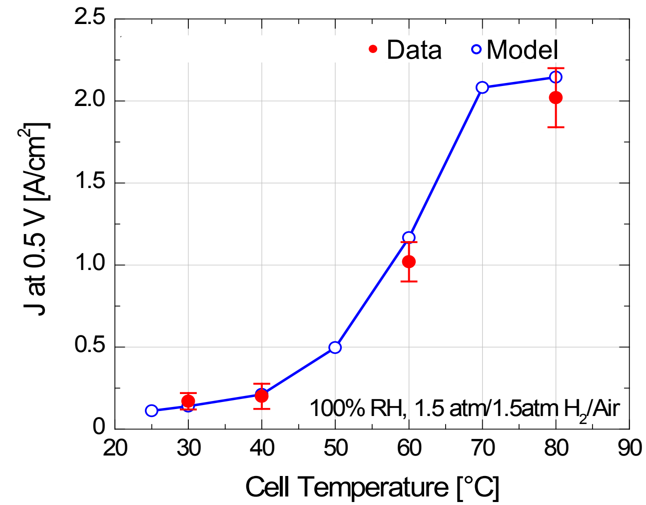


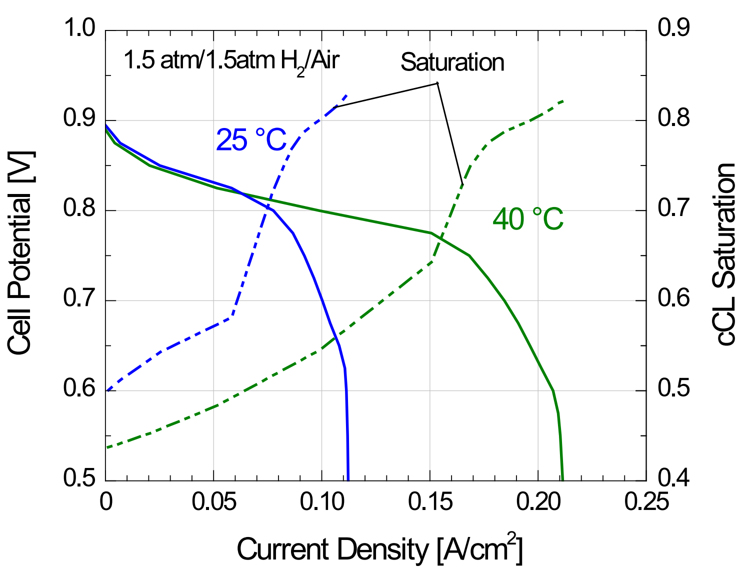
2/2.5 stoichiometry for H_2/Air
150/150 kPa outlet pressures

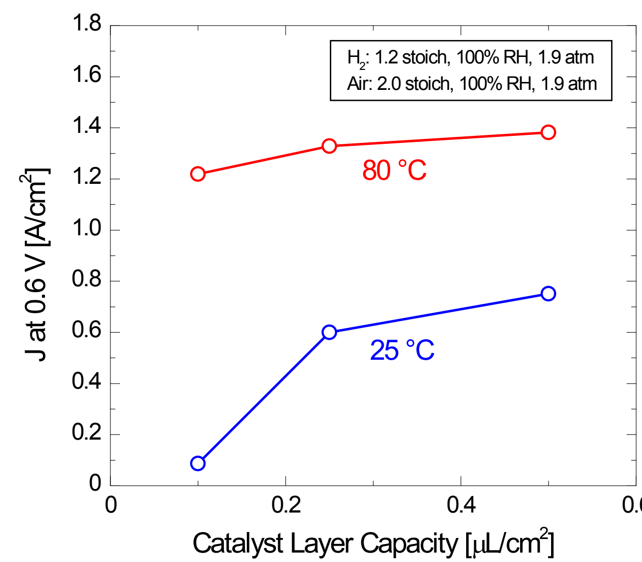
- Performance among the three cell-testing sites is converged
  - Lessons learned
    - Compression and cell assembly/hardware uniformity is critical
    - Need to run and condition NSTF properly

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

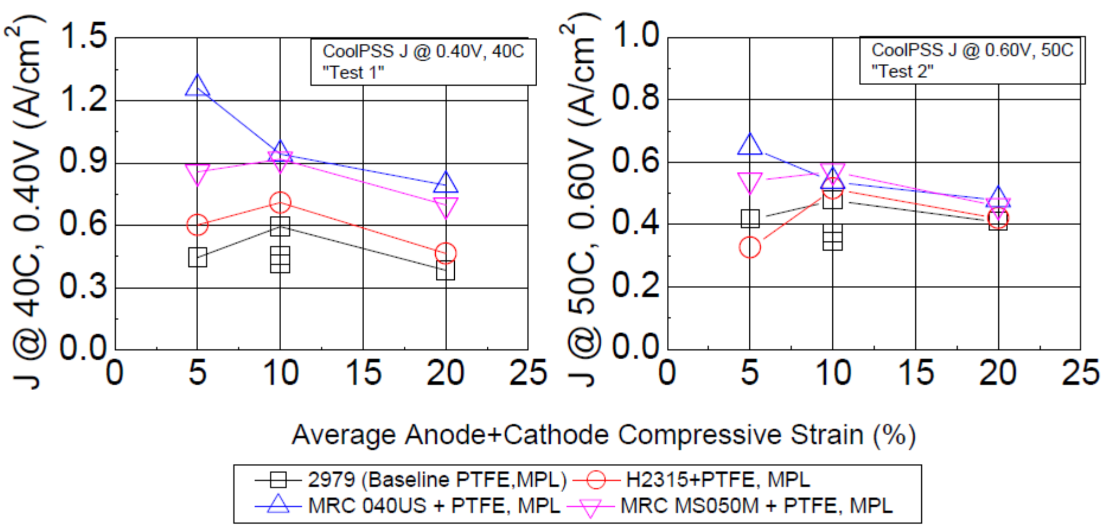


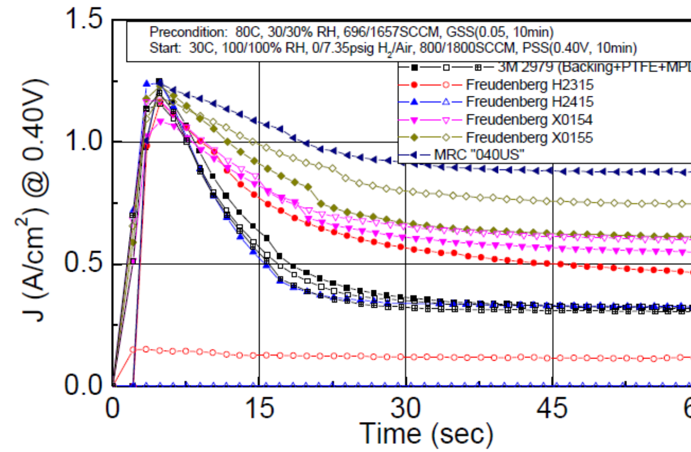




Anode GDL Studies

- 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



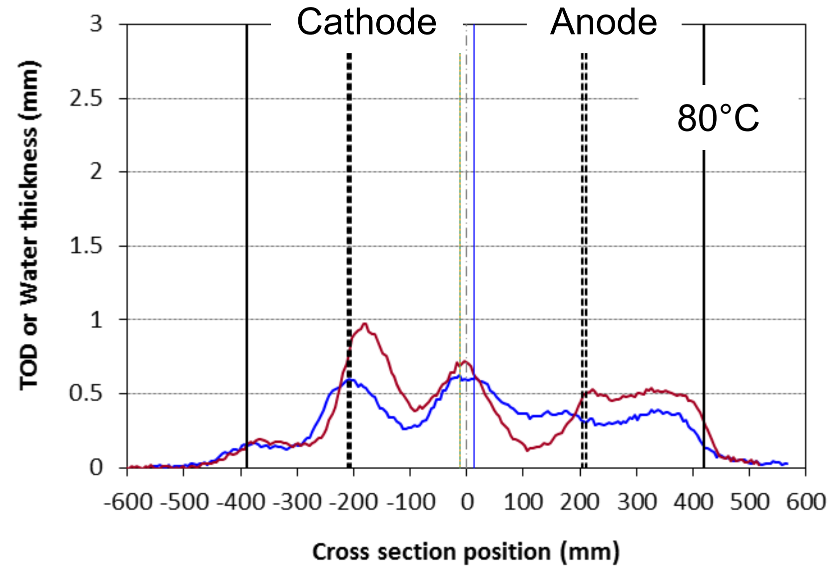


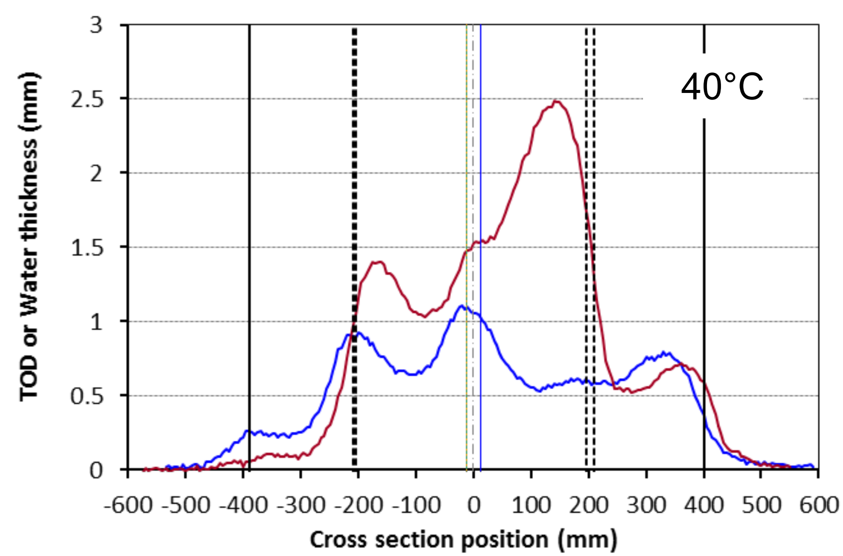
- Response generally decreases as compression increases from 10 to 20%, less consistent results for 5 to 10%

- 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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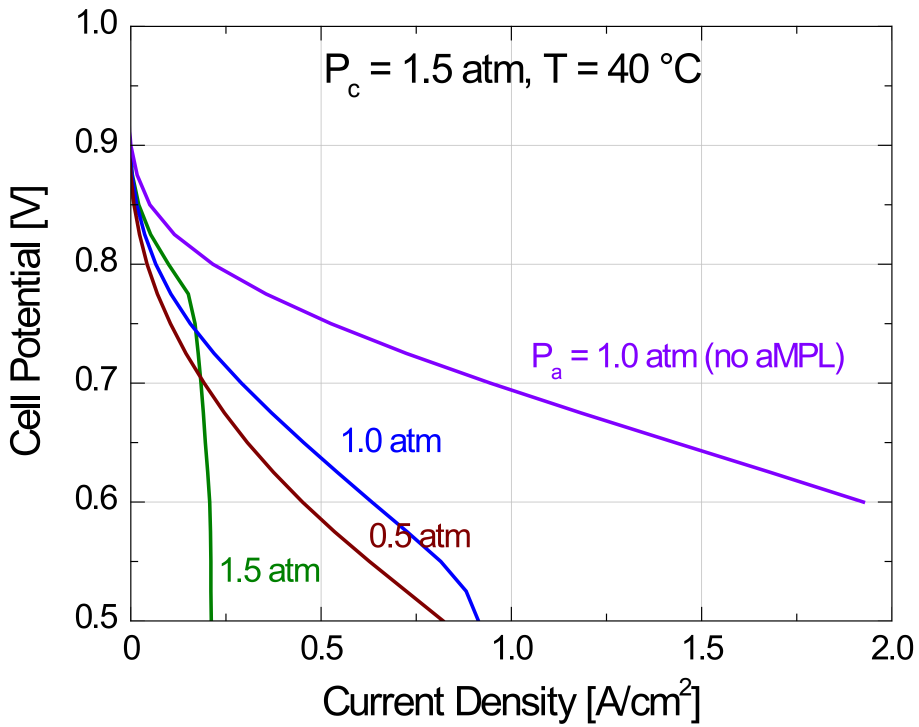
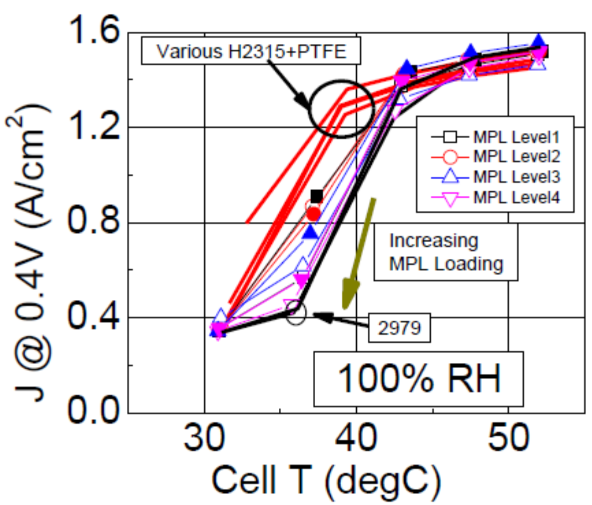
Anode GDL Studies

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

Model



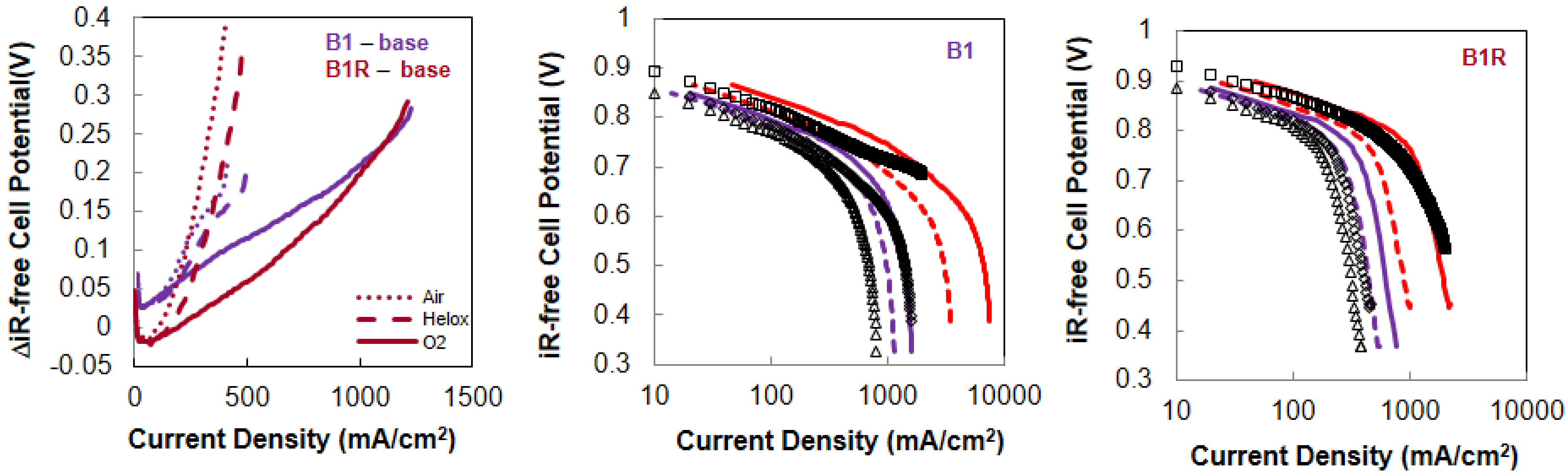
Data



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

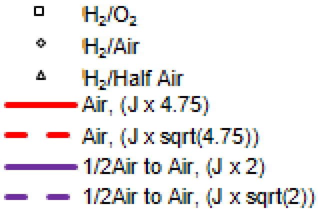
Oxygen-Gain Analysis

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



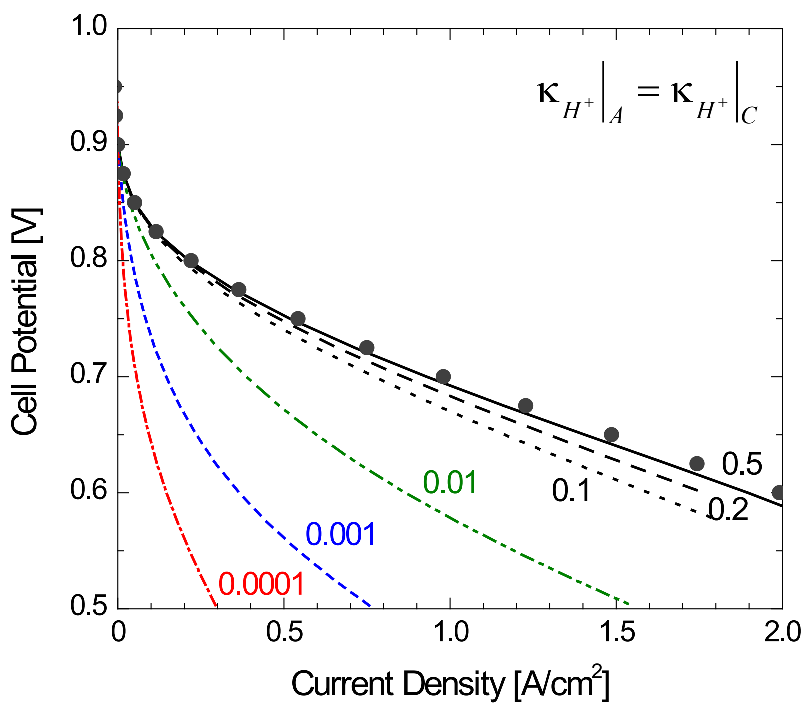
- Performance loss at low T appears to be due to transport limitations
  - Ionic limitation and not O_2?
  - Change in H_2 kinetics
  - Anode NSTF
    - Performance a function of oxidant
    - Ohmic limited at moderate current; limiting currents are ~ 1st order
  - Cathode NSTF
    - Different behavior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

	Anode (mg/cm^2)	Cathode (mg/cm^2)
B1	0.05 Pt/C	0.10 NSTF
Base	0.05 NSTF	0.10 NSTF
B1R	0.1 NSTF	0.05 Pt/C



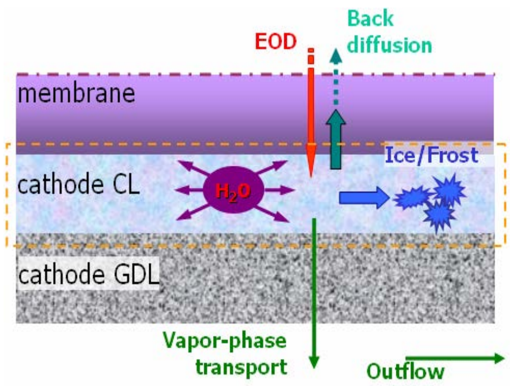
Impact of Proton Conductivity

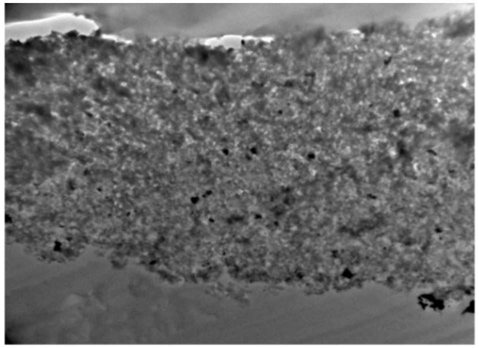
- Parametric study using **model** without aMPL at 40°C
  - NSTF proton conductivity has strong influence on the cell performance when conductivity is below 0.1 S/m



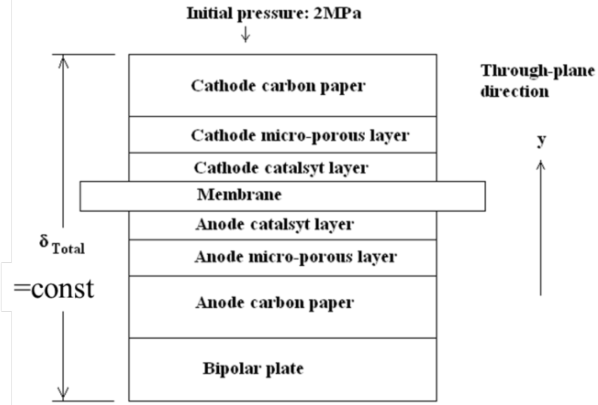
Mechanical Stress Modeling

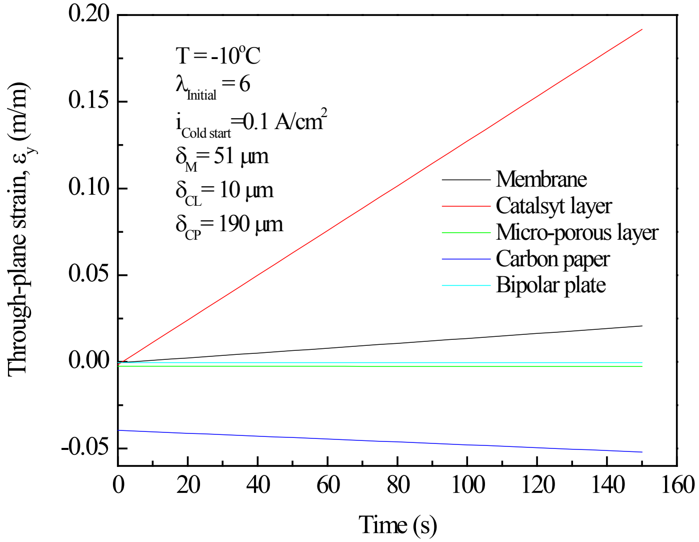
- Stress model of fuel-cell sandwich for purge and cold start

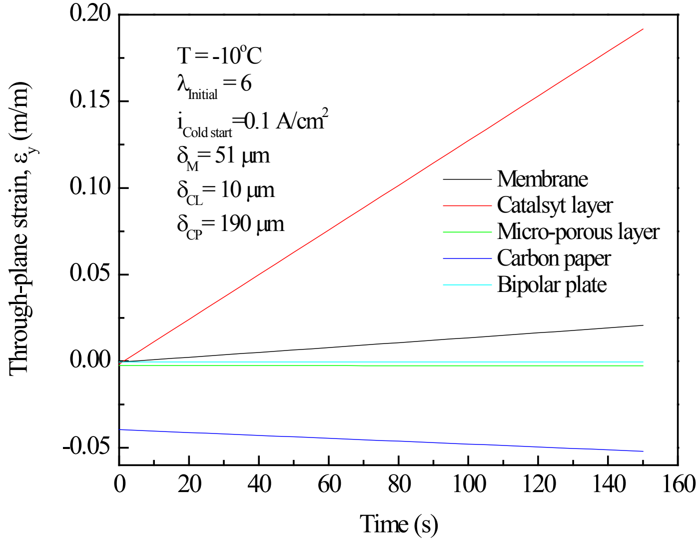




Interfacial delamination after 110 cycles of cold-start at 500 mA/cm²



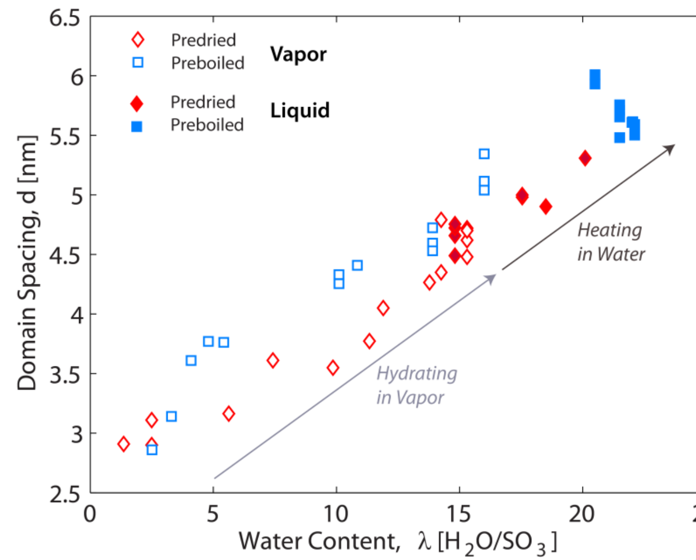


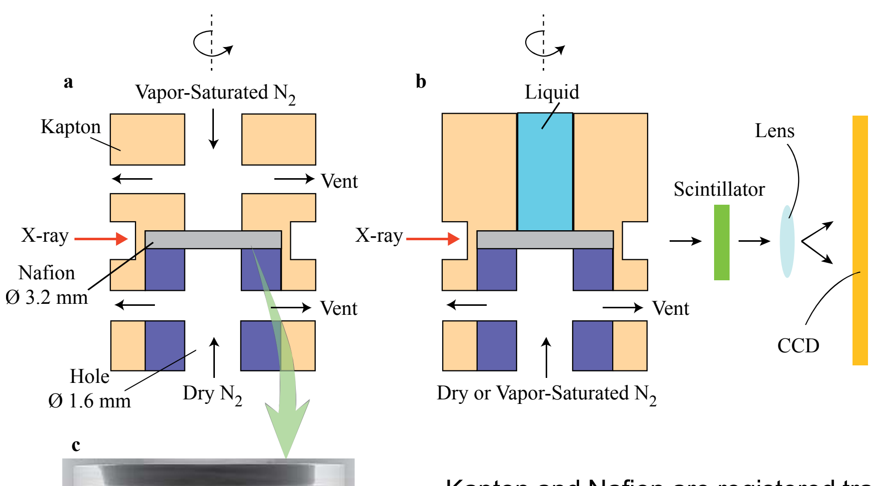


- During cold start, ice production yields very large strain in CL, which could cause CL/mem delamination and CL pore structure collapse
- Cold start from low temperatures leads to large mechanical stress, and high start current density leads to large strain in CL

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

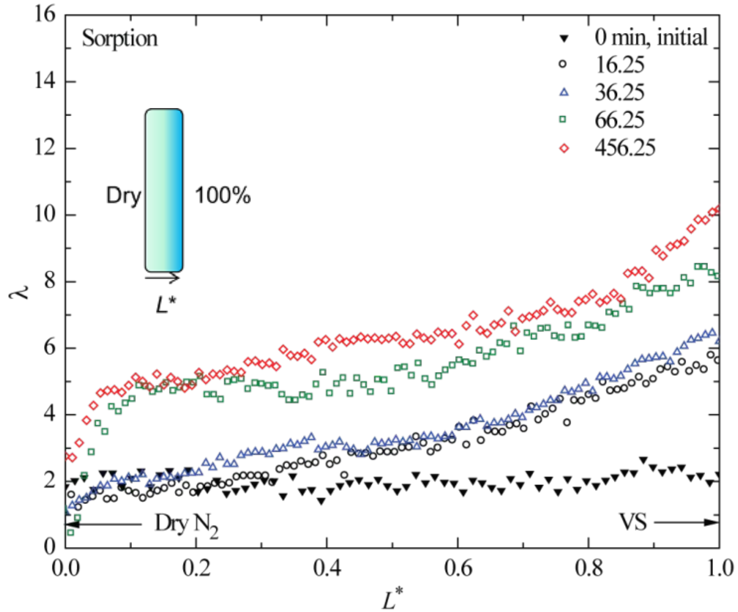




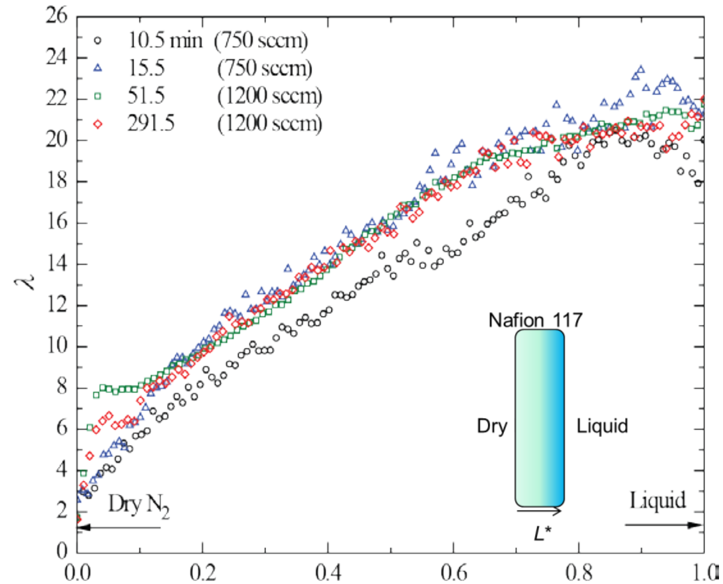
- Measure membrane water profile
  - Use x-ray computed microtomography
    - Good combined temporal (~min) and spatial (~µm) resolution

Membrane Water Profiles

Sorption from Dry to 100% RH



Sorption from Dry to Liquid

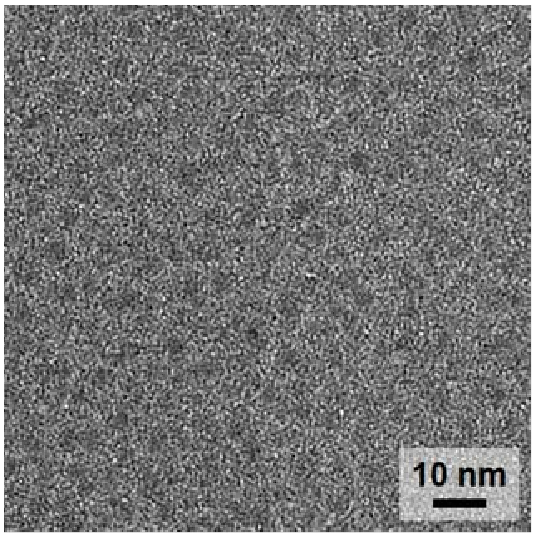


- With saturated vapor/dry, complex transient and steady-state profile
  - Shape changes from concave to convex with time
    - Agrees with different dependence of diffusion coefficient for dynamic and steady state
  - Lower values at boundaries suggest interfacial resistance
- With liquid/dry, rapid 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

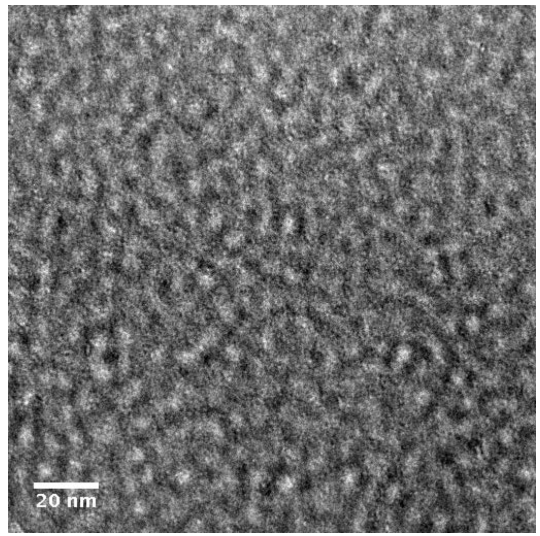
Membrane Morphology

- Examine morphology using SAXS and also TEM

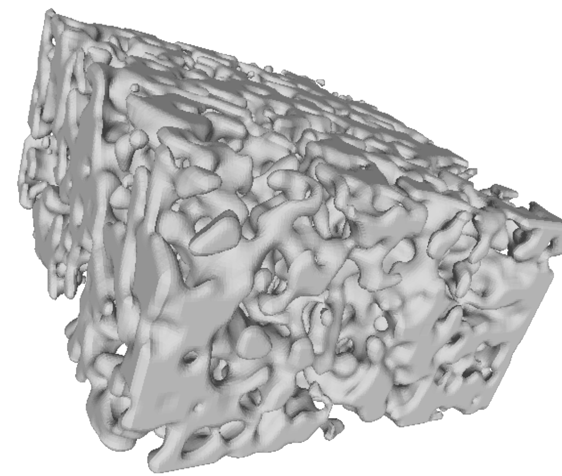
Dry (TEM)



Hydrated (cryoTEM)



Simulated from SAXS



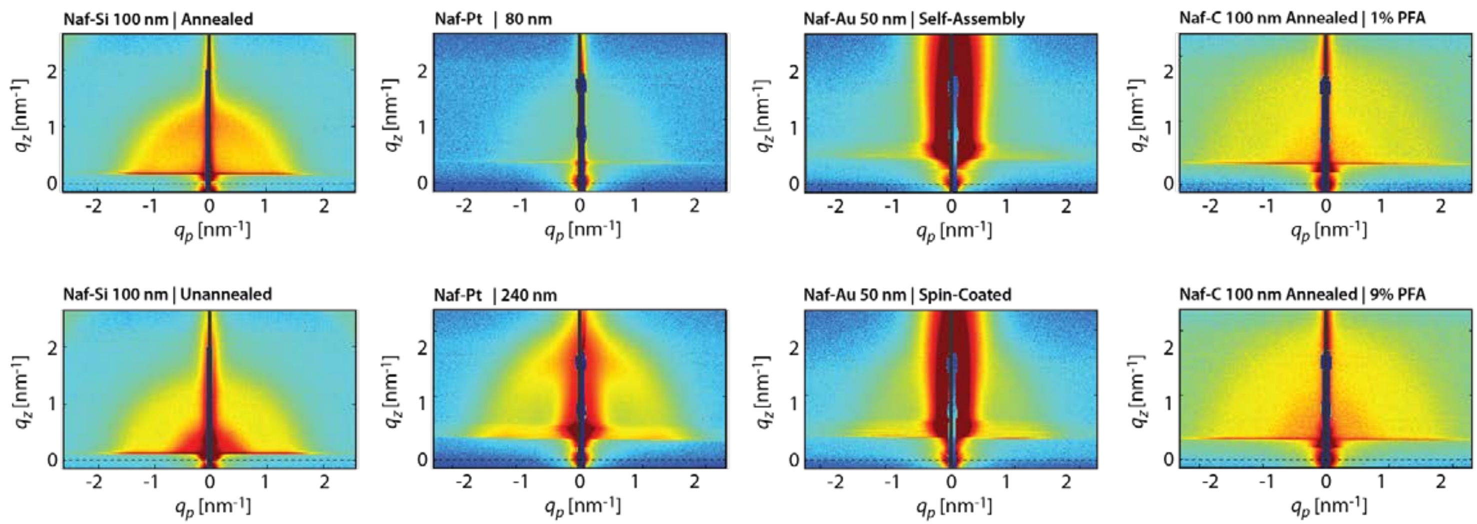
- Need to determine what the phases are using low-loss EELS
- Next would be to model transport through the morphology

Thin-Film Morphology

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

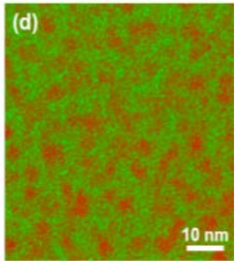
Nafion-Si	Nafion-Pt	Nafion-Au	Nafion-C
Annealing induces crystallinity in films	Thinner films lose phase separation	Sample preparation affects nanostructure	Carbon preparation method has no effect

GISAXS

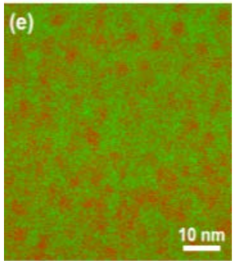


TEM

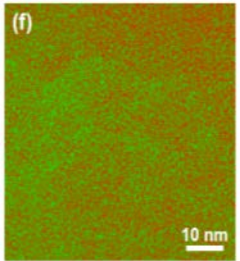
100 nm



20 nm



10 nm



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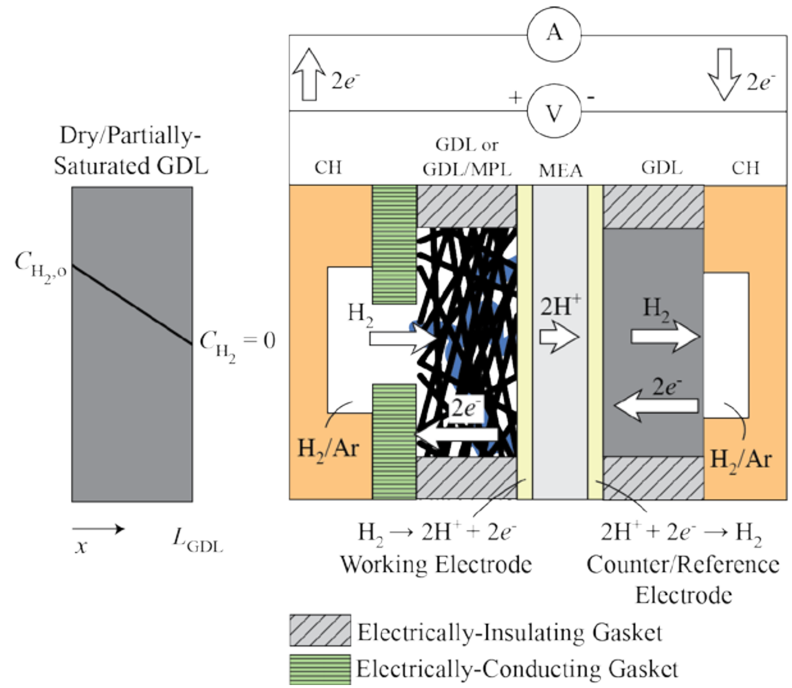
GDL Effective Diffusivity

- 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

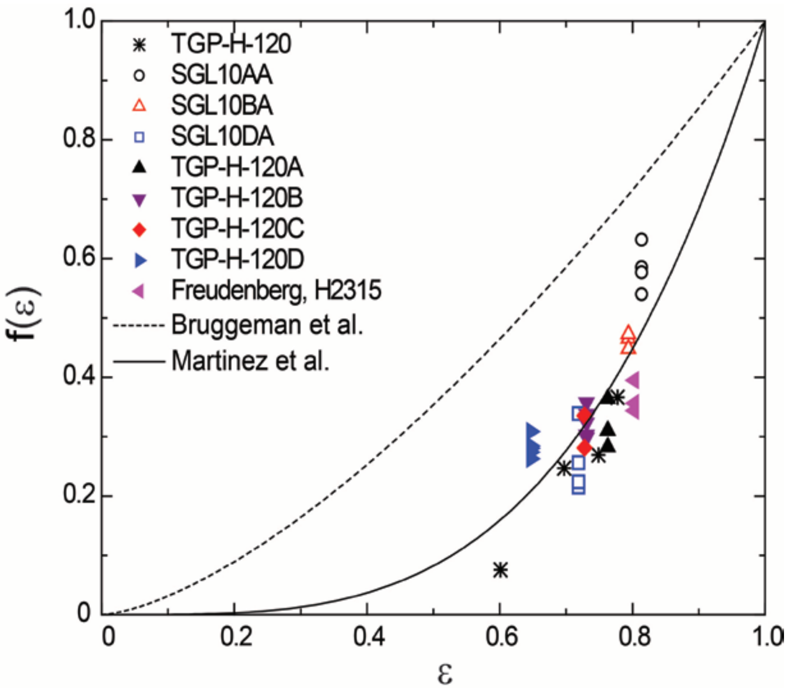


- Effective diffusivity is composed of dry and wet contributions

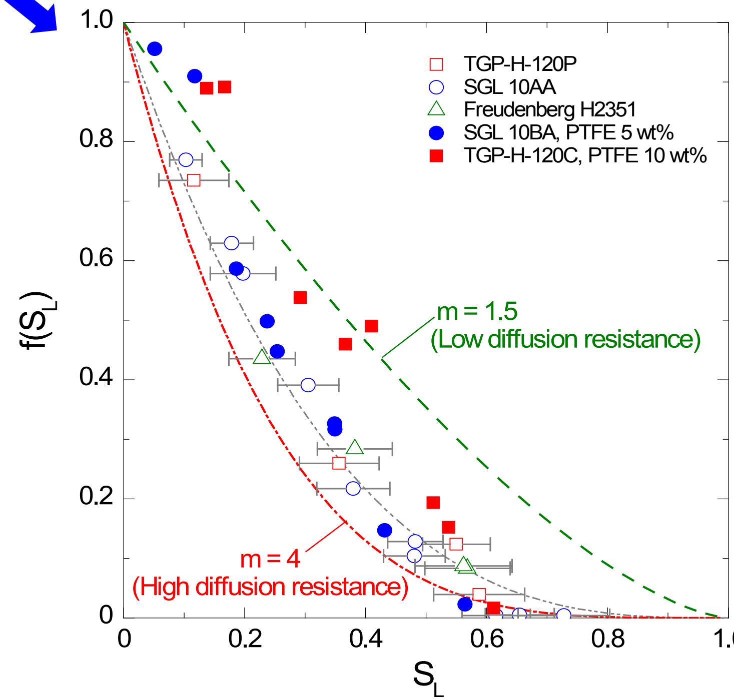
$$\frac{\langle D \rangle}{D} = f(\varepsilon) f(S_L)$$

GDL Effective Diffusivity

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



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



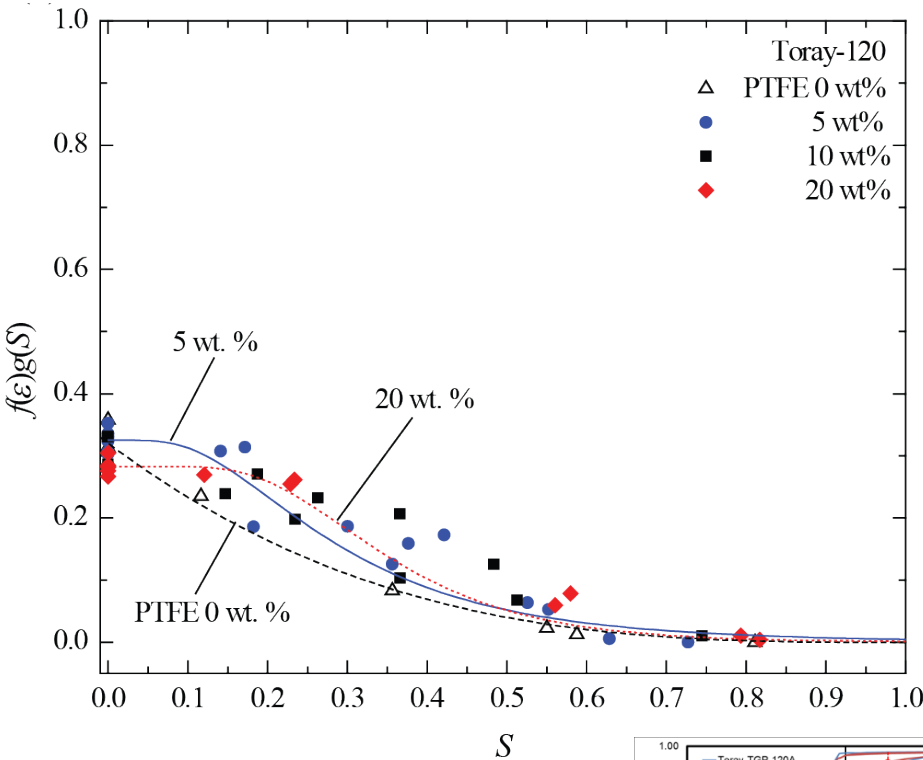
$$f(S_L) = (1 - S_L)^3$$

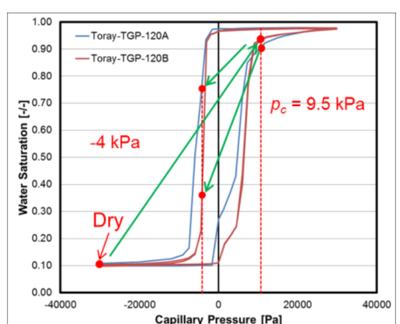
$$f(S_L) = \frac{1}{2}\{1 + \mathrm{erf}[-\frac{\ln(S_L) + a}{b}]\}$$ with PTFE

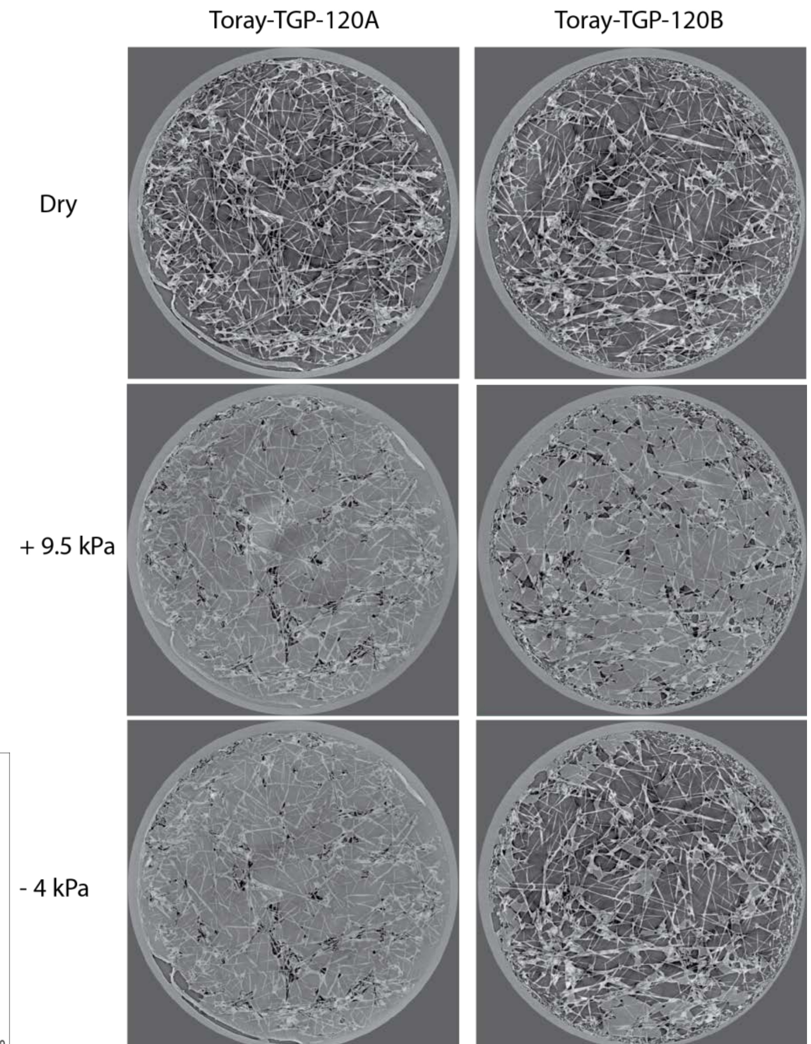
- Much higher tortuosity than expected
- Similar dependences for different papers
  - There is an impact of PTFE

GDL Effective Diffusivity

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



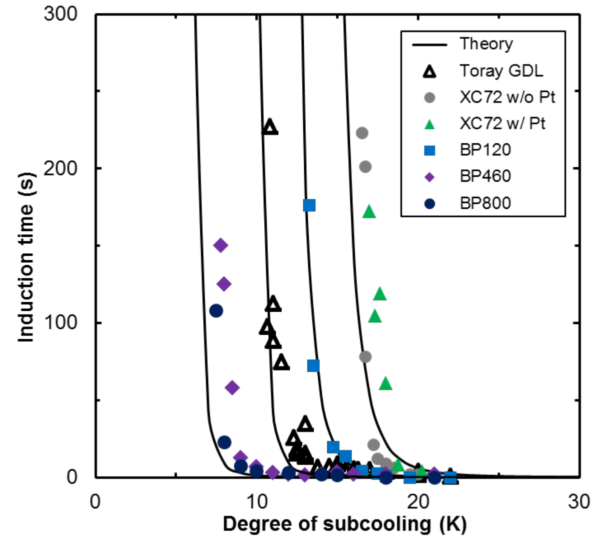




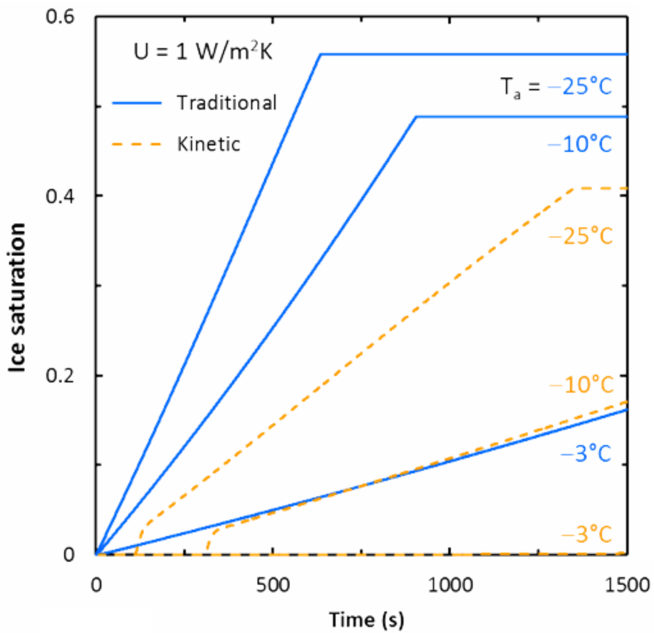
Freezing in Catalyst Layers

- 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

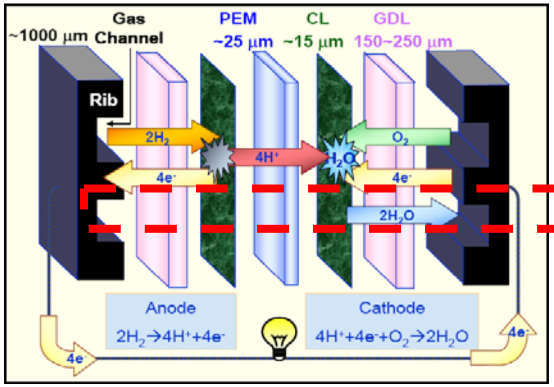
Summary

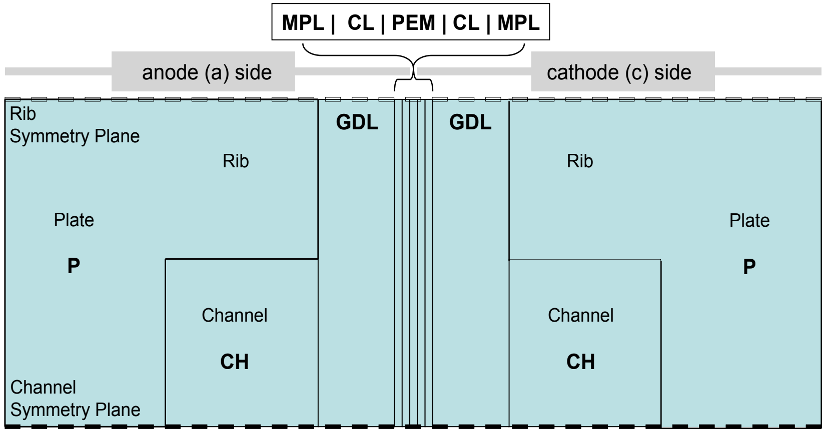
- **Relevance/Objective**:
  - Help enable, optimize, and mitigate failure in state-of-the-art materials through fundamental understanding of operation at low and subzero temperatures
- **Approach/Collaborations**:
  - Use synergistic combination of cell and component diagnostic studies with advanced 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

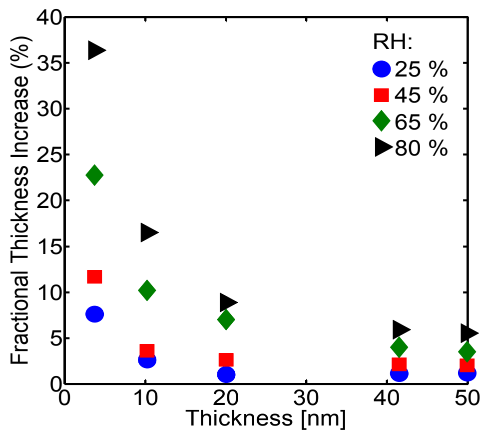
Properties

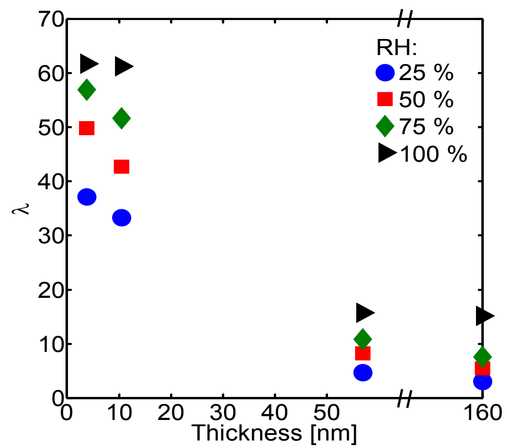
Function of *T*
and H_2O content

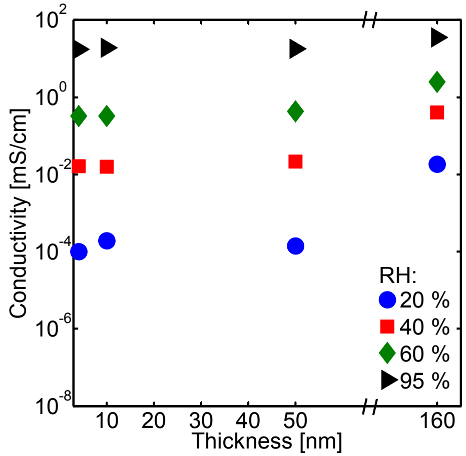
Equations (12): 7 2nd-order PDEs; 5 Algebraic equations

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

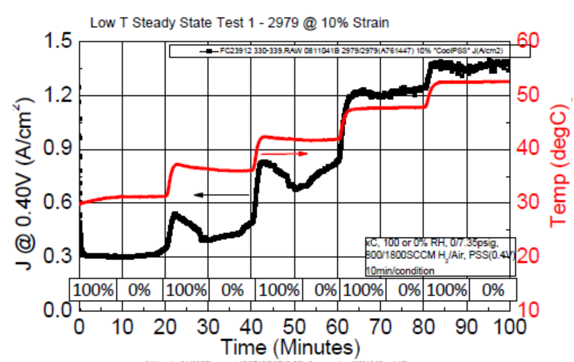
- Anode work consisted of 3 basic series (28 MEAs, 22 constructions)

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				

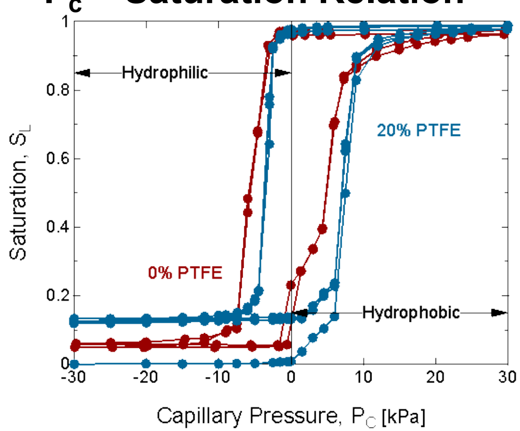
MEA: Roll Good CCM, one lot (Anode: 0.05mgPGM/cm2 PtCoMn/NSTF; Cathode: 0.15mgPGM/cm2 PtCoMn/NSTF; PEM: 3M 825EW 24u). Single cell and test station.



Model Kinetics and Transport Properties

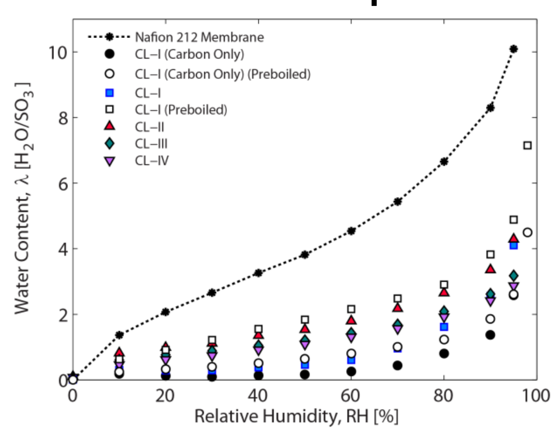
- Kinetic parameters
  - 3M and UTRC (NSTF MEA); Los Alamos (Pt/C MEA)
  - Literature (R.K. Ahluwalia et al., J. Power Sources, 215, 2012)
- Transport properties
  - Measured at LBNL (Pc – saturation relation, ionomer water uptake, effective gas diffusivity, effective thermal conductivity, etc.)
  -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

P_c – Saturation Relation



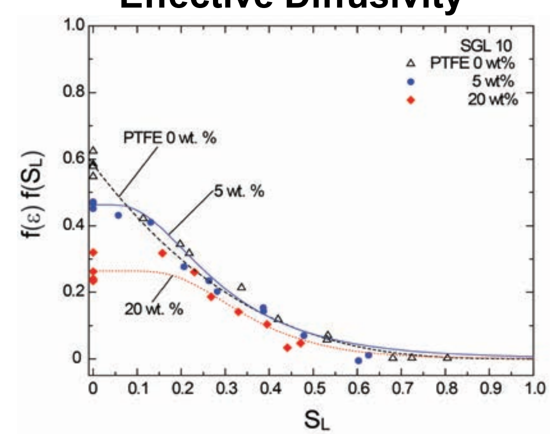
P.K. Das, A. Gripping, A. Kwong, and A.Z.Weber, *JES*, 159, B489-B496, 2012.

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.

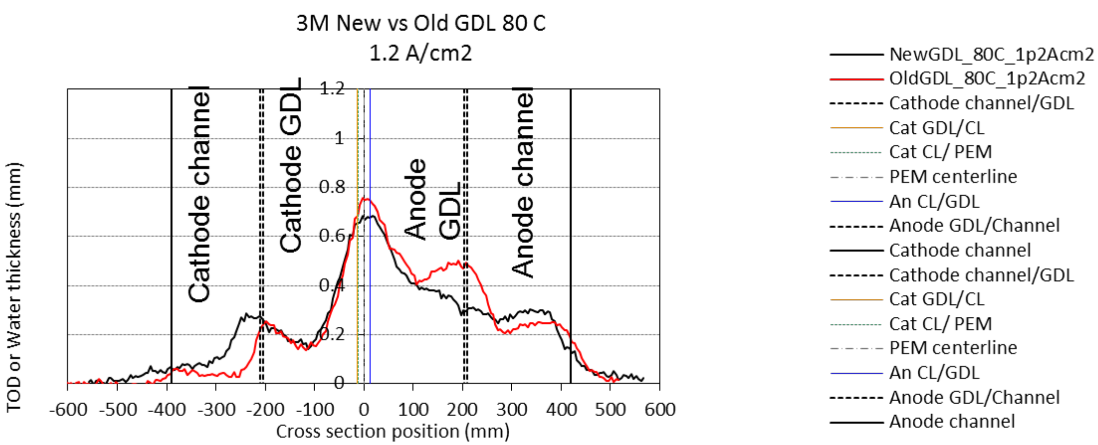
Neutron-Imaging Comparison

- 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