

Water Transport Exploratory Studies

2009 Fuel Cell Seminar

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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

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) – $\lambda = 14$ RH=100, $\lambda = 22$ 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.*

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

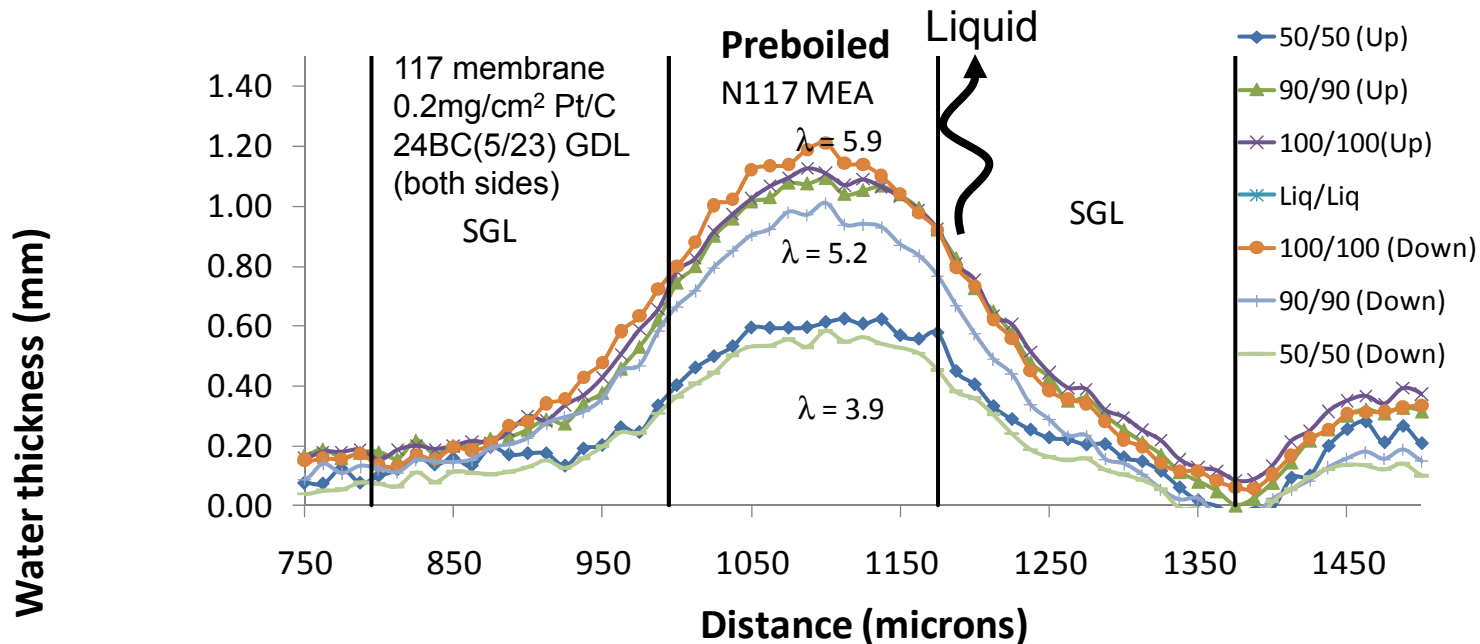
Predried membrane: $\lambda = 13-14$

Preboiled membrane: $\lambda = 23-24$

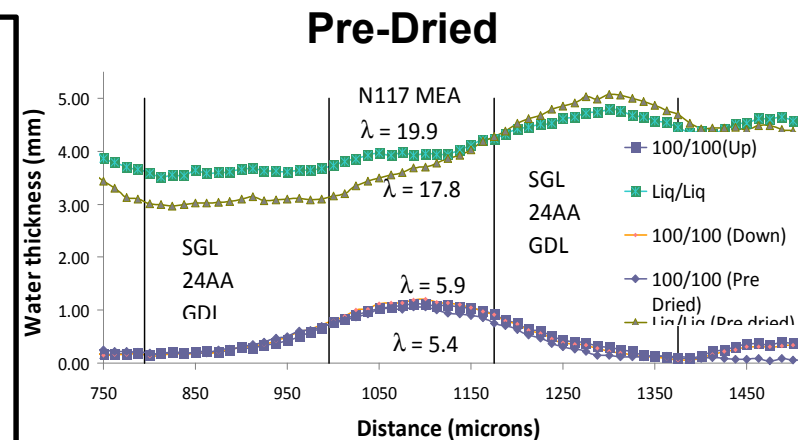
Membrane water content is a function of thermal history, with no difference in membrane water content between liquid water and vapor (100%) water

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

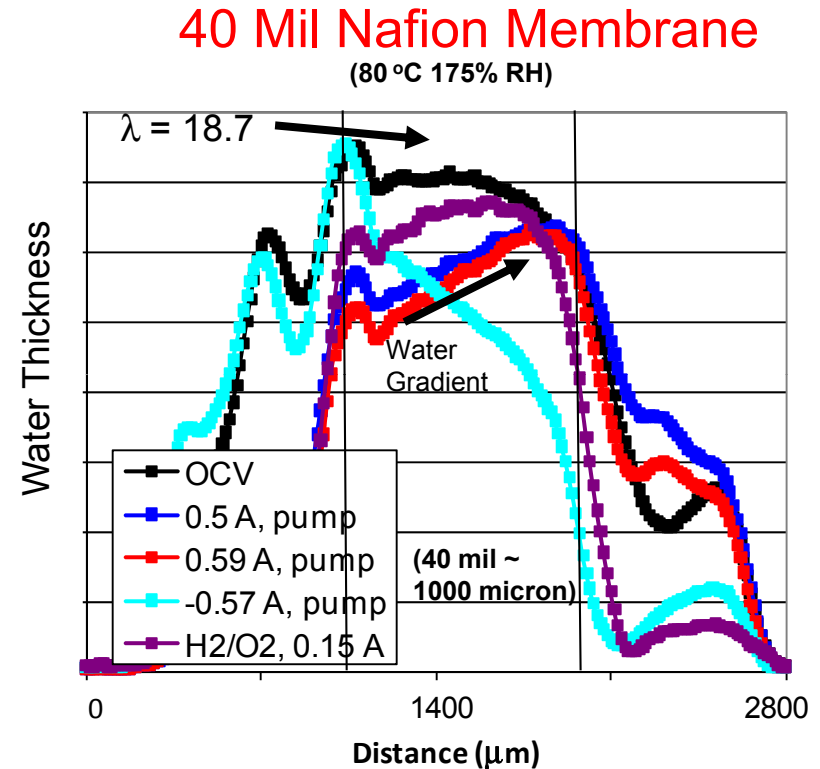
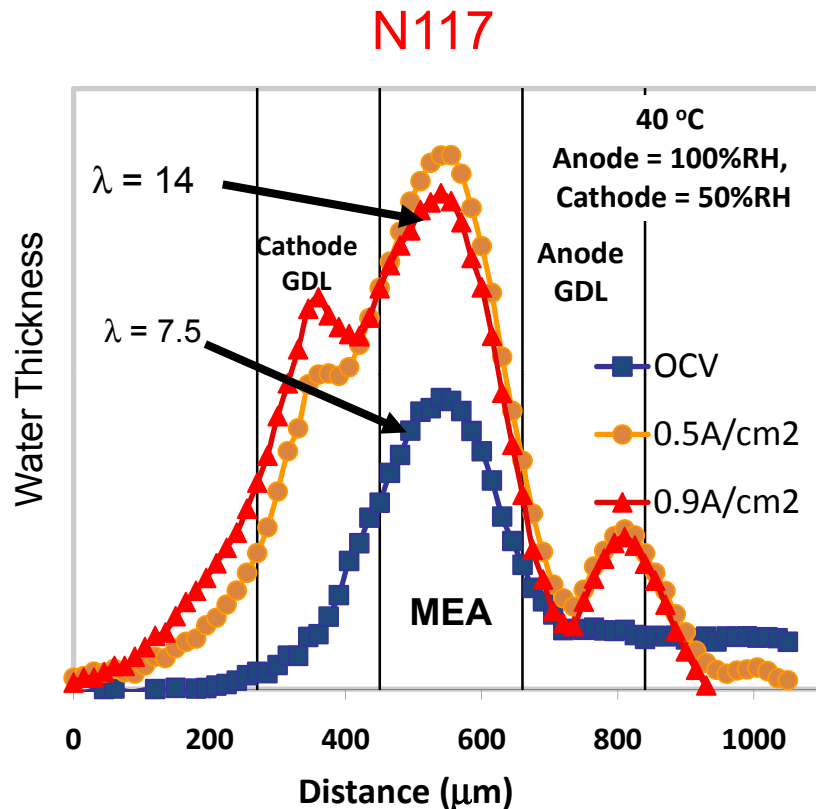
in situ Measurements Verifying Schroeder's Paradox



- 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 Schroeder's Paradox
- Preboiled and Predried Membranes show same dependence on membrane water content between vapor and liquid water



Water Profiles for Different Membrane Geometries



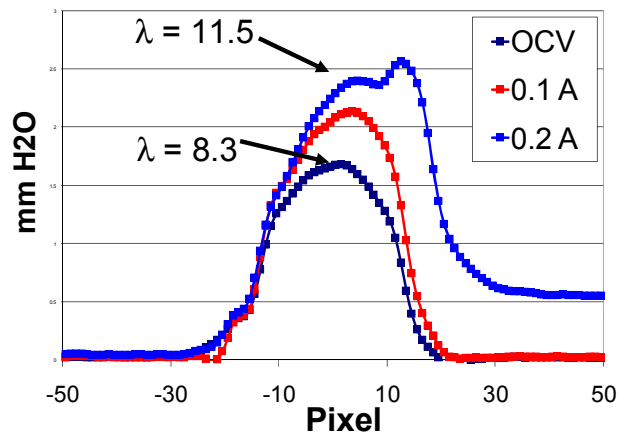
- Interface between membrane and catalyst layer maybe hydrophilic
 - Water peaks near each of the catalyst layers (liquid water in catalyst layer pores)
- Can clearly distinguish membrane profiles
 - FWHM ($\approx 100 \mu\text{m}$) is much smaller than membrane thickness ($\approx 585 - 1000 \mu\text{m}$)
- Water gradient formed at saturated conditions by H_2 pump

Acknowledge: Steve Grot, Ion Power

20 mil Nafion Membrane

(RH Equilibration, Fuel Cell and H₂ Pump Operation)

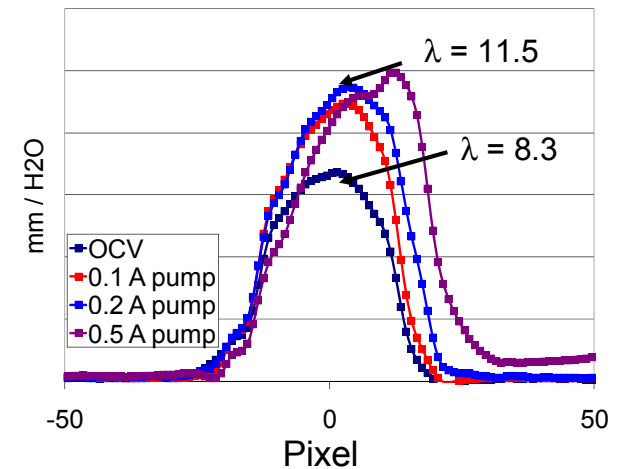
Fuel Cell Operation



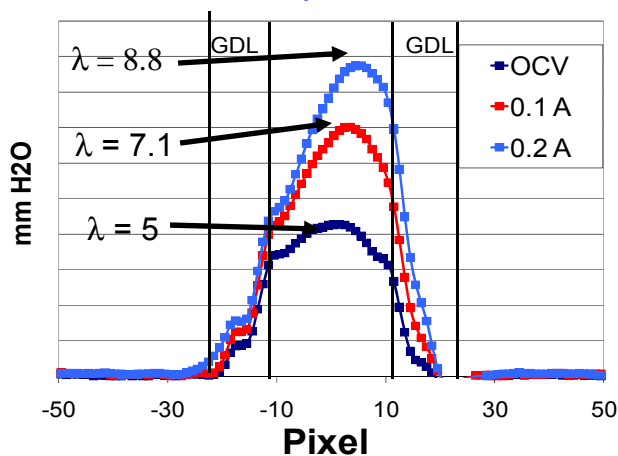
100/100 % RH 40 C

- 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

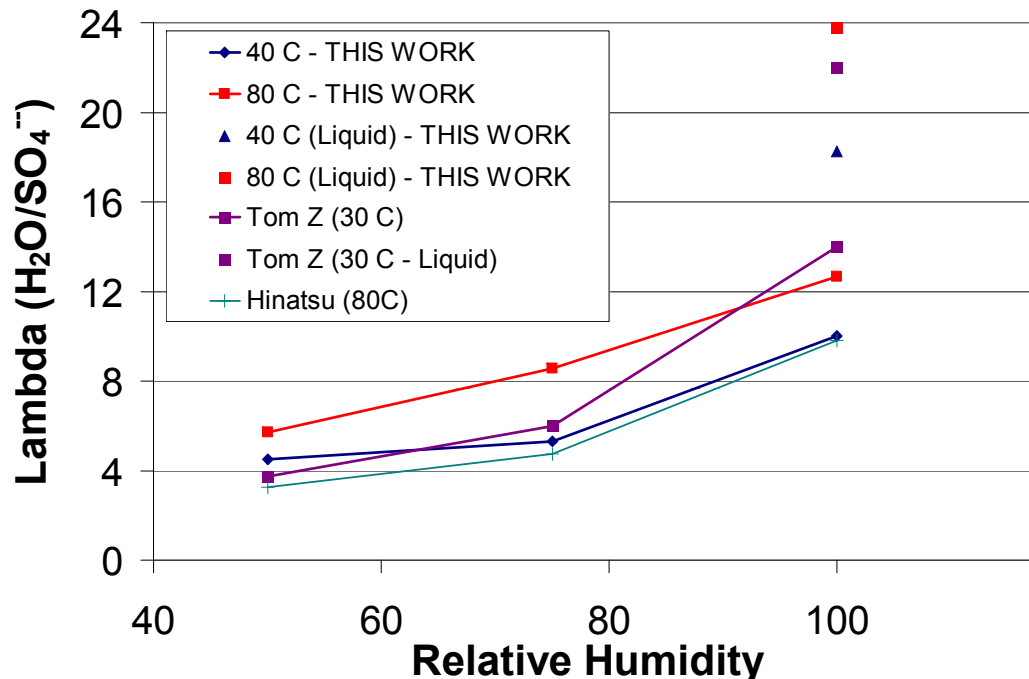


50/50 % RH, 40 C – Fuel Cell Operation



- 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:

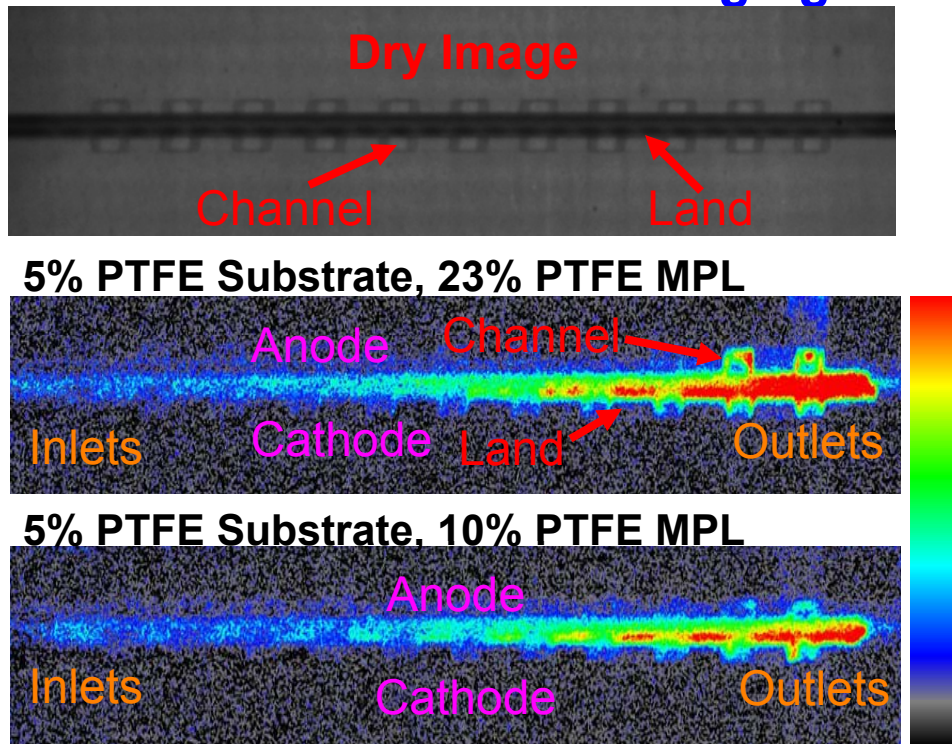
Tsushima, Shoji, **Water Transport Analysis by Magnetic Resonance Imaging**, LANL/AIST Meeting, San Diego, 2008

A. Isopo, V. Rossi Albertini, **An original laboratory X-ray diffraction method for *in situ* investigations on the water dynamics in a fuel cell proton exchange membrane**, Journal of Power Sources 184 (2008) 23–28

GDL Teflon Loading Effect on Water Content

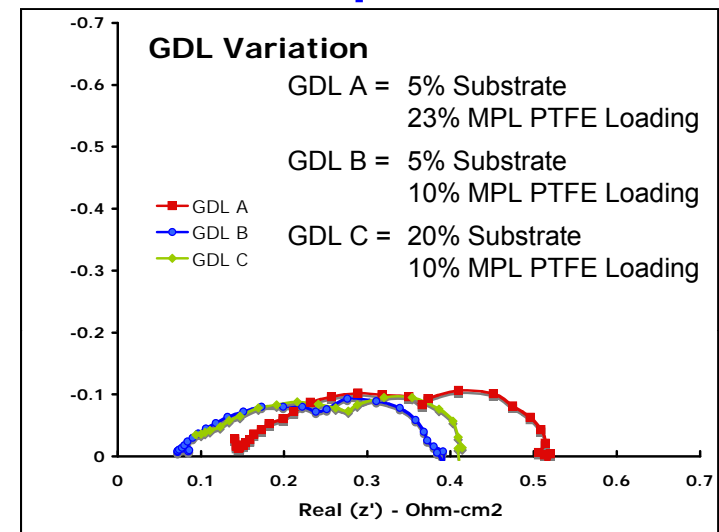
Monitored by Neutron Imaging and AC Impedance

Cross-section Neutron Imaging



- More PTFE in the MPL results in more water in GDLs and channels
- Mass transport limitations consistent with lower performance of fuel cells with high MPL Teflon loading at high current densities

AC Impedance

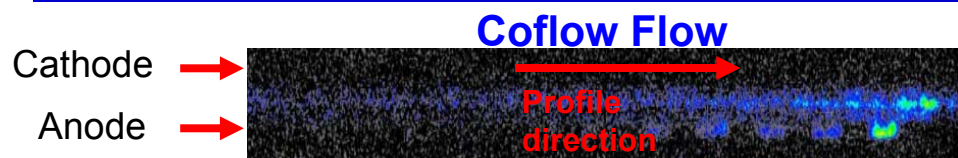


- Charge transfer resistance
 - Decreases with increasing current
 - Greater for GDL with 23% PTFE in MPL
- Mass transfer resistance
 - Increases with increasing current
 - Greater for GDL with 23% PTFE in MPL

Co-Flow, 80 °C, 172 kPa (abs)
 Anode: 1.1 stoich. / 50 % RH
 Cathode: 2.0 stoich / 100 % RH

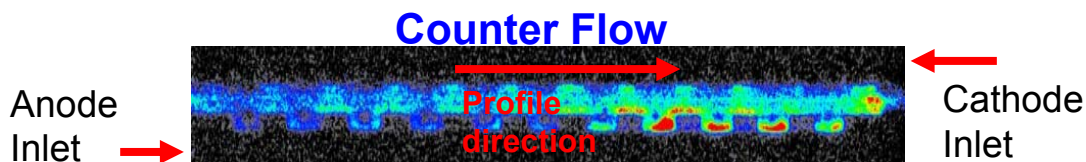
Cell Length Water Profiles

Co-flow vs. Counter flow



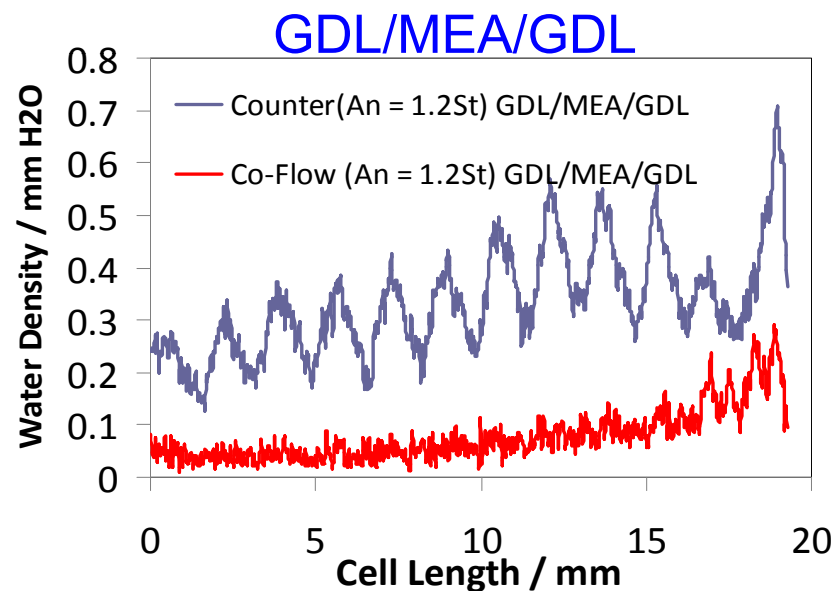
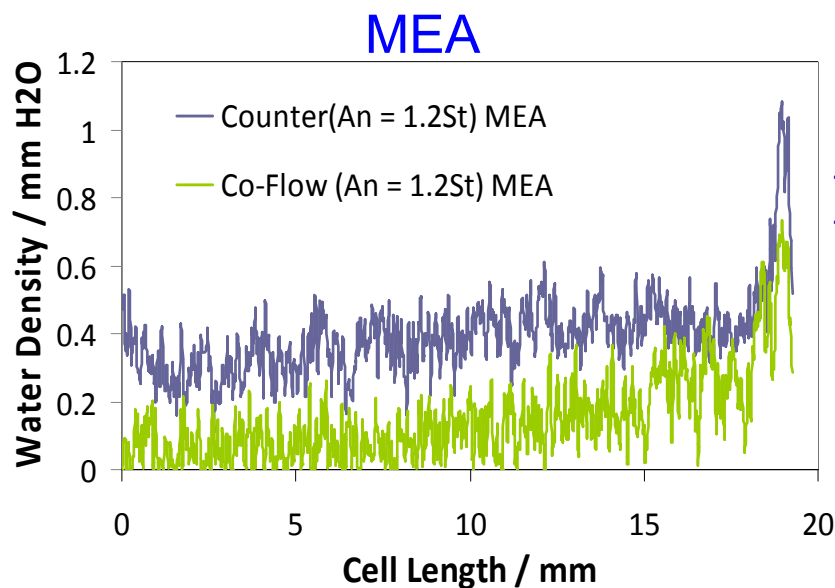
Co-flow :

$I = 1.41 \text{ A/cm}^2$; $V = 0.095 \text{ V}$
HFR = 0.10 Ohm.cm^2



Counter Flow :

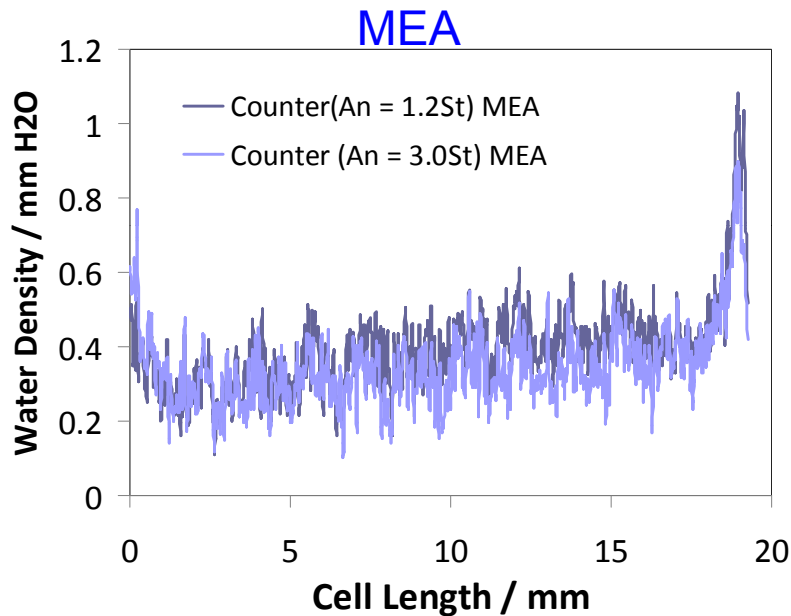
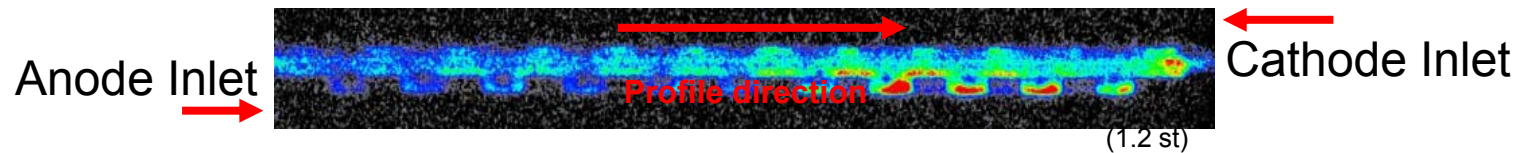
$I = 1.49 \text{ A/cm}^2$; $V = 0.27 \text{ V}$
HFR = 0.064 Ohm.cm^2



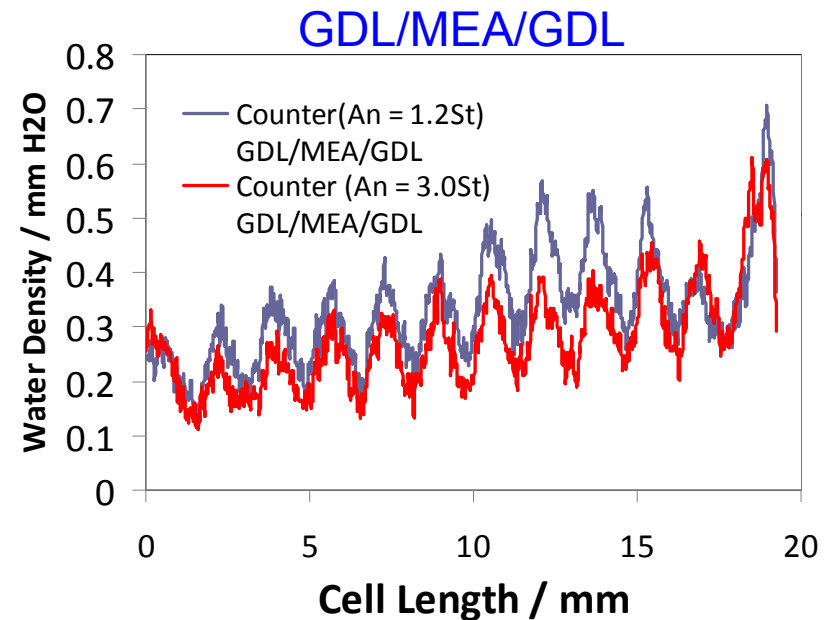
- Higher membrane water with counter flow
- Membrane water correlates to lower HFR and higher performance with counter flow

Cell Length Water Profiles

Anode Stoich comparison



100 / 0 % RH,
1.2 vs. 3.0 st.
simulating
anode recycle

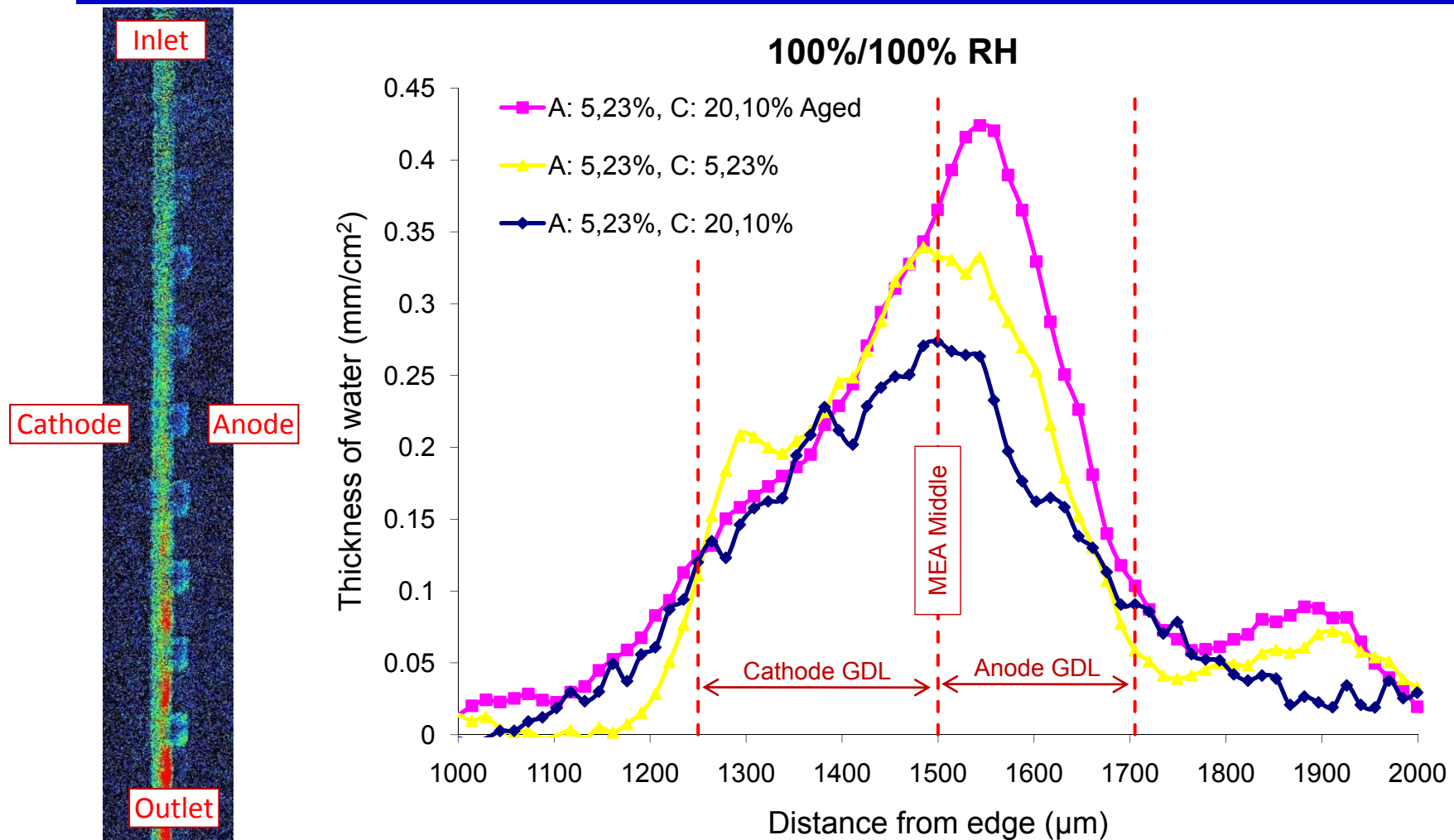


Counter Flow : 3.0St
I = 1.49; V = 0.27; HFR = 0.076

Counter Flow : 1.2St
I = 1.49; V = 0.27V; HFR = 0.064

- MEA water content ~ same
- Higher anode stoich: lower land water
- Similar Performance

GDL Hydrophobicity and Aging Effect on Water Concentration

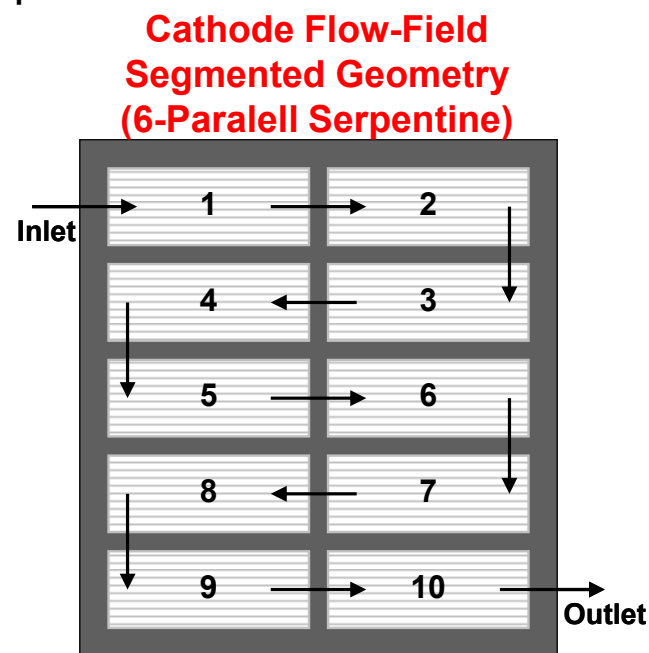


- Higher hydrophobicity shows lower water content
- Aged GDLs show more water on the anode side

In-Plane GDL Performance Improvement

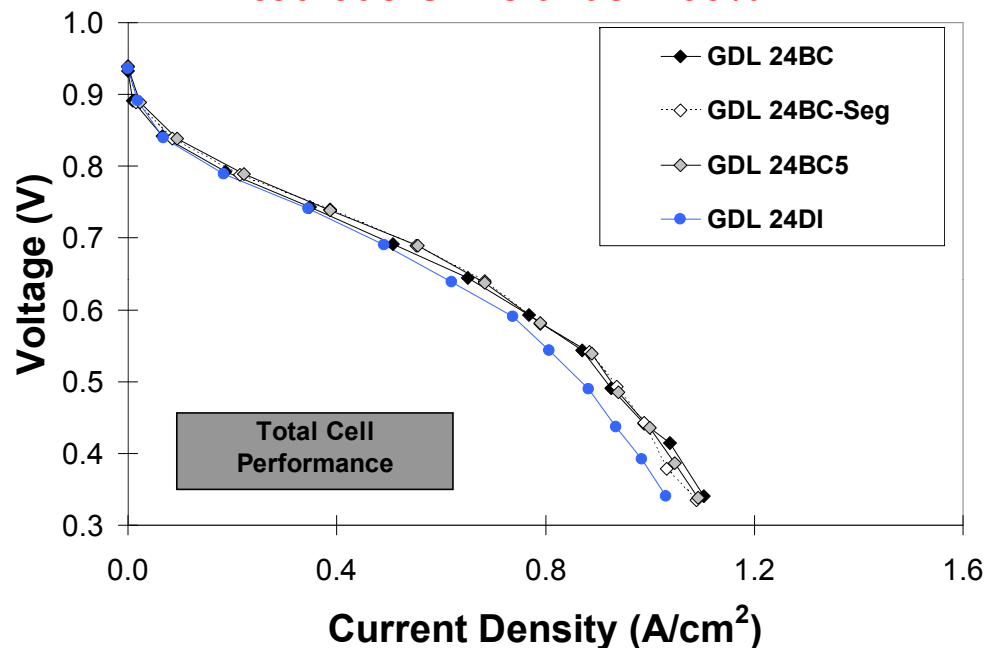
- Examining the cell performance with varying GDL materials in the different segmented regions
- Evaluate water and MT limitations with different operating conditions (100% RH and 50% RH)
- Design an improved in-plane GDL material
 - Basic principle selected GDL segments based on the 50% RH performance 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

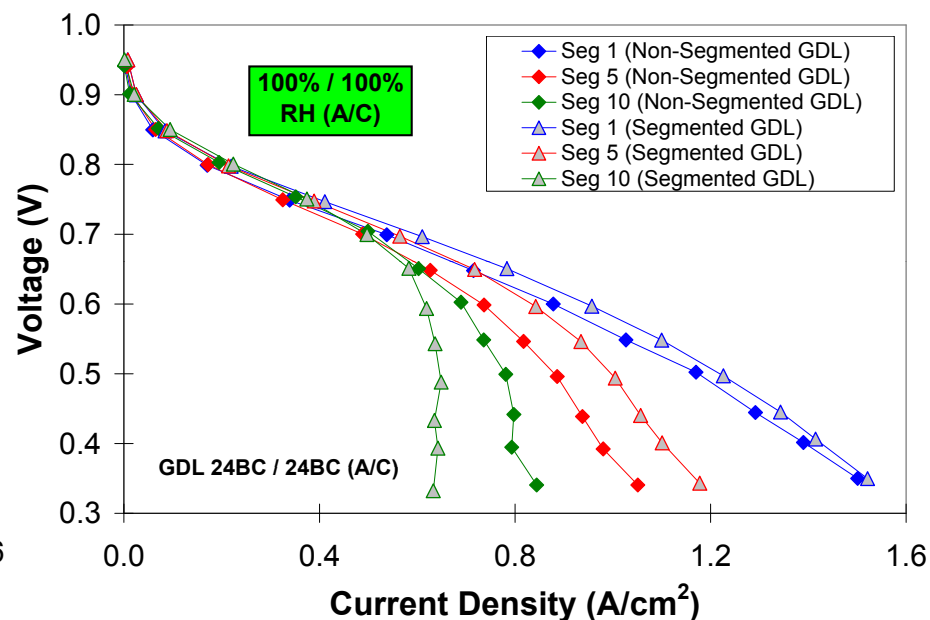


Segmented Cell Measurements (100% RH)

Total cell polarization data comparing cathode GDLs under 100% RH



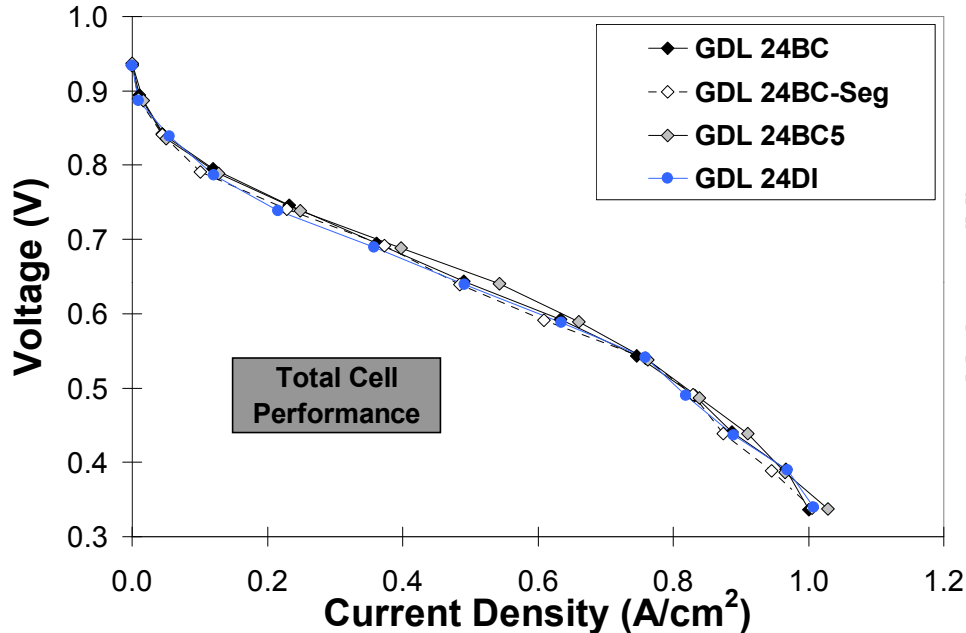
Segmented cell polarization data under 100% RH



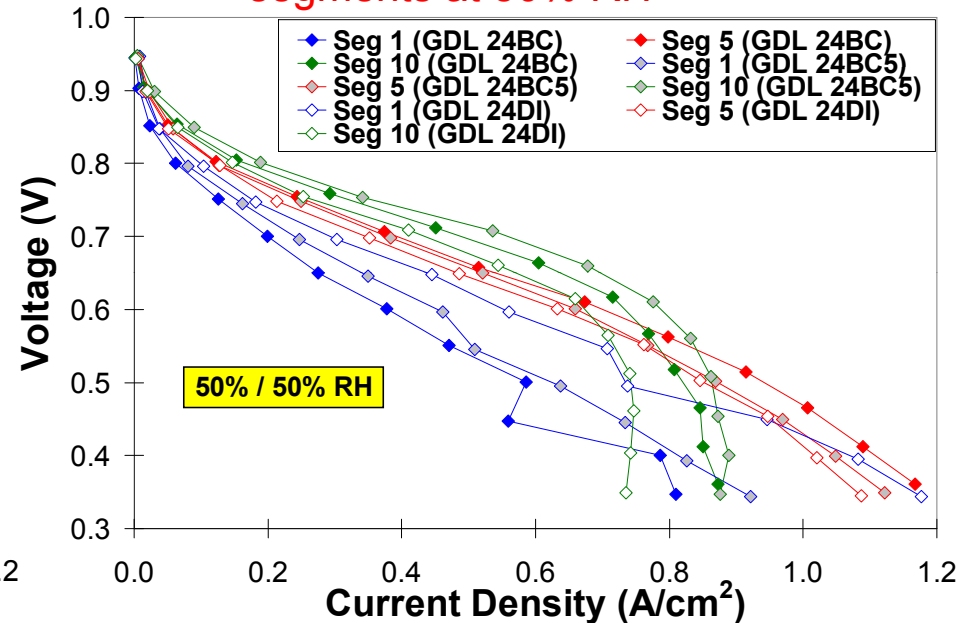
- Total cell performance nearly identical for 24BC, 24BC5, lower for 24DI
 - (24BC and 24BC-Seg are different experimental methods)
- Highest performance for all GDLs in segment 1
 - Later segments have reduced performance, especially at higher current densities due to MT limitations

Segmented Cell Measurements (50% RH)

Total cell polarization data comparing cathode GDLs under 50% RH



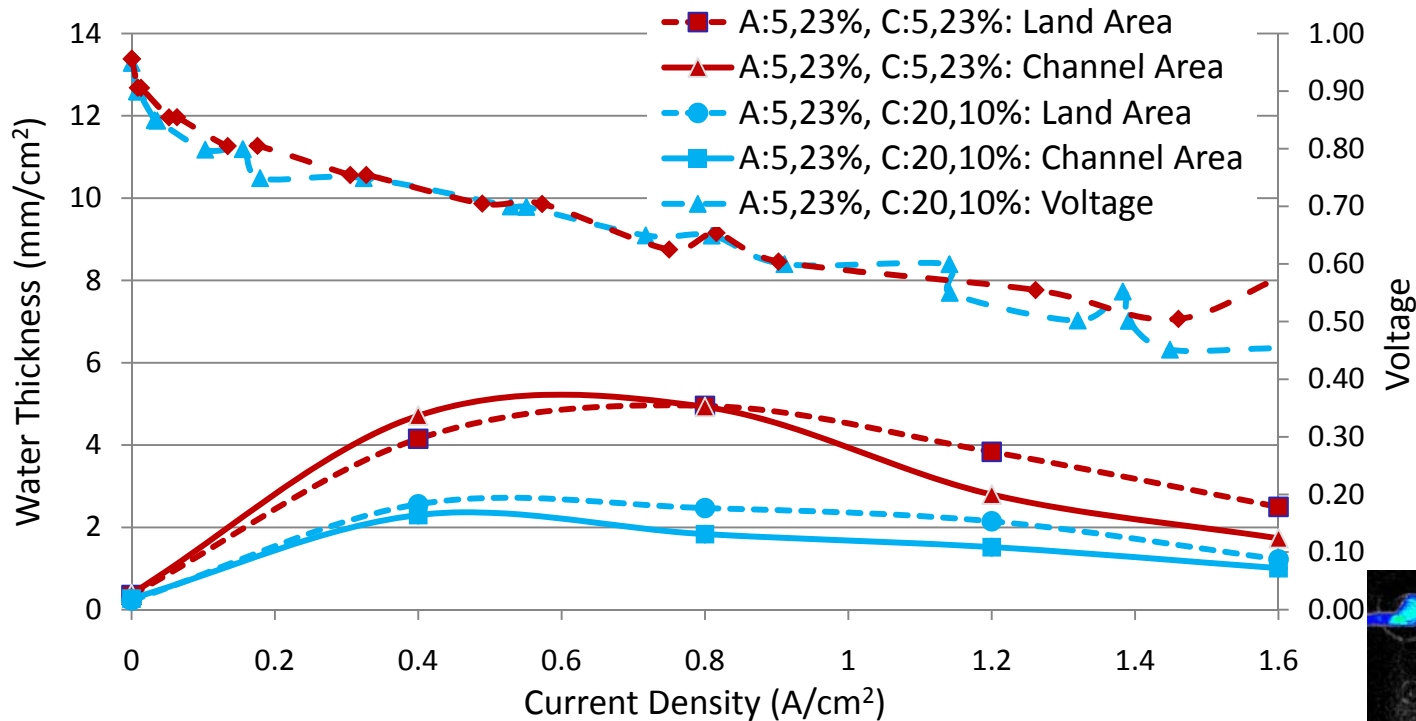
Polarization data for different segments at 50% RH



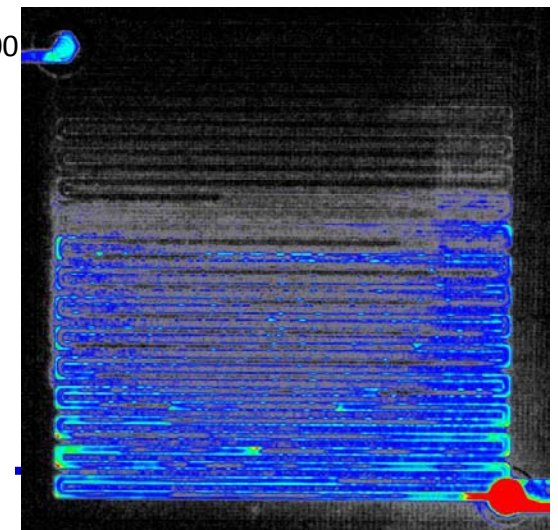
- At 50 % RH Total cell performance is ~ identical for 24BC, 24BC5, 24DI
- Highest low current performance for all GDLs in segment 10
- Highest high current performance occurs in the middle of the cell (~ segment 5)
 - Earlier segments have reduced performance due to limited membrane conductivity
 -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

Water Concentration Lands vs. Channels

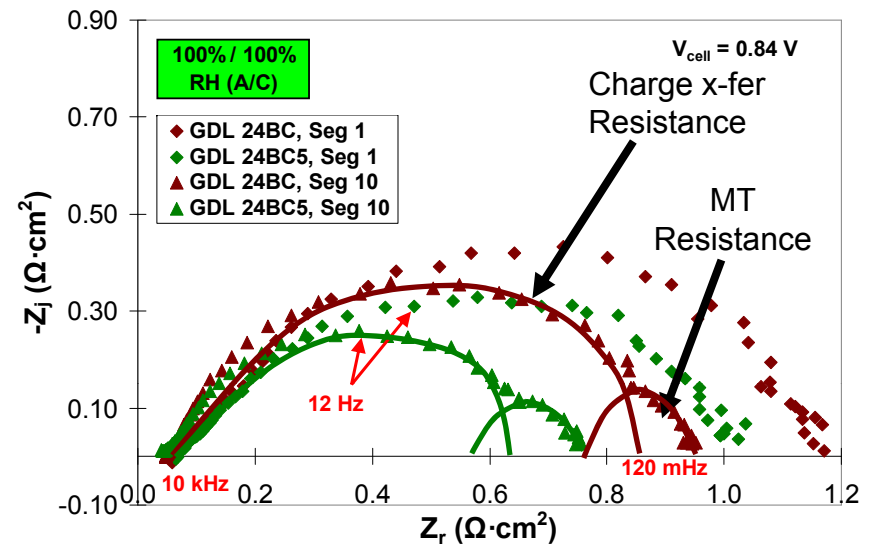
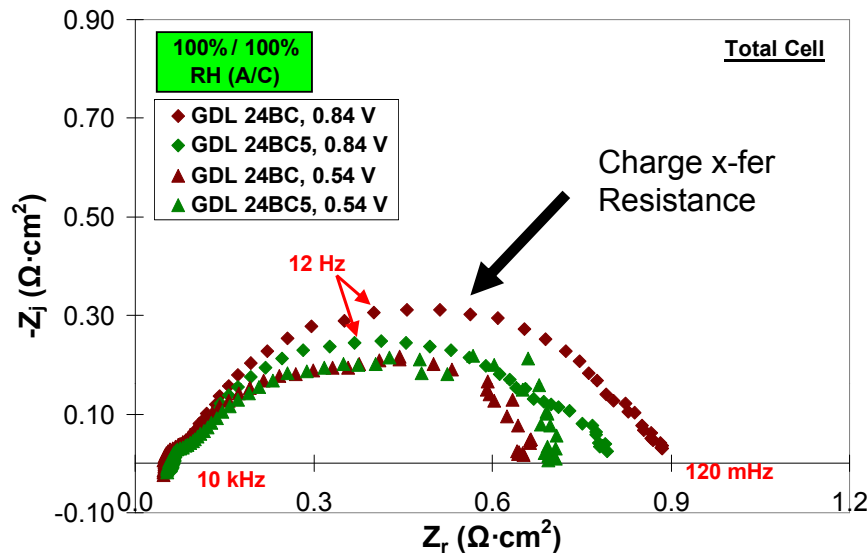
50 cm² Fuel Cells: 50%/50%RH



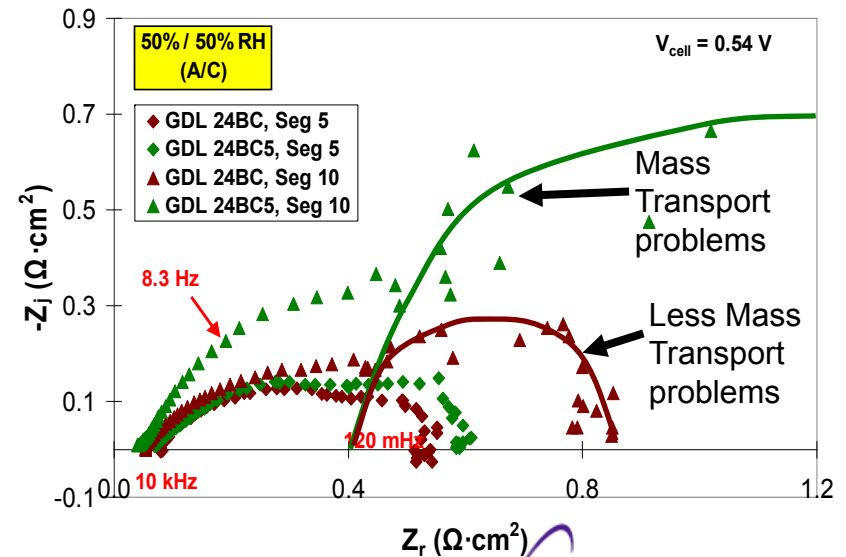
- Water is very different: 5/23%, 5/23% cell has much higher water content
 - Performance is similar
- From high-res analysis, we know that most of the water is on the cathode substrate



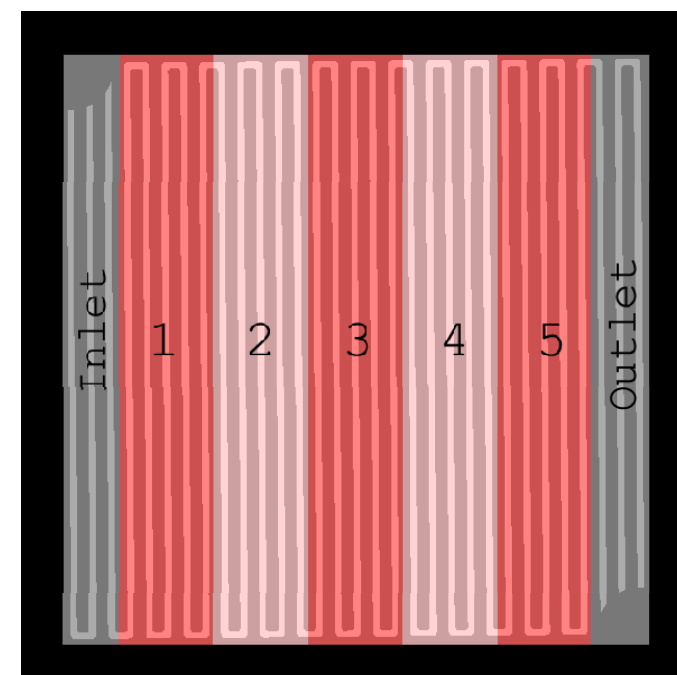
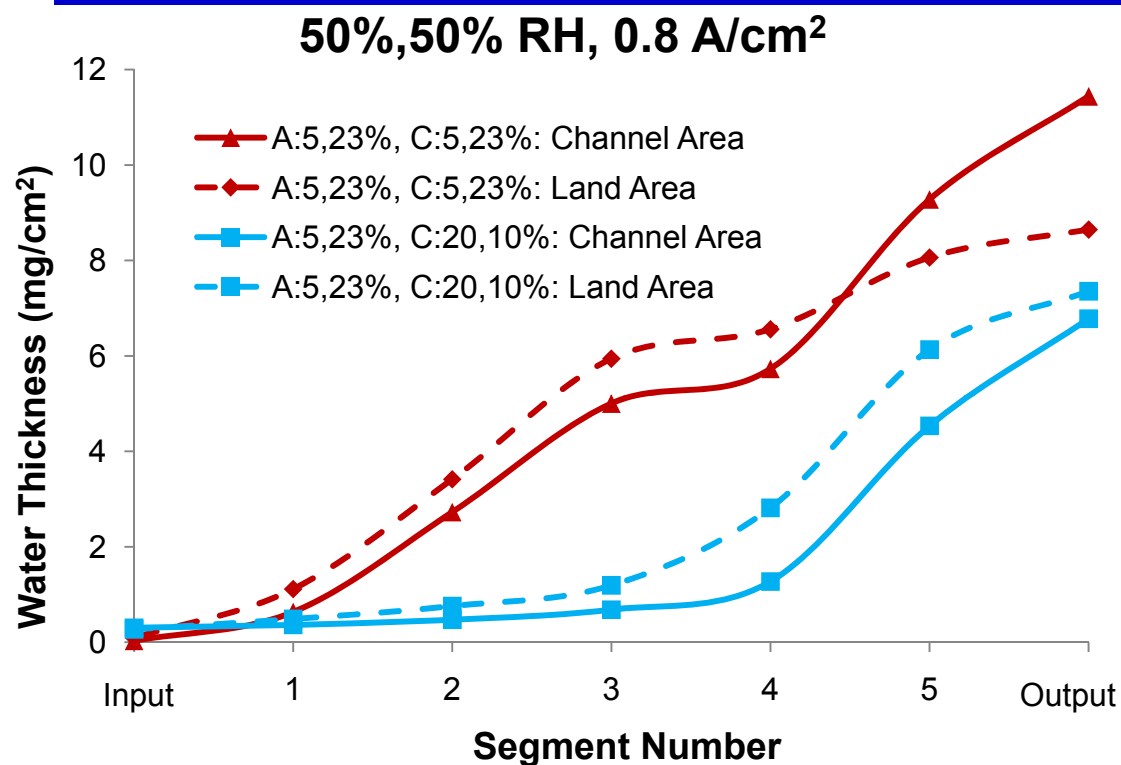
AC Impedance Data of Different Segments for Different Cathode *GDLs*



- 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.



Water Concentration Lands vs. Channels in Different Segments



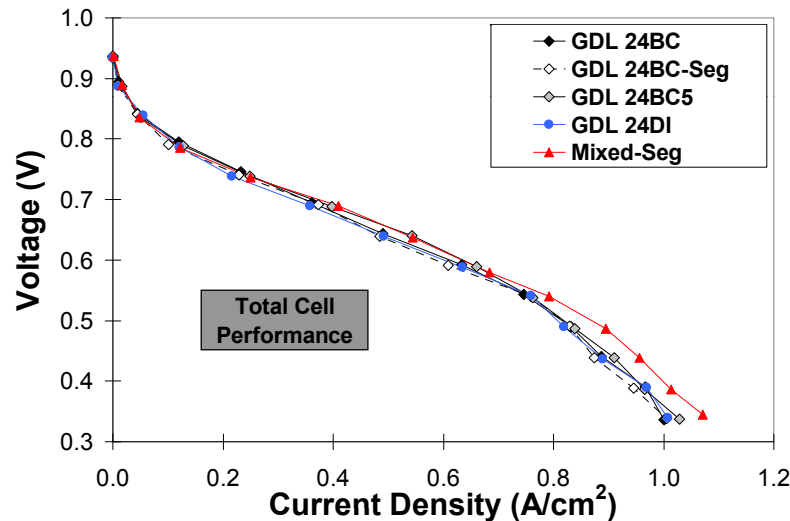
- Segmenting was done on the same cells from previous, and as shown in the above diagram
- The cells get wetter at an earlier point for the 5/23%, 5/23% cell

Simple Optimization Strategy

- At 50% RH:
 - Best inlet performance: GDL 24DI
 - Higher water holding capacity due to its high substrate PTFE loading. (20%)
 - Best middle cell performance : GDL 24BC
 - GDL with high water removal characteristics.
 - Best outlet performance at the outlet: GDL 24BC5
 - GDL with higher water removal characteristics (under dry conditions) because of its high surface energy MPL and low substrate PTFE loading.
- 1/3: GDL 24DI (20%/10%)
- 2/3: GDL 24BC (5%/23%)
- 3/3: GDL 24BC5 (5%/5%)

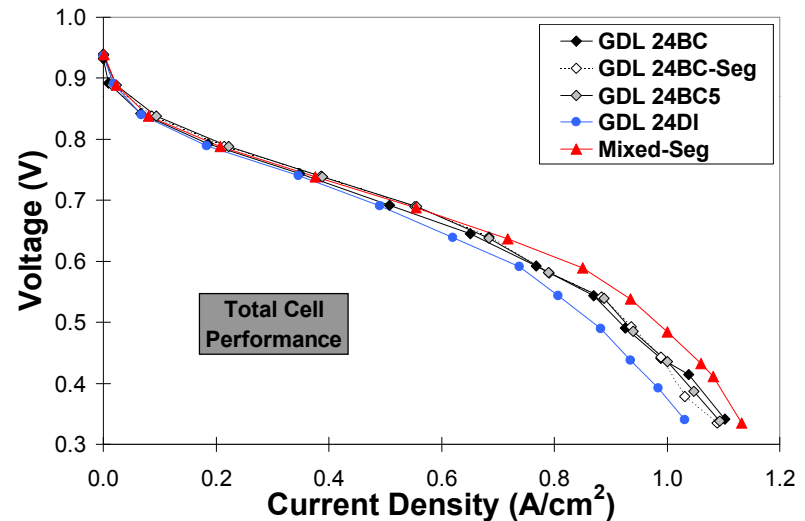
Mixed GDL Performance

Total cell polarization data comparing cathode GDLs at 50% RH



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

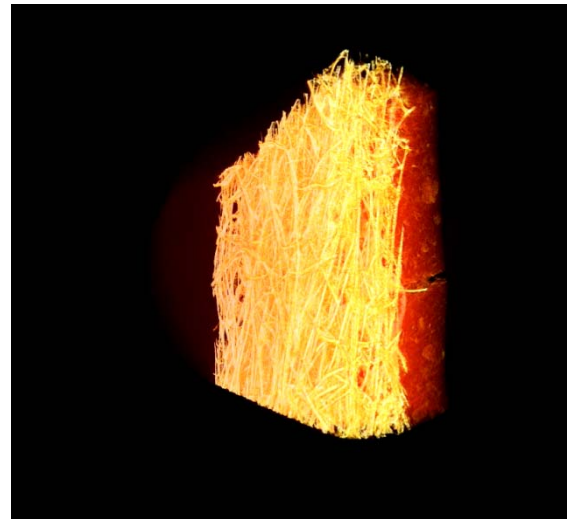
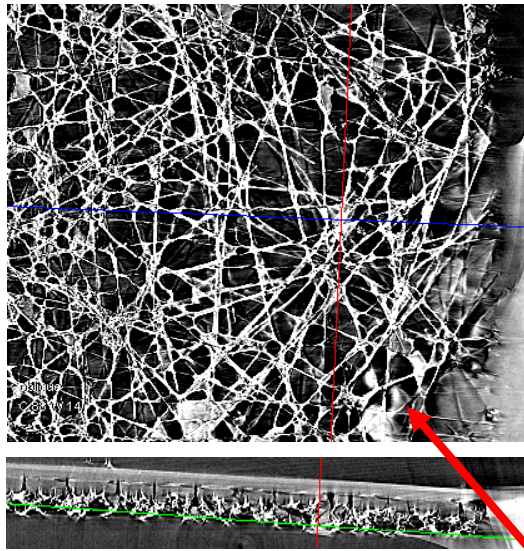
Total cell polarization data comparing cathode GDLs at 100% RH



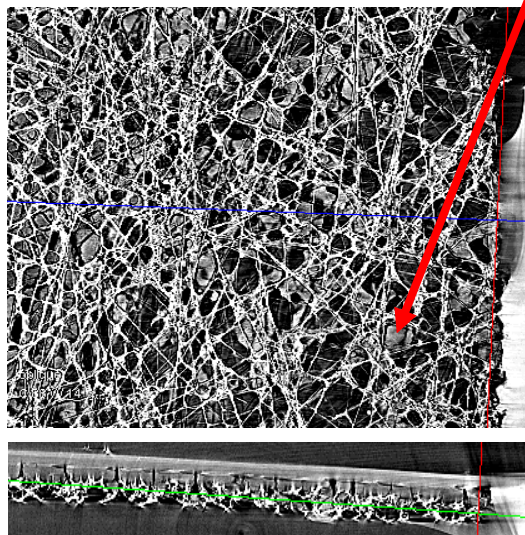
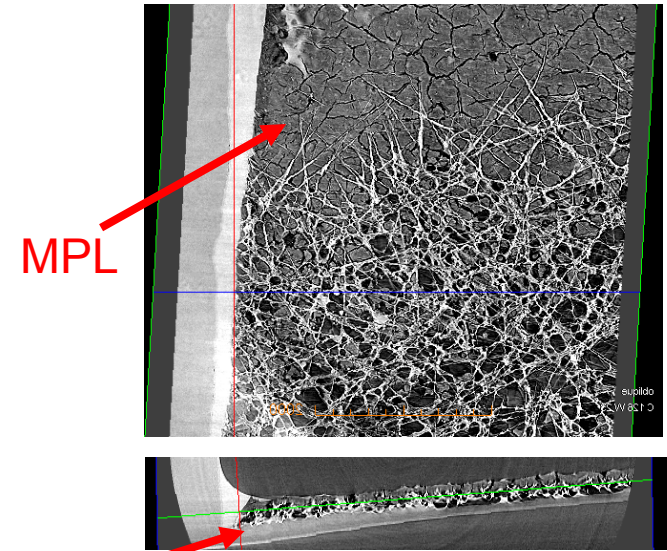
Mixed GDL:
GDL 24DI in segments 1-3
GDL 24BC in segments 4-7
GDL 24BC5 in segments 8-10

X-RAY Tomograph Image of water in GDL Pores

(23% PTFE MPL
20% Substrate)



5% PTFE MPL
5% Substrate)

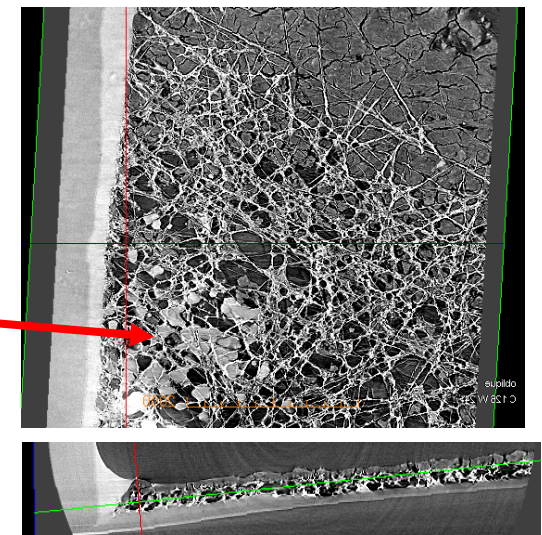


Water

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

Water

Water



Summary of Technical Accomplishments

Water management critical to optimal PEM fuel cell performance

- Varying MPL and substrate Teflon loadings and cell operating conditions
 - Using Neutron imaging, AC impedance to get data about water content and performance
 - When the three different GDL types were arranged in a mixed configuration, an improvement over the base case GDL 24BC (5/23 wt% PTFE substrate/MPL) of 11% and 8% in current density at 0.6 V was seen for wet and dry conditions, respectively.
- Equilibrium water content in the membrane, how membrane water content changes with RH, T, current and water production
 - Measured water content in membranes lower than ex situ equilibrium measurements
 - Verify existence of Shroeder's Paradox by in situ measurements
- 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

Thanks to

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