Fuel-Cell Fundamentals at Low and Subzero Temperatures

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June 10, 2015

Project ID #
FC 026

Overview

Timeline

- Project started FY09
  - September 2009
- Project end date*
  - September 2015

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: $7,172k
  - DOE share: $ 6,700k
  - Contractor share: $ 472k (6.5%)
- Funding Received in FY14: $900k
  - LBNL $596k; LANL $200k; UTRC $104k
- Planned Funding for FY15: $1100k
  - LBNL $900k
  - LANL $200k

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 and working groups (esp. TMWG)

*Project continuation and direction determined annually by DOE

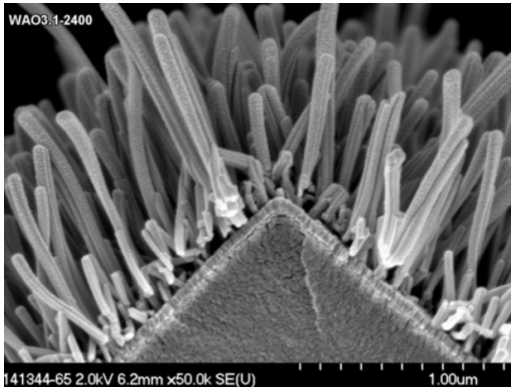
Collaboration: Organizations/Partners

- Lead
  - **Lawrence Berkeley National Laboratory**: Adam Weber, Ahmet Kusoglu, Michael Tucker, Dilworth Parkinson, Alexander Hexemer, Frances Allen, Iryna Zenyuk, Meron Tesfaye
- Subcontractors
  - **Los Alamos N.L.**: Rod Borup, Rangachary Mukundan, Dusan Spernjak
  - **3M Company**: Andy Steinbach, Michael Yandrasits
  - **United Technology Research Center**: Michael Perry
- 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)
- Other relationships (no cost)
  - **UC Berkeley/JCAP**: Nathan Lynd (Membrane scattering, properties, and other studies)
  - **University of Calgary:** Kunal Kuran (Nafion® thin-film data and samples)
  - **NIST**: Kirt Page, Chris Stafford (PFSA thin-film studies)
  - **McGill University**: Jeffrey Gostick (MPL and GDL modeling and measurements)
  - **TMWG and additional OEM industry discussions**

Relevance: Objectives

- Understand 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
  - Examine water management and key phenomena in the various fuel-cell components
  - Enable optimization strategies to be developed to overcome observed bottlenecks
    - » Operational
    - » Material

NSTF catalyst layer



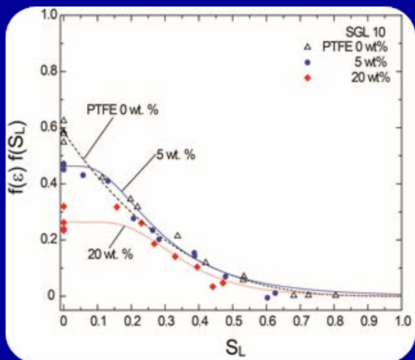
- Elucidate the associated degradation mechanisms due to cold and cool operation
  - Enable mitigation strategies to be developed

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

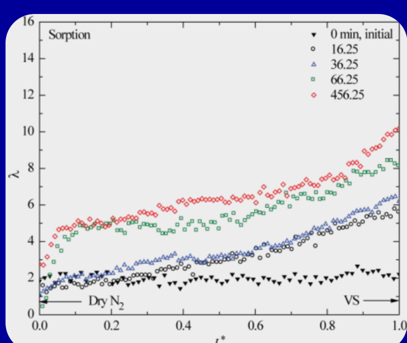
Approach

In/Ex-situ Diagnostics

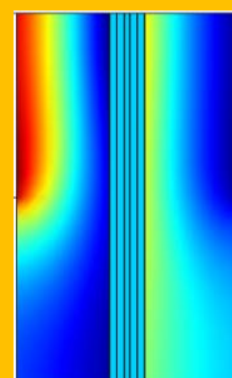
Component properties



Component phenomena

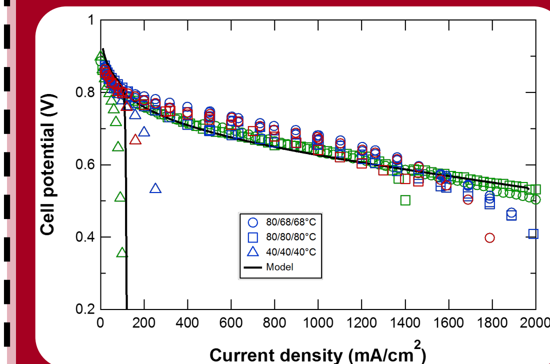


Cell Model

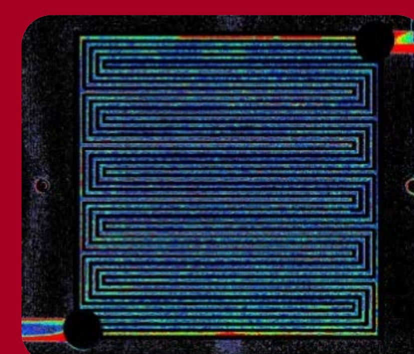


In-operando Studies

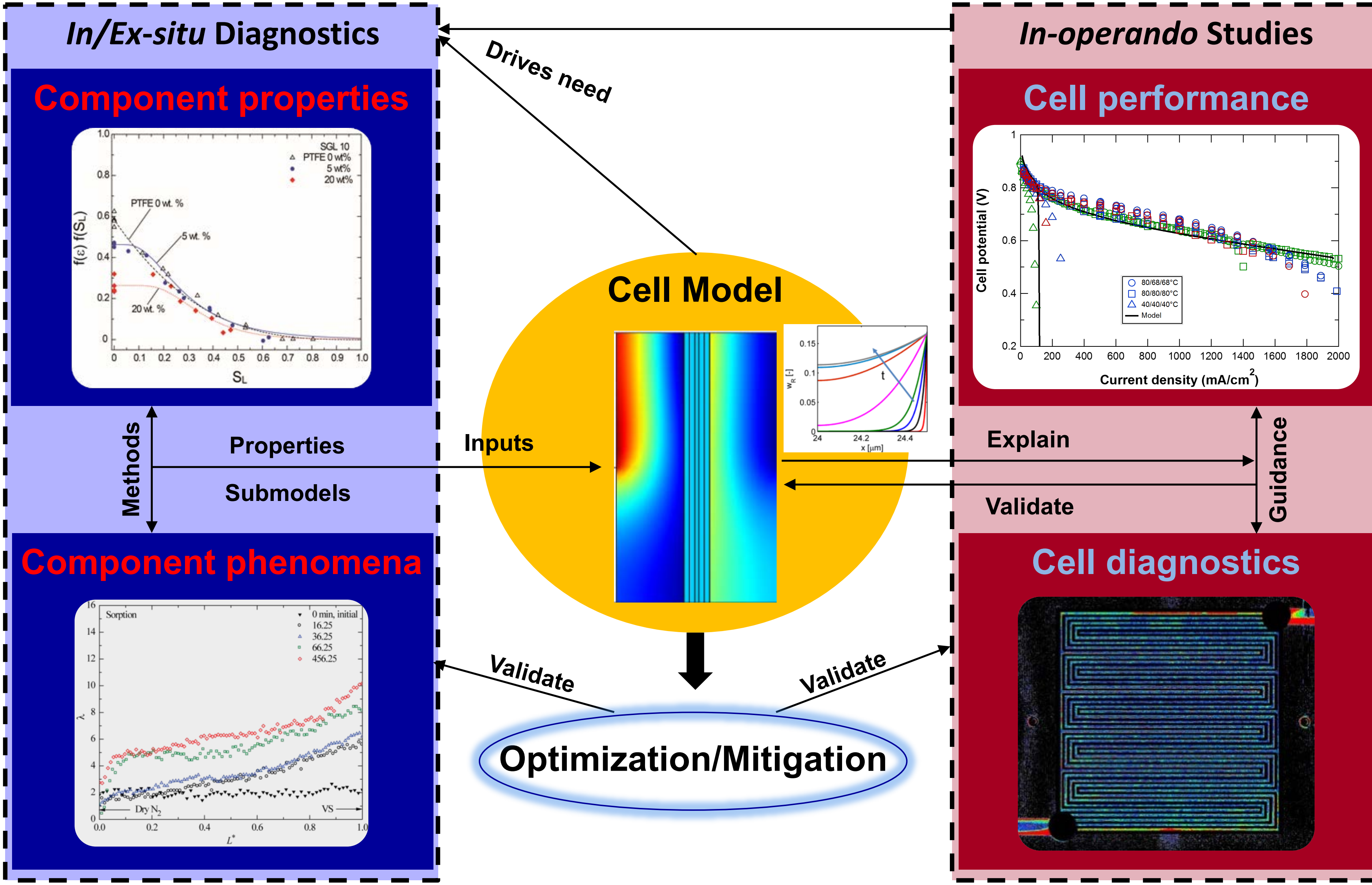
Cell performance



Cell diagnostics



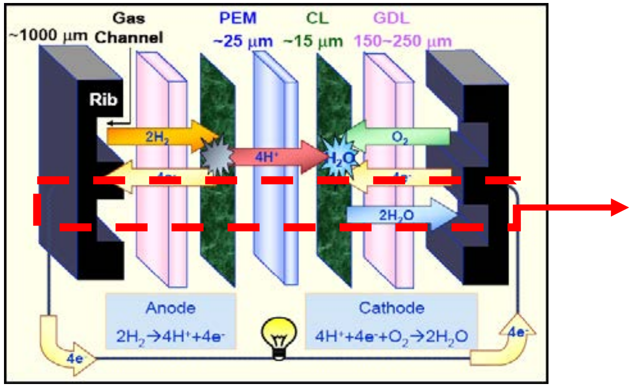
Approach

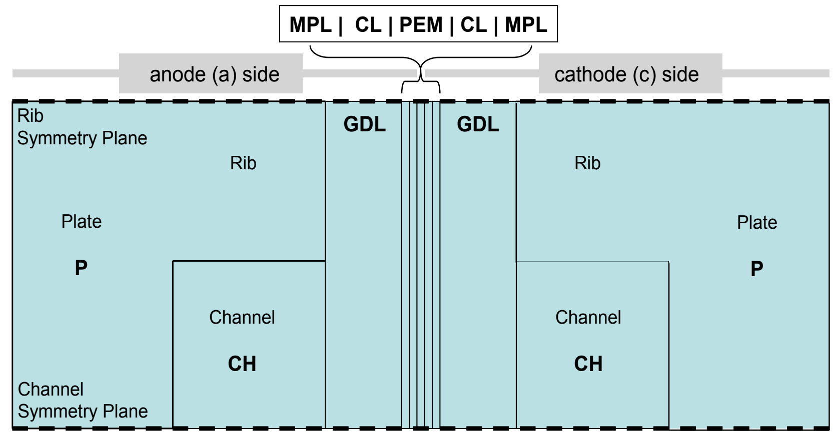


In/Ex-situ Diagnostics
Component properties
SGL 10
PTFE 0 wt%
5 wt%
20 wt%
PTFE 0 wt. %
5 wt. %
20 wt. %
f(ε) f(S_L)
S_L
Methods
Properties
Submodels
Component phenomena
Sorption
0 min, initial
16.25
36.25
66.25
456.25
Dry N2
VS
λ
L*
Drives need
Inputs
Cell Model
x [μm]
t
Optimization/Mitigation
Validate
Validate
In-operando Studies
Cell performance
Cell potential (V)
Current density (mA/cm2)
80/68/68°C
80/80/80°C
40/40/40°C
Model
Explain
Validate
Guidance
Cell diagnostics

Approach: 2-D Cell Model

- **Model Geometry**





- **Model physics**

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

Thermodynamics

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

Kinetics

Butler-Volmer for HOR and
double trap for ORR
H_2O phase change between

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

Key is describing the governing critical phenomena

Approach: Work Plan / Organization

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

Task 1. Cool-start model	Task 2. Degradation model	Task 3. Cell characterization	Task 4. Water imaging	Task 5. Model deployment	Task 6. Component characterization
LBNL	**LBNL,**	**UTRC** LANL, 3M	**LANL, LBNL**	**LBNL**	**LANL** LBNL, 3M
Steady state Startup Boundary conditions	Property degradation Mechanical stress	Performance evaluation Failure analysis	Neutron X-ray	Cool-start optimization Performance loss Failure mitigation	Membrane Catalyst layer Diffusion media

LBNL

- Project management and coordination
- Model development
- GDL and membrane characterization
- Ionomer thin-film diagnostics

LANL

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

UTRC

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

3M

- Material supplier and testing knowledge including conditioning procedures

Other

- Unique materials and diagnostics
- Real-world guidance

FY15 Project Timeline

Begin 10/14	P1,P2 12/14	P3,P4 03/15	P5,P6 06/15	M7,M8 09/15	End 09/15

Major Milestones/Deliverables/Progress Measures

P1: Along-the-channel model framework developed and coded impacts (*completed*)

P2: Complete power and humidity transients in segmented cells for 2 GDLs and 2 MEAs (*completed with improved MPL GDLs and baseline GDLs as well as NSTF and Gore MEAs*)

P3: Adiabatic-cell startup transient results for both NSTF and traditional MEAs at two starting temperatures and two current densities impacts (*completed included subzero startup case*)

P4: Measure catalyst layer water content in thick catalyst layers (*completed with neutron imaging*)

P5: Boundary condition identified for water interaction at the GDL and land/channel interface (*partially complete using adhesion force and force balance condition to predict liquid pressure*)

P6: Complete full impedance measurements for low loaded catalyst layers (*on track*)

M7: Determine if impedance measured in a differential cell can be used for model validation instead of the 10 segment cell at various current densities (*on track*)

M8: Model agreement (< 10% deviation in current density) with segmented-cell data for operation at 60 and 80C and inlet humidities of 30, 60, and 100 % relative humidity using NSTF MEAs, demonstrating that the discretized model can be used for optimization and evaluation studies (*on track*)

Accomplishments

In/Ex-situ Diagnostics

Component properties

- ❖Measured GDL properties
  - Detachment velocity, effective diffusivity, thermal conductivity
- ❖Measured CL properties
  - Water uptake in ionomer
  - Effective gas resistance

Component phenomena

- ❖ Examined 3M ionomer thin films
- ❖ Water imbibition in GDLs
  - X-ray tomography of water profiles under compression
  - Modeled using Lattice-Boltzmann
  - ❖ Studied ionic limitations in NSTF electrodes

Cell Model

- ❖Initially validated transient model
- ❖Developed along-the-channel (2D+1) model
- ❖Incorporated properties and diagnostic information
- ❖Explained anode GDL improvement

In-operando Studies

Cell performance

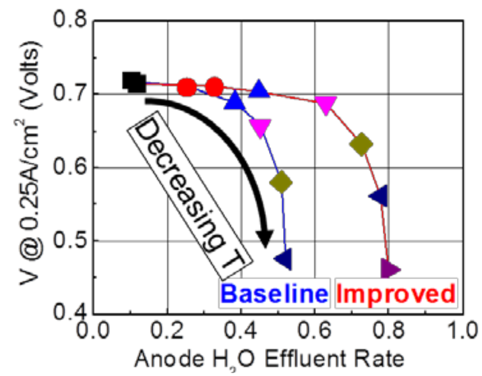
- ❖ Understanding and optimizing operation with NSTF
- ❖ Examined new MPLs
- ❖ Impacts of low-loaded catalyst layers
- ❖ Adiabatic cell and transient studies including subzero

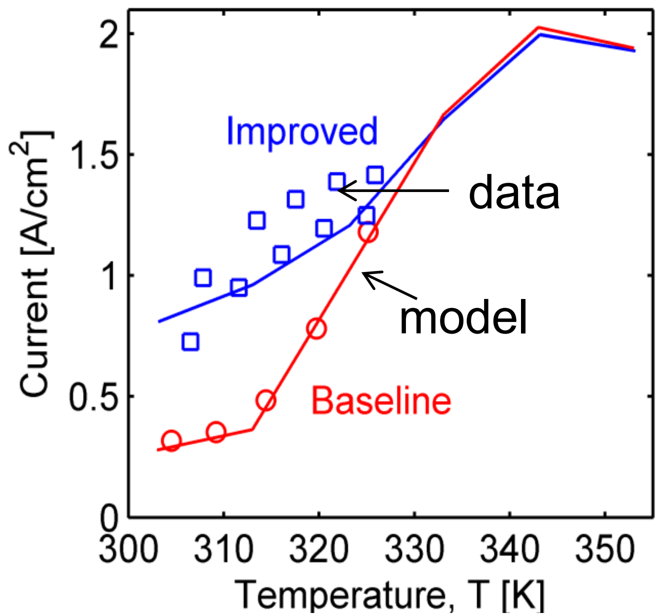
Cell diagnostics

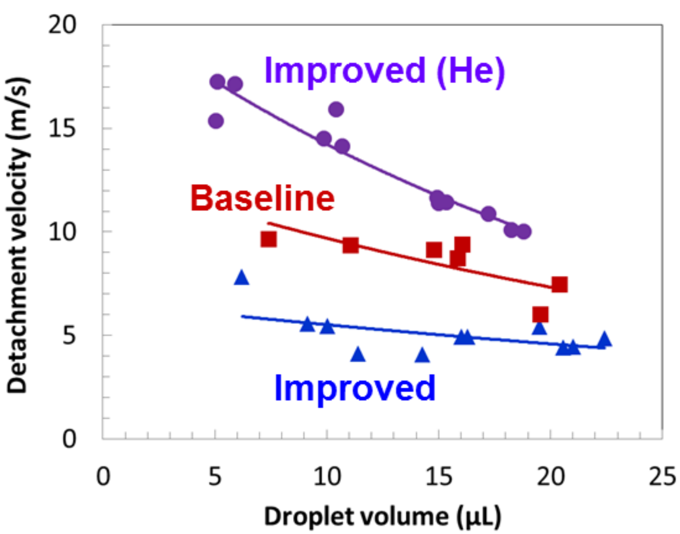
- ❖ High-res neutron imaging with different GDLs and CLs
- ❖ Segmented cell studies during transient operation
- ❖ Water-balance studies for different banded GDLs

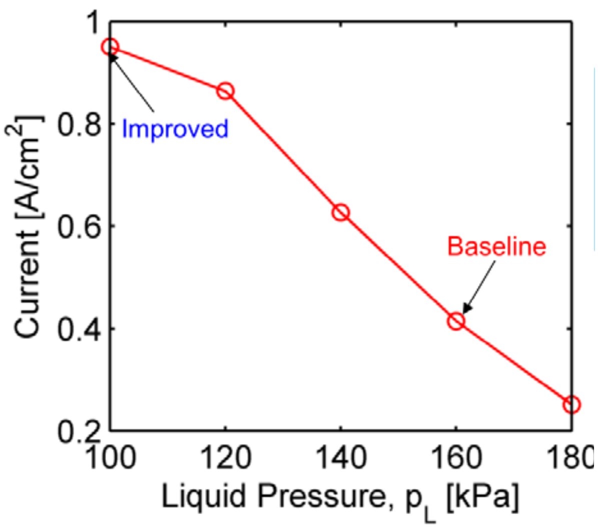
Modeling Results

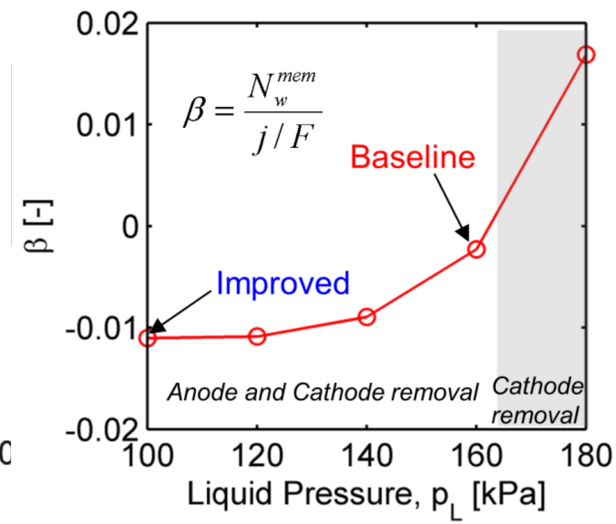
- GDL measured properties incorporated into model
  - Improved GDL modeled with lower adhesion force at GDL|channel interface
  - Detachment velocity dependent on gas
- Model agreement for NSTF temperature sensitivity







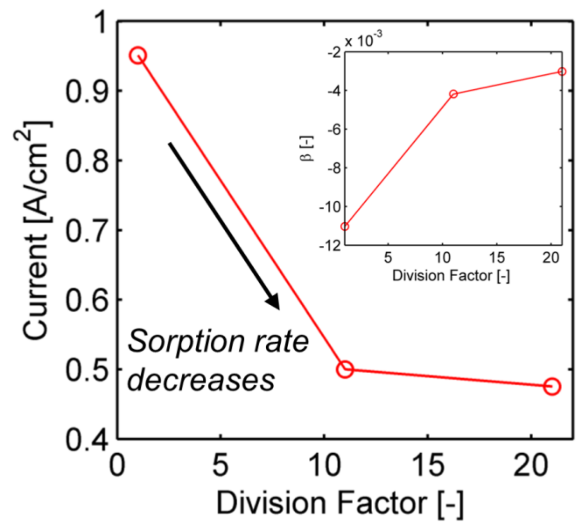




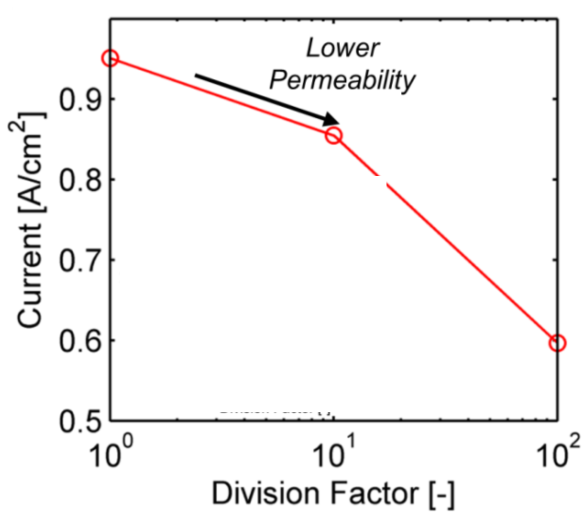
Model Exploration

- For effective water removal through anode need to worry about water driving forces and resistances
  - Sensitive to transport in membrane and GDL adhesion force, less sensitive to GDL permeability

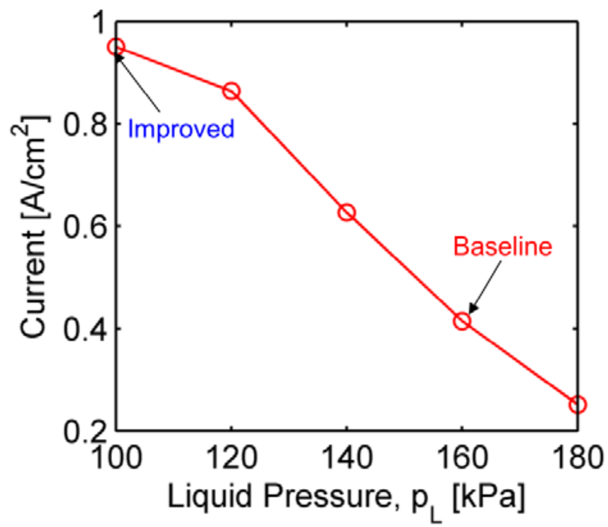
Membrane water sorption



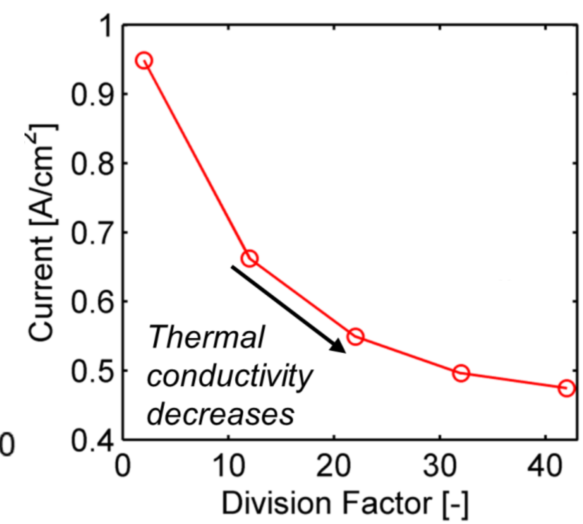
GDL permeability



Adhesion force

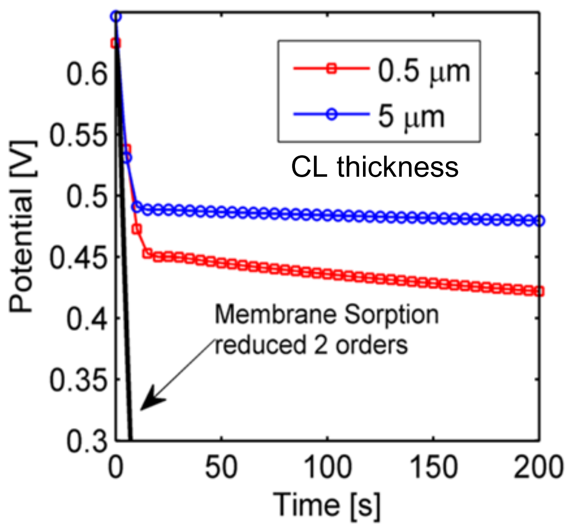


Membrane thermal conductivity



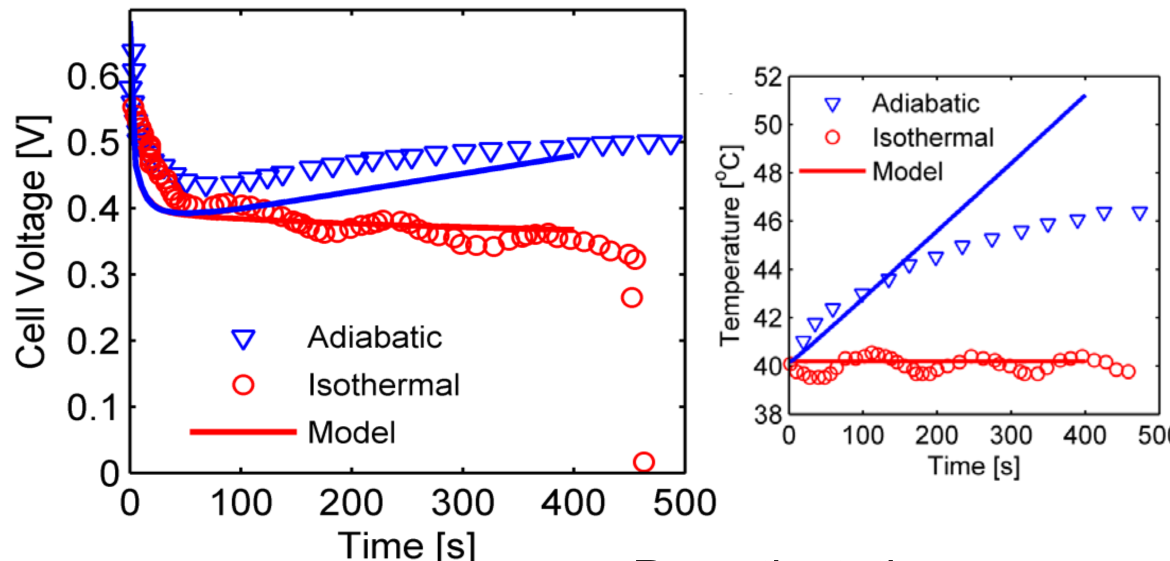
Cell Transients and Model

- NSTF start depends on thermal and pressure boundary conditions
  - 2x X0155 shows highest current due to water redistribution
  - Initial model agreement with galvanostatic transients
    - Model shows impact of design and material variables

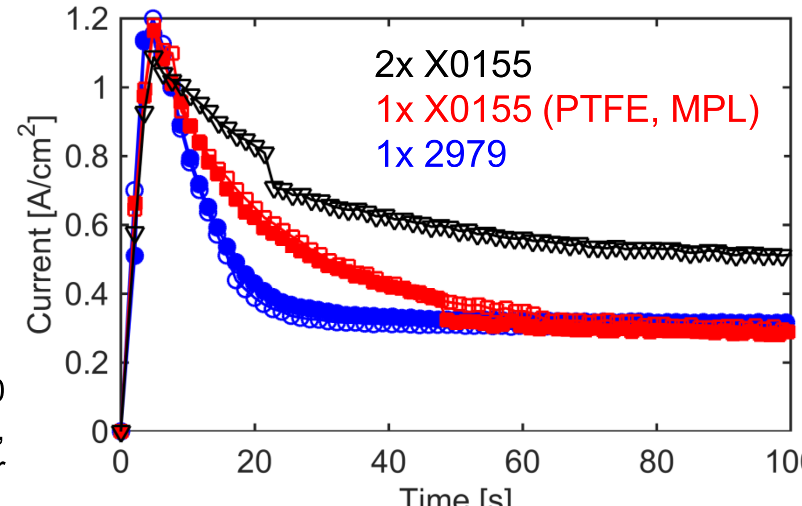


Galvanostatic

0.25 A/cm², 40 C, 100/100 kPa, 100/100 %RH

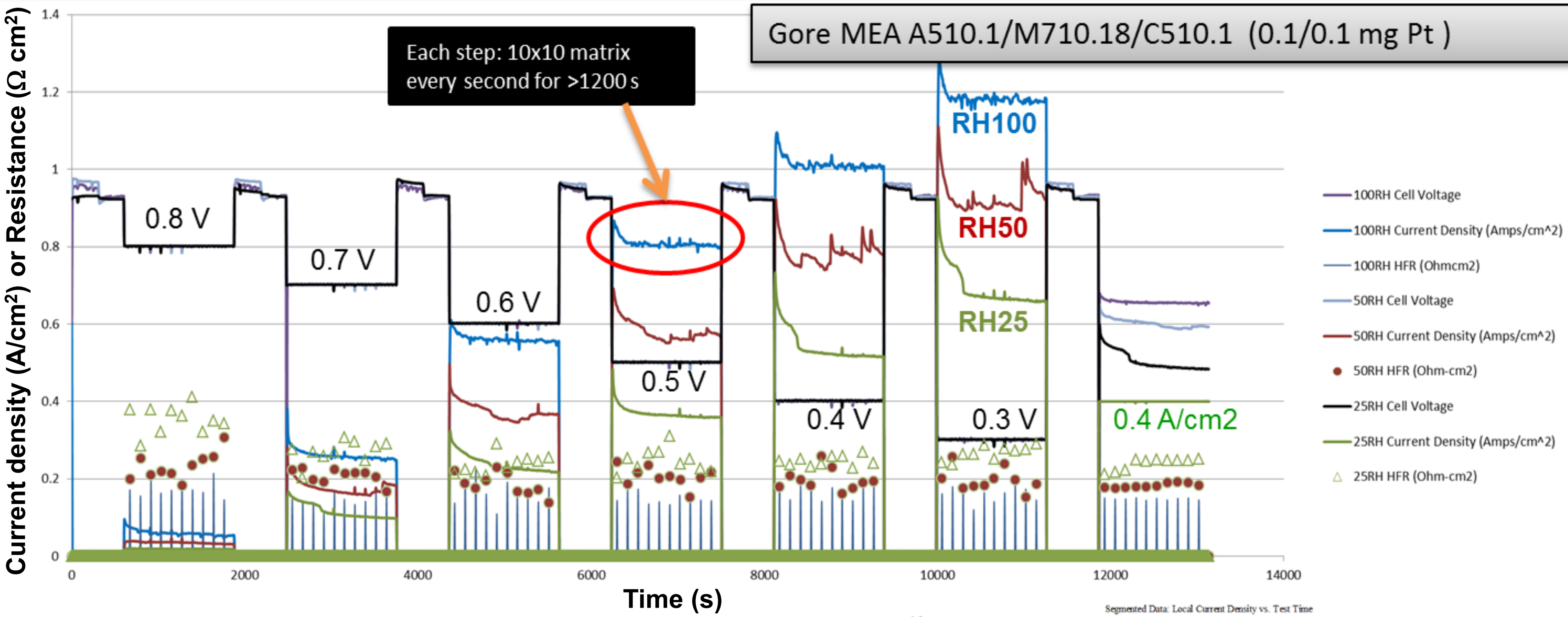


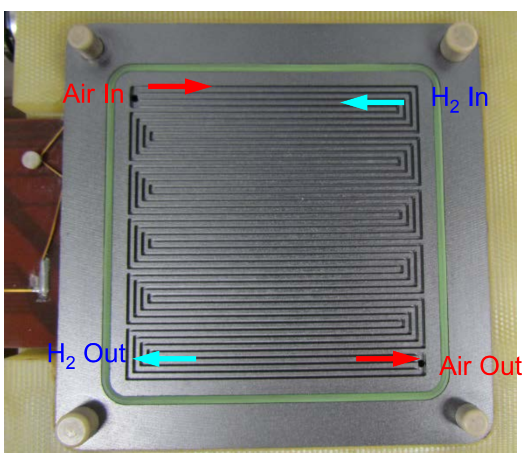
Potentiostatic

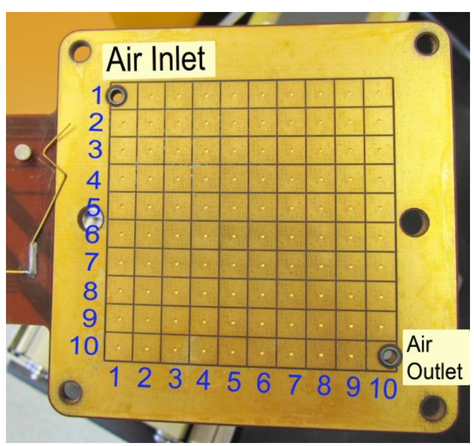


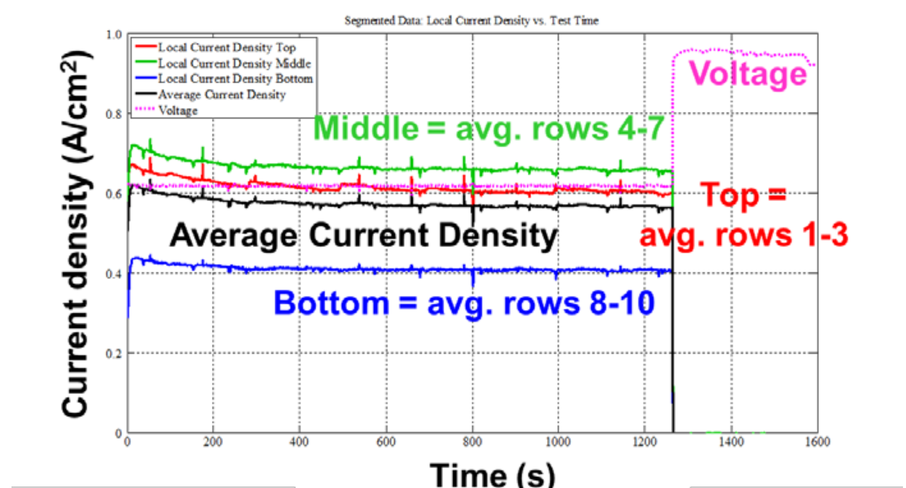
0.4V, 30 C, 100/150 kPa, 100/100 %RH, 2/2 H_2/Air

Segmented Cell Transients





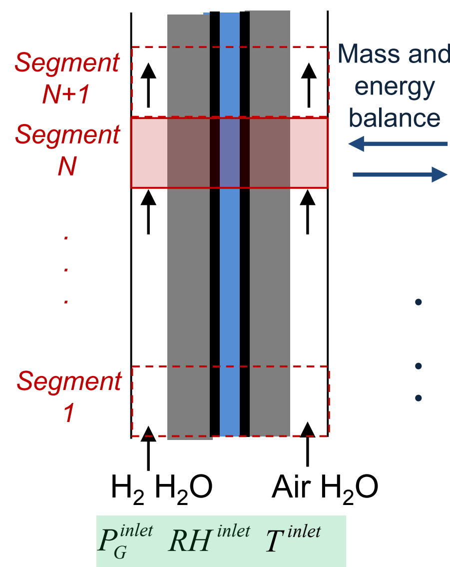




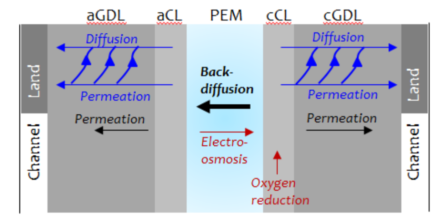
Along-the-Channel Model

- Along-the-channel steady-state model developed for segmented cell data
  - ↳ Iterative loop for RH computation
- Model will complement segmented cell results and serve as predictive tool, especially for low RH inlets

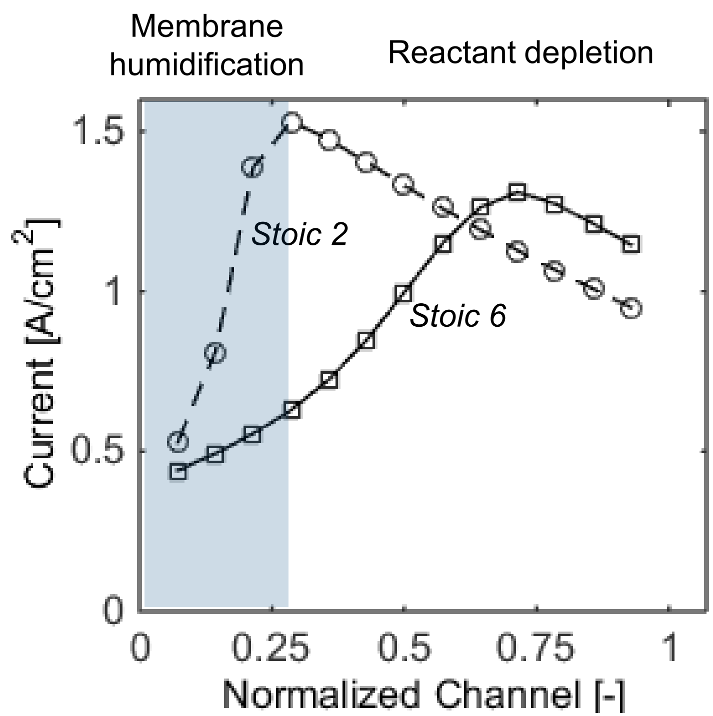
Along-the-channel 1D

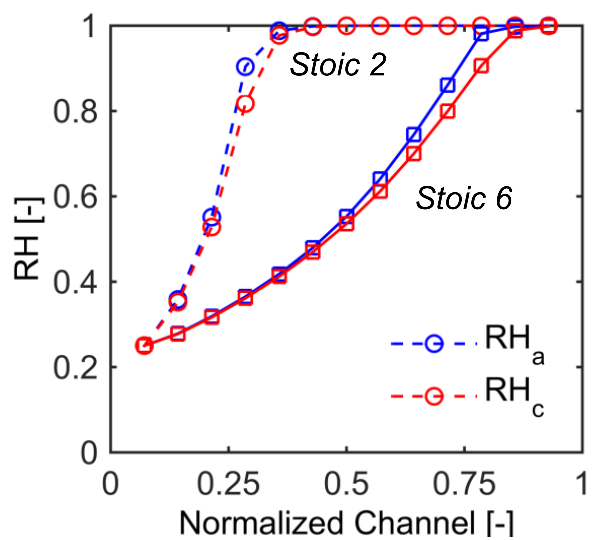


2D sandwich model



- Mass, energy balance, condensation/evaporation
- Co-flow
- 20-40 segments, 10 cm channel

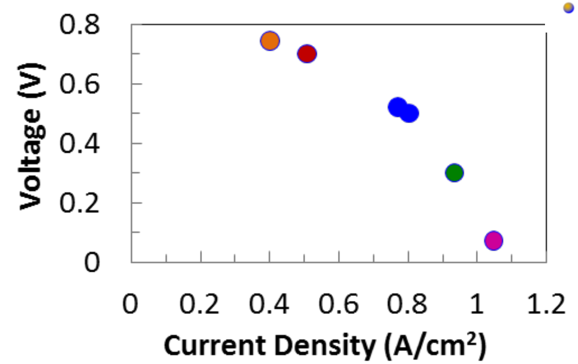


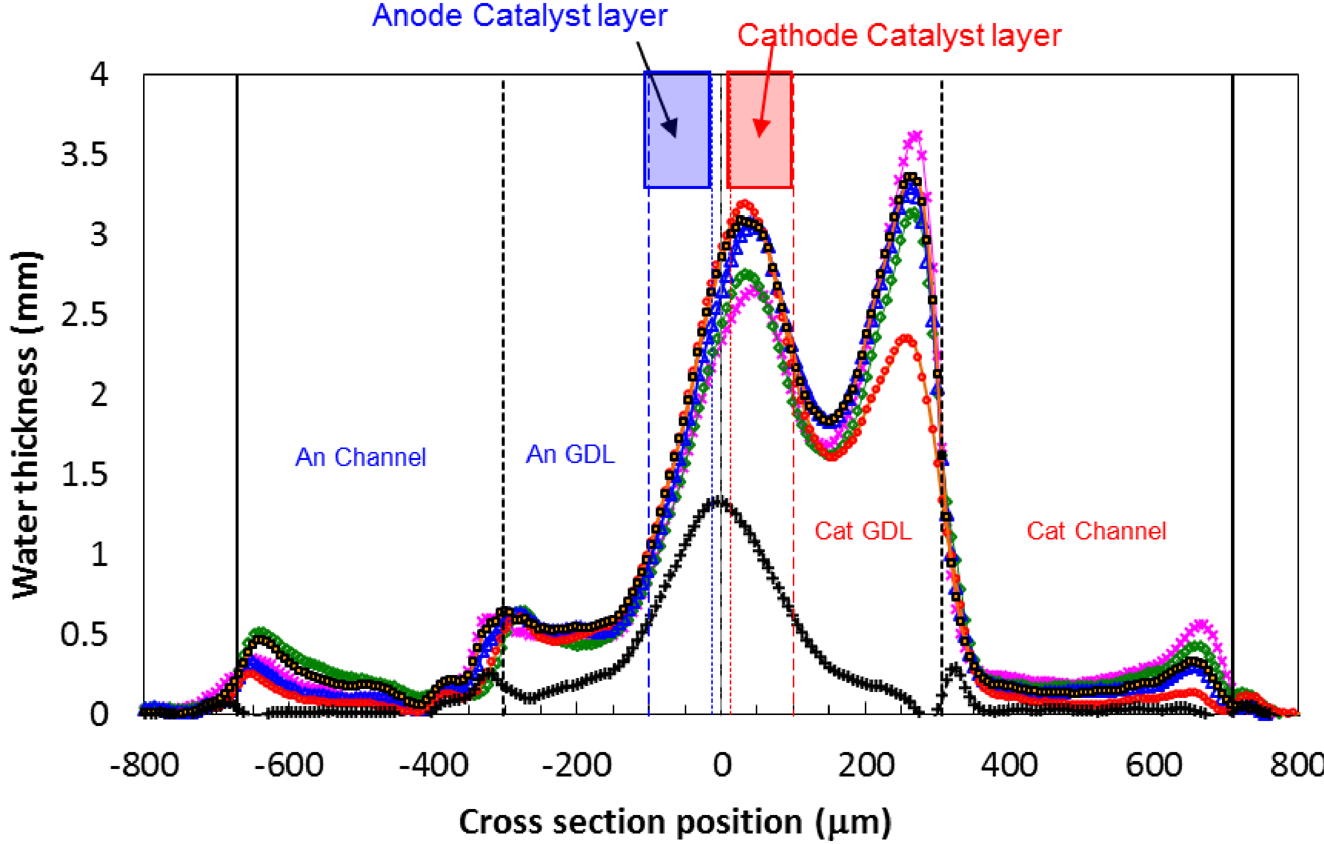


RH: 0.99/0.99, P_g: 100/150 kPa, T: 40 C, Stoic: 4/2, V= 0.4 V RH_{in}: 25%/25%

Measuring Catalyst-Layer Saturation

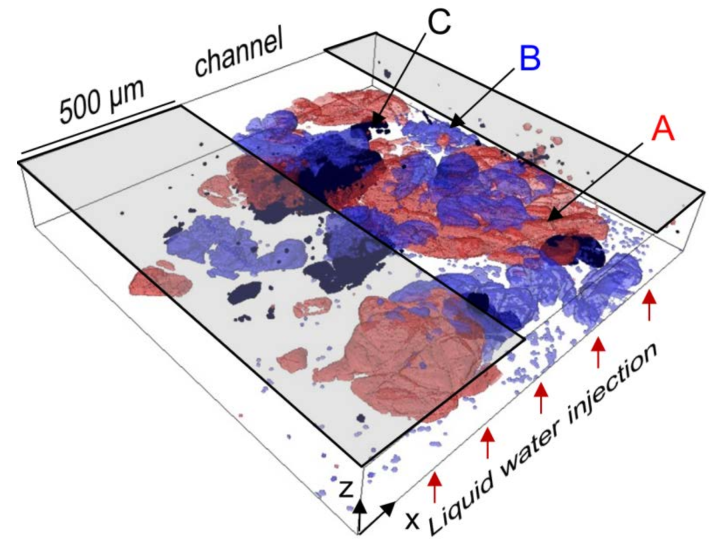
- At open circuit (OCV): symmetric water profile
- At current >= 0.4 A/cm^2, clear water peaks in cathode CL (also in cathode GDL substrate)
- Water content in the cathode CL steady in moderate range of current/voltage
- Cathode CL decreases at lower voltage due to phase-change-induced flow (increase in GDL)
- Anode CL appears like extension of membrane

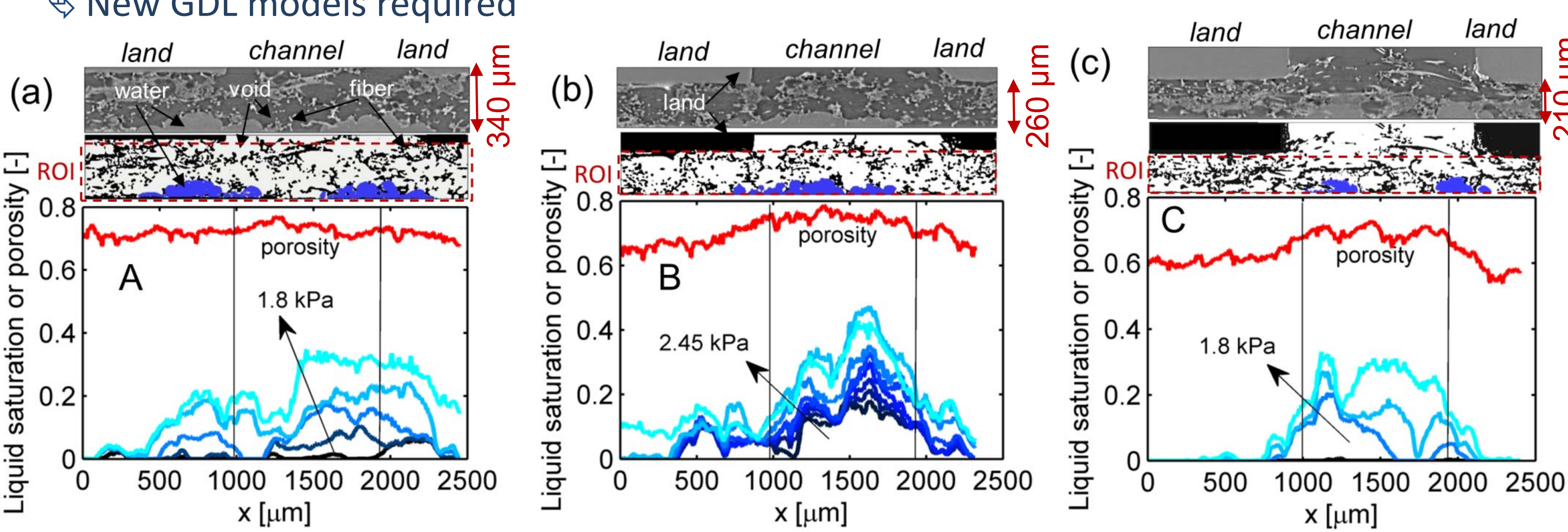




X-Ray Tomography of GDLs

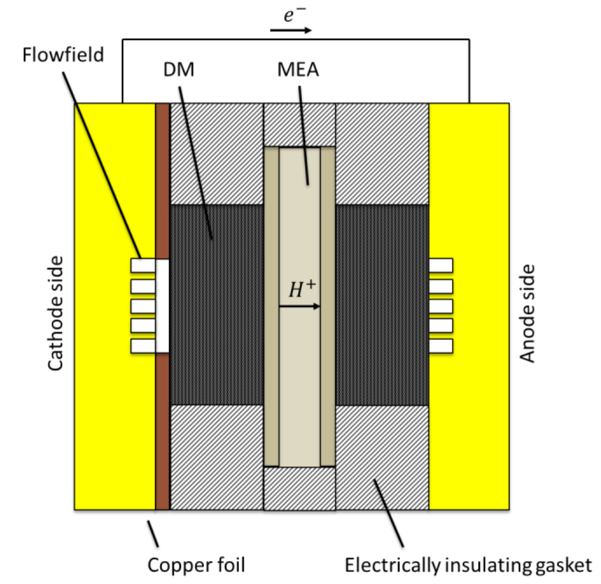
- Understanding water distribution under compressed land|channel geometry enables GDL optimization for effective water removal
  - With increased compression water clusters decrease in size and appear only under the channel
    - Becomes correlated to porosity
- Water profile at breakthrough shows only small liquid-front penetration
  - New GDL models required

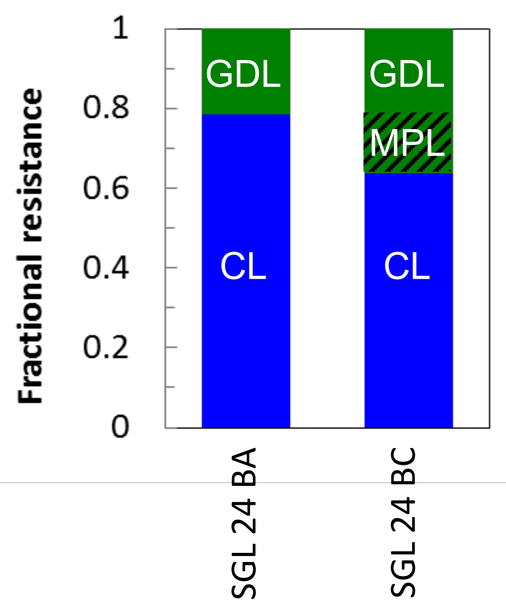


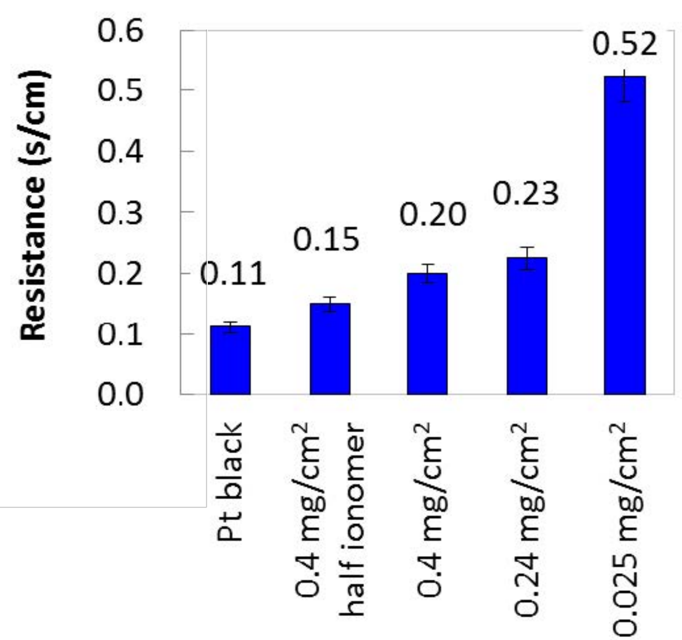


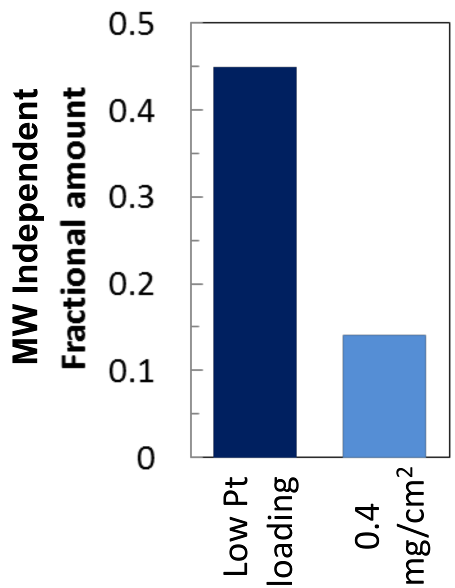
Catalyst-Layer Resistance

- Adapt effective diffusivity hydrogen pump setup for CL
  - CL is dominant diffusion resistance compared to *dry* GDLs
    - DM makes up about 20 to 40% of total resistance
  - Use of deuterium helps separate molecular weight dependent and independent processes
    - For low loadings, MW independent becomes important
  - Local CL resistance increases with lower Pt loadings









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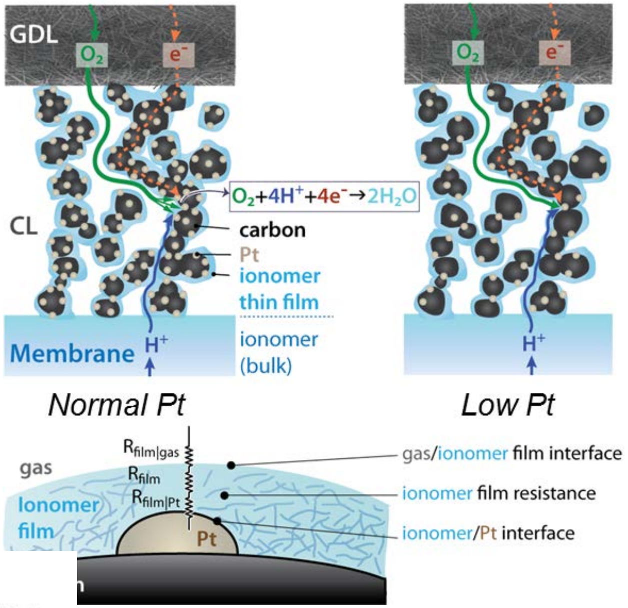
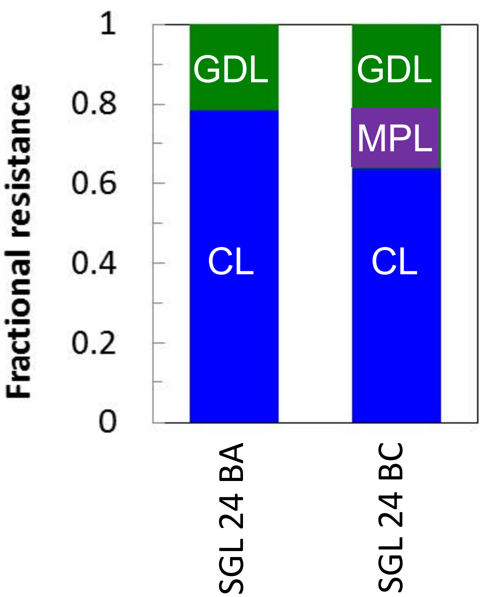
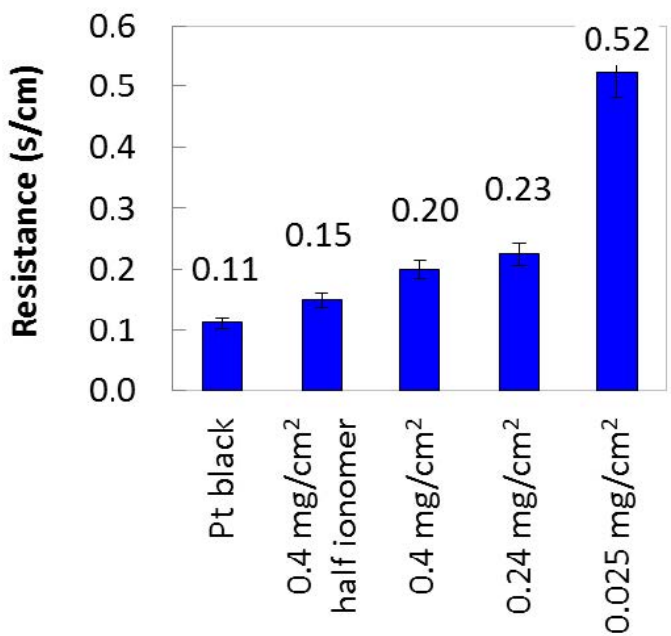
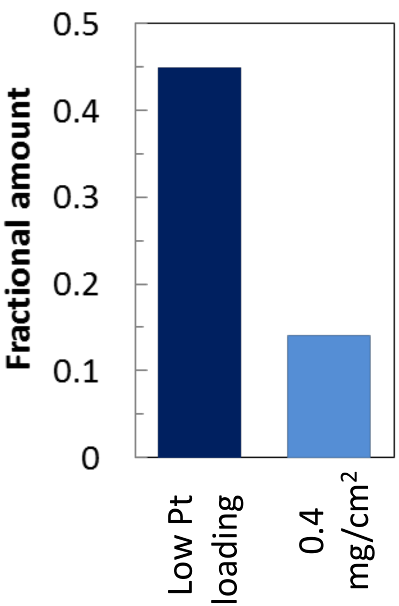


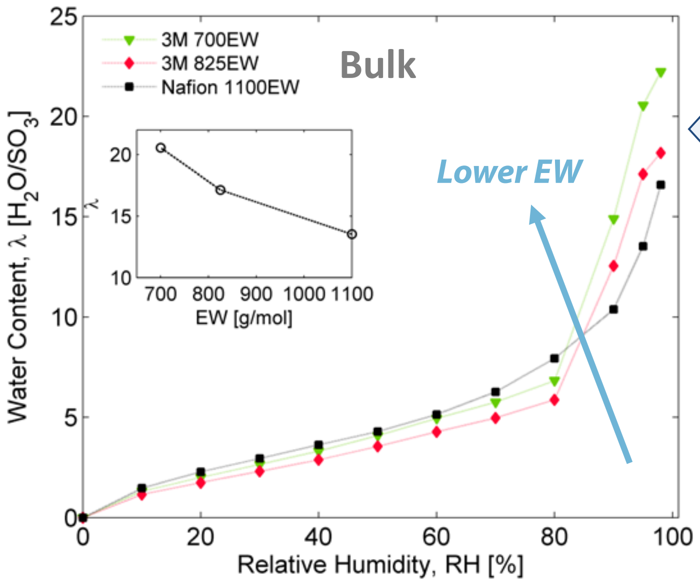


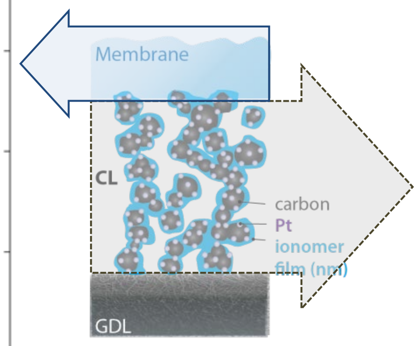




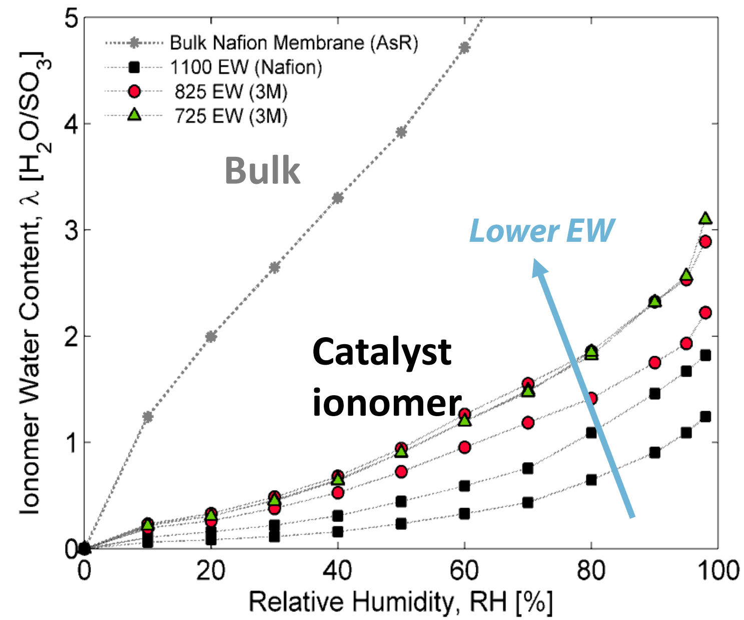
Impact of EW: Bulk vs.CL ionomer

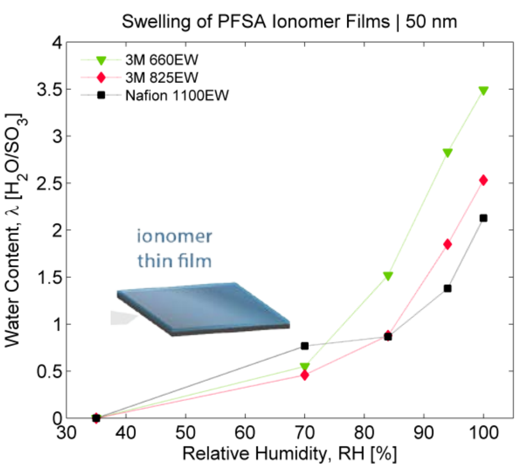
- **Bulk:** EW → high uptake at high RHs

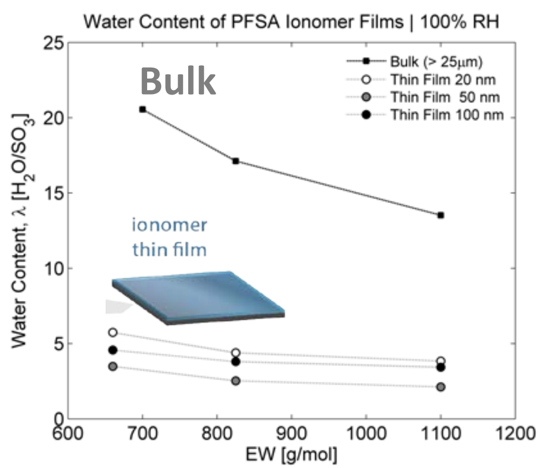




- **CL ionomers:** Significant reduction in uptake, EW effect is still preserved and pronounced







- **Thin films** on model substrates exhibit similar swelling to catalyst-layer ionomer

Responses to Previous Year Reviewers' Comments

- The fundamental understanding of freeze-thaw and of NSTF water management issues will be of strategic value to the community as a whole. Without temporal and spatial effects in the developed model, its application … will only be to provide qualitative trends.
  - We have initially validated the transient model and have focused on developing an along-the-channel model to predict spatial variations in water management and allow comparisons for a wider range of conditions.
- The proposed future work is generally solid, but the research team should consider a more even split between NSTF and conventional electrodes, despite the originally proposed project scope.
  - Throughout the project we have also examined issues and models with traditional Pt/C catalyst layers and are planning to do more of this in the future including ionomer films, visualization of liquid water distribution, etc. The knowledge gained should also benefit novel catalyst-layer architectures like extended surface or ultra-thin ones in general.
- The project seems very focused on basic science; there is not enough application of what has been learned to investigate what a next-generation material or future operating strategy should be.
  - As presented, the characterization and diagnostics are all designed with application in mind to uncover the key performance bottlenecks and determine ways to overcome them. For example, the ionomer thin films or x-ray tomography of GDLs both directly assess performance issues with liquid-water management. In addition, modeling the cell and water management requires knowledge of the underlying phenomena, which is gained from detailed studies that, in some cases, may appear to be basic science but is much more application and need driven.
- The project could benefit from closer collaboration with a system integrator or original equipment manufacturer (OEM), who could provide insight into issues related to full-size stack hardware.
  - We have and continue to reach out to material suppliers and system integrators, including inviting OEMs to help advise during our annual project review/planning meeting as well as possibly holding a workshop.

Remaining Challenges and Barriers

- Still not understood what limits NSTF and ultra-thin catalyst layers at lower temperatures and how protons conduct
- Need to optimize performance of ultra-thin catalyst layers, especially transient operation
- Water and thermal management at interfaces is poorly characterized and not typically modeled
- Need to overcome mass-transport resistances for low Pt loadings

Proposed Future Work

- **Cell Performance**
  - UTRC to run cool and cold starts using adiabatic cell hardware
  - Examine possible interlayers and multilayer electrodes
  - LANL to run NSTF and Gore cells with different diffusion media and operation conditions
    - Segmented cell and NIST imaging including thick catalyst layers
- **Component Characterization**
  - Traditional CLs
    - Measure transport resistance, especially for low Pt loadings
  - NSTF CLs
    - Determine proton conductivity on platinum
  - Diffusion media
    - Measurement of key properties including PSD, liquid-water pathways, adhesion force, etc. for new GDLs
  - Ionomer
    - Measure transport properties of ionomer films, especially low EW ones
    - Characterize reinforced membranes
- **Modeling**
  - Exercise model to determine critical properties and guide material development and design targets
  - Incorporate more advanced interfacial and kinetic models
  - Examine pore-scale models and new GDL model possibilities
- **Understand and increase the operating window with thin-film CLs**
  - Focus on solutions and strategies derived from the integrated model and cell and component studies
- **Solicit input and advice from OEMs and material companies**

Technology Transfer Activities

- This project now incorporates activities and discussion at the Transport Modeling Working Group, which allows for free dialogue and discussion with OEMs and researchers on critical issues related to water and thermal management

- Interact with industry
  - Participate in FCTO tech to market activities including events at the Fuel Cell Seminar and ECS meeting
  - Industry days at SLAC and LBNL
  - Streamlined CRADA process through CalCharge
  - Conduct site visits to OEMs and have them participate in annual progress meetings

- A provisional patent filed around novel flow cell that is currently being advertised for licensing

- Developed diagnostics have been transferred to industry

Summary

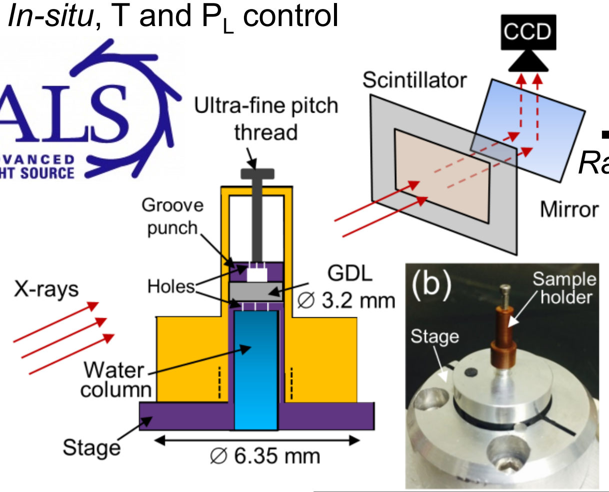
- Relevance/Objective:
  - Help enable and optimize, and mitigate failure in state-of-the-art materials through understanding of operation at low and subzero temperatures
- Approach/Collaborations:
  - Use synergistic combination of cell and component diagnostic studies with advanced mathematical modeling at various locations (national laboratories, industry, and academia)
- Technical Accomplishments:
  - Combined modeling and experiment to understand low-temperature performance of NSTF
    - Examined transient operation showing how the membrane properties and GDL interface are the most sensitive parameters for water out of the anode scheme
    - Increased water out the anode lowers cathode flooding and is driven by morphological features that decrease GDL surface adhesion force
  - Developed along-the-channel model to correlate spatially varying results
  - Investigated water movement and existence in diffusion media
    - Water-imbibition front and catalyst-layer water content imaged
    - Novel MPLs examined
  - Investigated traditional catalyst-layer resistance and importance of ionomer mass-transport resistance at low catalyst loadings
- Future Work:
  - Understand liquid-water movement and interactions in fuel-cell components and cells
  - Identify optimal materials and engineering solutions to overcome elucidated critical bottlenecks for transient and steady-state cell performance

Technical Back-Up Slides

Work-flow and Potential for XCT Tomography GDLs

XCT imaging

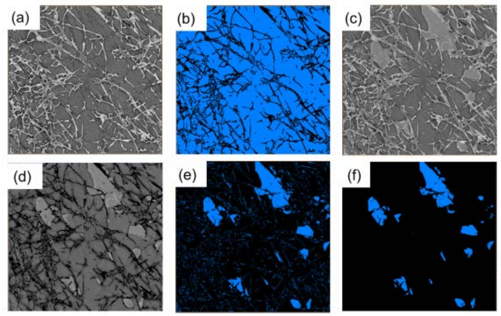
- 1.3 µm resolution
- *In-situ*, T and P_L control



Raw data

Image Reconstruction and Segmentation

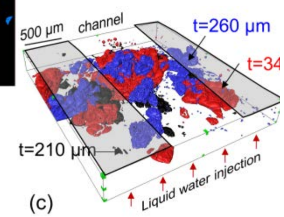
- Avizo, ImageJ, Octopus, Matlab® Image Processing toolbox

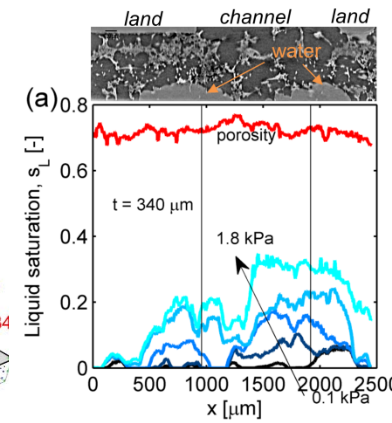


Binary image stacks

Morphology and Spatial Distributions

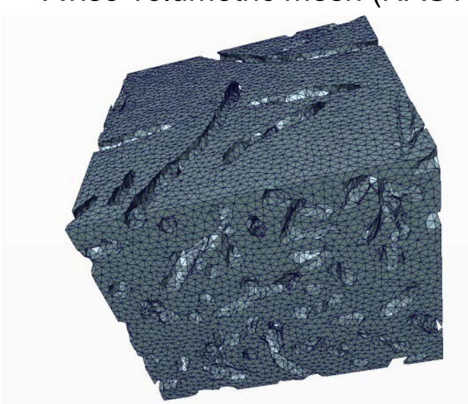
Binary image stacks of GDLs and water





3D Volumetric Mesh

- Tetragrid generation of void-space
- Aviso volumetric mesh (NASTRAN file)



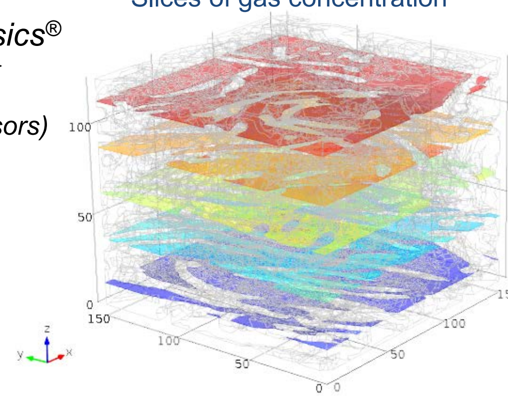
Mesh into Comsol Multiphysics®

CRAY CX1™, 4 blades, 24 GB RAM/blade, 2.93 GHz (2 processors) per blade, 12 cores each

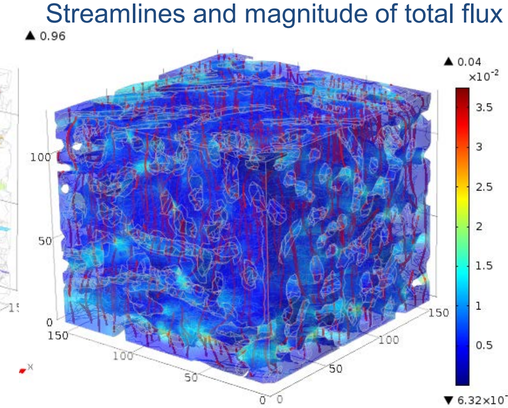
Morphological Transport Properties

- Effective diffusion coefficient
- Optimal transport pathways

Slices of gas concentration

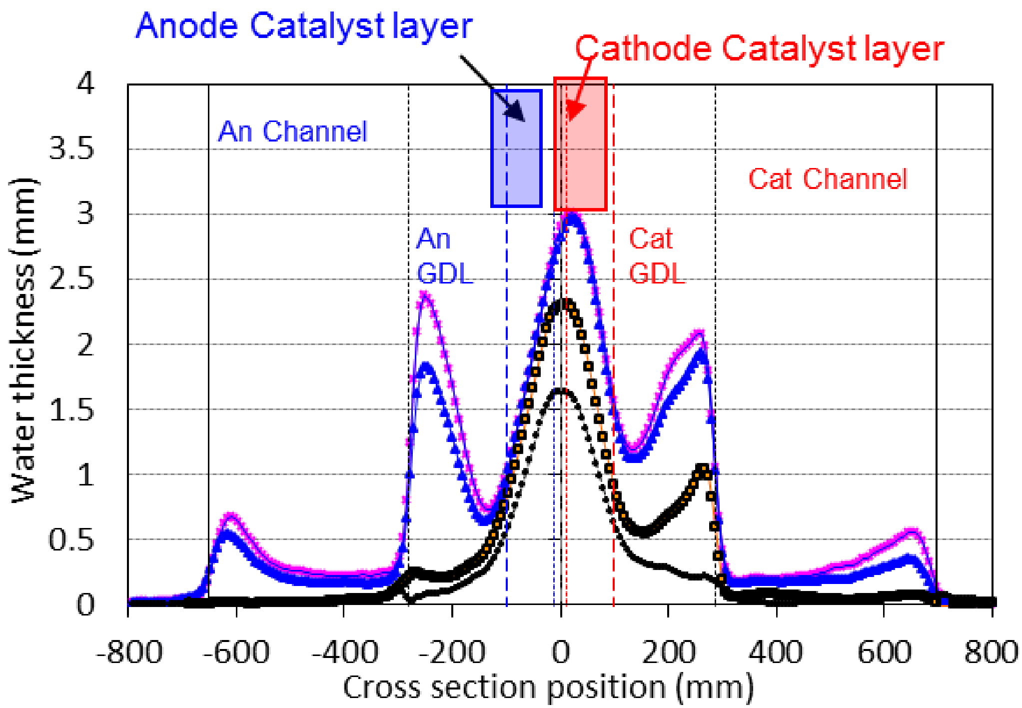


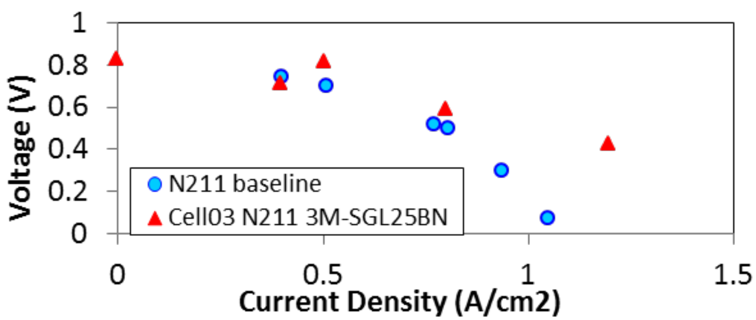
Streamlines and magnitude of total flux

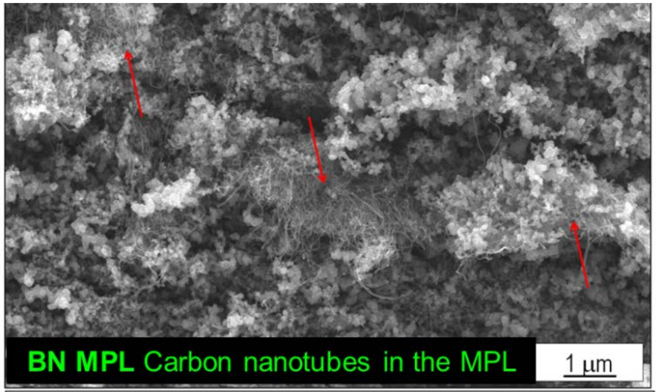


Improved GDL Combination

- Cathode SGL25BN and anode 3M improved GDL demonstrate
  - Improved performance
  - Same or lower saturation in the cathode catalyst layer compared to baseline
  - The peak in the water content in cathode catalyst layer shifts slightly to the anode side compared to the baseline case
  - GDL water: At current >0.4 A/cm2, water content shifts from cathode GDL to the anode GDL







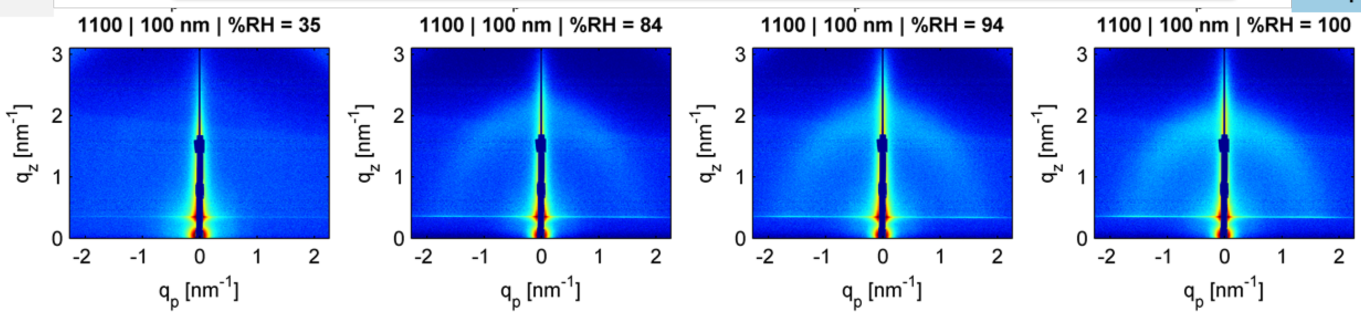
MPL comprised of loosely packed carbon black particles that surround CNT "bundles" (red arrows) – CNTs are not homogeneously distributed within the MPL.

3M Thin-Film Ionomer Studies

No Phase-Separation

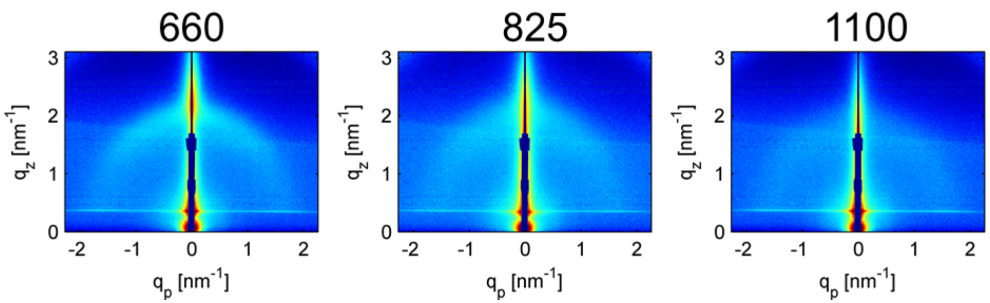
Decreasing Humidity / Swelling

Phase-Separation

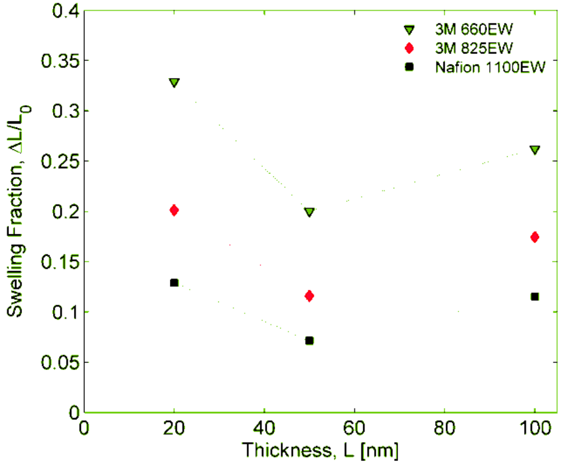


Lower EW / Higher IEC

Weak Phase-Separation

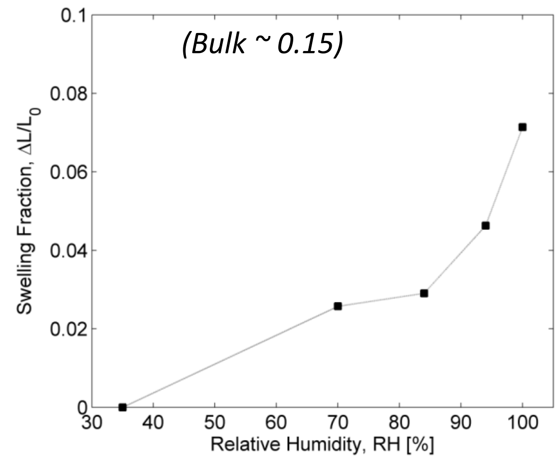


No Phase-Separation



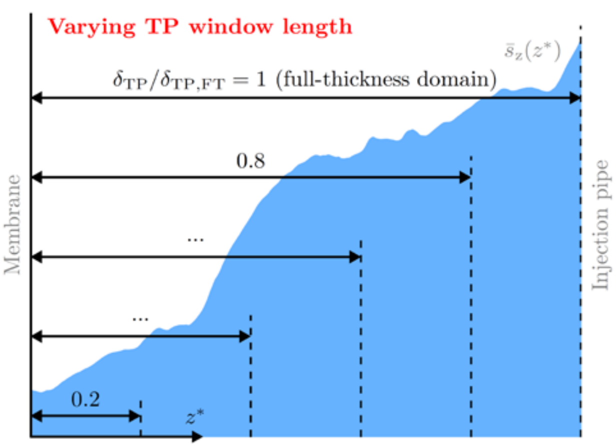
- Structure vs. Swelling
  - Not much swelling below 80% RH
  - Higher IEC results in better phase separation
    - Higher water uptake

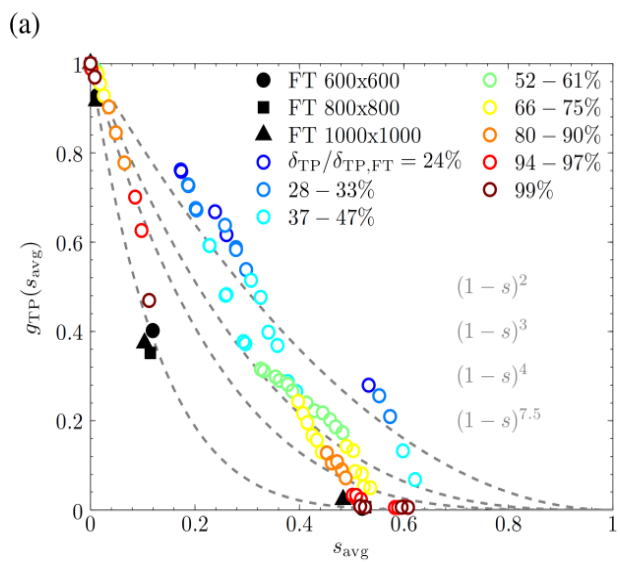
      20 nm > 100 nm > 50 nm
    - Seen even at the same water content

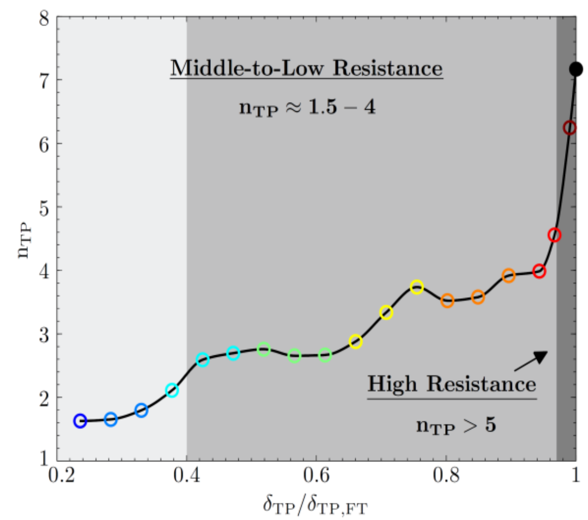


GDL Simulations

- Capillary pressure – saturation does not apply locally
  - ↳ Need to obtain values only from flat regions for continuum upscaling
- LBM simulations from XCT images show the large difference depending on what you assume for your bounding volume
  - ↳ Need more complicated GDL models







A Path Forward for Extended-Surface Catalysts

- Extended-surface *catalyst architectures* offer potential for excellent durability
  - However, robust performance with these novel catalysts has ***not*** been demonstrated
- Relative to Pt/C-based MEAs with low loadings, NSTF MEAs exhibit these *major issues*:
  - Significantly higher temperature sensitivities
  - More sensitive to some contaminates (*e.g.*, species that are prone to adsorption on Pt)
  - Highly susceptible to flooding, especially under transient conditions
  - Poor ionic conductivity in electrodes (air performance similar to half-air performance)
- These issues could all potentially be addressed with ***catalyst-layer architectures*** that have:
  - **Additional porosity, surface area, and ionic conductivity**
- These attributes could potentially be enabled by adding components to the catalyst layers:
  - **Carbon** (not decorated with Pt and therefore less prone to corrosion)
    - Enables a catalyst layer with more porosity (void volume to store/release water, as needed)
    - Enables additional surface area (which can preferentially adsorb some contaminates)
  - **Ionomer** (should be highly dispersed; *i.e.*, added during production of CL)
    - Enables a catalyst layer with higher level of water storage (and adds porosity)
    - Enables ionic conductivity (that is not highly temperature sensitive)
- Ultra-low loaded CLs are not typically limited by transport losses through thickness of the CL
  - Addition of these materials will increase CL thickness, but should actually decrease mass-transport losses (since they address what is actually limiting the performance)