Water Transport Exploratory Studies

DOE 2010 Annual Merit Review Meeting

June 7 - 11, 2010

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

This presentation does not contain any proprietary or confidential information

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Project Overview

Timeline

- Project initiated FY07
  - **Start March '07**
- 4 year Project Duration
  - **End March '11**
- ~> 85 % complete

Budget

- Total project funding
  - DOE Cost: $6,550,000 (over 4 yrs)
  - Cost Share: $290,811
- Funding for FY10

LANL	$1000k
Partners (Univ. & Ind.)	$250k
Other National Labs	$350k
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

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Collaboration: Organizations / Partners

- **Los Alamos National Lab:** **Rod Borup, Rangachary Mukundan, John Davey, Roger Lujan, Joe Fairweather, Dusan Spernjak, 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 Univ. / Univ. Tenn:** **Tom Zawodzinski, Che-Nan Sun**
- **SGL Carbon Group:** **Peter Wilde, Ruediger-Bernd Schweiss**
- **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** (visiting student)**:** **Jeremy Meyers, Peter Olapade**
- **Nuvera:** **James Cross, Amedeo Conti, Keven Beverage, Robert Dross**

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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

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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

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GDL: Improved Water Transport Properties

- GDL Materials
  - Data taken on GDLs varying Teflon® loading
  - GDL Characterization
  - Measured water profiles for various materials
  - Measured transport limitations by AC Impedance
  - New materials with varying porosity and MPL materials and properties.

- Optimizing spatial GDL properties
  - Segmented measurements of performance and mass transport limitations
  - Vary XY spatial GDL composition

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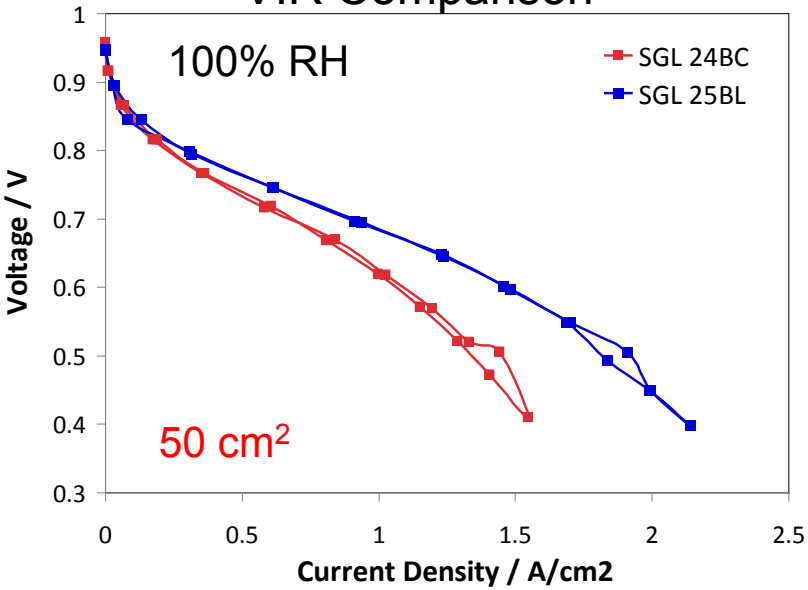
GDL Cell comparison, with/without Hydrophilic Cathode MPL Treatment

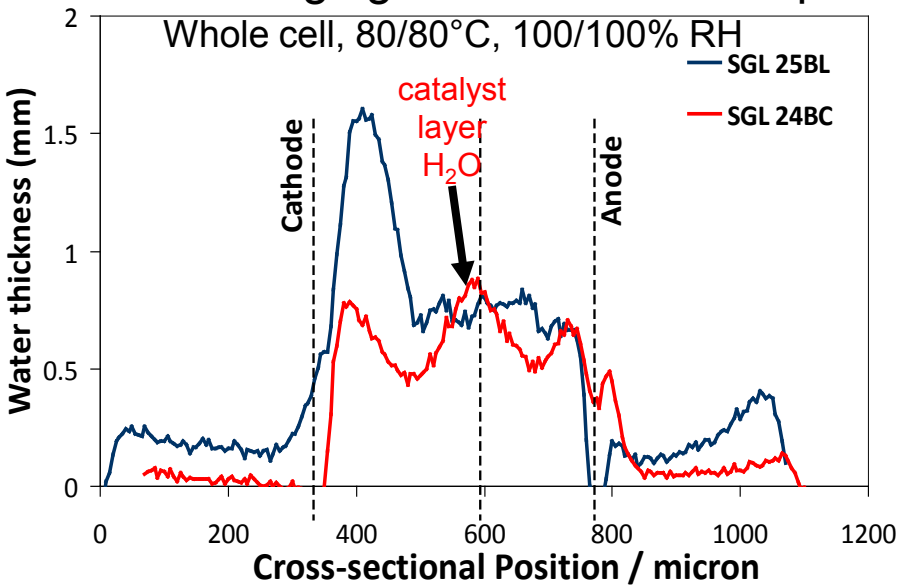
Cathode GDLs:

- 24BC and 25BL both 5% PTFE substrate/23% PTFE MPL Loading
- 25BL had additional hydrophillic MPL treatment

VIR Comparison



Neutron Imaging Water Profile Comparison



- GDL with hydrophillic treatment in MPL shows improved performance at high current densities
- Water profile from neutron imaging shows lower cathode catalyst layer region water content

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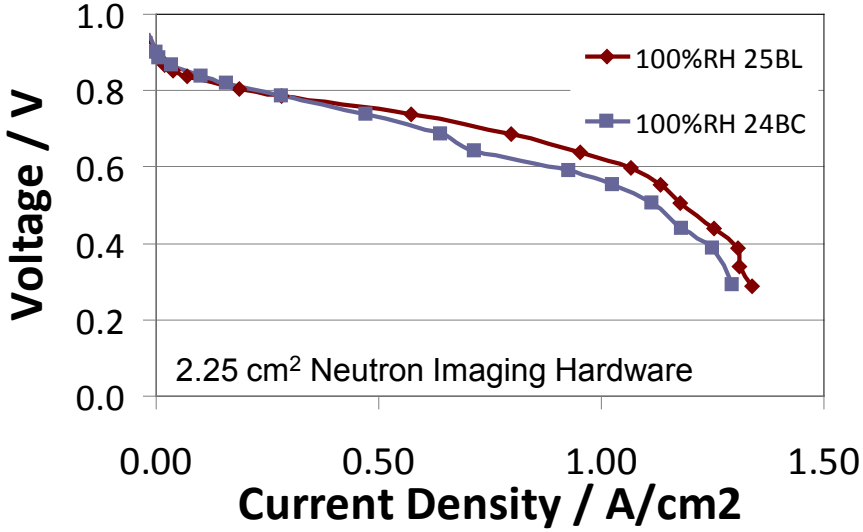
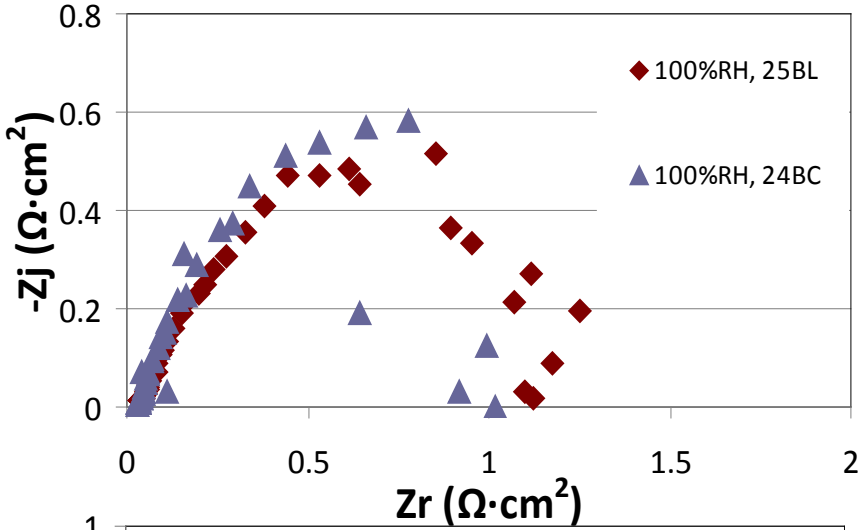
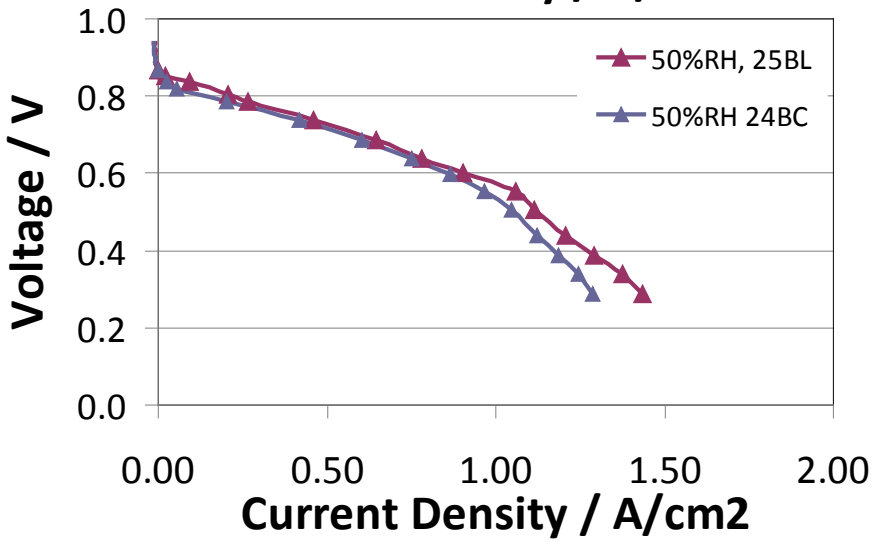
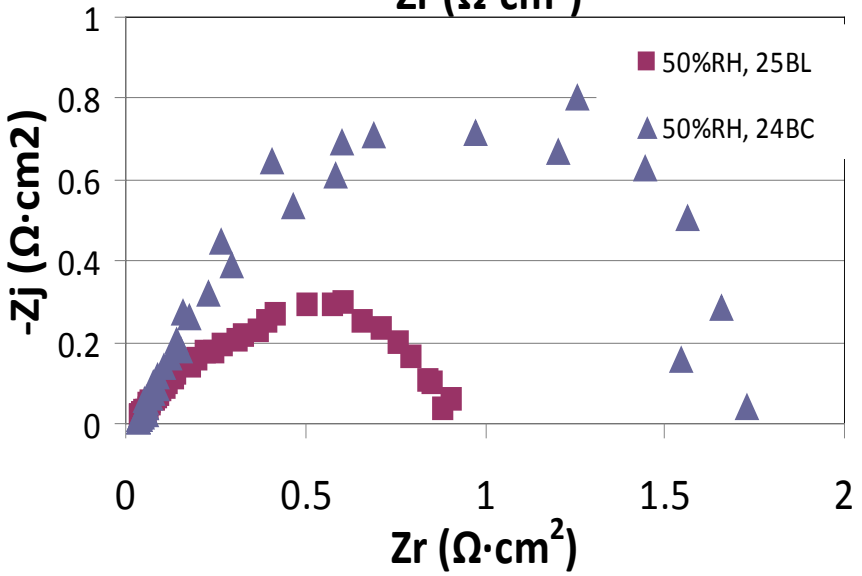
VIR and Impedance Comparison of 24BC vs. 25BL









- 25BL shows improved performance at both 100% and 50%RH
- Shows lower mass transport limitations at high currents
- Correlates AC Impedance and lower cathode water content

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In-Plane GDL Performance Improvement

- Examining the cell performance with varying GDL materials in the different segmented regions
- Evaluate water and MT limitations with different operating conditions (100% RH and 50% RH)
- Measure over-all performance, performance spatially, and mass-transport limitation spatially and as a function of current density
- Design an improved in-plane GDL material
  - Basic principle: Selected GDL segments based on the 50% RH performance without compromising the 100% RH performance

Cathode GDL Configurations				
Cell ID	**Segmented GDL**	**GDL Type**	**Substrate PTFE wt%**	**MPL wt%**
G-103	No	GDL 24BC	5	23
G-104	No	GDL 24BC5	5	5
G-105	No	GDL 24DI	20	10
G-106S	Yes	GDL 24BC	5	23

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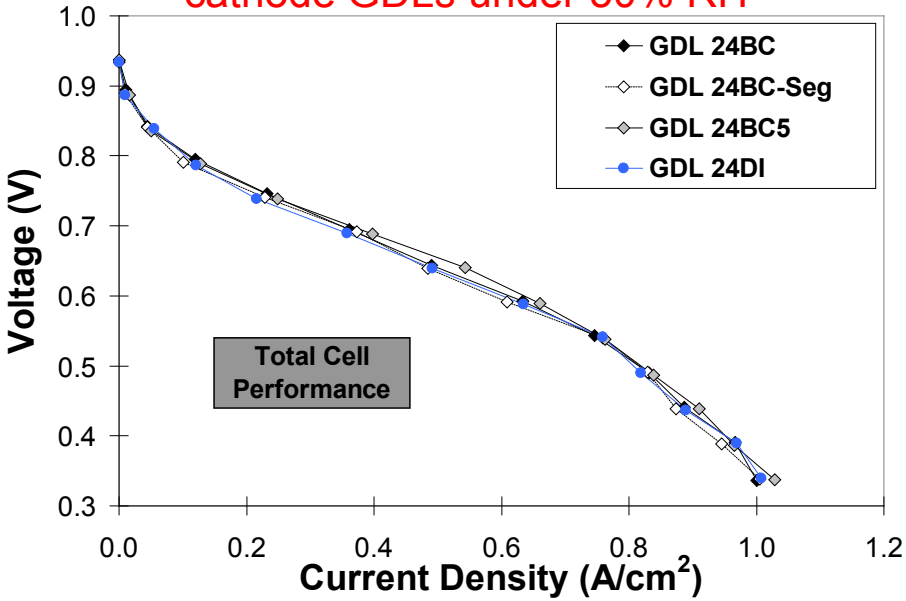
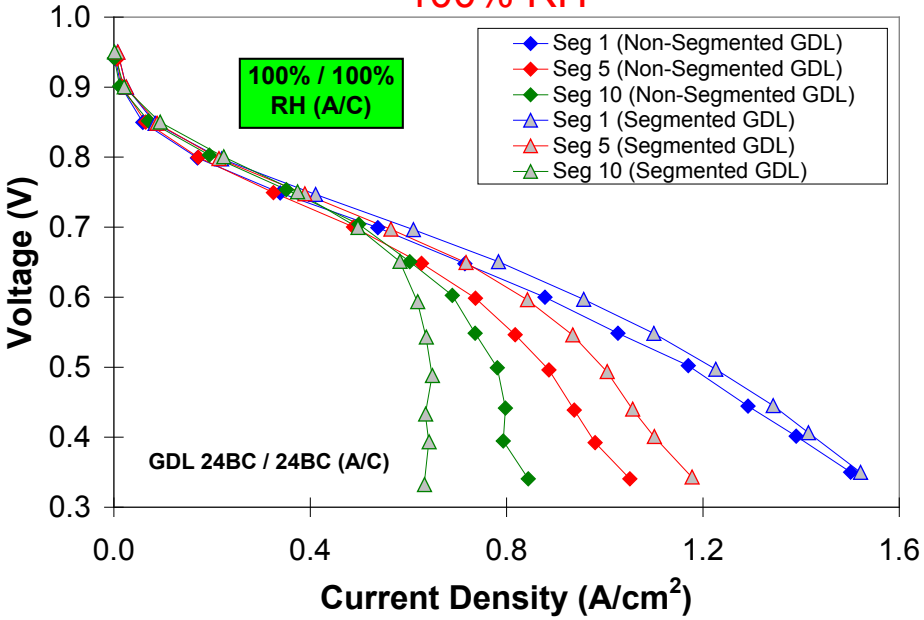
Segmented Cell Measurements

Total cell polarization data comparing cathode GDLs under 50% RH



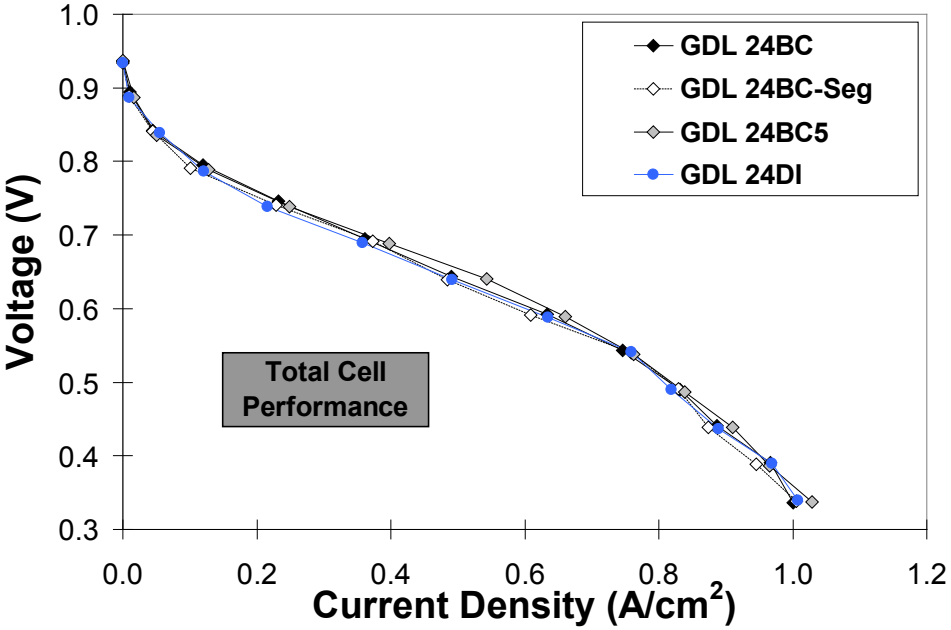
Segmented cell polarization data under 100% RH



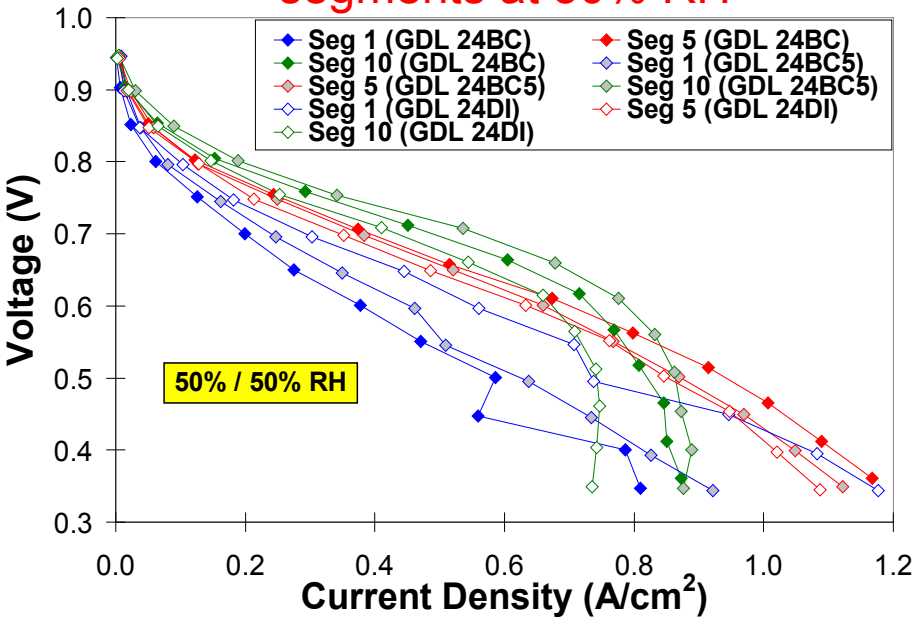
- Total cell performance nearly identical for 24BC, 24BC5, lower for 24DI
  - (24BC and 24BC-Seg are different experimental methods)
- At 100% RH - highest performance for all GDLs in segment 1
  - Later segments have reduced performance, esp. at high current (MT limitations)

Segmented Cell Measurements (50% RH)

Total cell polarization data comparing cathode GDLs under 50% RH

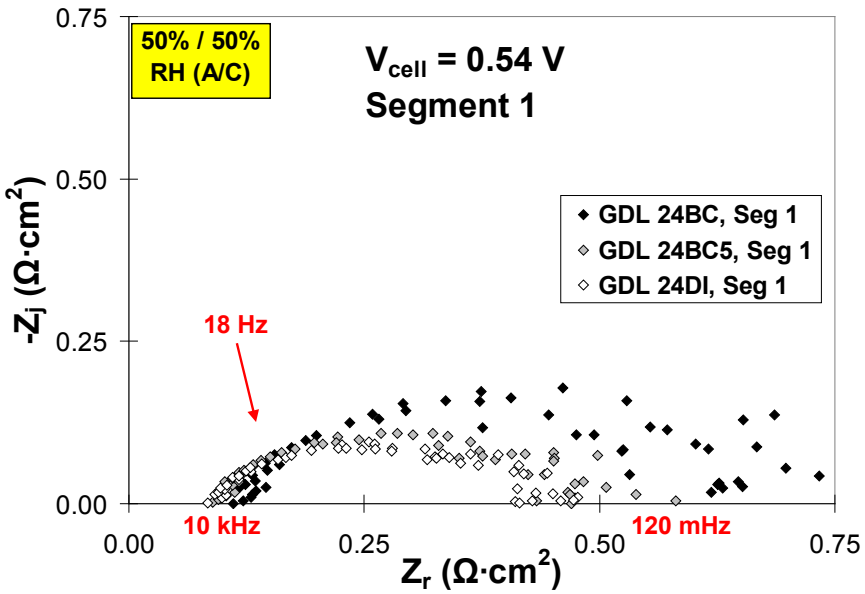


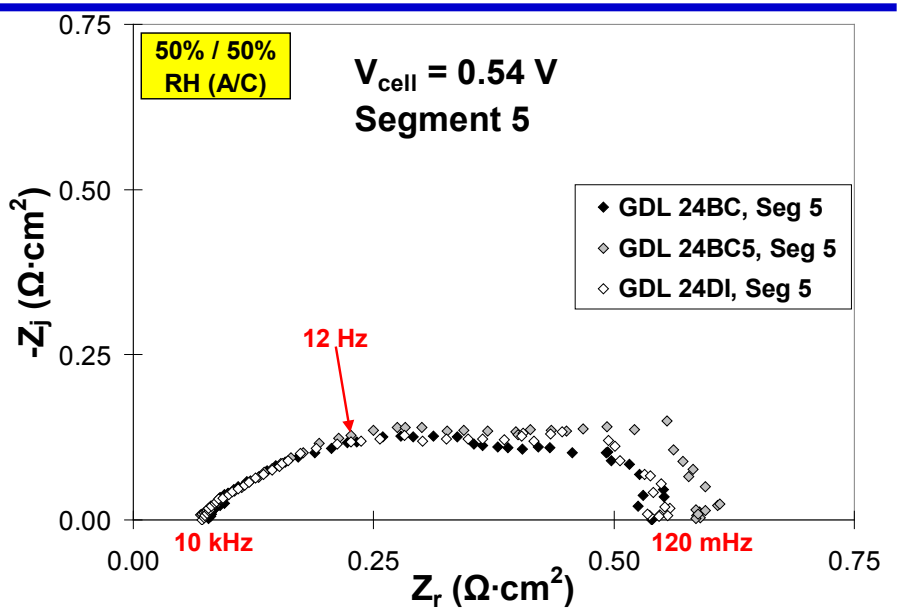
Polarization data for different segments at 50% RH

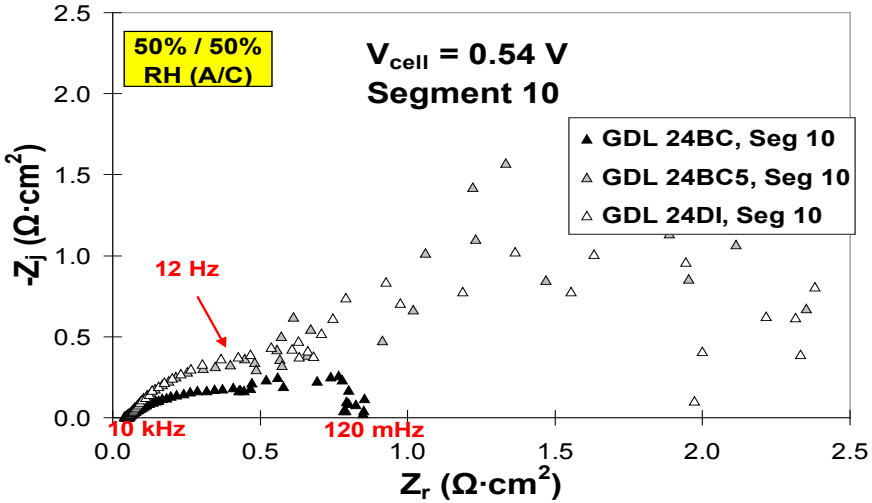


- At 50 % RH Total cell performance is ~ identical for 24BC, 24BC5, 24DI
  - Highest low current performance for all GDLs in segment 10
  - Highest high current performance occurs in the middle of the cell (~ segment 5)
  - Earlier segments have reduced performance due to limited conductivity
  - Late segments have reduced performance at high currents due to MT limitations

Segmented Impedance







- Impedance comparison at different cell locations
  - Inlet segments show higher catalyst layer resistance when the catalyst layer is dry.
  - Outlet segments show higher mass transport limitations (due to water accumulation and O_2 depletion)
  - Lower electrolyte ionomer conductivity and higher O_2 reduction resistance under drier conditions.
  - Membrane resistance is not very different since HFR is about the same.

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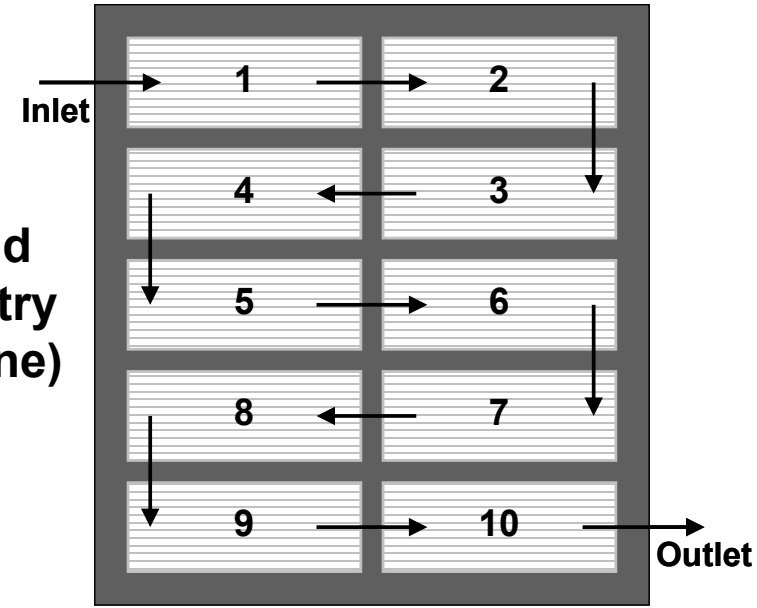
Basic Optimization Strategy

- At 50% RH:
  - Best inlet performance: GDL 24DI
    - Higher water holding capacity
  - Best middle cell performance : GDL 24BC
    - GDL with high water removal characteristics
  - Best outlet performance at the outlet: GDL 24BC5
    - GDL best high water content performance

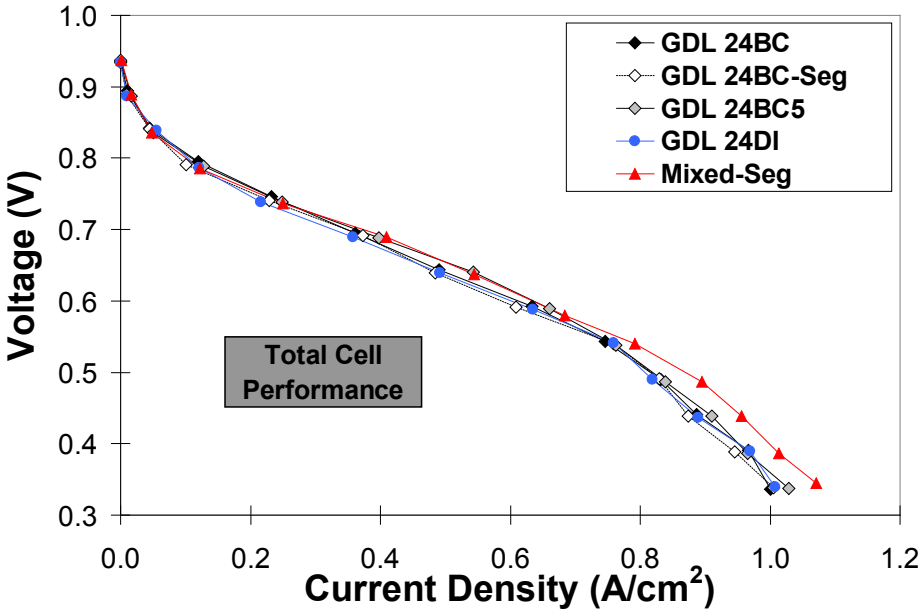
- Build cell with :
  - Inlet: GDL 24DI (3 segments)
  - Middle: GDL 24BC (4 segments)
  - Outlet: GDL 24BC5 (3 segments)

Cathode Flow-Field Segmented Geometry (6-Parallel Serpentine)

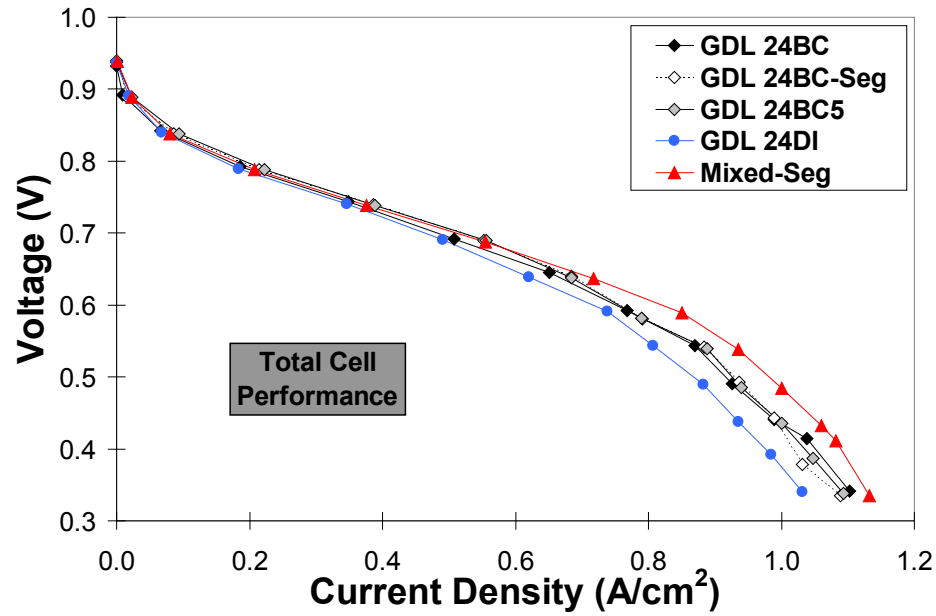


Mixed GDL Performance

Total cell polarization data comparing cathode GDLs at 50% RH



Total cell polarization data comparing cathode GDLs at 100% RH



- Mixed GDL configuration shows:
  - 11% improvement at 100% RH
  - 8% improvement at 50% RH
    (based on GDL 24BC @ 0.6 V)

Mixed GDL:

GDL 24DI in segments 1-3
GDL 24BC in segments 4-7
GDL 24BC5 in segments 8-10

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Schroeder's Paradox

100% RH and liquid water have activity of water = 1. Membrane water uptake should be equivalent at these conditions. However, many measurements have been made indicating that this is not true.

Zawodzinski, et al., *J. Electrochem. Soc.,* Vol. 140, No. 4, April 1993

(λ as a f(RH) – λ = 14 RH=100, λ = 22 Liq.)

In 1903, Schroeder reported that gelatin had less water uptake from 100% relative humidity (RH) water vapor than from liquid water immersion at the same temperature. This observation, known as Schroeder's paradox, is inconsistent with thermodynamics because the chemical potential of saturated water vapor is equal to that of liquid water at the same temperature; therefore, at equilibrium, the water content of gelatin in contact with saturated water vapor should be the same as that when in contact with liquid water.*

Recent Papers Indicate that Schroeder's Paradox does not exist:

JN. Cornet, G. Gebel et A. de Geyer***. Phys. IV France* 8 (1998)**

Sandra Jeck, Philip Scharfer, Matthias Kind, Journal of Membrane Science, 337 (2009) 291–296

L.M. Onishi, J.M. Prausnitz and J. Newman, *J. Phys. Chem. B* **2007,** *111,* 10166-10173*

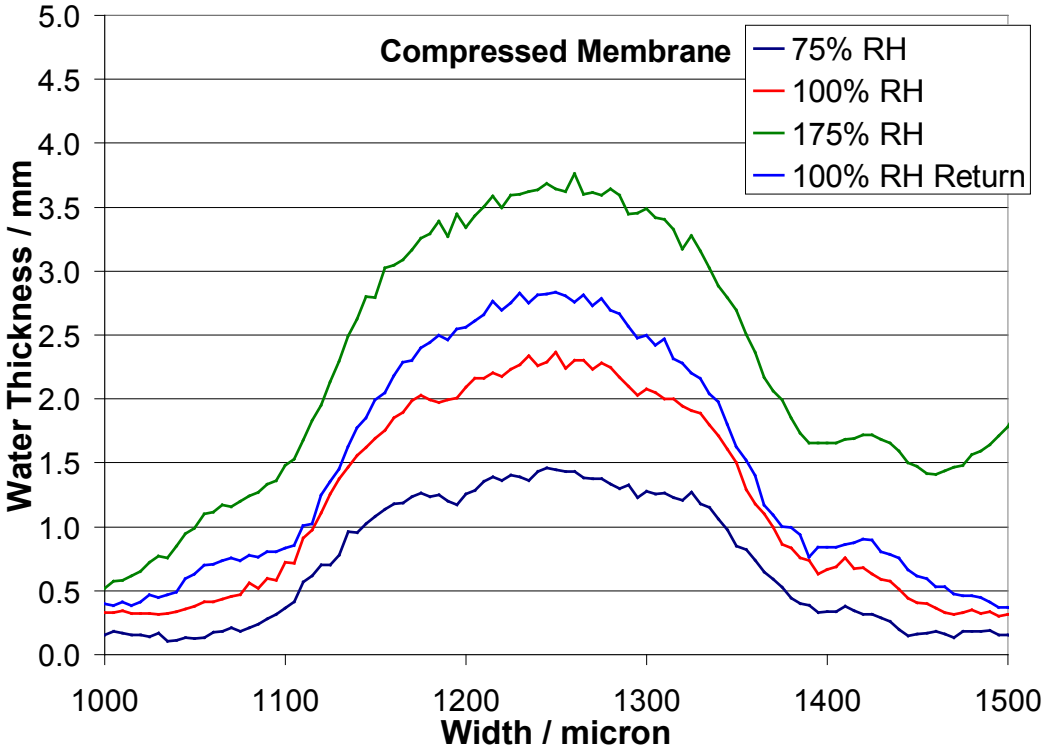
Predried membrane: λ = 13-14

Preboiled membrane: λ = 23-24

Membrane water content is a function of thermal history, with no difference in membrane water content between liquid water and vapor (100%) water

in situ Measurements Verifying Schroeder's Paradox

Used NIST's new high resolution detector (10 micron) and N117 (175 micron membrane) to measure water content with varying RH and liquid water reproducible and reversibly *in situ*.



- Measured Membrane water equilibrated with 50, 90, 100% RH, then liquid water then reversed the humidity
- Membrane water content decreases from Liquid to water vapor, thus verifying existence of Schroder's Paradox
- Preboiled and Predried Membranes show same dependence on membrane water content between vapor and liquid water

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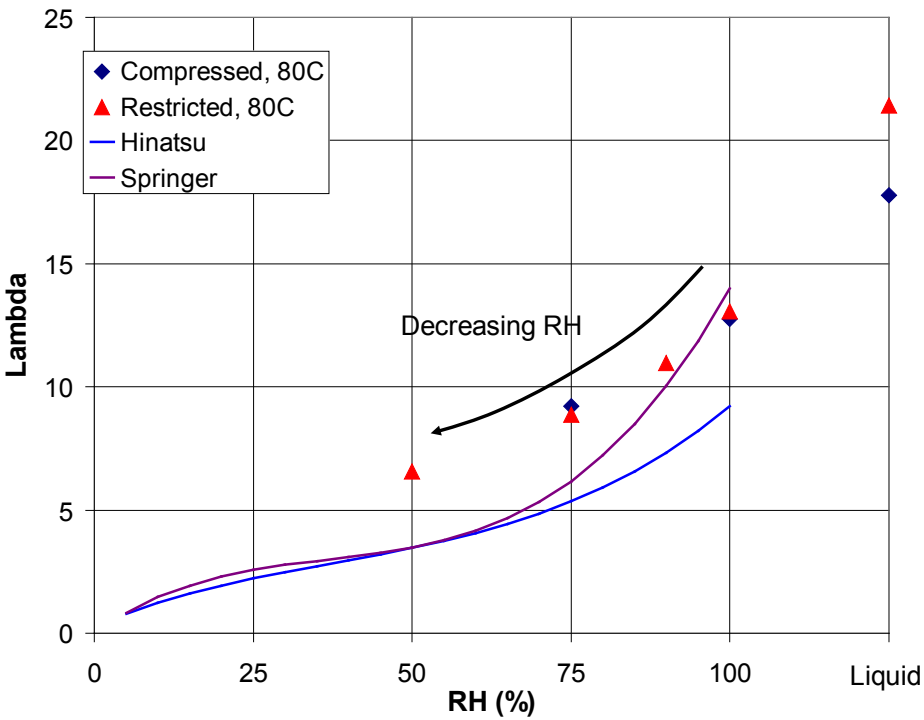
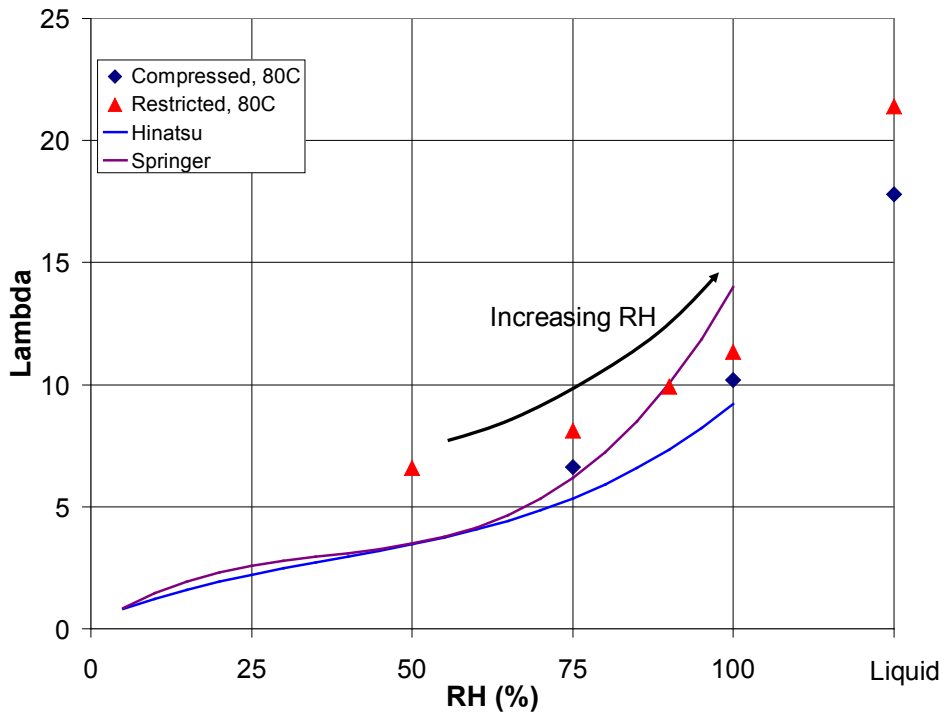
Membrane
Lambda Measurements with compression

- Comparison of measured membrane water content
  - Measured by neutron imaging at RH and liquid water (175%)
- Comparison of
  - Compressed membrane (GDLs applied compression forces (~> 400 psi)).
  - Restricted membrane (low membrane compression (< 140 psi), - membrane not free to swell)

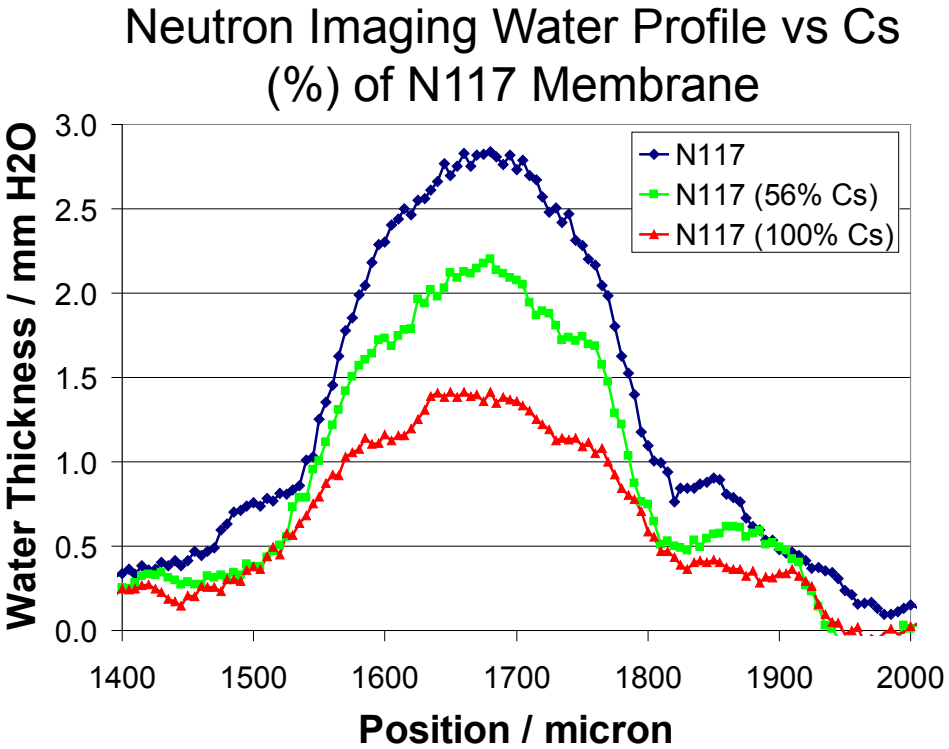


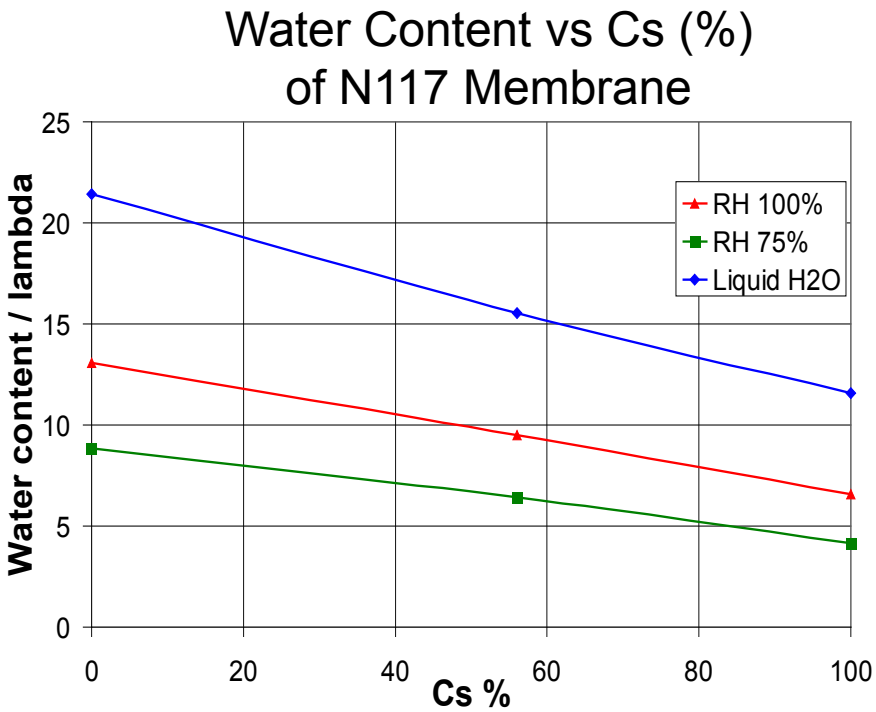


- Restricted and compressed membranes have similar water content with exception of liquid H_2O
  - Longer for liquid to equilibration times or swelling putting pressure membrane
- New detector gives more pixels in N117 → measurements are accurate

Hinatsu et al., J. Electrochem. Soc., Volume 141, Issue 6, pp. 1493-1498 (1994)
Springer et al., J. Electrochem. Soc., Volume 138, Issue 8, pp. 2334-2342 (1991)

Cation Effect on Membrane Water Content





- Membrane water content measured *in situ* by neutron imaging
  - N117 and N117 sulphonic acid sites exchanged with Cs (56% and 100%)
- Cation contamination greatly reduces membrane water content
  - Reduced protonic conductivity due to lack of sulphonic acid sites

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Freeze: Isothermal Operation

- Shut down
  - Dry water in channels with N_2 purge (2-5 L/min for 0.5 - 5 min)
  - Cool to -10, -20, -30 or -40 ^oC
- Operate
  - Constant current at high stoich. of dry H_2/ dry air till V = 0
  - CVs before and after, and HFR or AC impedance

Cells Tested			
Cell Designation	MEA	Anode and Cathode GDLs	Tests performed
1 (LANL MEA / Cloth GDL)	LANL MEA (Nafion® 212)	ELAT GDL : Double sided (An), Single sided (Ca)	5 starts at -10 ^oC 5 starts at -20 ^oC 3 starts at -40 ^oC
2 (LANL MEA / Paper GDL)	LANL MEA (Nafion® 112)	SGL GDL : 24 B"C" (5% PTFE in substrate and MPL)	5 starts at -10 ^oC 5 starts at -20 ^oC 2 starts at -40 ^oC
3 (Gore MEA / Cloth GDL)	Gore Primea® MESGA (18 μm membrane)	ELAT GDL : Double sided (An), Single sided (Ca)	4 starts at -10 ^oC 4 starts at -20 ^oC 4 starts at -40 ^oC
4 (Gore MEA / Paper GDL)	Gore Primea® MESGA (18 μm membrane)	SGL GDL : 24 B"C" (5% PTFE in substrate and MPL)	7 starts at -10 ^oC 3 starts at -20 ^oC 2 starts at -30 ^oC
5 (Gore MEA / Paper GDL)	Gore Primea® MESGA (18 μm membrane)	SGL GDL : 24 BC (5% PTFE in substrate and 23% in MPL)	5 starts at -10 ^oC 5 starts at -20 ^oC 5 starts at -40 ^oC

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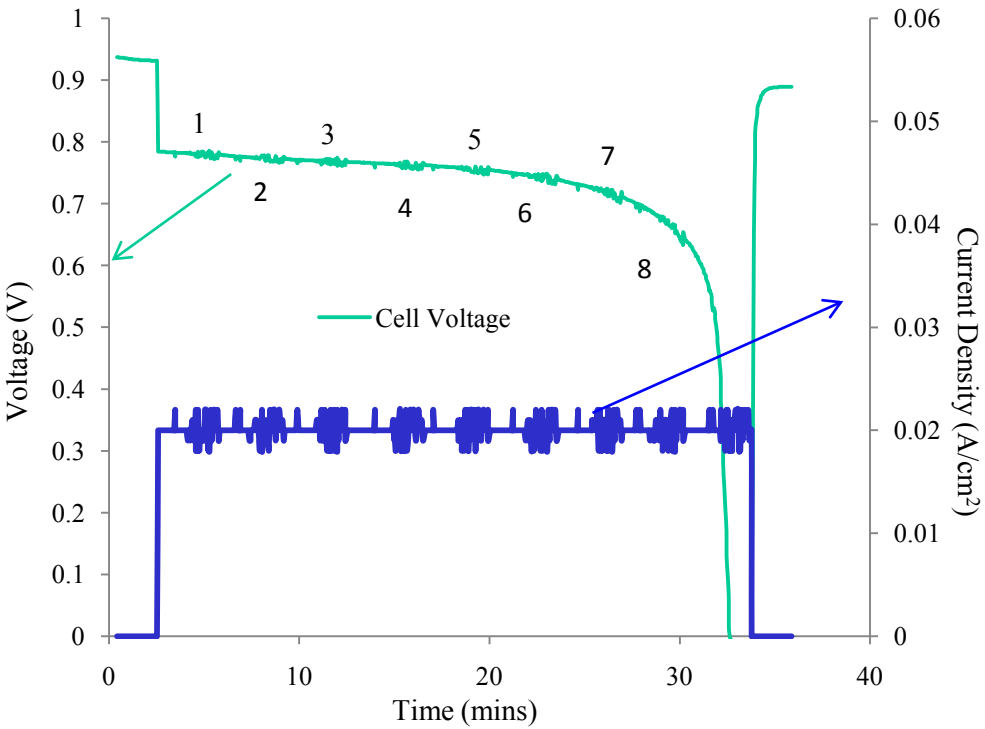
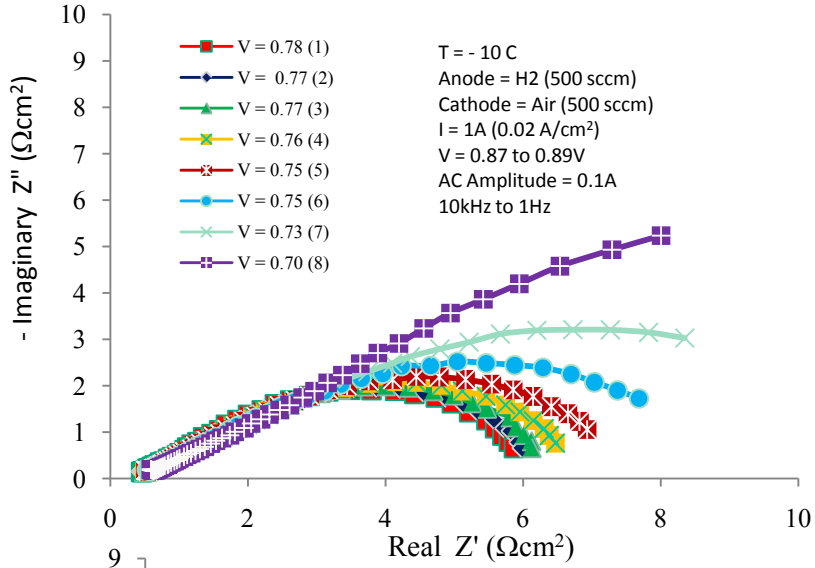
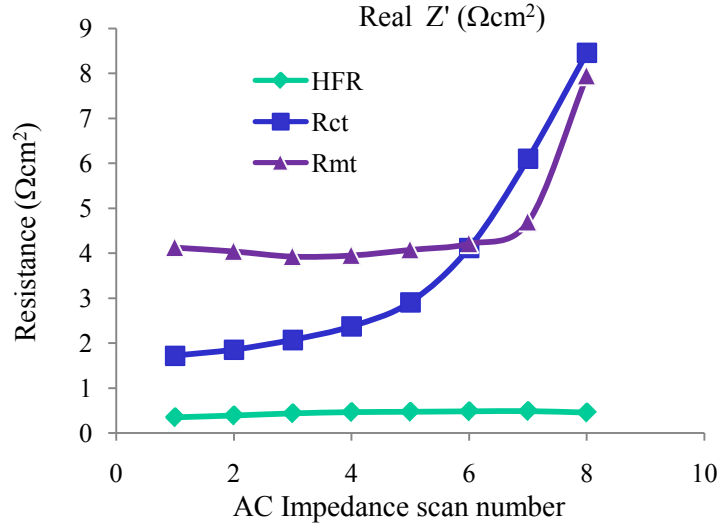
Typical Isothermal Start







- Steady increase of Rct
- Steep increase in Rmt when cell voltage drops dramatically
- HFR (constant when started from a fully hydrated condition)

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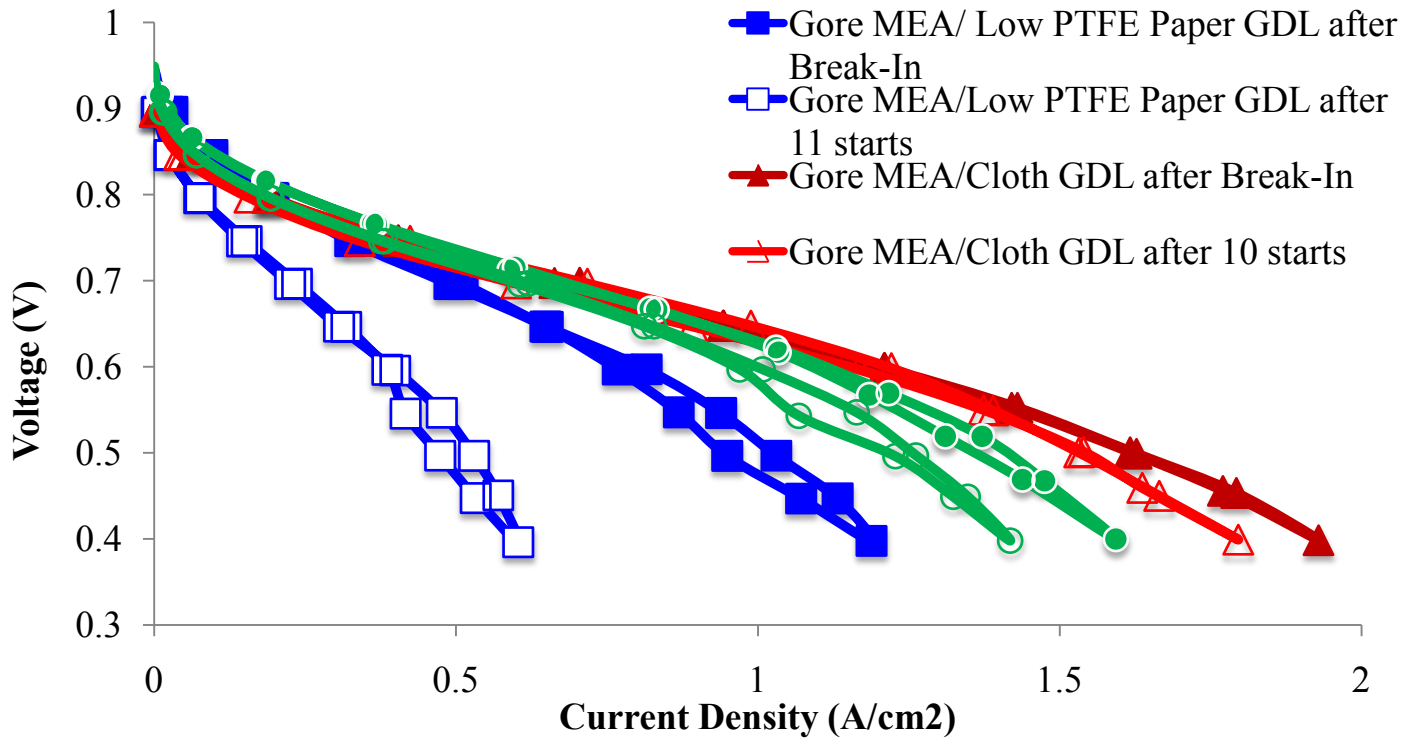
Durability (VIR)



- Low PTFE paper shows high degradation (46% loss in ECSA after 4 isothermal starts @ -10°C)
- High PTFE paper exhibits better durability (21% loss in ECSA after 4 isothermal starts @ -10°C)
- Cloth shows similar durability (27% loss in ECSA after 4 isothermal starts @ -10°C)
- High MPL PTFE content is critical for freeze durability (Keeps water out of cathode catalyst layer)

Increased ice holding capacity @

- Higher operating temperature
- Lower operating current
- Lower initial hydration (shutdown from lower RH)

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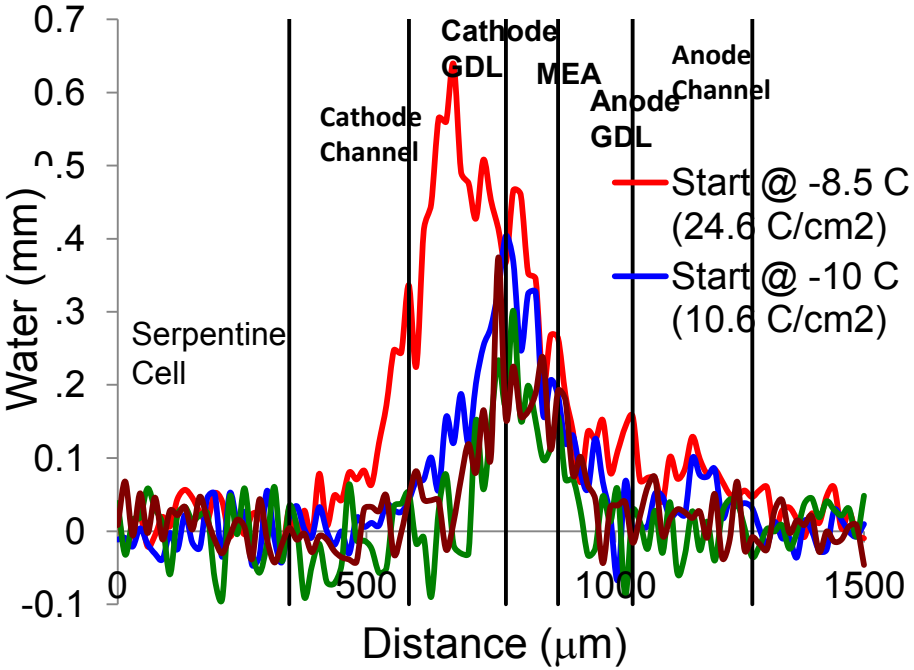
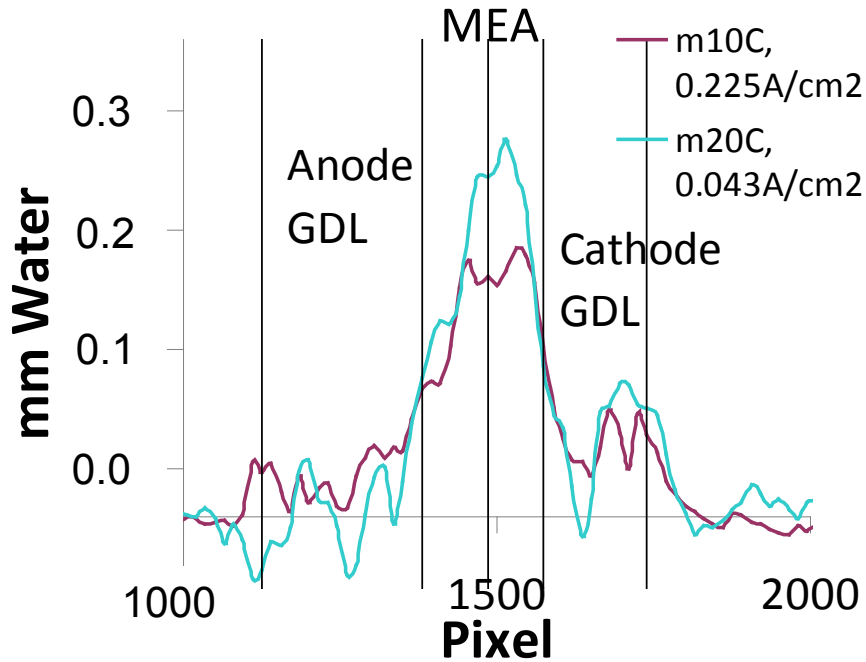
Freeze: High resolution imaging





- 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
  - More water/ice accumulation when operated from lower membrane lambda and lower current density
  - Membrane does not reach maximum lambda before V = 0 (More water can be put in the membrane if cell is allowed to reverse)

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Future Work

Experimental and Characterization

- Segmented cell measurements of new optimized GDL materials (25BL) and varying flow conditions
  - Expand segmented cell measurements to included performance measurements during AST testing
- Use pneumatic pressure control to change in situ GDL compression and measure GDL compression effect on water transport
- X-Ray radiography/tomography of GDL substrates measuring water movement through GDL pores
  - Use water activity gradients to induce water transport in GDL materials
  - Correlate measured water movement with GDL porosimetry and water capillary measurements
  - Validate water transport models

Modeling

- Wrap up work on analyzing through-plane water distribution and transport in MEA-GDL regions.
  - Simulate water profile measurements with varying conditions and GDL hydrophobicity measured by neutron imaging
- Wrap up multiphase transient model for simulating ice thawing or melting and water transport during PEM fuel cell start-up from subzero temperatures.

Transport Projects

- Support new transport projects and distribute measurements to 2008 funded projects
  - LBNL
  - SNL

Conclusions

GDL Materials

- New materials with modified MPL properties show better water removal characteristics
- When the three different GDL types were arranged in a mixed configuration, improved performance compared with the individual GDLs
- Demonstrated performance improvement can be realized by varying the in-plane GDL type in relation to its flow-field position

Membrane Water Content Measurements (Neutron Imaging)

- Measured water content in membranes lower than ex situ equilibrium measurements
- Cell compression of membrane influences membrane water content
- Verified existence of Shroeder's Paradox by in situ measurements
  - Reversible in situ measurements of membrane water content

Freeze

- 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
- Cycling results in loss of catalyst surface area, increase in porosity of catalyst layer and mass transfer limitations
- Cell durability to freeze/thaw cycling is influenced by
  - High PTFE in MPL results in better durability
  - Keeps water out of catalyst layer
- Location of frozen water (ice) depends on
  - Temperature of operation, current density, cell configuration

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Thanks to

- U.S. DOE -EERE Fuel Cell Technologies Program for financial support of this work
  - Technology Development Manager: Nancy Garland

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Supplemental Slides

FY2010 Milestones

Mon Yr	Milestone	
Dec 2009	Demonstrate fuel cell performance improvement by segmented cell operation with in-plane variation GDL Teflon loading	☑
Mar 2010	Examine flow geometry of operating anode with dead-end flowfield on the cross-sectional water profile in the operating fuel cell (completed with Univ. of Michigan)	☑
Mar 2010	Obtain the saturation profiles of GDLs while measuring limiting current, to relate gas permeability directly to saturation levels.	~☑
Mar 2010	Compare AC impedance spatially of operating fuel cells for high and low water content inlets (50% and 100% inlet RH).	☑
Jun 2010	Identify location of ice formation and level of membrane hydration in a N117 MEA operated isothermally under sub-freezing conditions	☑

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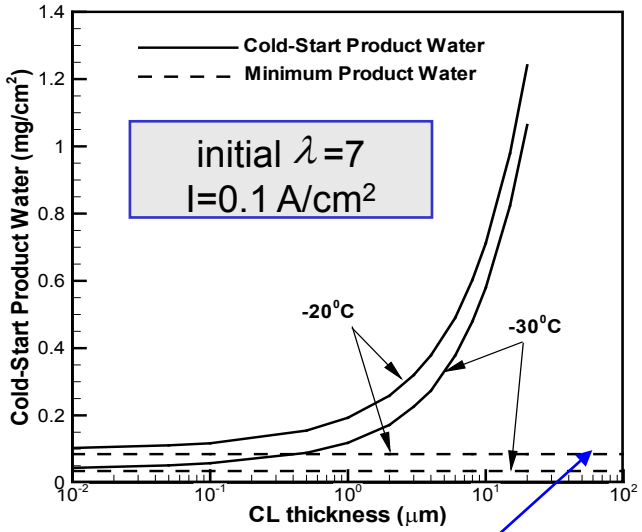
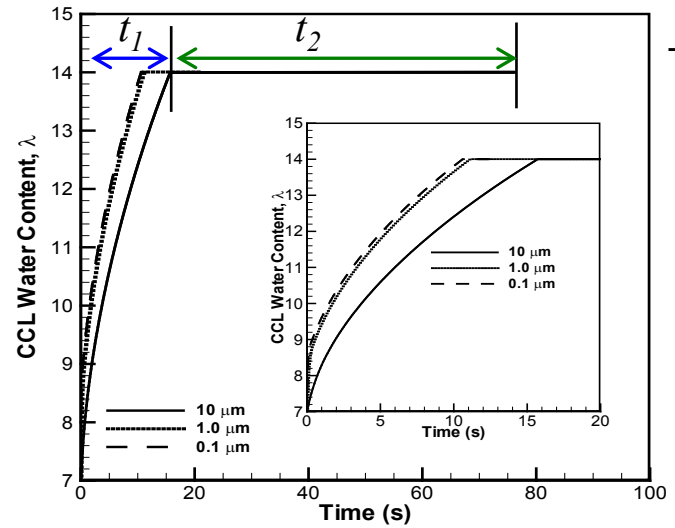
CCL Thickness Significantly Affects Isothermal Cold Start Performance!

CCL = Cathode Catalyst Layer





corresponds to a minimum operation time ~ 9 s

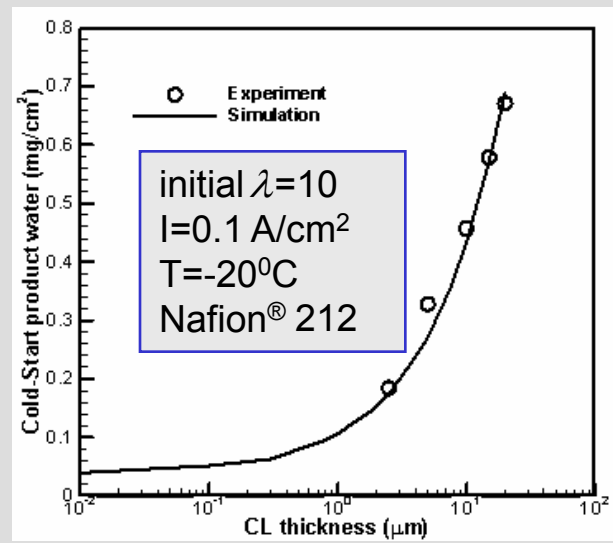
Cold-start product water reaches asymptotically to a minimum nonzero value as CCL is made infinitesimally thin!

$$t = \begin{cases} t_1 \\ + \\ t_2 \end{cases}$$

- Time taken by CCL to reach $\lambda = 14$
- Asymptotic in nature

- ice precipitation time
- $\sim$ proportional to CL thickness

Experimental Validation



Purge process: 2 min dry purge with N_2 at 55^{0}C

Reference:

A.Nandy, F. Jiang, S. Ge, C.-Y. Wang, and K. S. Chen, "Effect of cathode pore volume on PEM fuel-cell cold start", *J. Electrochemical Society*, 157 (5) 1-XXXX (2010).

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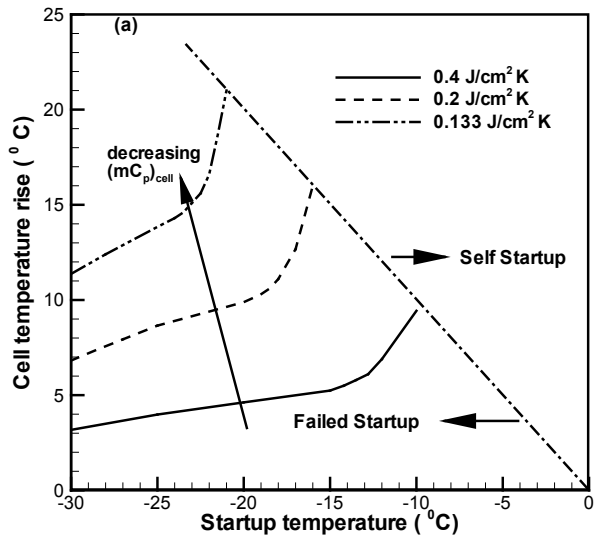
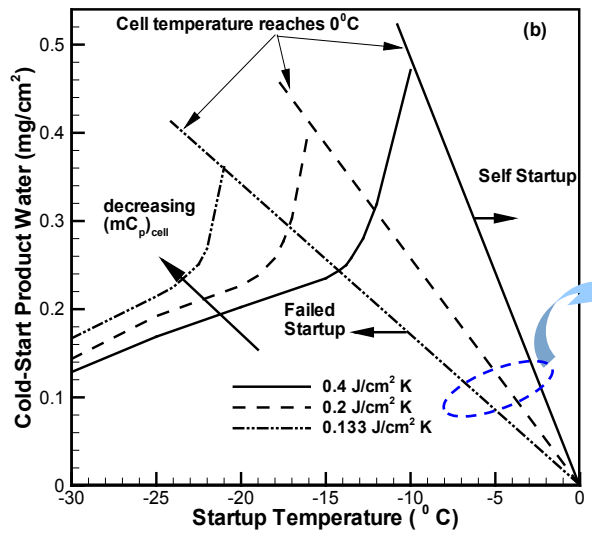
Case Studies of Cold Start with Thin (1μm) CCL:
Effects of Cell Thermal Mass and Membrane Water Activity

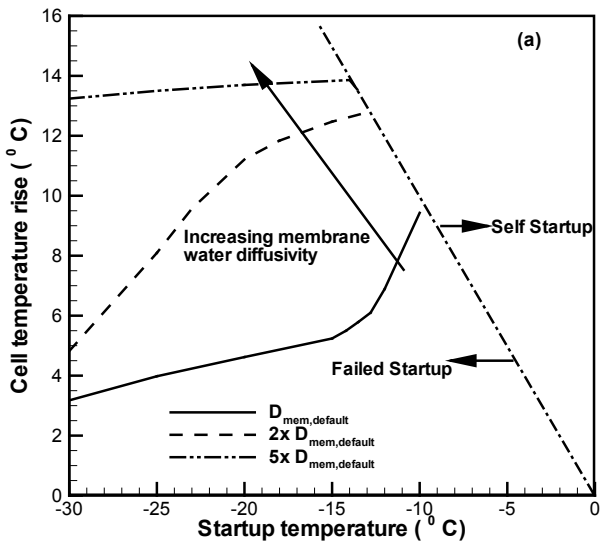


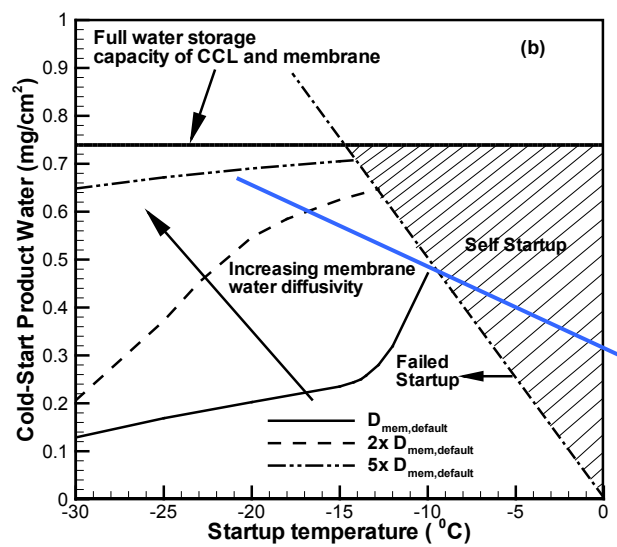


Effect of cell thermal mass

initial λ=7
$S_{ice,0}$ =0
I=0.1 A/cm²

Slope of these lines are directly proportional to the cell thermal mass!





Effect of membrane water diffusivity

initial λ=7
$S_{ice,0}$ =0
I=0.1 A/cm²
$(mC_p)_{cell}$=0.4 J/cm²K

Almost full utilization of membrane and CL water storage capacity owing to faster water absorption into membrane and prolonged cell operation!

Reference:

A.Nandy, F. Jiang, S. Ge, C.-Y. Wang, and K. S. Chen, "Effect of cathode pore volume on PEM fuel-cell cold start", *J. Electrochemical Society*, 157 (5) 1-XXXX (2010).

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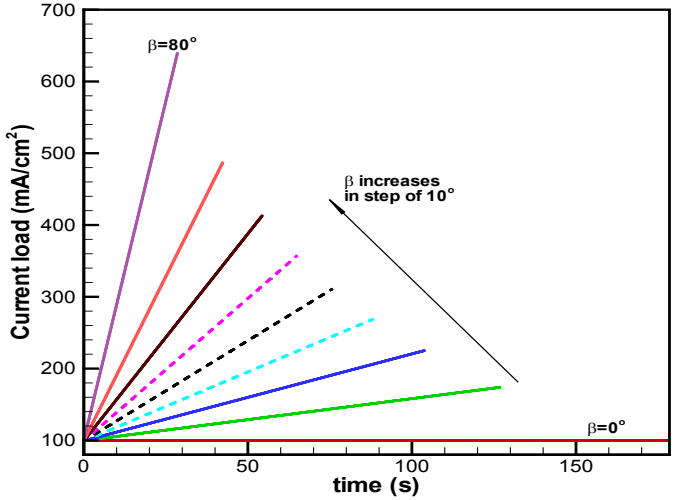
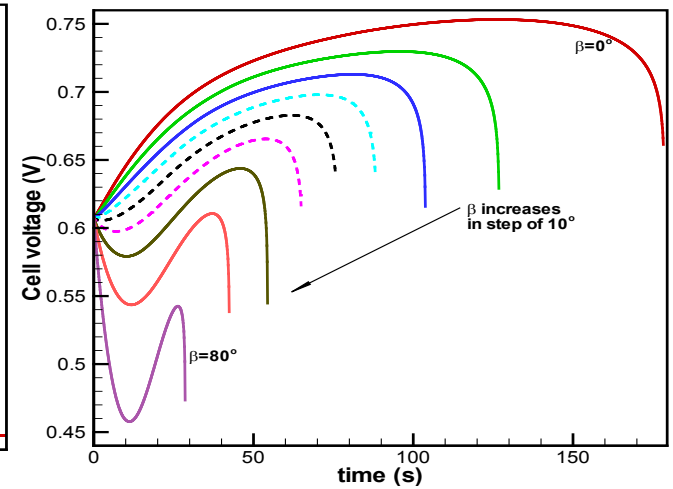
Current Ramping Rate Has Significant Effect on Whether or not A PEMFC can be Started up Successfully from Subzero Temperatures

Define current density *I* in current-ramping startups as:

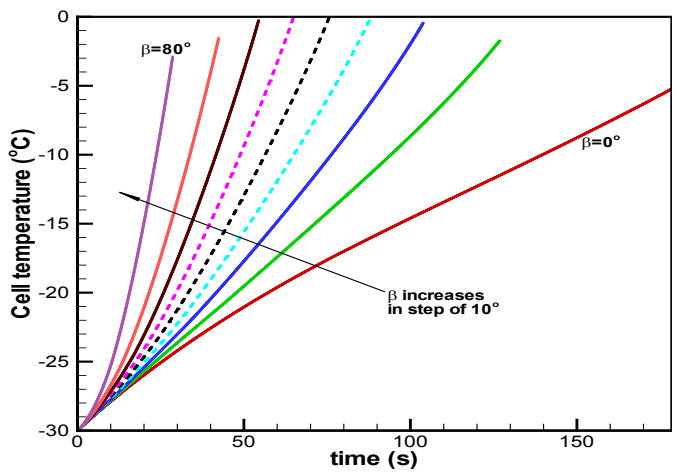
$$\frac{I}{I_0} = 1 + (\frac{t}{30}).\tan(\beta)$$

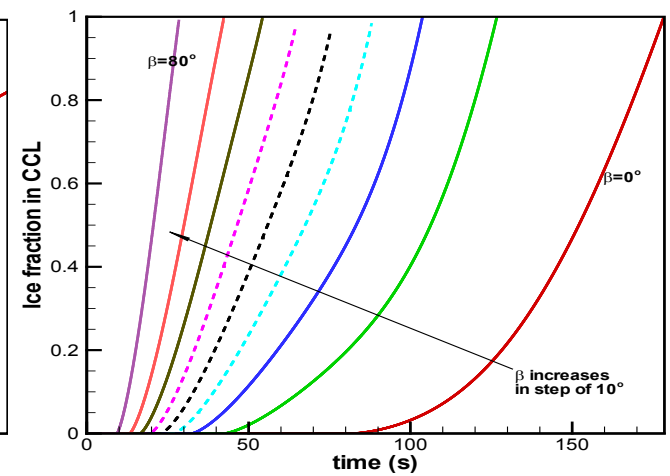
where I_0 *is* initial current density and β is current ramping angle.





- Intermediate values of β (30°–50°) lead to successful startups. When β is smaller than 20°, the slowly ramping current density cannot ensure a sufficiently fast cell temperature rise, leading to shutdown. When β is larger than 60°, the speedily ramping current density results in too fast water production rate, eventually leading to shutdown.





Reference:

F. Jiang, C.-Y. Wang, and K. S. Chen, "Current ramping: strategy for rapid start-up of PEMFCs from subfreezing environment", *J. Electrochemical Society*, 157 (3) B342-B347 (2010).

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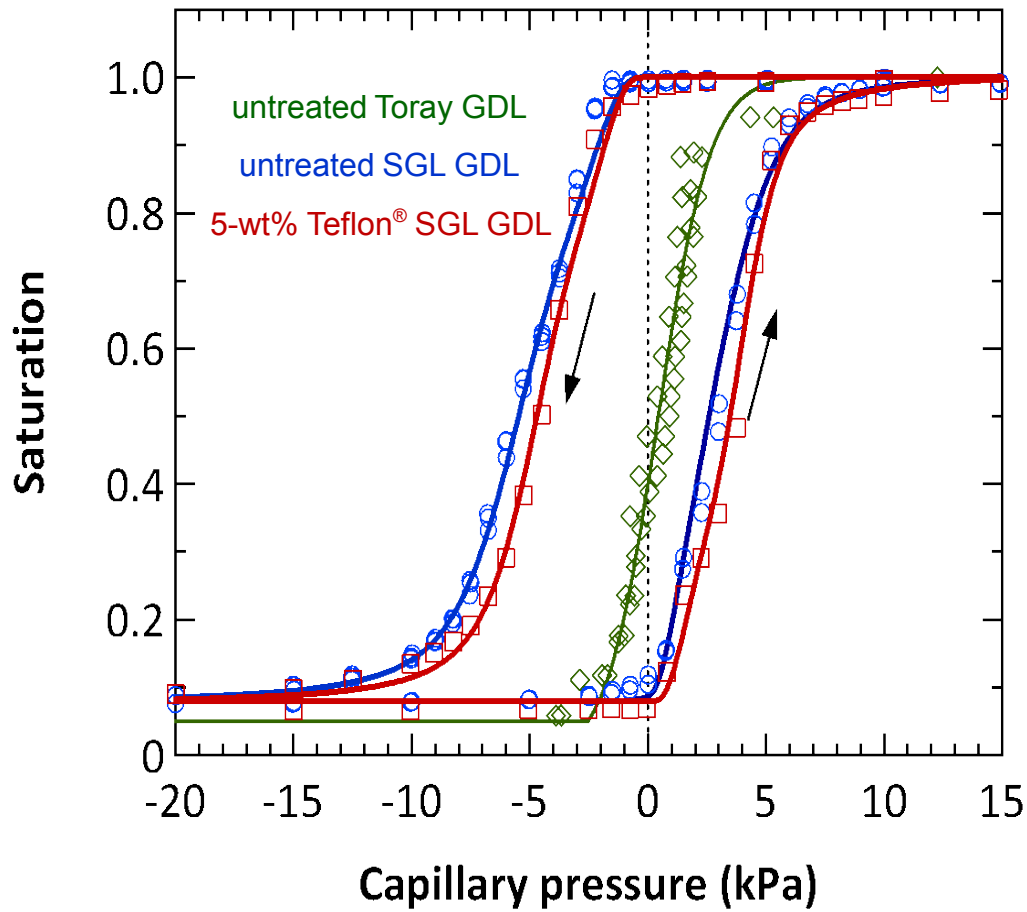
Capillary Pressure vs. Saturation

- Measured capillary pressure – saturation profile is the **key** DM metric



- Fit data with self-consistent model using a pore-size (PSD) and a contact-angle (CAD) distribution

$$Y = \iint \Psi(\theta) Y(r) V(r) \mathrm{d}r \mathrm{d}\theta$$

Weighting function

  - PSD is fit to measured one

$$V(r) = \sum_k f_{r,k} \left\{ \frac{1}{r s_k \sqrt{2\pi}} \exp\left[-\left(\frac{\ln r - \ln r_{o,k}}{s_k \sqrt{2}} \right)^2 \right] \right\}$$

  - CAD fit to Pc vs. S data using fit PSD and above formula

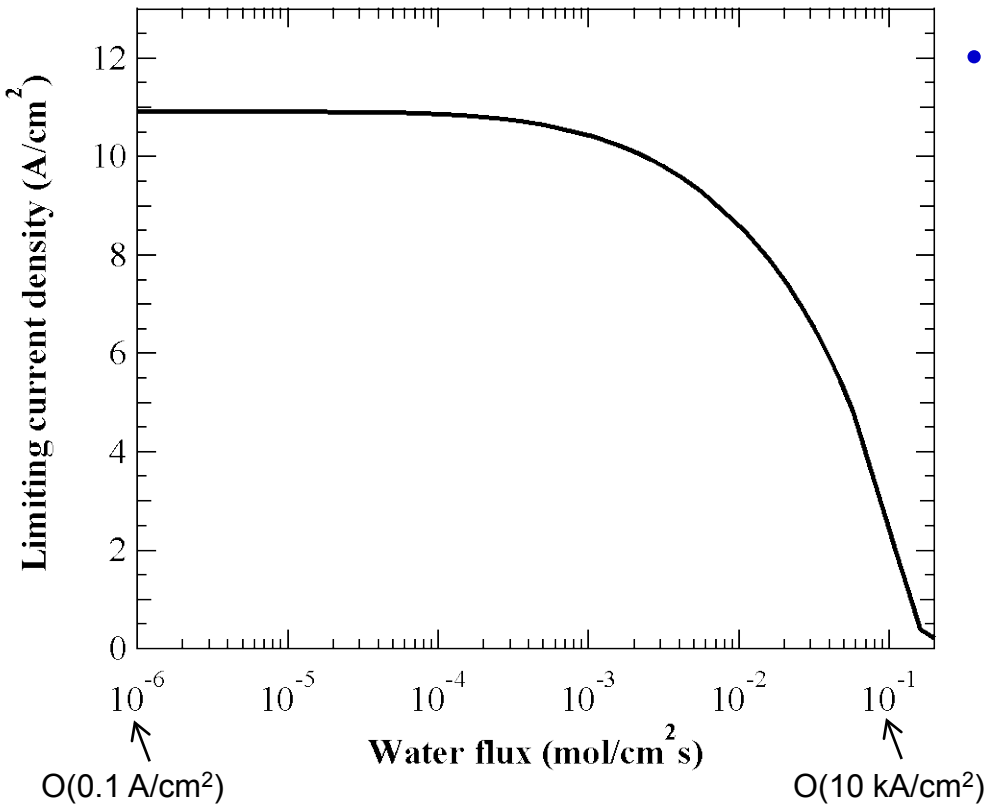
$$\Psi(\theta) = \sum_n f_{\theta,n} \left\{ \frac{1}{\sigma_n \sqrt{2\pi}} \exp\left[-\frac{1}{2} \left(\frac{\theta - \theta_{o,n}}{\sigma_n} \right)^2 \right] \right\}$$

References: J.T. Gostick, et al., *JPS*, in press (2009); P. Cheung, et al., *JPS*, 187, 487 (2009); K. G. Gallagher, et al., *JES*, 155, B1225 (2008)

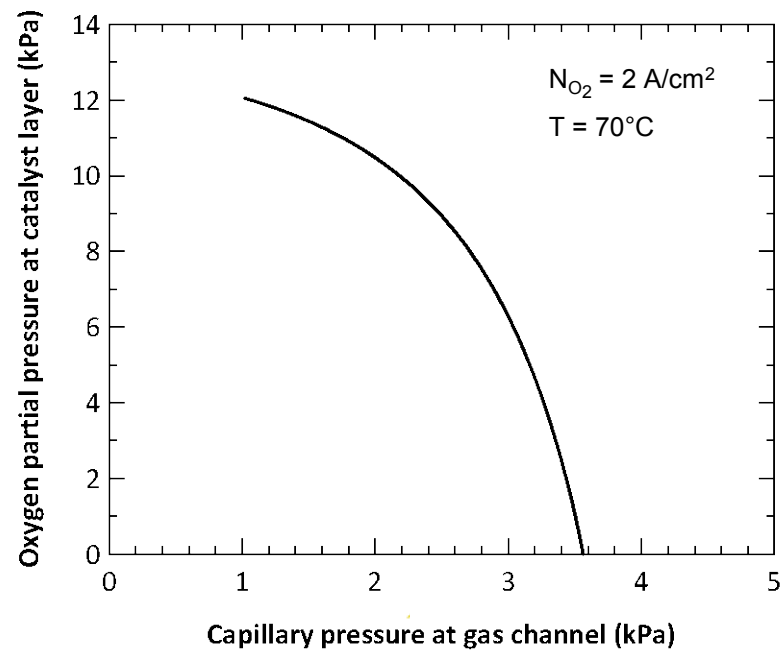
Los Alamos

GDL Simulations

- Examine mass-transfer limiting current as a function of inlet water flux
  - High limiting currents and very flat in practical range
- Bulk transport (convection) does **not** lead to mass-transfer limitations
  - Effective permeability remains too high
  - Once have water pathway, it can sustain practical liquid-water fluxes

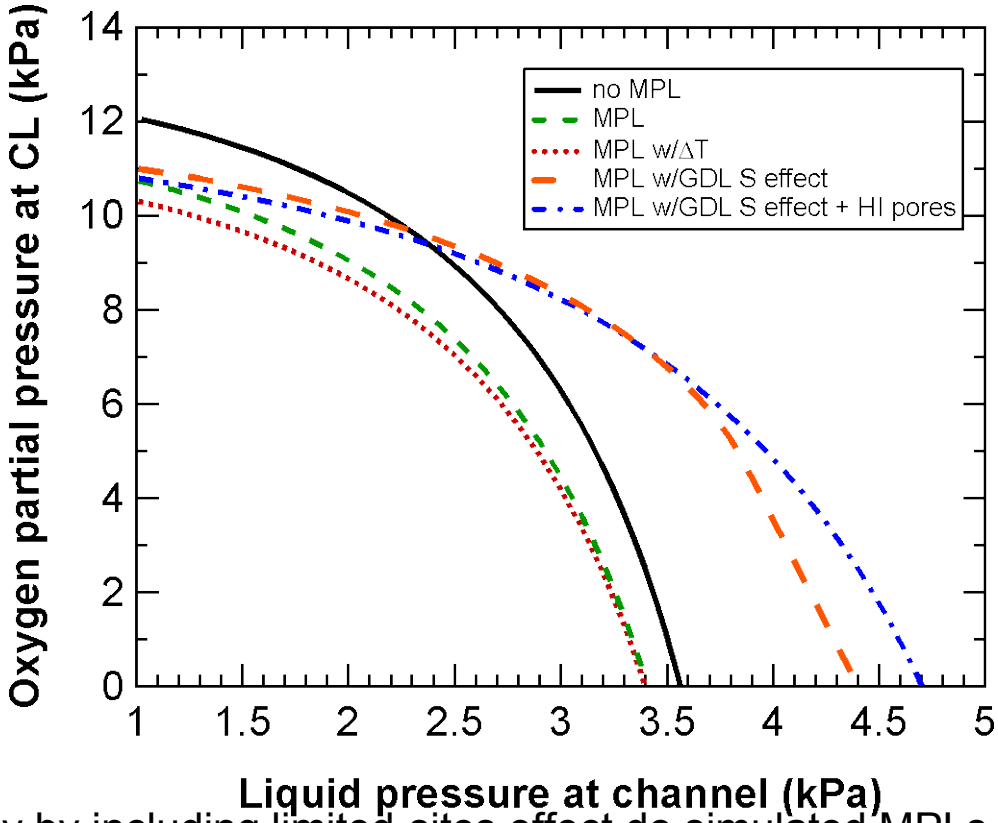


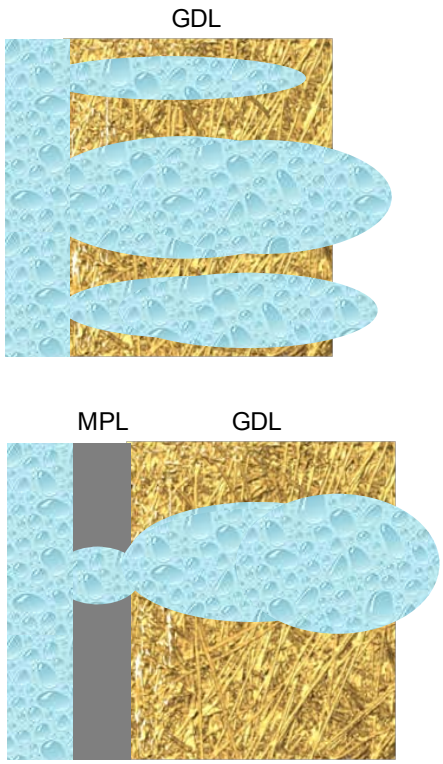
- However, **interfacial conditions** can lead to flooding



MPL Simulations

- MPL functions by limiting the site access of water from the into the GDL
  - Cracks and some hydrophilic pathways





  - Only by including limited-sites effect do simulated MPLs show better performance
  - Might be able to increase performance by engineering such connections

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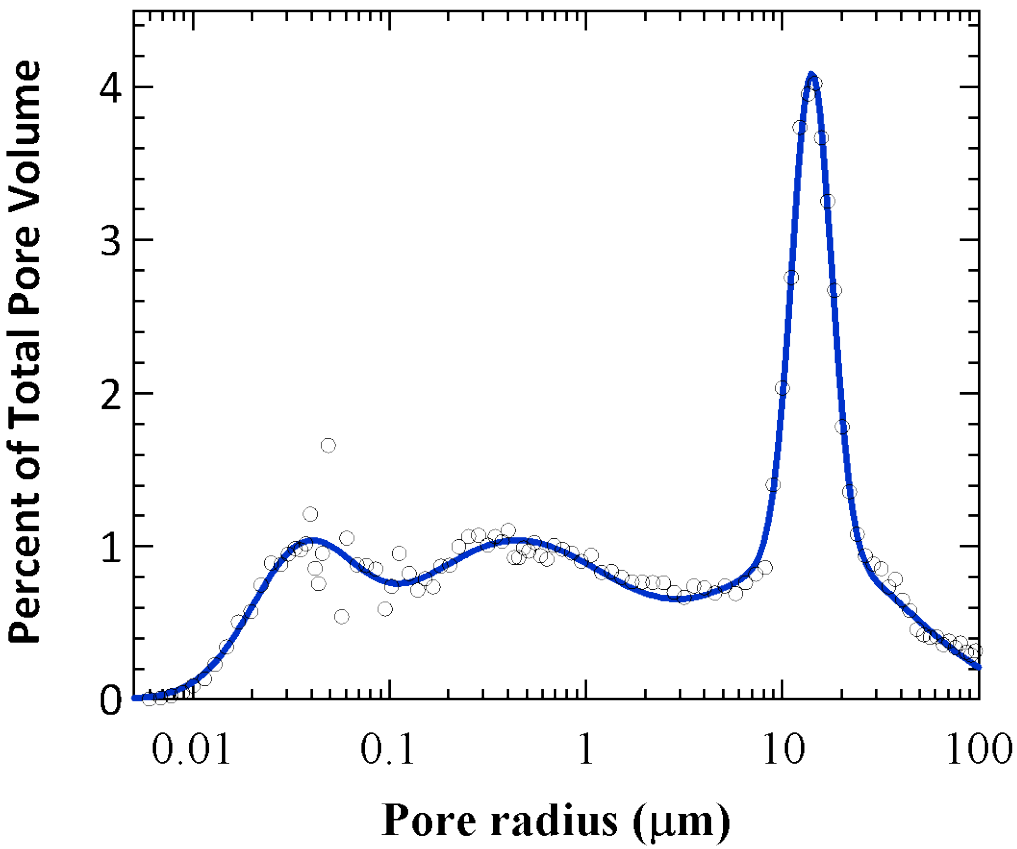
Modeling Approach

- Macrohomogeneous where average over microstructure
- Describe the DM as a function of a structural and chemical part
  - Structure is the pore-size distribution (PSD)
    - Example: DM composed of MPL and GDL

$$V(r) = \sum_k f_{r,k} \left\{ \frac{1}{r s_k \sqrt{2\pi}} \exp\left[-\left(\frac{\ln r - \ln r_{o,k}}{s_k \sqrt{2}} \right)^2 \right] \right\}$$



Los Alamos

Modeling Approach

- Macrohomogeneous where average over microstructure
- Describe the DM as a function of a structural and chemical part
  - Structure is the pore-size distribution (PSD)
  - Chemical is the wettability, which cannot be readily measured so need to infer
    - Use a normal distribution for a contact-angle distribution (CAD)

$$\Psi(\theta) = \sum_n f_{\theta,n} \left\{ \frac{1}{\sigma_n \sqrt{2\pi}} \exp\left[-\frac{1}{2} \left(\frac{\theta - \theta_{o,n}}{\sigma_n} \right)^2 \right] \right\}$$

    - Integrate to determine the property of interest

$$Y = \iint \Psi(\theta) Y(r) V(r) \mathrm{d}r \mathrm{d}\theta = \int_0^{90} \Psi(\theta) \int_0^{r_c} Y(r) V(r) \mathrm{d}r \mathrm{d}\theta + \int_{90}^{180} \Psi(\theta) \int_{r_c}^{\infty} Y(r) V(r) \mathrm{d}r \mathrm{d}\theta$$

Weighting function

$$r_c = -\frac{2\gamma \cos\theta}{p_L - p_G} = \frac{2\gamma \cos\theta}{p_C}$$

    - Fit the property to available experimental data

  - Assume uniform structural and chemical properties

Los Alamos

Water in electrode structures: NMR studies

Che-Nan Sun and Tom Zawodzinski
Case, UT-Knoxville and ORNL

- NMR provides the possibility of probing water motion over various length scales to:
  - Reveal porosity and behavior of water in pores
  - Probe water interaction with ionomer, carbon
  - Provide indirect information on ionomer structure: is transport different within ionomer?

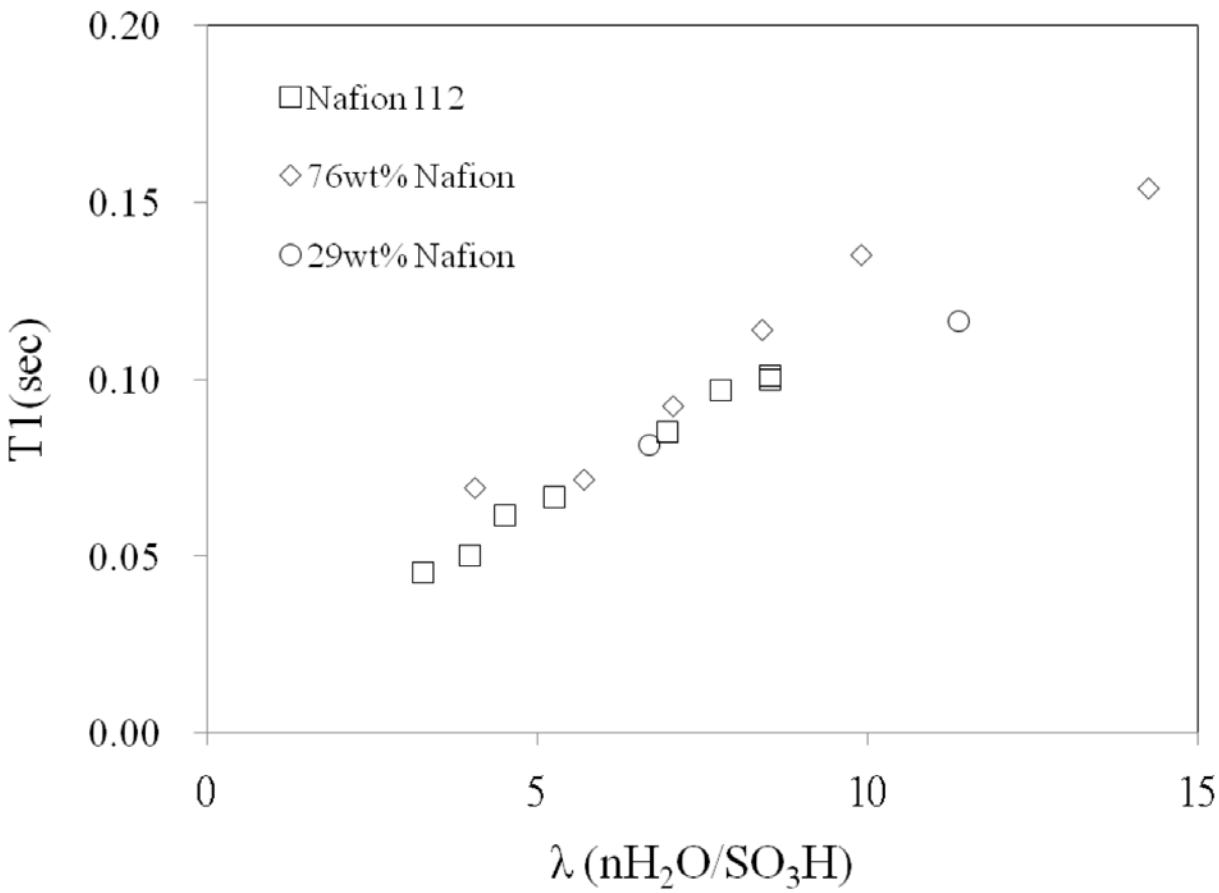
Method determines length scale probed

Relaxation: Nano-scale motion; Diffusion: um-scale motion

Can we even do NMR on Composite Electrodes?

- NMR methods will require well-controlled rf, field gradient pulses
- RF problems: skin depth of conductors
- Gradient pulses: introduce local eddy currents, warp gradient
- Recently introduced technique modifications to remove these effects

Results from NMR Relaxation Measurements on Composite Electrodes (hand-made, in-house)

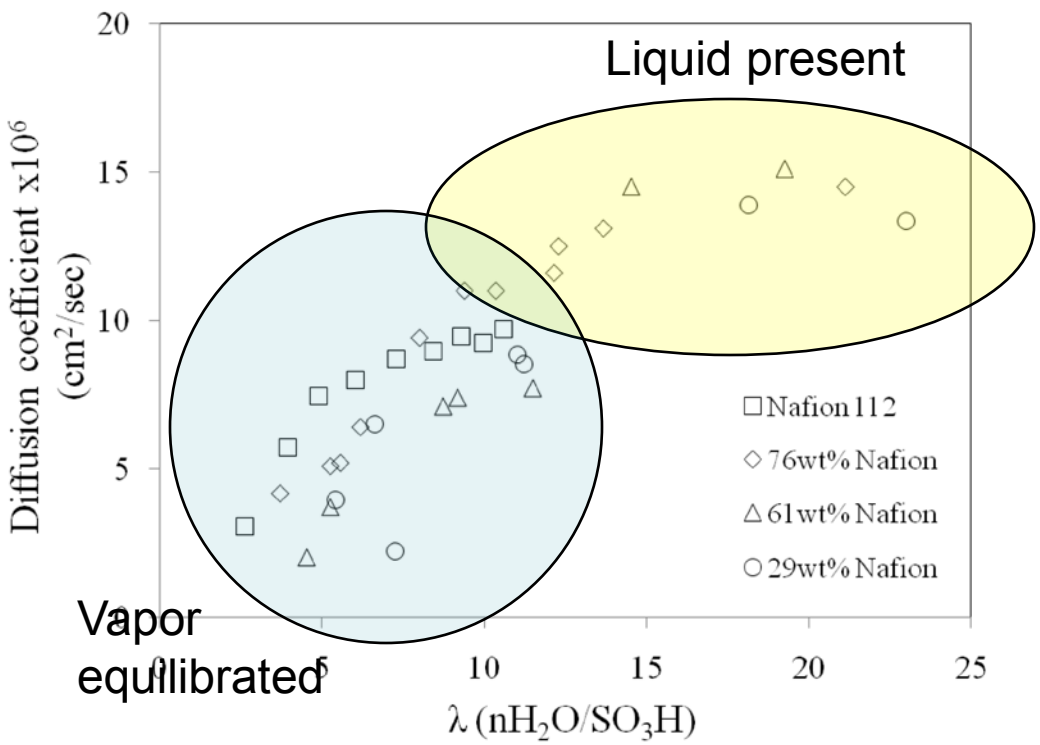


Water motion at short range (nano-scale) is similar to that in bulk Nafion®

→Water rotational motions are controlled by solvation effects

→At higher lambda, water motion is still similar to bulk

Results from NMR Diffusion Measurements on Composite Electrodes (hand-made, in-house)



Vapor Equilibrated: Long-range (micron) water motion is lower than water motion in Nafion® at a given lambda—tortuosity effect

Liquid present: Approaches 'free" water motion

Conclusions:

(1) Nafion® present in distributed bulk-like phases

(2) Water pores/ Nafion® well-connected