

Water Transport Exploratory Studies

2009 DOE Hydrogen Program Review

May 18-22, 2009

Presented by: **Rod Borup**

Solicitation Partners:

Los Alamos National Lab, National Institute of Standards and Technology, Sandia National Lab, Oak Ridge National Lab, SGL Carbon, W.L. Gore, Case Western Reserve University

Additional Partners/Collaborations:

University of Texas-Austin, Lawrence Berkeley National Lab, Nuvera Fuel Cells

FC_35_Borup

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project Overview

Timeline

- Project initiated FY07
 - **Start March '07**
- 4 year Project Duration
 - **End March '11**
- ~> 50 % complete

Budget

- Total project funding
 - DOE Cost: \$6,550,000
(over 4 yrs)
 - Cost Share: \$290,811
- Funding for FY09

LANL	\$1100k
Partners (Univ. & Ind.)	\$200k
Other National Labs	<u>\$350k</u>
FY09 Total	\$1650k

Barriers

- Water management is critical for optimal operation of PEM Fuel Cells
- Energy efficiency
 - Power density
 - Specific power
 - Cost
 - Start up and shut down energy
 - Freeze Start Operation

Partners

- Direct collaboration with Industry, Universities and other National Labs (see list)
- Interactions with other interested developers
- Project lead: Los Alamos National Lab

Collaboration: Organizations / Partners

- **Los Alamos National Lab:** Rod Borup, Rangachary Mukundan, John Davey, David Wood, Partha Mukherjee, Jacob Spendelow, Tom Springer, Tommy Rockward, Fernando Garzon, Mark Nelson
- **Sandia National Laboratory:** Ken Chen & C.Y Wang (PSU)
- **Oak Ridge National Lab:** Karren More
- **Case Western Reserve University:** Tom Zawodzinski
- **SGL Carbon Group:** Peter Wilde
- **National Institute of Standards and Technology (no-cost):** Daniel Hussey, David Jacobson, Muhammad Arif
- **W. L. Gore and Associates, Inc.:** Will Johnson, Simon Cleghorn
(Purchase request basis)
- **Lawrence Berkeley National Lab:** Adam Weber, Haluna P. Gunterman
(directly funded)
- **Univ. Texas-Austin** (additional sub-contract): Jeremy Meyers
- **Nuvera:** James Cross, Amedeo Conti (Technical Assistance – freeze workshop)

Relevance: Objectives

- **Develop understanding of water transport in PEM Fuel Cells (non-design-specific)**
 - Evaluate structural and surface properties of materials affecting water transport and performance
 - Develop (Enable) new components and operating methods
 - Accurately model water transport within the fuel cell
 - Develop a better understanding of the effects of freeze/thaw cycles and operation
 - Develop models which accurately predict cell water content and water distributions
 - Work with developers to better state-of-art
 - Present and publish results

Approach

- **Experimentally measure water *in situ* operating fuel cells**
 - Neutron Imaging of water
 - HFR, AC impedance measurements
 - Transient responses to water, water balance measurements
 - Freeze measurement / low temperature conductivity
 - Understand the effects of freeze/thaw cycles and operation
 - Help guide mitigation strategies.
- **Characterization of materials responsible for water transport**
 - Evaluate structural and surface properties of materials affecting water transport
 - Measure/model structural and surface properties of material components
 - Determine how material properties affect water transport (and performance)
 - Evaluate materials properties before/after operation
- **Modeling of water transport within fuel cells**
 - Water profile in membranes, catalyst layers, GDLs
 - Water movement via electro-osmotic drag, diffusion, migration and removal
- **Develop (enable) new components and operating methods**
 - Evaluate materials effects on water transport

In situ Measurement of Membrane Water

- Membrane conductivity is a f(water content)
(λ = # of Water molecules per # of sulphonic acid sites)
 - Large literature base measuring water in Nafion®
 - Vast majority of studies were conducted ex situ
- T. E. Springer, T. A. Zawodzinski, and S. Gottesfeld, Polymer Electrolyte Fuel Cell Model, *J. Electrochem. Soc.*, Vol. 138, No. 8, 1991 2334
(λ = 14 at Cathode interface)
- Zawodzinski, et al., *J. Electrochem. Soc.*, Vol. 140, No. 4, April 1993
(λ as a f(RH) – λ = 14 RH=100, λ = 22 Liq.)
- J. T. Hinatsu, M. Mizuhata, and H. Takenaka, *J. Electrochem. Soc.*, Vol. 141, No. 6, June 1994
(λ as a f(RH) at 80 oC by thermogravimetric)
- L.M. Onishi, J.M. Prausnitz and J. Newman, *J. Phys. Chem. B* 2007, 111, 10166-10173
(Membrane water content is a f(thermal history)
 λ = 13-14 (predried), λ = 21 +/- 1 (preboiled)
(Suggest why 26 papers are 'incorrect')

Prior Neutron Imaging and modeling based off of literature results show large discrepancy (Factor of 4 difference)

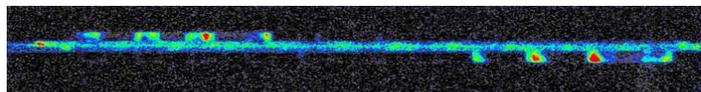
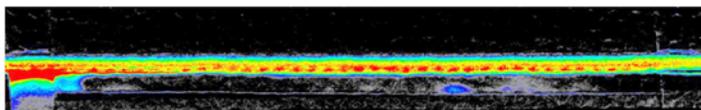
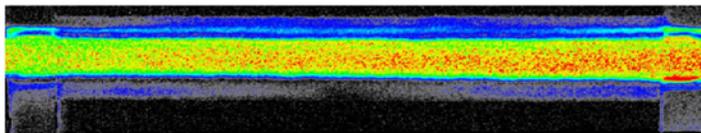
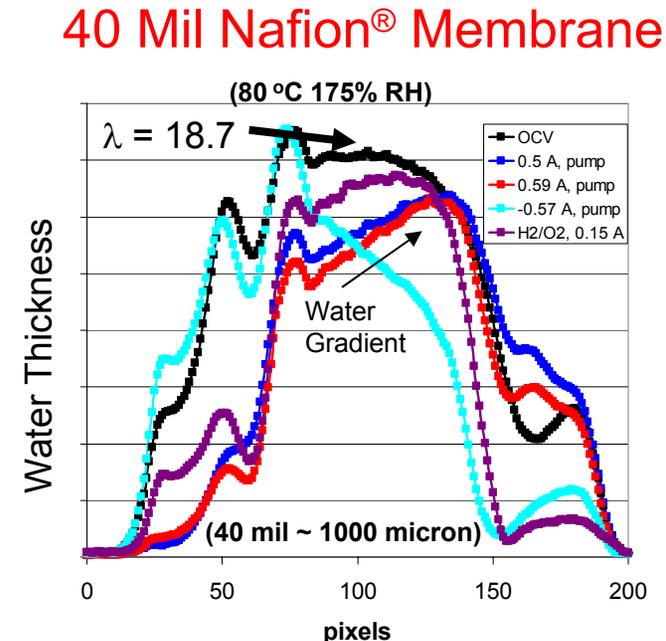
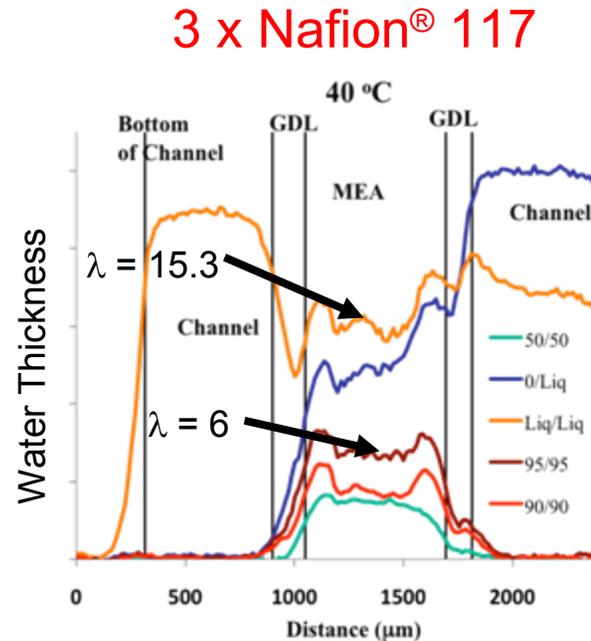
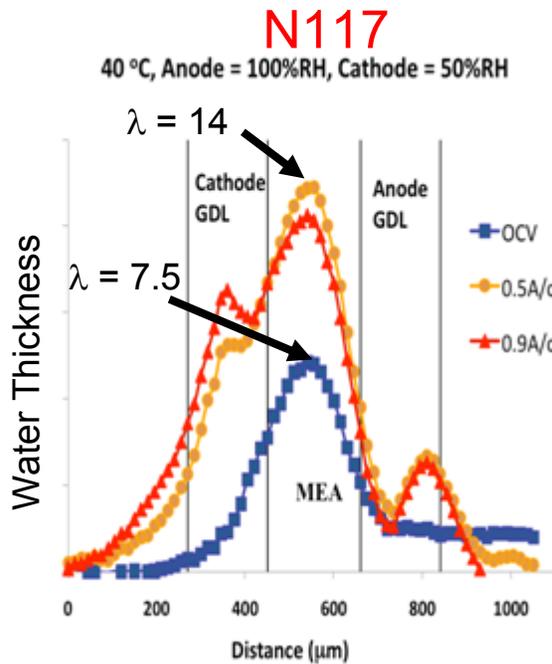
A.Z.Weber, M.A. Hickner, *Electrochimica Acta* 53 (2008) 7668.

Worked with NIST to *in situ* evaluate membrane water

- Measured through-plane water content:
 - Gore 18 micron membrane
 - N212
 - N117
 - N117 3-layer sandwich
 - 20 mil Nafion® Membrane
 - 40 mil Nafion® Membrane

Equilibrated with RH, Liquid water, under fuel cell operation, under H₂ pump operation.

Water Profiles for Different Membrane Geometries



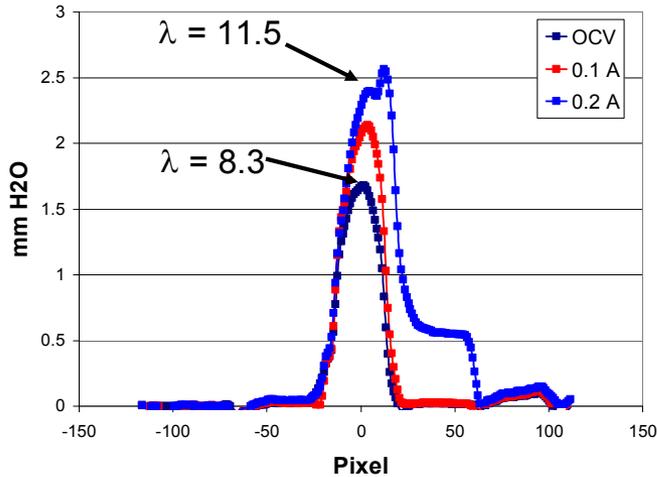
- Interface between membranes is hydrophobic
 - Water peaks in the middle of each Nafion[®] 117 membrane slice
- Interface between membrane and catalyst layer maybe hydrophilic
 - Water peaks near each of the catalyst layers (liquid water in catalyst layer pores)
- Can clearly distinguish membrane profiles
 - FWHM ($\approx 100 \mu\text{m}$) is much smaller than membrane thickness ($\approx 585 - 1000 \mu\text{m}$)
- Water gradient formed at saturated conditions by H₂ pump

Acknowledge: Steve Grot, Ion Power

20 mil Nafion® Membrane

(RH Equilibration, Fuel Cell and H₂ Pump Operation)

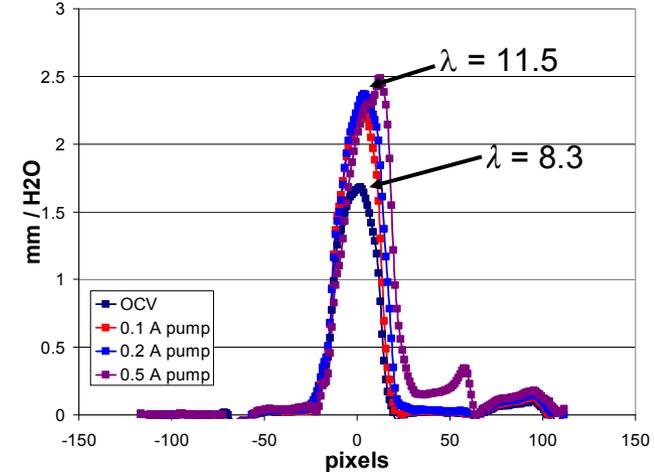
Fuel Cell Operation



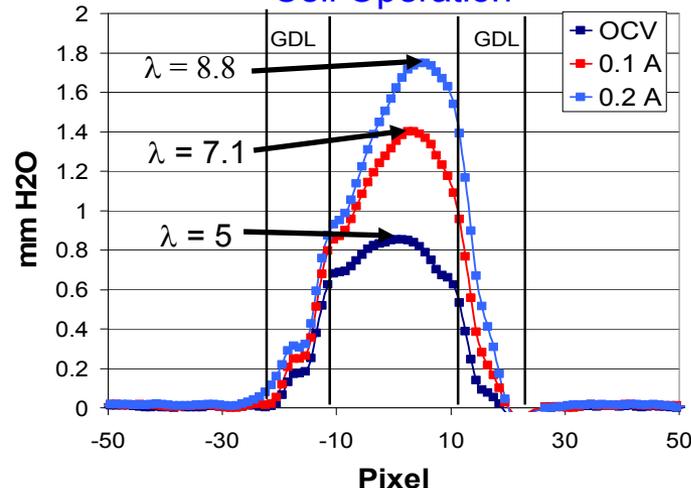
100/100 % RH 40 C

- Single Nafion® 20 mil electrolyte
- 6mg/cm² Pt on cathode and anode
- SGL Sigracet® 24 AA (Hydrophilic no MPL)
- Vertical setup
- Water profile is not flat at OCV. → due to edge effects.
- Middle 7 pixels vary by <4% for the 50/50 case and <5% for the 100/100 case.

Hydrogen Pump

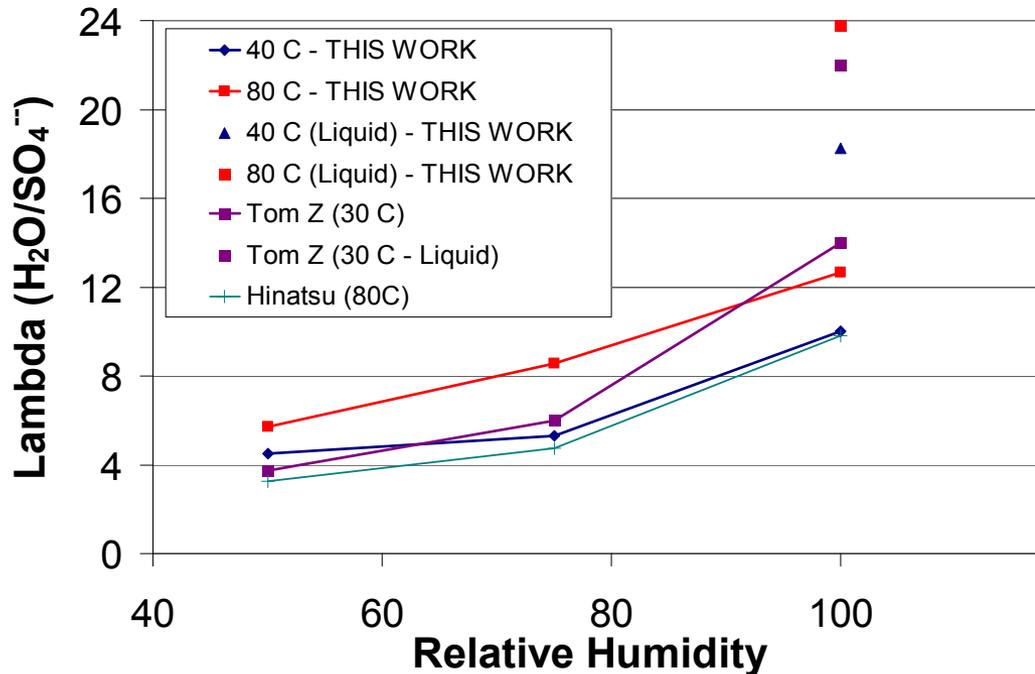


50/50 % RH, 40 C – Fuel Cell Operation



- Membrane hydration is observed to be
 - $\lambda = 5.0$ (50/50%) and 8.3 (100/100%)
 - λ increases with water production (Fuel Cell) and with H₂ pump (liquid water formation, electro-osmotic drag)
 - Observed differences with 40 mil membrane at 80 °C & super-saturated conditions
- At 100/100, 0.1 A there is no discernible difference between pump operation and normal operation
- At 100/100, 0.2 A cathode flow field become wet when the cell is operated in fuel cell, however not in H₂ pump mode
- Increasing pump current causes decreasing water on the anode and increasing water on the cathode side.

λ Comparison



λ Measurement Summary:

$\lambda \sim 10-12$ at 100% RH

$\lambda \sim 18-24$ liquid H_2O

Fuel Cell current increases λ :

at 50/50 % RH's $5 \rightarrow 8.8$

at 100/100% $8.3 \rightarrow 11.5$

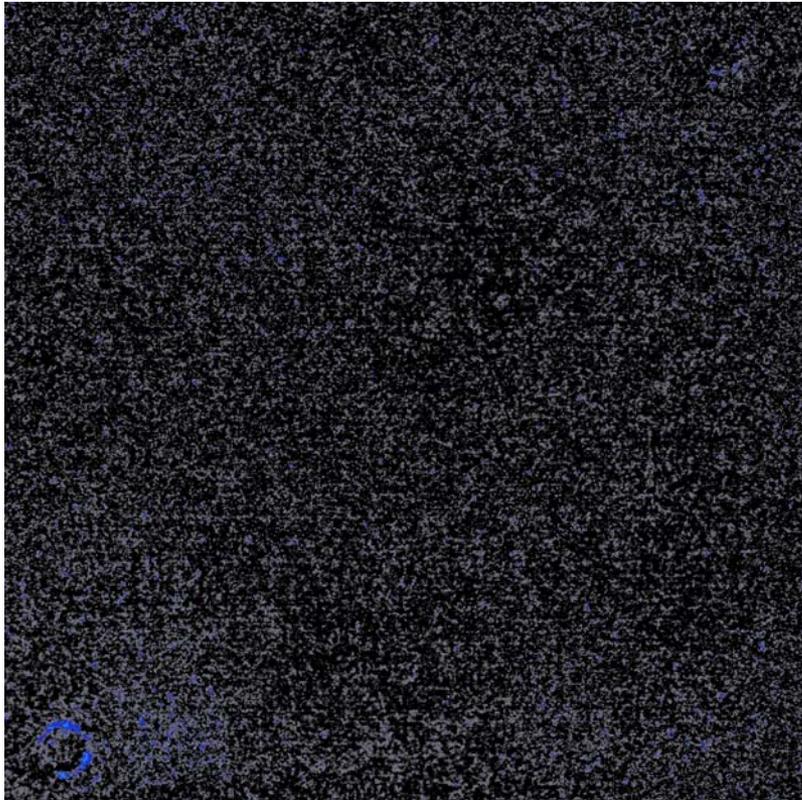
(depends upon current)

- Cathode under-saturated - Membrane water increases from $\lambda \approx 6$ to $\lambda \approx 10$ with current
- Membrane water gradients observed, much less than in modeling literature
- Reasonable agreement with some literature data at low RH
 - Do not measure absolute reliance on 'membrane thermal history'
 - Membranes will equilibrate at different λ for 100% RH and liquid water
 - Observe higher λ at equivalent water activity at higher temperatures
- Other recent literature on in situ measurements of membrane water content:

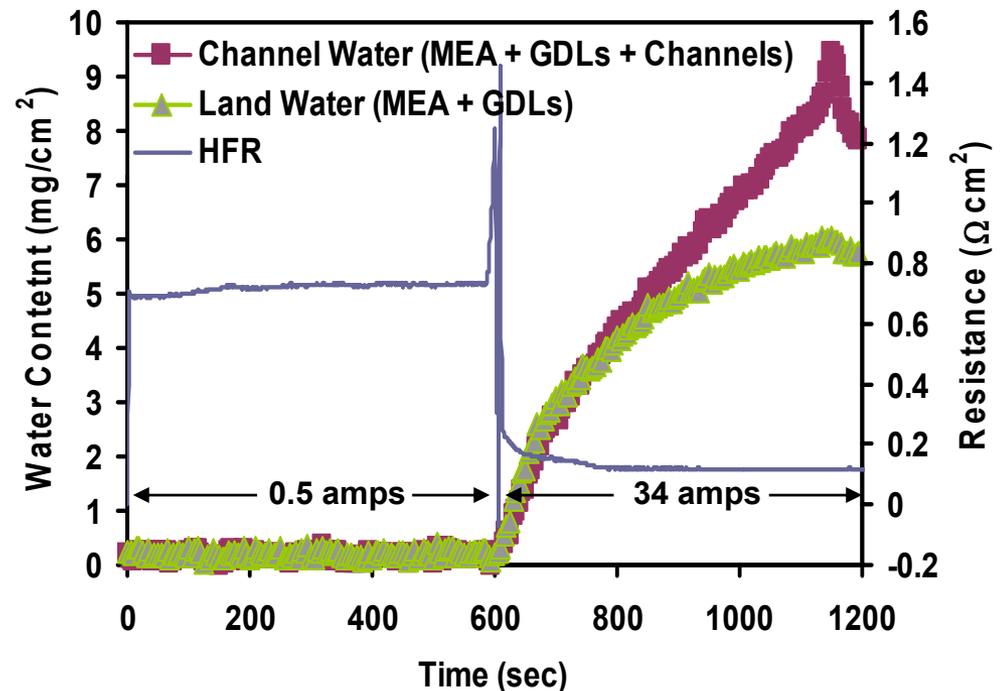
Wetting Transient

Wetting from 0.5A to 34A 40C and 0/0 inlet RH

Neutron Images of Cell Wetting
During Current Transient



Integrated Water Content from
Neutron Images During Current
Transient

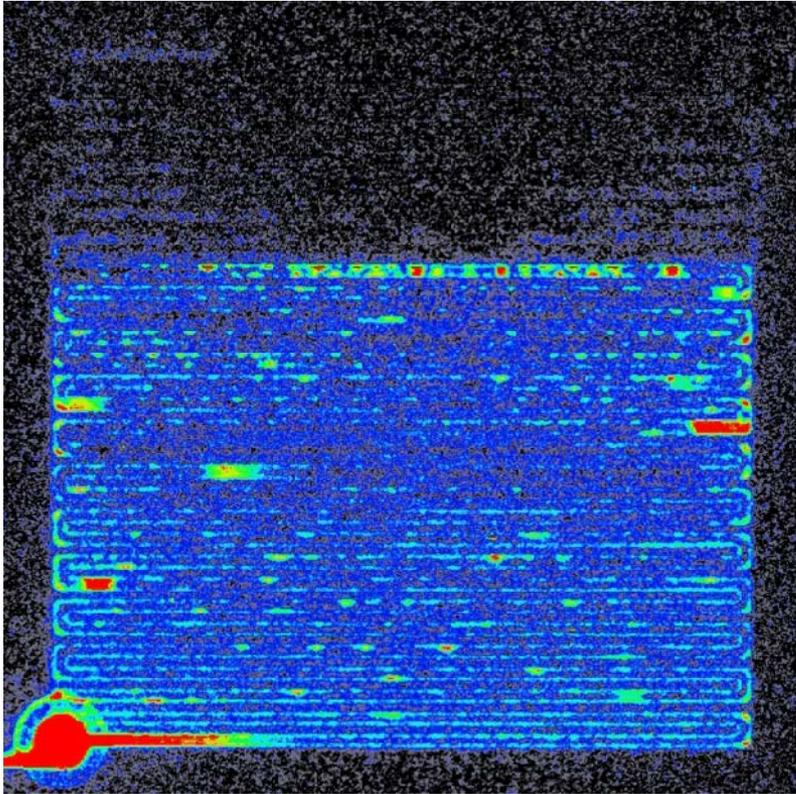


Minimum flows at 82cc/min and 333cc/min at the anode and cathode @ 0.5A. At 34A it is 1.2 and 2.0 stoich flows.

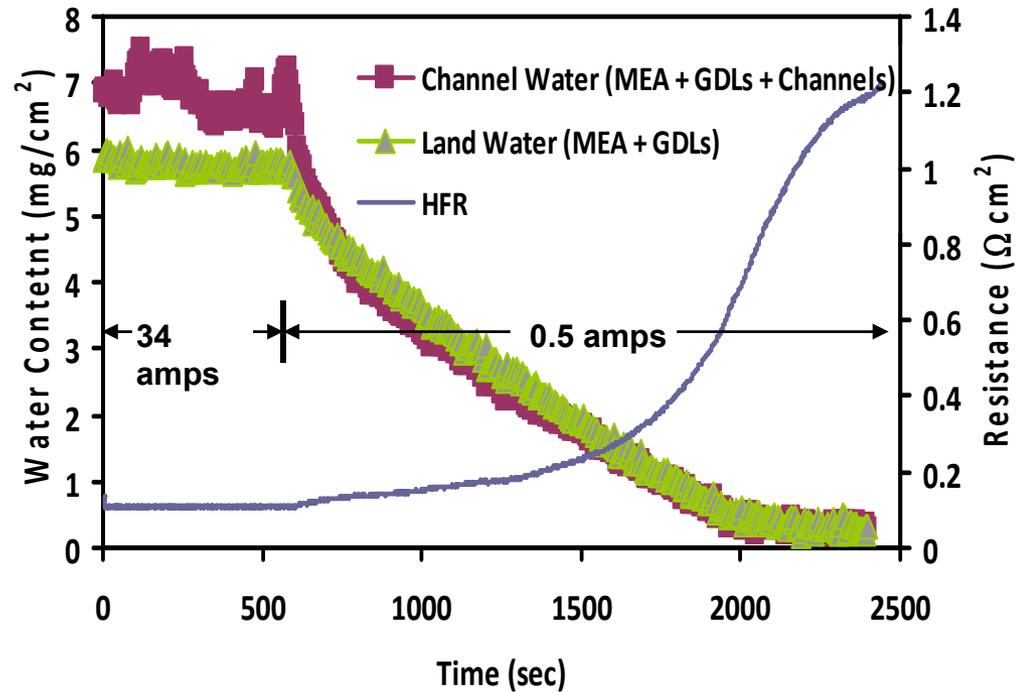
Drying Transient

Drying from 34A to 0.5A 40C and 0/0 inlet RH

Neutron Images of Cell Drying
During Current Transient

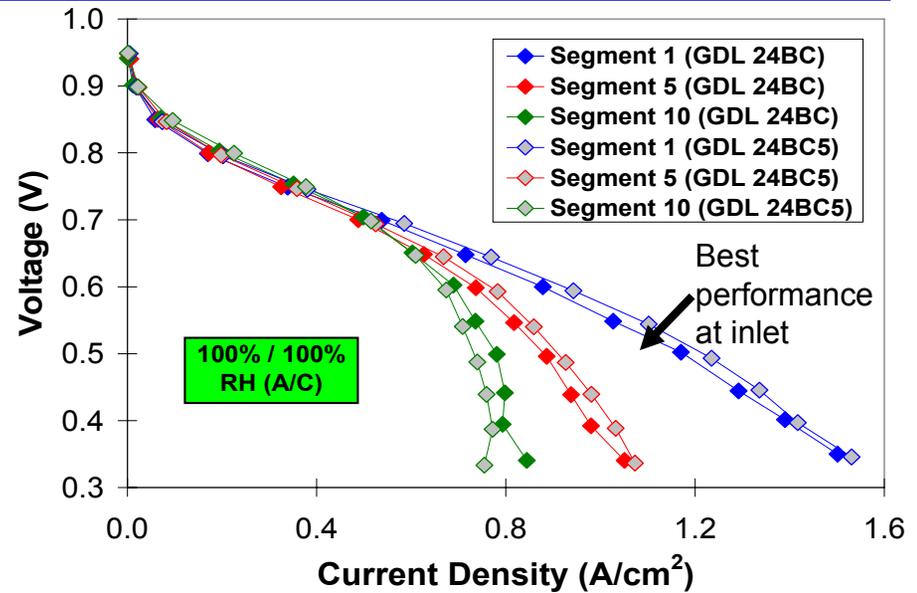
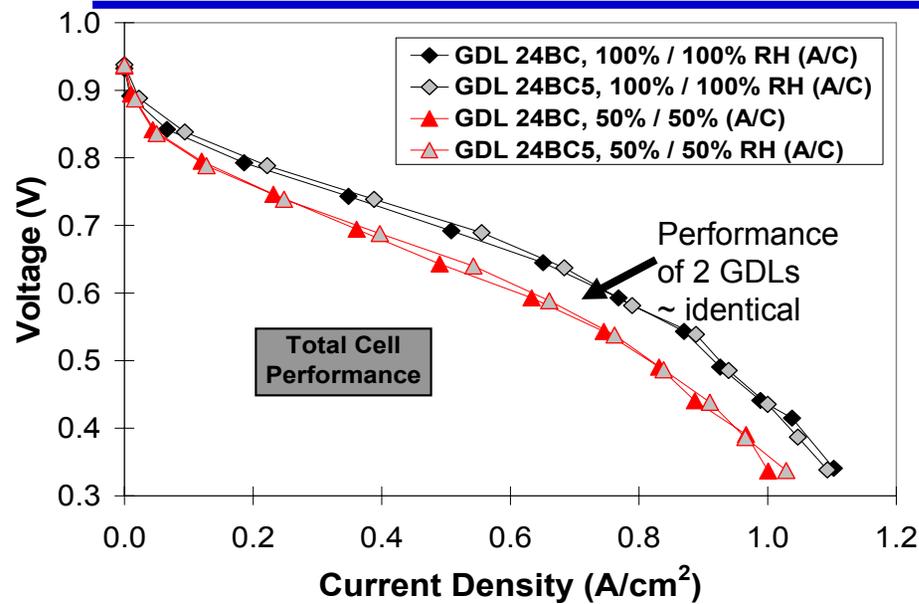


Integrated Water Content from
Neutron Images During Current
Transient



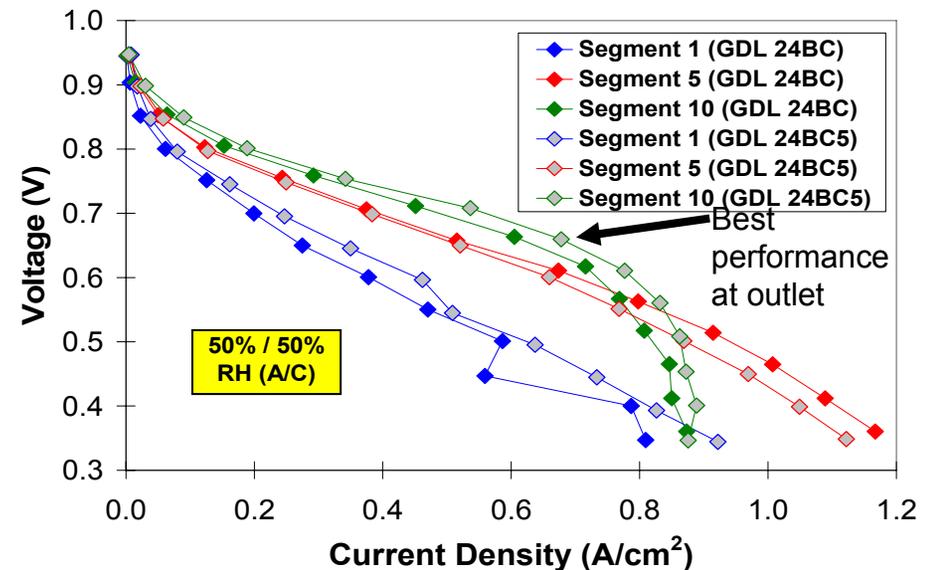
- Wetting response is faster (10 – 30 sec) than the reciprocal drying response (~ minutes)
 - Wetting response is the result of water produced at cathode which quickly back diffuses to into the membrane.
 - Drying response requires water to move out of the MEA through wetted GDLs.

Segmented Polarization Data for Different Cathode GDLs

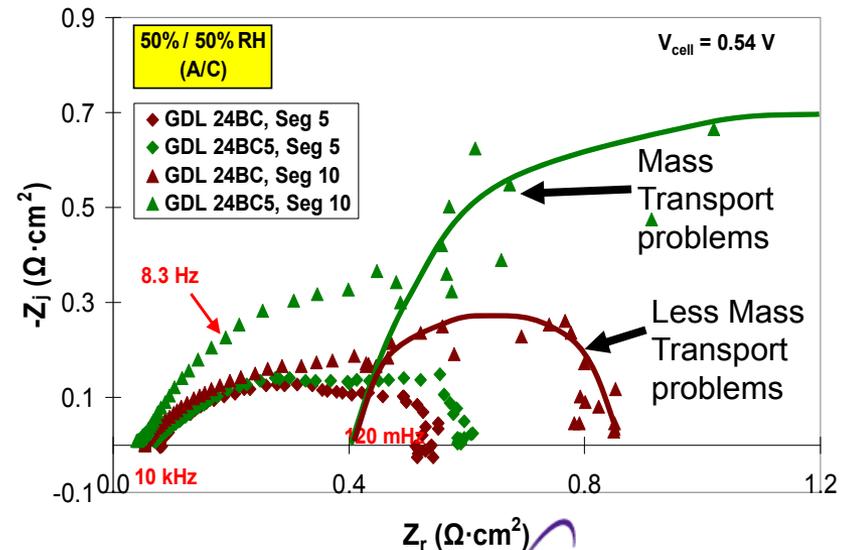
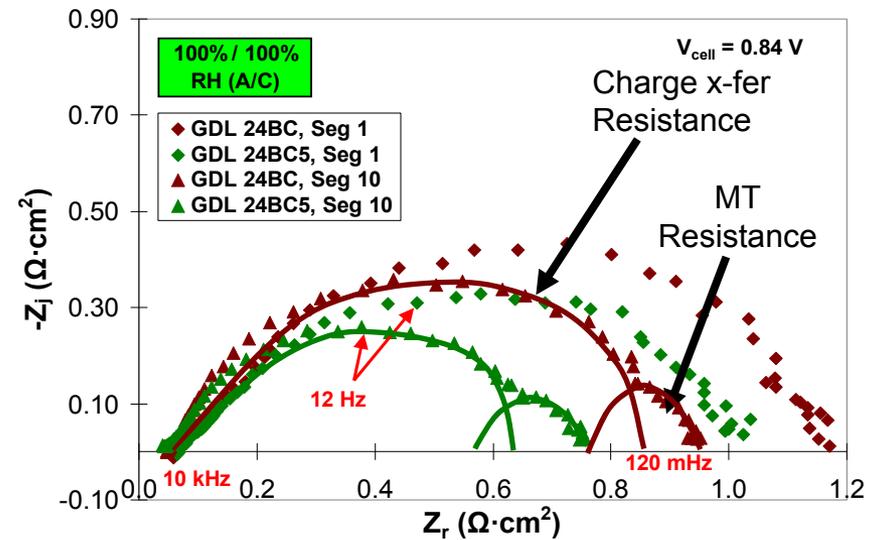
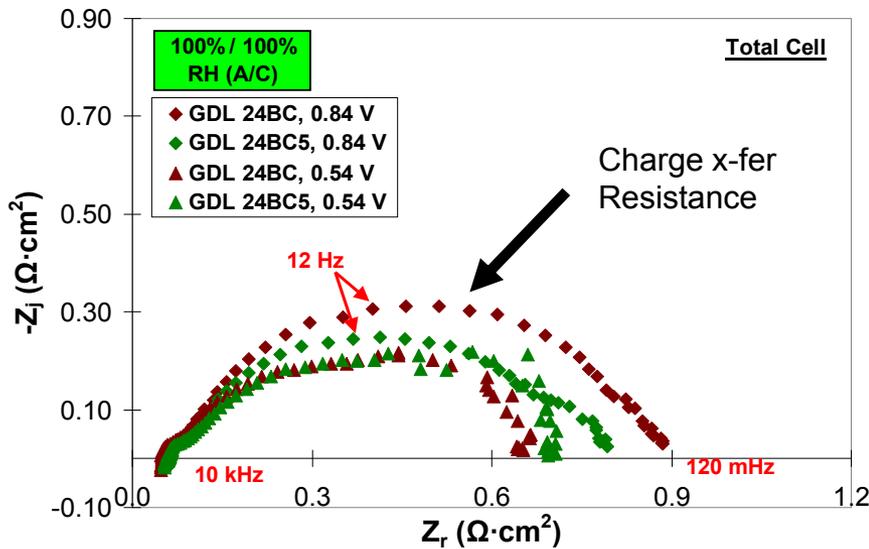


Segmented Cell Measurements show where Mass Transport losses dominate versus where IR losses, and kinetic occur

- Cathode GDL:
 - GDL 24BC (5/23 wt% PTFE substrate/MPL)
 - GDL 24BC5 (5/5 wt% PTFE substrate/MPL)
- Anode GDL:
 - GDL 24BC (5/23 wt% PTFE substrate/MPL)

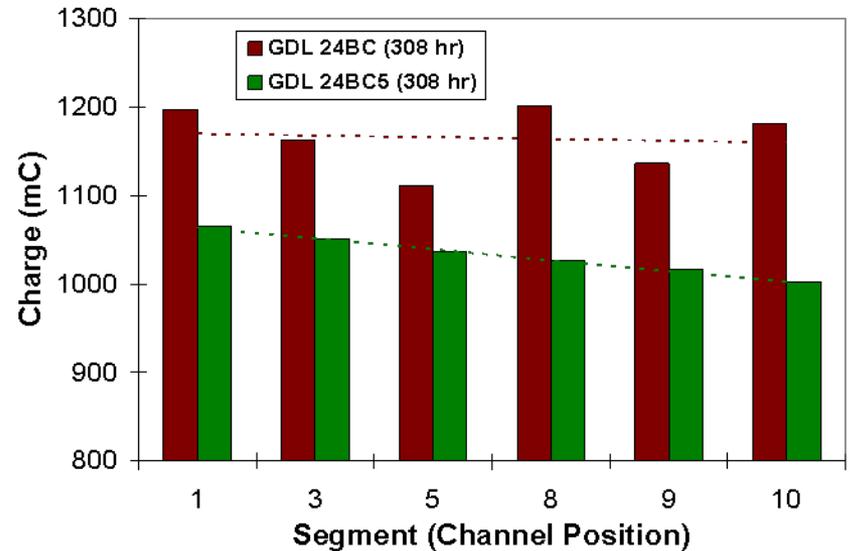
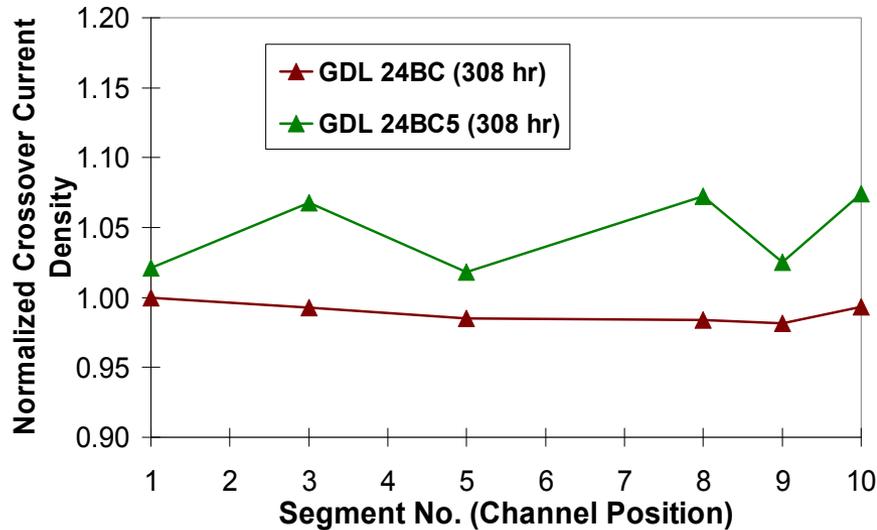


AC Impedance Data of Different Segments for Different Cathode *GDLs*



- GDL 24BC5 maintains higher water content in catalyst layer at high V and high RH (i.e. lower impedance).
- GDL 24BC has better water management at low V and low RH.

Interrelation of GDL, Catalyst and membrane



- Increasing ECSA loss with segment position due to greater water content
- Greater increase in membrane crossover and lower ECSA for 24BC5 compared with 24BC (over 308 hrs)
 - higher liquid water content in cathode catalyst layer with 24BC5.
- Demonstrates interrelated durability effects between GDL (water content), membrane and catalyst.

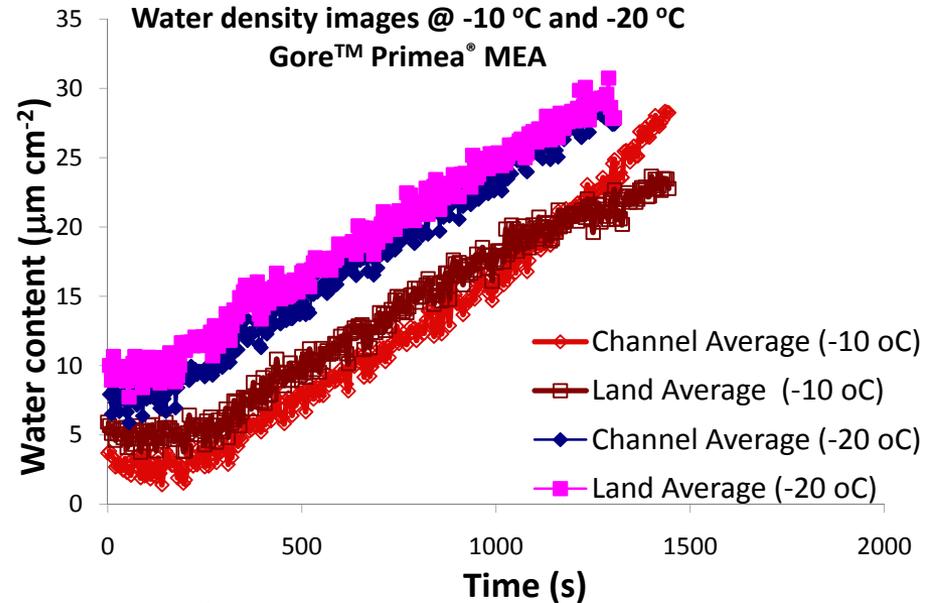
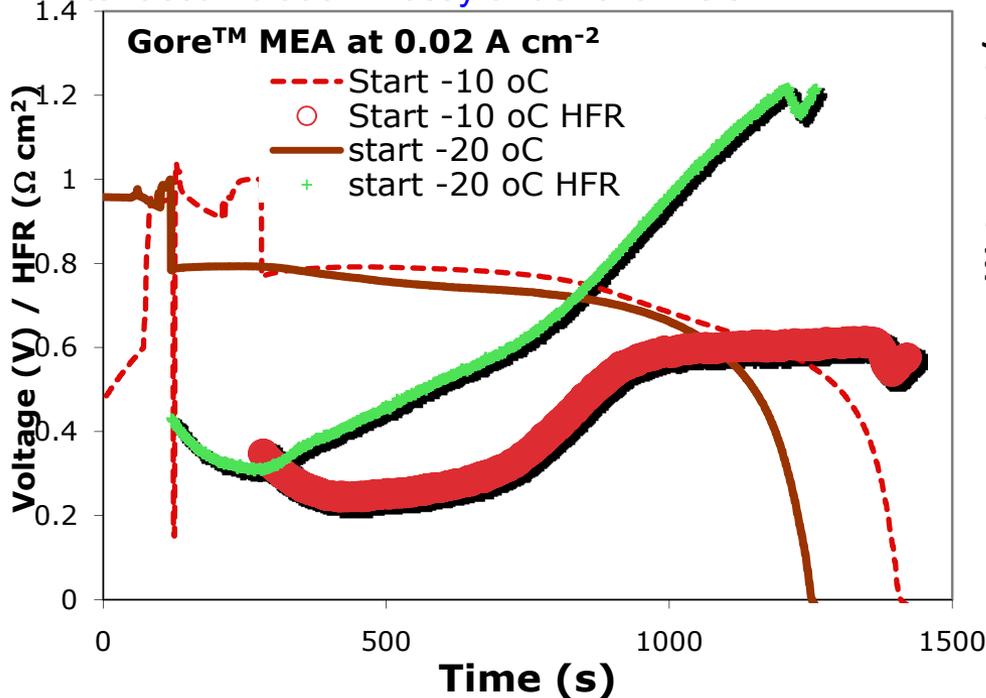
Freeze: Low resolution imaging

-10 °C

Increase of HFR stops after a time

Water under land almost stops accumulating

Water accumulation mostly under channels



- 20 °C

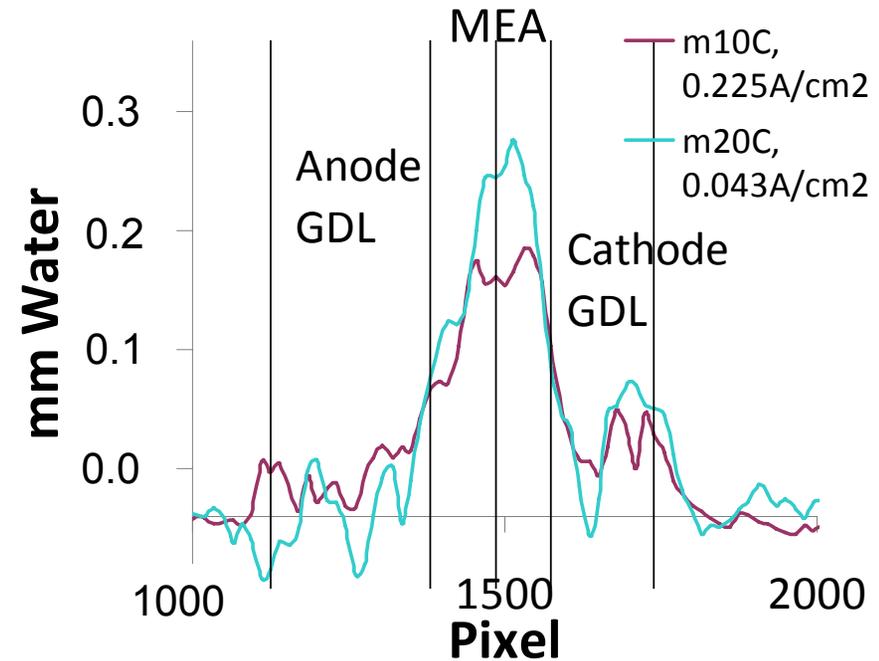
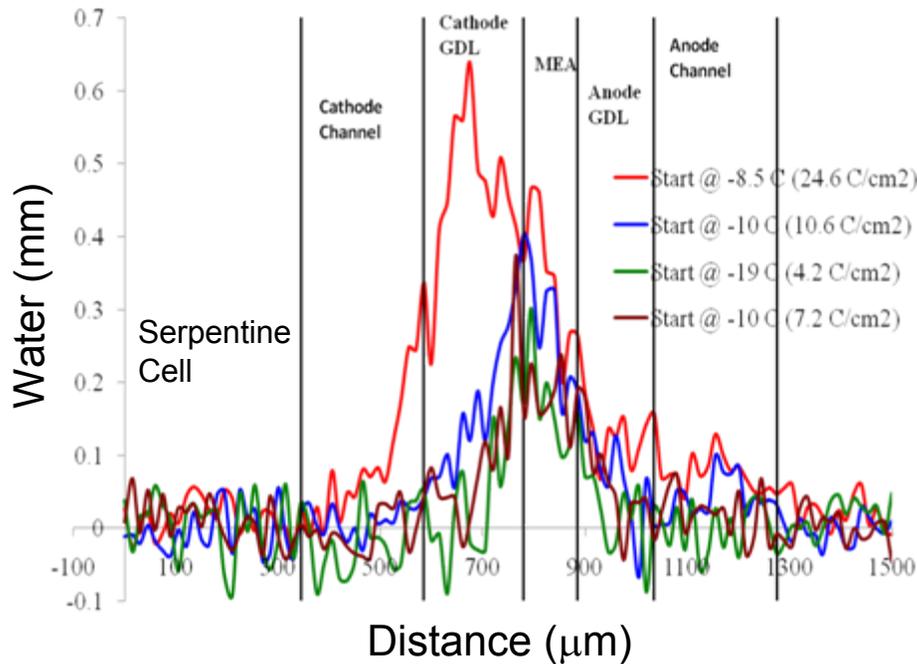
Water distribution always even between land/channel

Water probably in the MEA or GDL

HFR continuously increases

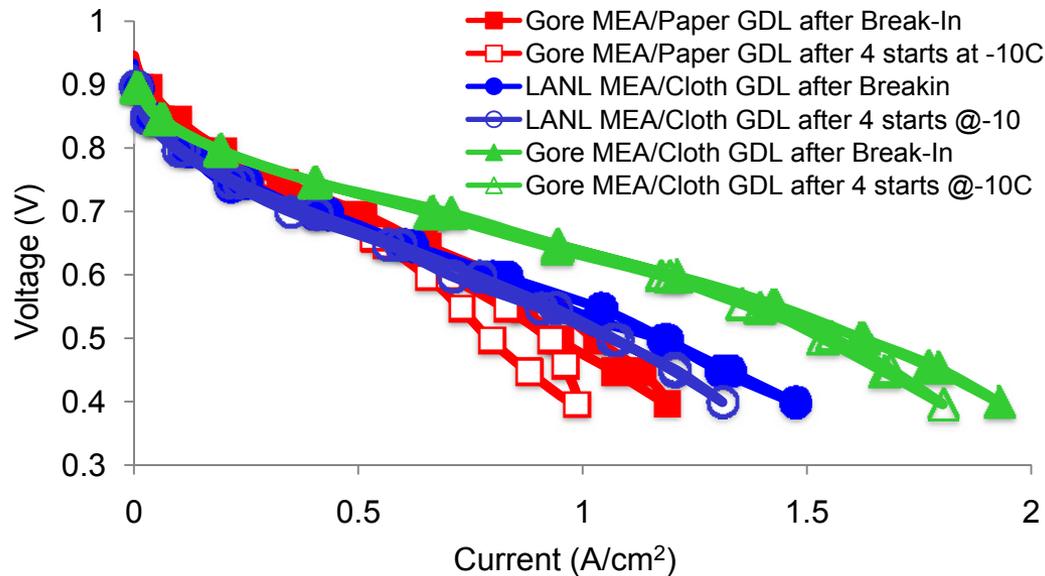
- Membrane hydration due to the generated current and back diffusion is dominant at sub-freezing temperatures
- Ice build up results in charge transfer and mass transfer resistance increases

Freeze: High resolution imaging

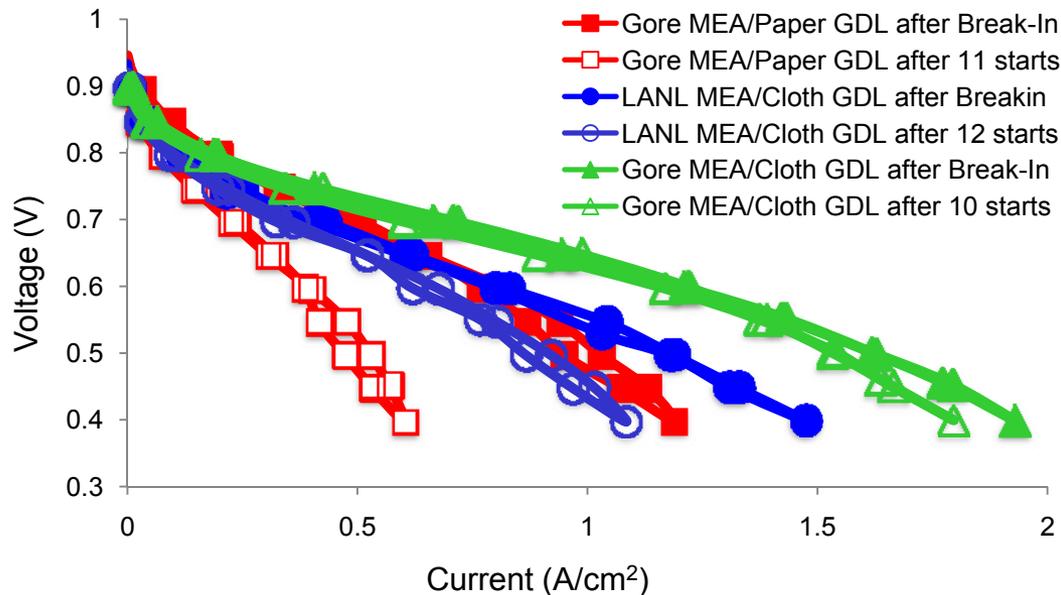


- Location of frozen water (ice) depends on operating temperature and current density
 - Water distribution closer to the cathode catalyst layer with:
 - Decreasing temperature
 - Increasing current
 - Greater water formation possible at higher temperatures and lower current densities

Freeze Durability



Durability after 4 starts @ -10C is dependant on MEA
 Gore MEA/Cloth GDL loses 27% cathode ECSA
 LANL MEA/Cloth GDL loses 7% cathode ECSA
 Gore MEA/Paper GDL loses 46% cathode ECSA

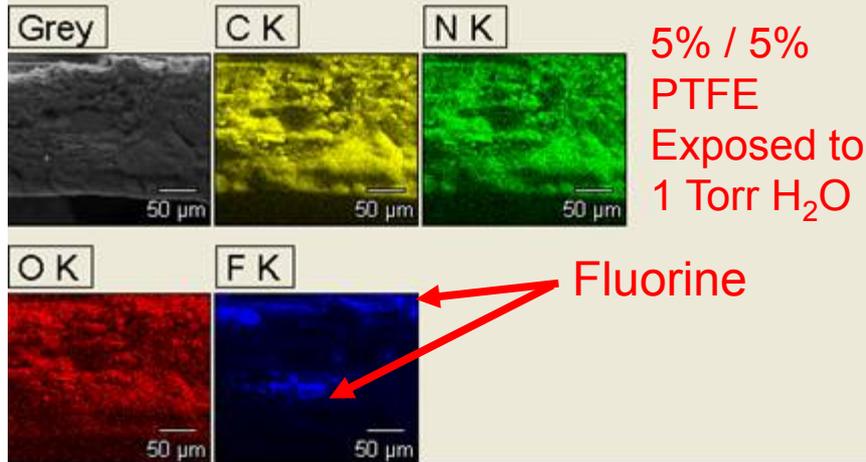


Durability after ≥ 10 starts @ -10C $> T > -40C$ is also dependant on MEA
 Paper GDL shows maximum loss in performance
 Mass transport losses in addition to kinetic losses

ESEM (Environmental SEM) GDL Cross-Section Water Mapping

SGL GDL 24DC (24DI)

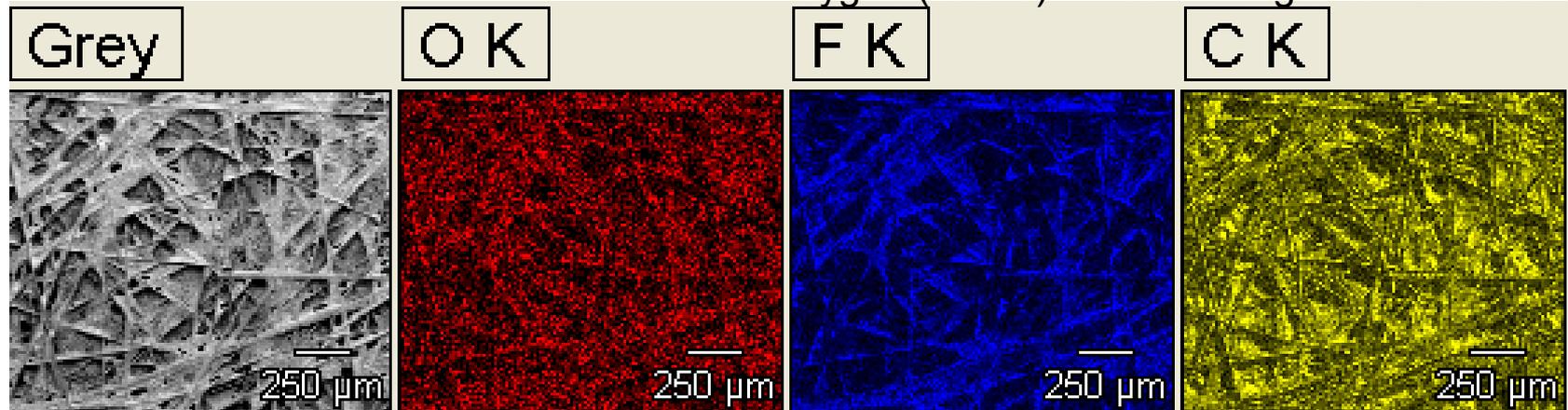
SGL area 2 - Counts (30 Frame(s))



- Fluorine distribution uneven
 - Fluorine at outer edges of GDL
- Less H₂O in center of GDL

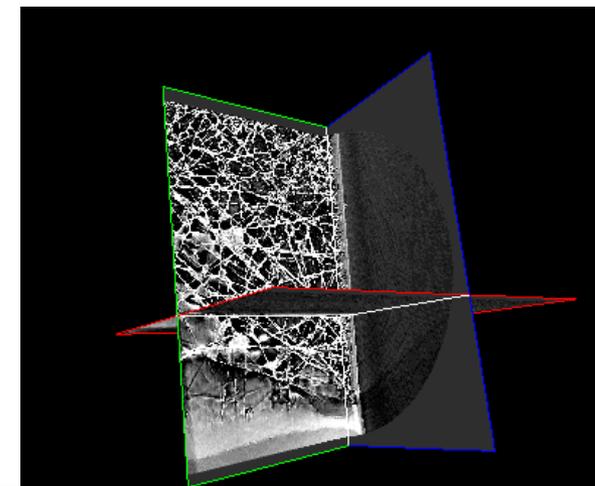
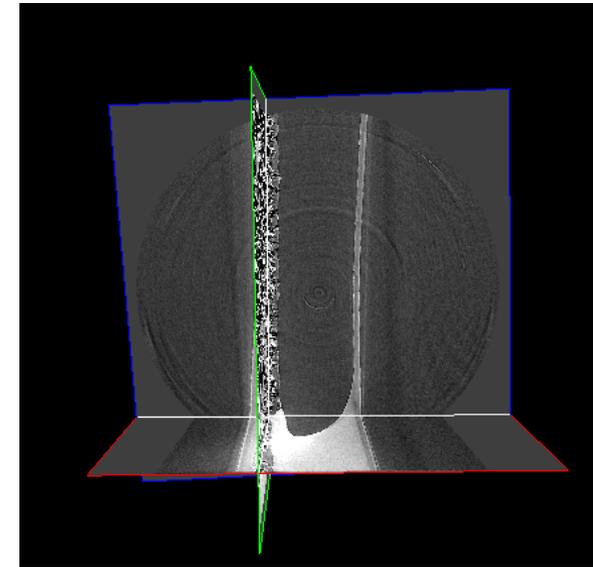
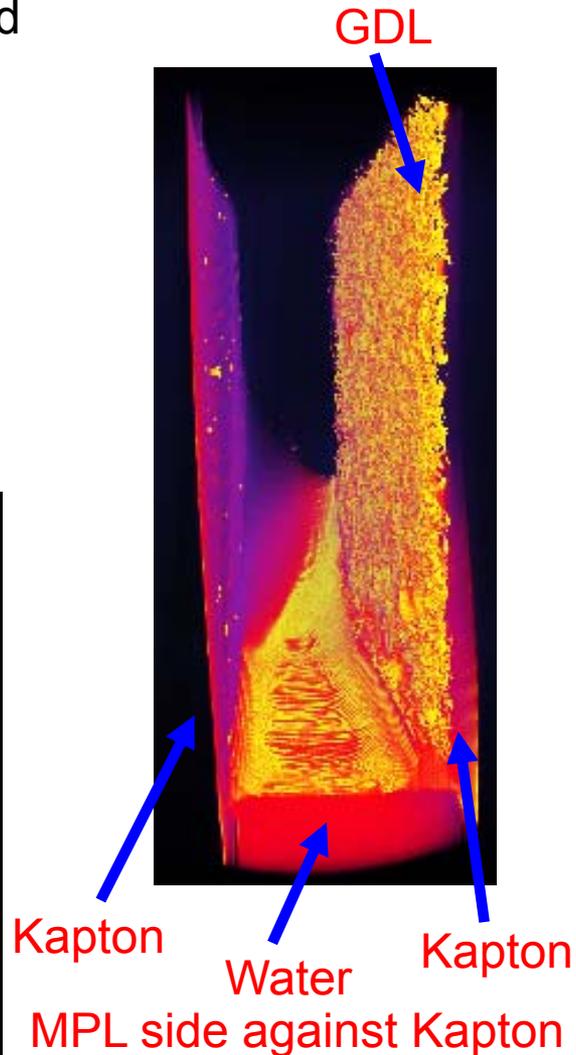
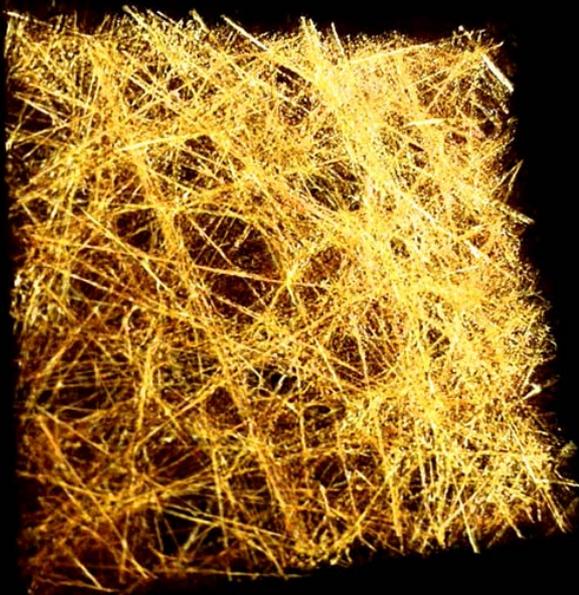
Exposed to 0.75 Torr H₂O

- Fluorine distribution uneven with carbon
- Oxygen (Water) seems to align on carbon fibers



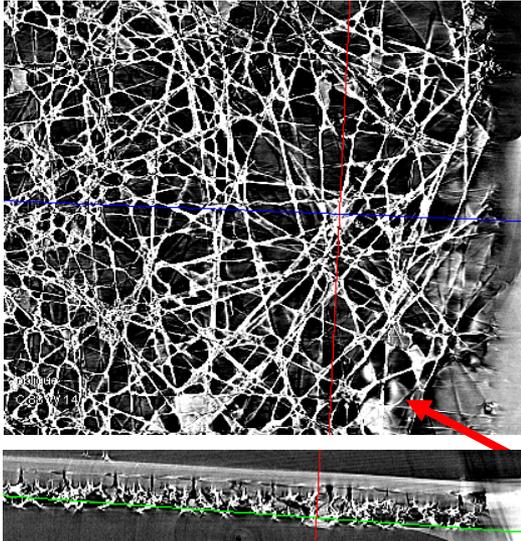
X-RAY Tomograph Image of water in GDL Pores

- Evaluate pore size density and distribution
- Observe GDL compression
- Observe/monitor water diffusion
- Evaluate water wetting and water diffusion pathways

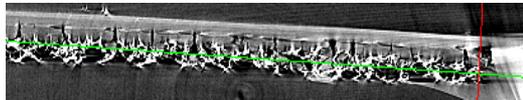
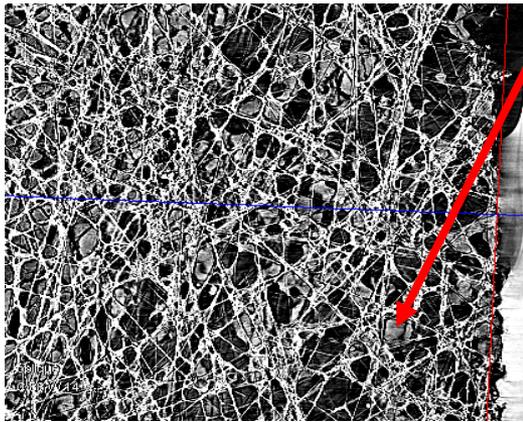


Water Inside SGL GDL Pores

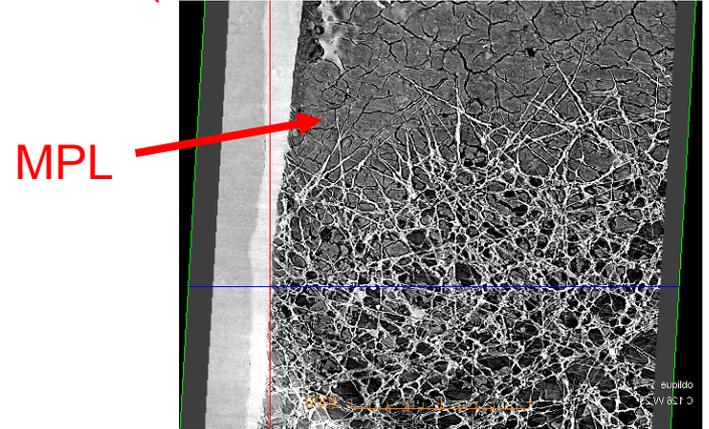
(23% PTFE MPL, 20% Substrate)



Water

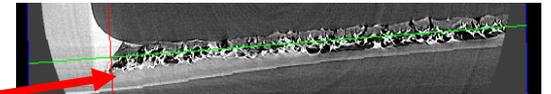


(5% PTFE MPL, 5% Substrate)



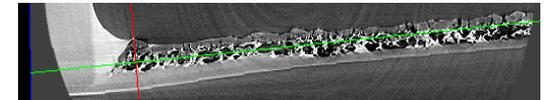
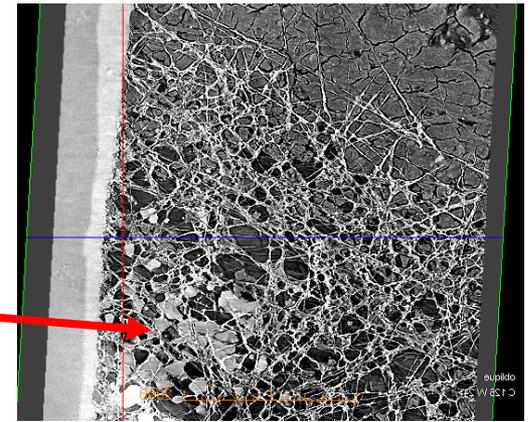
MPL

Water

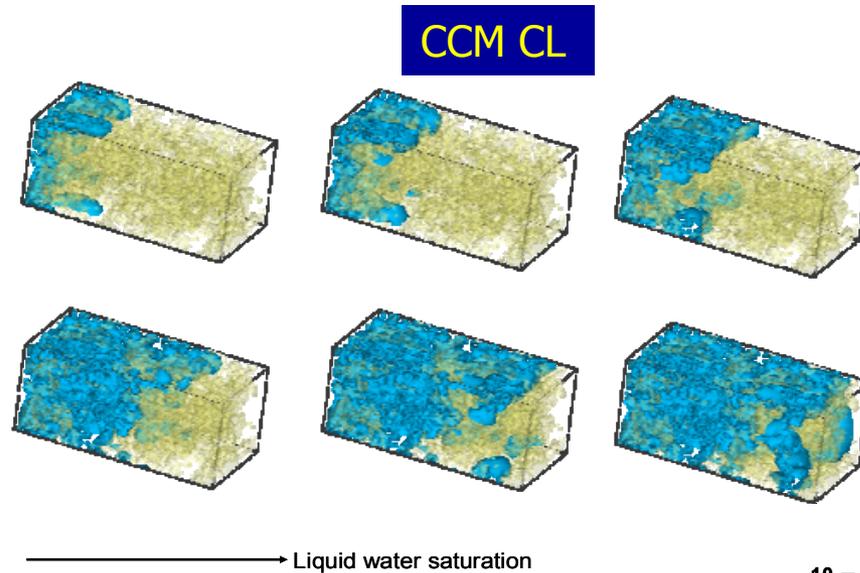


Significantly more water in GDL pores as cross-section approaches water layer

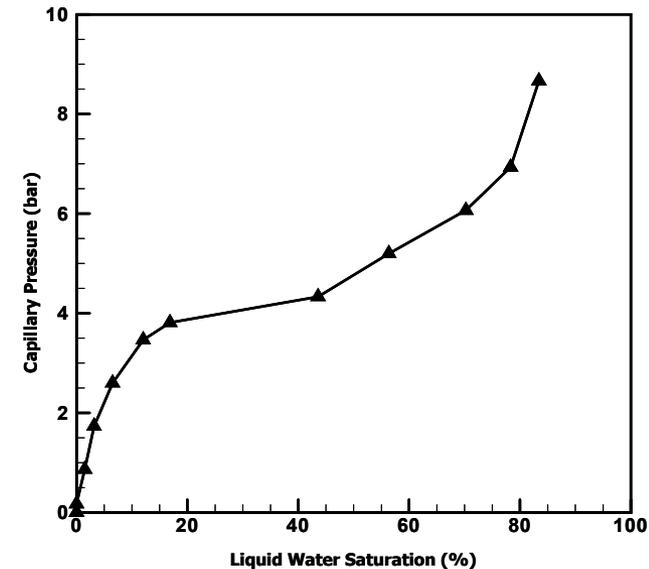
Water



Modeling: Capillary Pressure Simulation



- LB model simulates liquid water transport through the CL, insight into underlying two-phase dynamics.
- Capillary pressure and relative permeability as functions of liquid water saturation are employed in macroscopic two-phase fuel cell models.
- Other modeling activities described in supplemental slides (Ken Chen Sandia; Adam Weber LBNL, Jeremy Meyers UTA)



Future Work

Experimental and Characterization

- 3-D X-Ray tomography during operation observing water transport in GDL pores
 - Identify hydrophobic pores vs. hydrophilic pores
 - Identify liquid water pathways in GDLs
- Incorporate 3-D X-ray tomography PSD into Capillary Pressure Simulation
- Conduct segmented cell measurements varying the GDL PTFE loading as a function of cell location and with counter-flow inlets configurations.
- Measure the effect of compression and GDL substrate porosity
- Better identify GDL loss of hydrophobicity degradation mechanism
 - Surface characterization (TEM) and surface species identification (DRIFTS)
- Measure capillary pressure in GDLs with concurrent counter flow of water and gas
 - (Collaboration with LBNL → LANL visiting student from LBNL)

Modeling

- Develop a multiphase model for simulating ice formation and thawing during start-up, and investigating the effects of cell design (e.g., catalyst-layer thickness, pore volume) on PEMFC startup under sub-zero temperatures.
- Using modeling parameters, correlate impact of diffusion-media wettability on fuel-cell performance and demonstrate agreement with NIST water images
- Effects to examine
 - Heterogeneous structures
 - Separate hydrophobic and hydrophilic PSDs
 - Anisotropy
 - Structural and chemical changes within a GDL
 - Compression
 - Transients including hysteresis

Summary of Technical Accomplishments

Providing fundamental information on water transport

- Varying MPL and substrate Teflon[®] loadings and cell operating conditions
 - Using Neutron imaging, AC impedance to get data about water content and performance
 - Use data to develop comprehensive GDL water transport model in addition to the existing membrane/electrode model
- Equilibrium water content in the membrane, how membrane water content changes with RH, T, current and water production
- Segmented cell operation
 - How water varies as a function of GDLs, inlet RH, cell position, and the effect that water content has on membrane durability and catalyst durability
- Response of GDL and membrane water to transients
 - Fast membrane wetting
 - Slow GDL de-wetting, followed by membrane drying
- GDL Characterization
 - Profiling the GDL in 3-D
 - Observing the location in the GDL structure where water exists
 - Correlating water with Teflon[®] content in the GDL
- Freeze
 - Durability
 - Monitoring where water freezes as a function of operating variables

Thanks to

- U.S. DOE -EERE Hydrogen, Fuel Cells and Infrastructure Technologies Program for financial support of this work
 - Program Manager: Nancy Garland

Additional Slides

Milestones

Mon Yr	Milestone
Dec 08	Demonstrate isothermal operations at -10°C, -20°C, -30°C and -40°C. Report on degradation due to sub-freezing isothermal operations. <i>(ECS Transactions (2008), 16(2), 1939-1950)</i>
Mar 09	Correlate water content data to ex situ membrane and electrode conductivity results <i>(Neutron imaging of water content as f(RH, T, current))</i>
Mar 09	Provide accurate water balance data to verify models <i>(Modified: Provided water content in X,Y,Z as function of operating variables)</i>
Mar 09	NIST to provide z-direction imaging capability (Go/No Go). <i>(Using the cross-section (25 micron) and field view (150 micron) detectors to understand water content in 3-d).</i>
Jun 09	Quantify effects of varying GDL hydrophobicity <i>(Already have used multiple variation of GDL PTFE loadings, will continue to expand matrix)</i>

✓

✓

✓

✓

✓



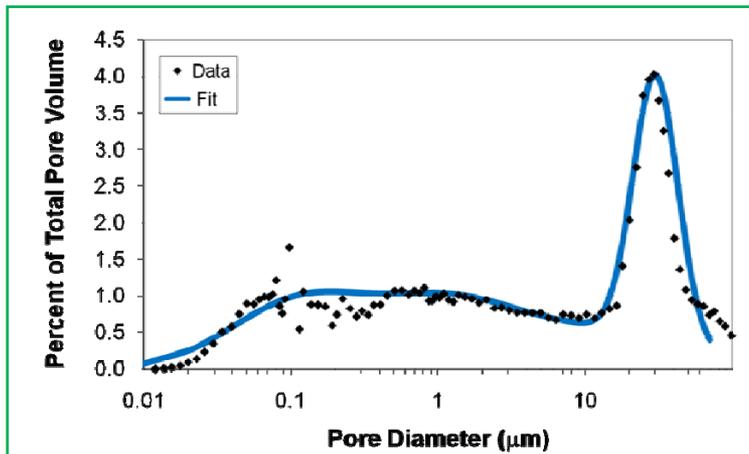
Modeling Flow in Diffusion Media

- Goal is to model the impact of wettability and two-phase flow
 - Previous model framework* is being modified to include contact-angle distribution

*A.Z. Weber, et al., *JES*, **151**, A1715 (2004).

- Input parameters

- 1. Fit the material properties to data (e.g., PSD of SGL24BC)



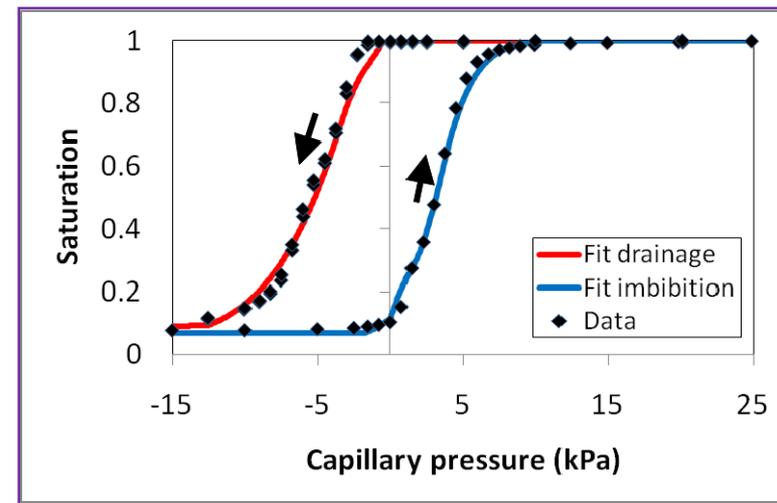
2-pt log-normal distribution

$$S = \iint \Psi(\theta) \mathcal{V}(r) dr d\theta$$

← *2-pt normal distribution*

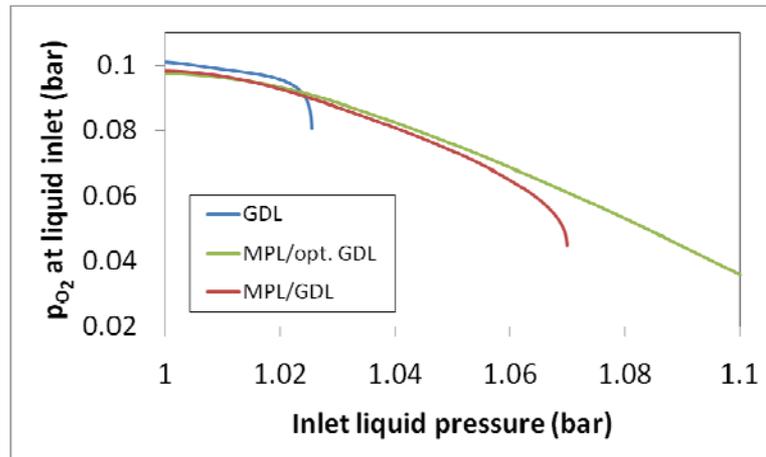
Data provided by J. Gostick

- 2. Fit a contact-angle distribution to capillary-pressure vs. saturation data
 - Hysteresis needs to be considered
 - Majority of the curve (saturation) is due to the GDL and not MPL pores

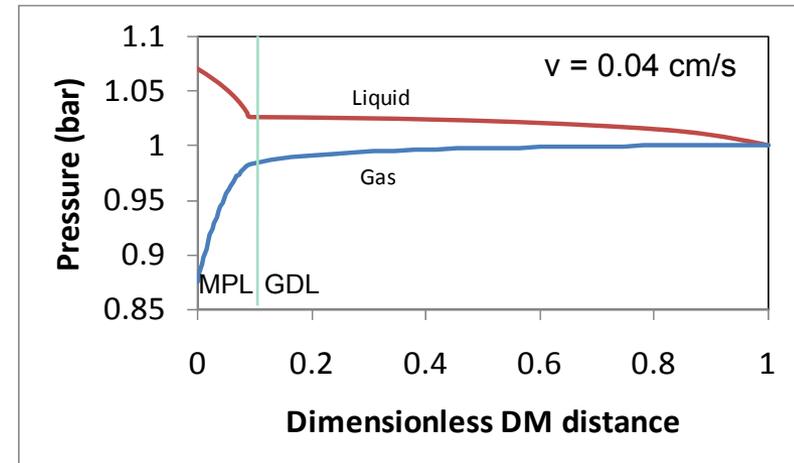


- Simulations of cathode DM

- Explore two-phase flow effects and DM signature by setting oxygen flux and changing liquid pressure at inlet (i.e., catalyst-layer side)
 - Mimics what happens in fuel-cell operation
 - Example: Equivalent oxygen flux set at 2 A/cm^2 at 80°C , 100% RH, 1 bar, $\Delta T=1^\circ\text{C}$



- MPL can support higher pressures
- Develop optimum DM structures
 - Optimum contains separate small pore hydrophobic network
- Optimization depends on operating regime



- Resistance mainly in MPL even though saturation dominated by GDL
- Gas pressure as important as liquid pressure since capillary pressure is their difference

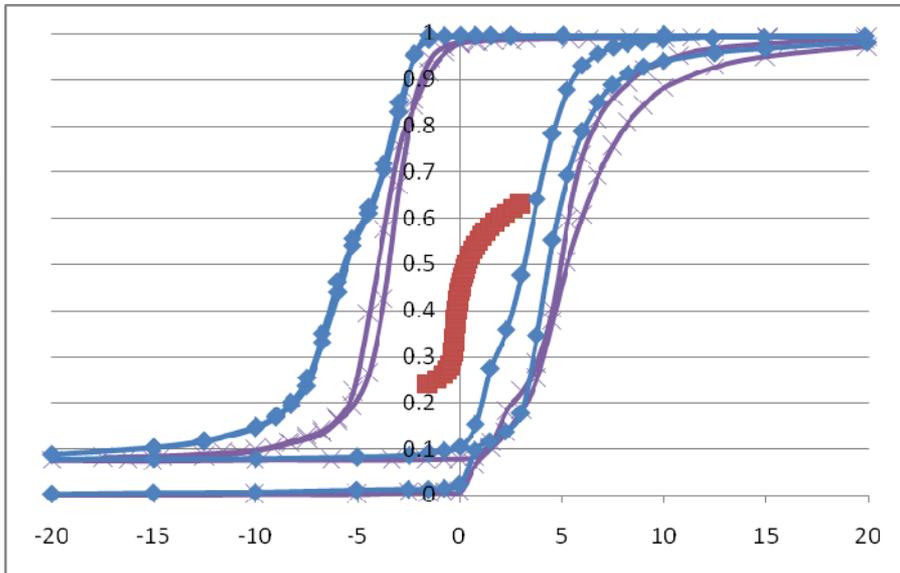


Modeling Flow in Diffusion Media

- Future Work
 - Using modeling parameters, correlate impact of diffusion-media wettability on fuel-cell performance and demonstrate agreement with NIST water images
 - Effects to examine
 - Heterogeneous structures
 - Separate hydrophobic and hydrophilic PSDs
 - Anisotropy
 - Structural and chemical changes within a GDL
 - Compression
 - Transients including hysteresis
 - Impact of boundary conditions

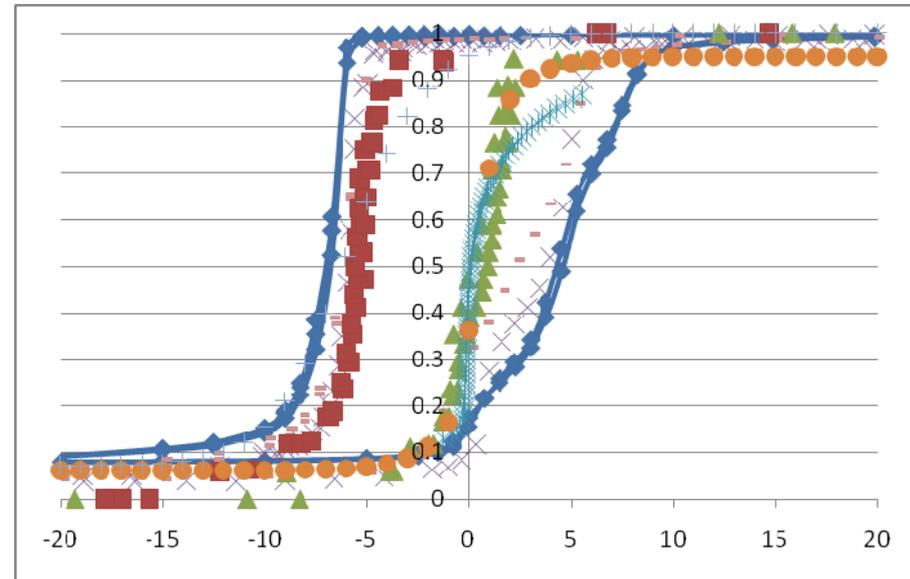
Pc vs. S

SGL



- 0% (blue) and 5% Teflon[®] (purple) from Gostick
- Red from Nguyen
- Data from Mench not shown

Toray



- Data from Schwartz, Nguyen, Gostick, Darling



Unanswered Questions

- Is our approach okay?
 - Can we decouple the two effects...is it reasonable?
- Are there interfacial effects
 - CL, flooding and mass-transport resistance
 - Matching of pore sizes (capillary condensation, intrusion)
 - Droplet removal into the channel
 - Impacted by CAD or PSD?
- Impact of other things
 - Anisotropy in properties
 - Different structural zones
 - Mechanical properties and compression
 - Changes in absolute permeability
- What to do with hysteresis
- Aging?
 - Same PSD (if Teflon[®] does not migrate) but change CAD to make it more hydrophilic



Calculating Properties

$$r_{c,h} = -\frac{2\gamma \cos\theta_h}{p_C}$$

- Previous saturation

$$S = f_{HI} S_{HI} + (1 - f_{HI}) S_{HO} = f_{HI} \int_0^{r_{c,HI}} V(r) dr + (1 - f_{HI}) \int_{r_{c,HO}}^{\infty} V(r) dr = f_{HI} \sum_k \frac{f_{r,k}}{2} \left[1 + \operatorname{erf} \left(\frac{\ln r_{c,HI} - \ln r_{o,k}}{s_k \sqrt{2}} \right) \right] + (1 - f_{HI}) \sum_k \frac{f_{r,k}}{2} \left[1 - \operatorname{erf} \left(\frac{\ln r_{c,HO} - \ln r_{o,k}}{s_k \sqrt{2}} \right) \right]$$

- Now

$$S = \iint \Psi(\theta) V(r) dr d\theta = \int \Psi(\theta) \int V(r) dr d\theta = \int \Psi(\theta) \sum_k \frac{f_{r,k}}{2} \left[1 + \mathfrak{g}_h \operatorname{erf} \left(\frac{\ln r_{c,h} - \ln r_{o,k}}{s_k \sqrt{2}} \right) \right] d\theta$$

$$= \int_0^{90} \sum_k f_{r,k} \left\{ \frac{1}{\sigma_k \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{\theta - \theta_{o,k}}{\sigma_k} \right)^2 \right] \right\} \sum_k \frac{f_{r,k}}{2} \left[1 + \operatorname{erf} \left(\frac{\ln \left(-\frac{2\gamma \cos\theta}{p_C} \right) - \ln r_{o,k}}{s_k \sqrt{2}} \right) \right] d\theta + \int_{90}^{180} \sum_k \dots$$

- Do the above using a Gauss-Legendre integration method so have

$$S = \sum_{i=1}^{20} w_i \sum_k f_{r,k} \left\{ \frac{1}{\sigma_k \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{\theta_i - \theta_{o,k}}{\sigma_k} \right)^2 \right] \right\} \sum_k \frac{f_{r,k}}{2} \left[1 + \operatorname{erf} \left(\frac{\ln \left(-\frac{2\gamma \cos\theta_i}{p_C} \right) - \ln r_{o,k}}{s_k \sqrt{2}} \right) \right] + \sum_{i=1}^{20} w_i \dots$$

- A 20 term series is used and the w_i 's and θ_i 's are calculated between the range 0 to 90 and 90 to 180
 - Refinement is to use ± 4 standard deviations (σ_k) to increase accuracy

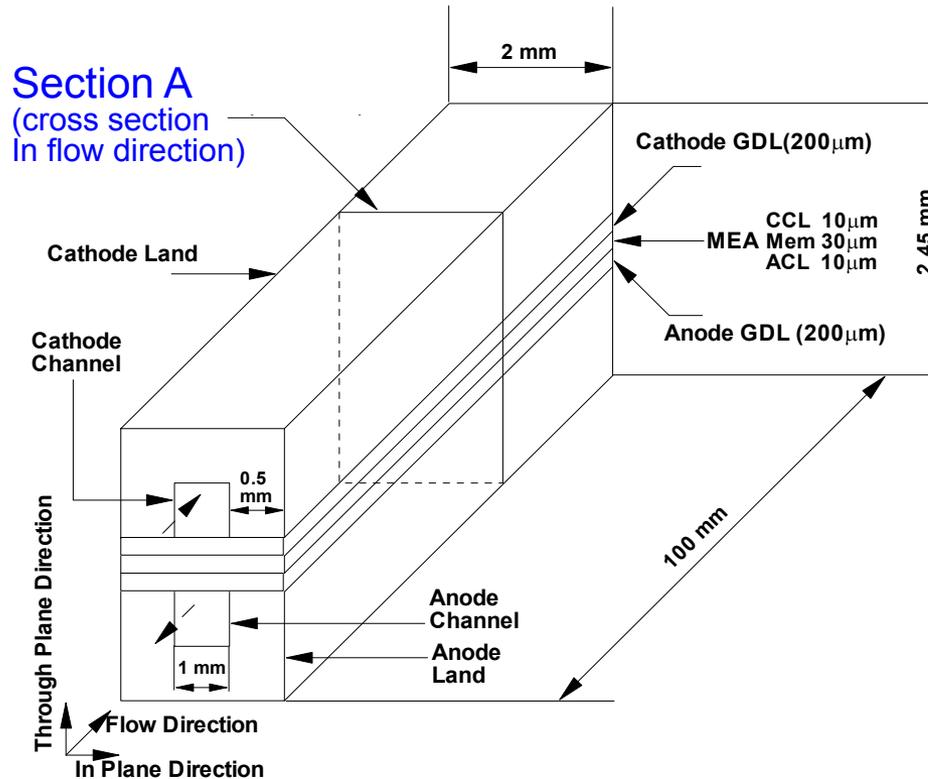
- f_{HI} can be seen as

$$f_{HI} = \int_0^{90} \sum_k f_{r,k} \left\{ \frac{1}{\sigma_k \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{\theta - \theta_{o,k}}{\sigma_k} \right)^2 \right] \right\} (1) d\theta = \sum_k \frac{f_{r,k}}{2} \left[1 + \operatorname{erf} \left(\frac{90 - \theta_{o,k}}{\sigma_k \sqrt{2}} \right) \right]$$

Modeling Phase Change in a PEM Fuel Cell: (water vapor \leftrightarrow liquid water)

Motivation: it is critically important to elucidate the dynamic phenomena inside the PEM fuel cell: **Where does water vapor condense? Where does liquid water evaporate? Under what process conditions do condensation/evaporation occur?**

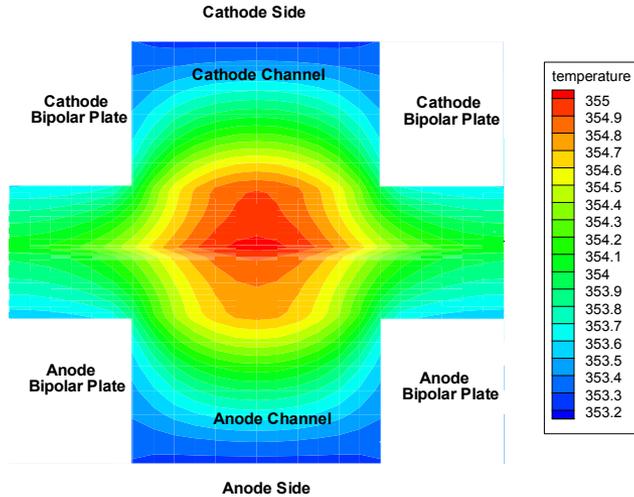
Model geometry and cross sections for analysis



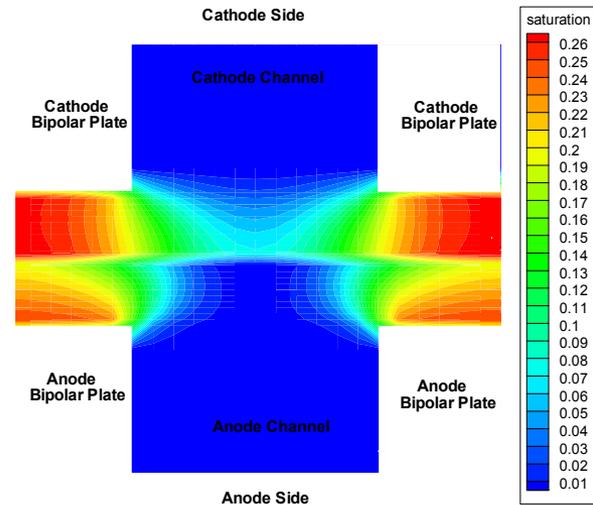
Modeling results: computed temperature, saturation, phase-change rate

(1.0A/cm², Stoic (A/C) =2.0, RH=100%)

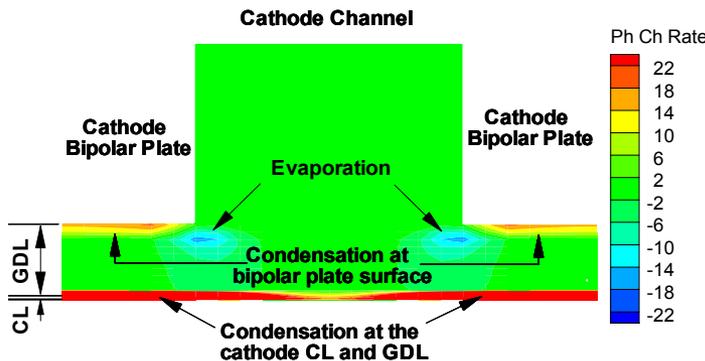
Temperature contours



Saturation contours



Phase-change rate contours (cathode side only)

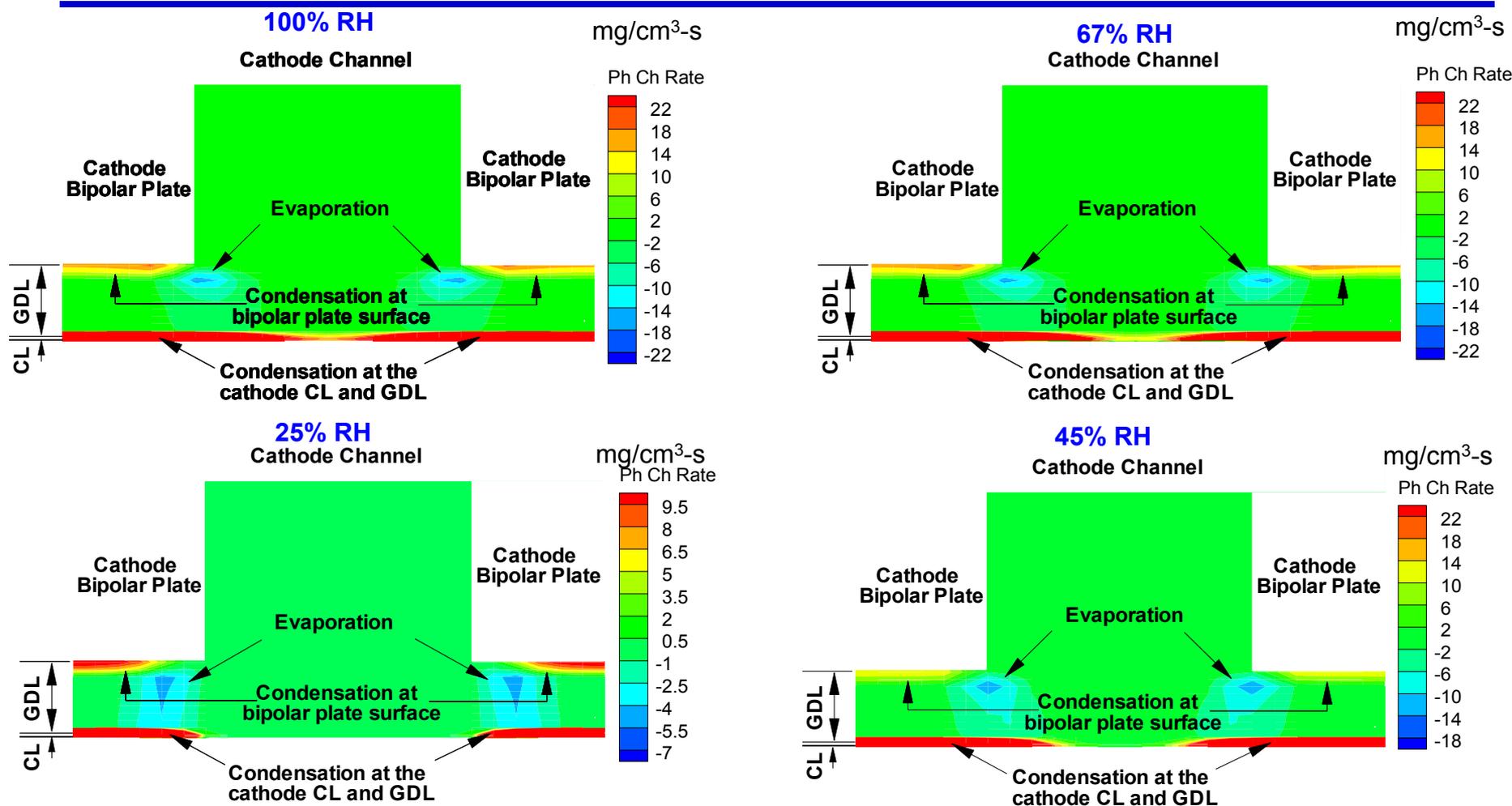


- Temperature is high above/below the channels whereas low above/below the lands due to higher conductivity of the bipolar plate.
- Evaporation takes place in the GDL underneath the channel near the channel-land boundary.
- Condensation mainly occurs within the cathode catalyst layer and in GDL near CL/GDL interface.
- Water also condenses on the cooler land surface.

*Reference: S. Basu, C.-Y. Wang, and K. S. Chen, "Phase change in a polymer electrolyte fuel cell", accepted for publication in *J. Electrochem. Soc.*

Effect of Inlet Humidity on Phase-Change Rate

($I = 1.0\text{A/cm}^2$, Stoic = 2.0, at Section A)



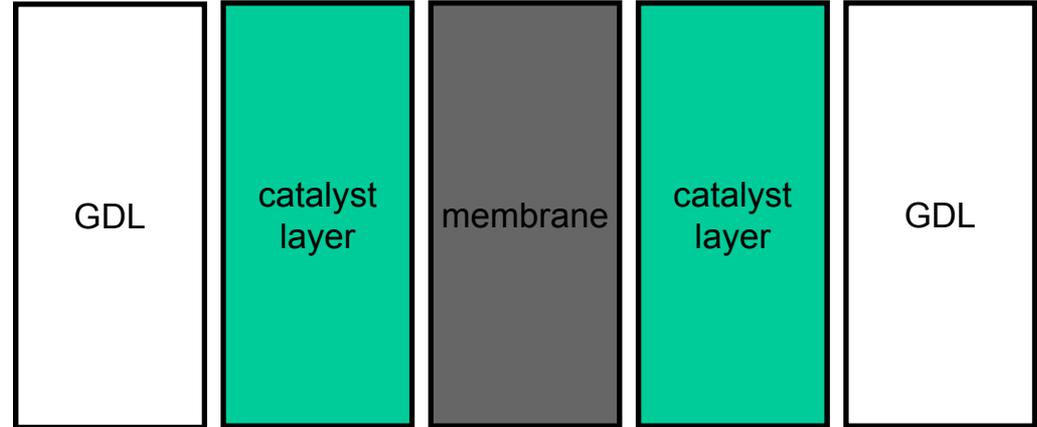
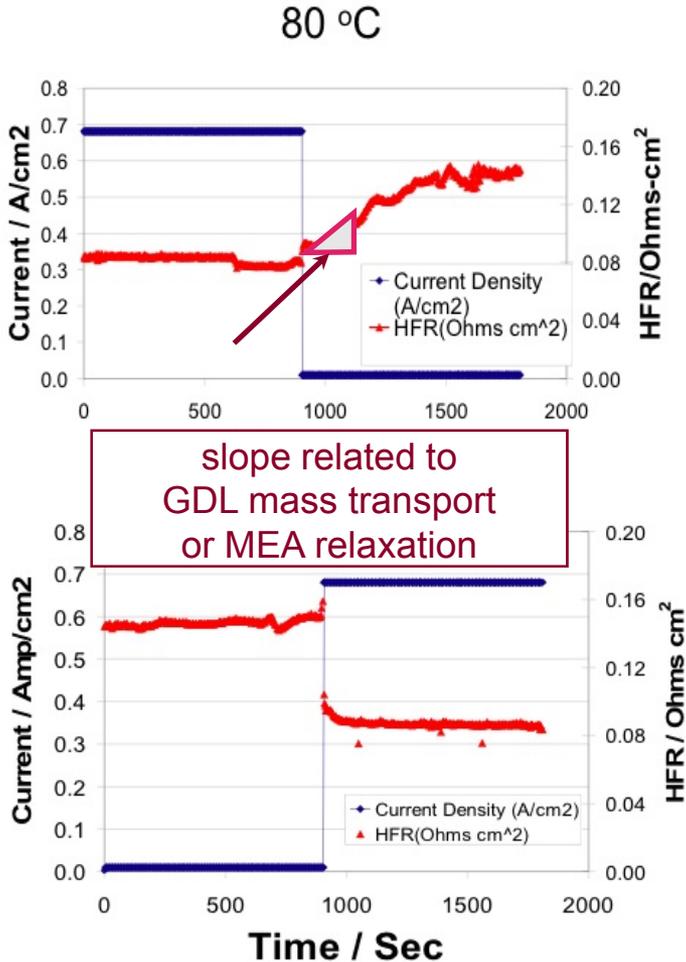
- Water vapor condenses on the cooler land surfaces.
- Condensation region at cathode CL & GDL shrinks in size as inlet humidity is lowered.
- Evaporation regions increase in size when inlet humidity is lowered.

*Reference: S. Basu, C.-Y. Wang, K. S. Chen, accepted for publication in *J. Electrochem. Soc.*

Transient Water Management Modeling

UT Austin On-going Work

Modeling of HFR Transient Response to Step in Current



$$Z = -\frac{\Delta\tilde{\Phi}}{\tilde{i}} = \int \frac{dx}{\kappa(x)} + \frac{1}{F} \int \xi \frac{d\tilde{\mu}_0}{\tilde{i}}$$

HFR modeled by neglecting interfacial resistance, and by appropriate timescales of transient processes: quasi-steady state in gas phase; liquid and polymer-phase water profile relaxation