in situ PEM Fuel Cell Water Measurements

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Presented by: Rod Borup

Los Alamos National Lab

Rod Borup, Rangachary Mukundan, John R Davey, Jacob Spendelow, Partha Mukherjee, Roger Lujan

National Institute of Standards and Technology

David Jacobson, Daniel Hussey, Muhammad Arif

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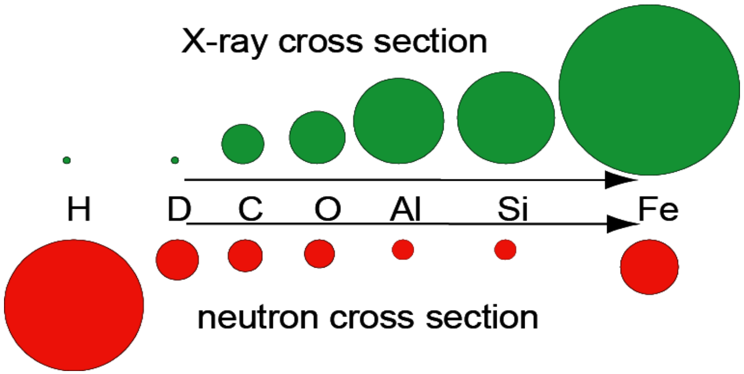
Approach

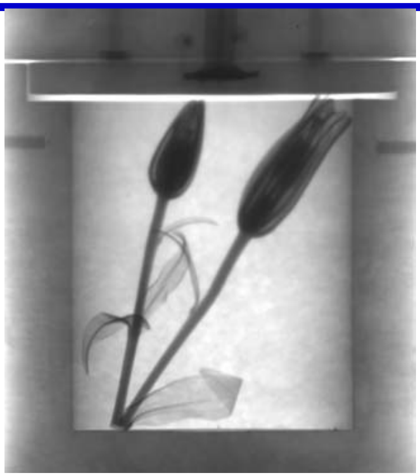
- **Experimentally measure water *in situ* operating fuel cells**
  - Neutron Imaging of water
  - HFR, AC impedance measurements
  - Segmented Cells (coupled with AC impedance)
  - X-Ray tomography

- **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

Neutron Imaging & PEMFCs





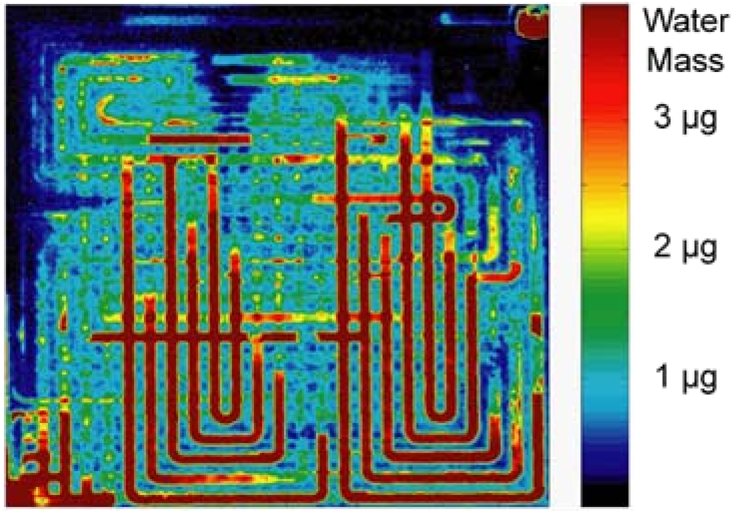
$I = Io \exp(-\mu t)$

Io = reference (dry) image

I = attenuated (wet) image

m = attenuation coefficient of water

T = water thickness

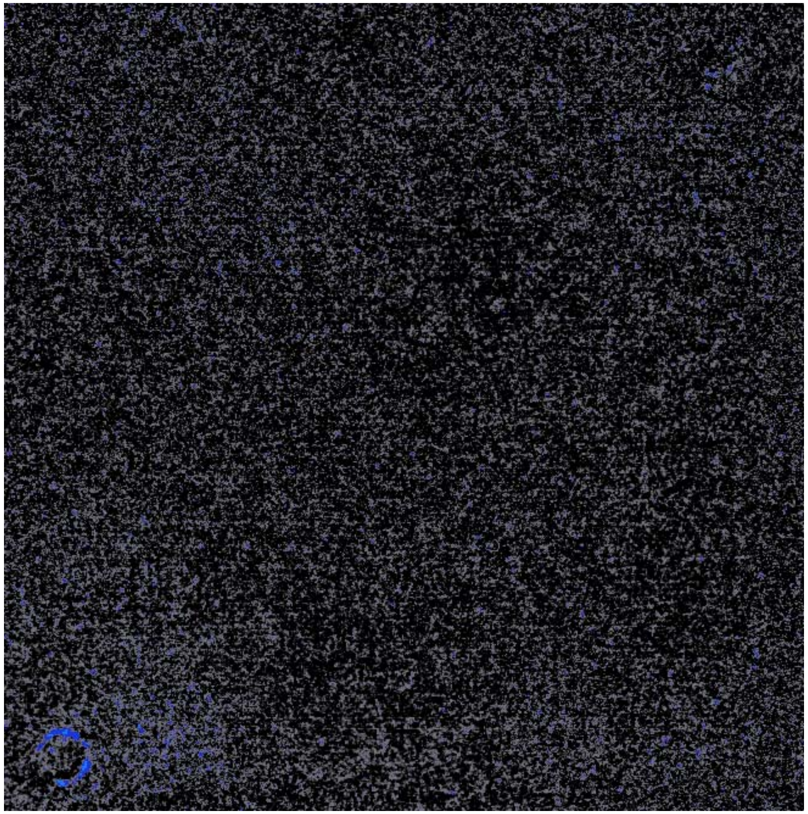


- Subtle changes in the water distribution inside a fuel cell impact performance and durability
- Neutron Imaging measures small changes at video frame rate
  - (amorphous Si Detector)

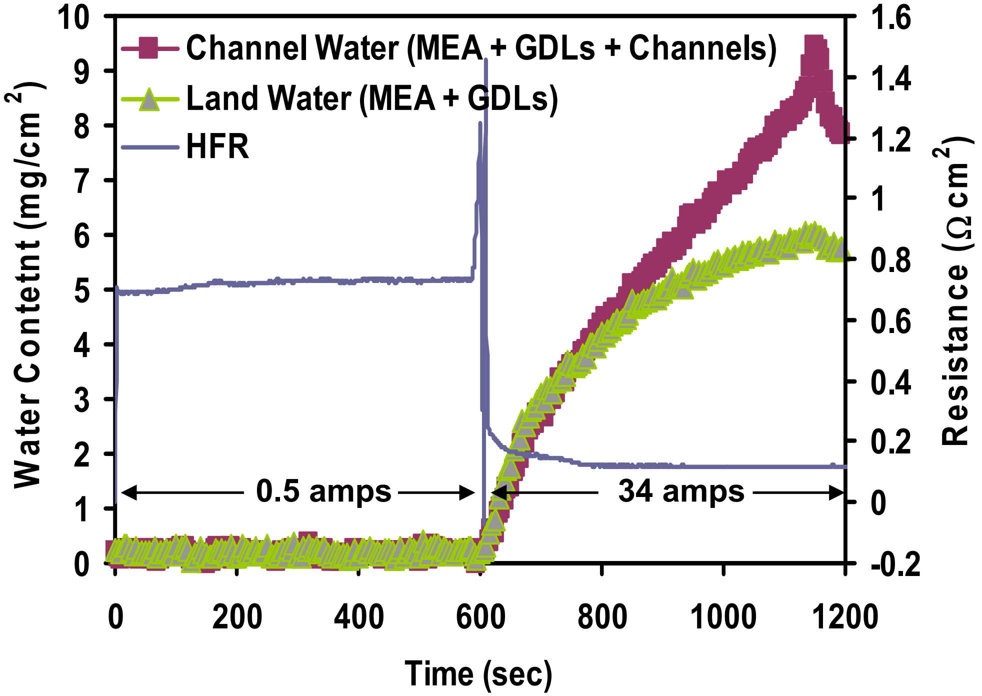
Wetting Transient

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.

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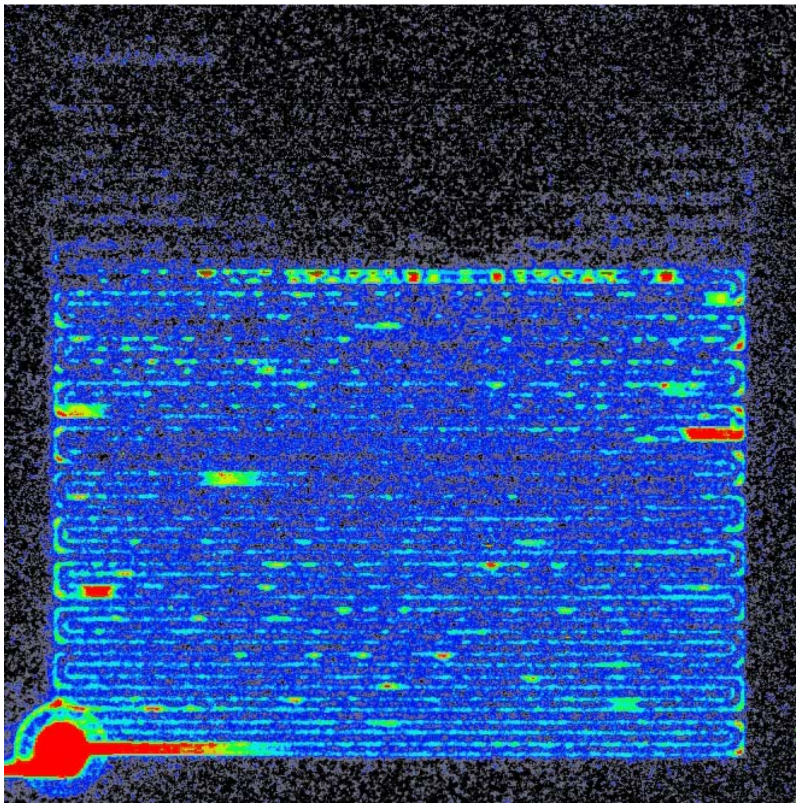
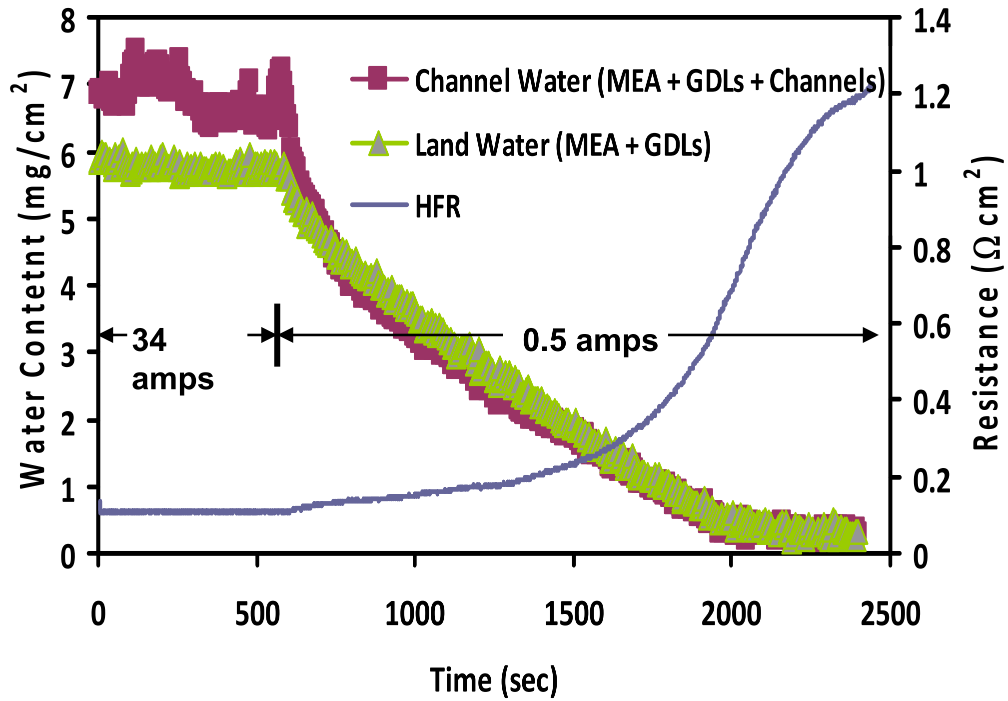
Drying Transient

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

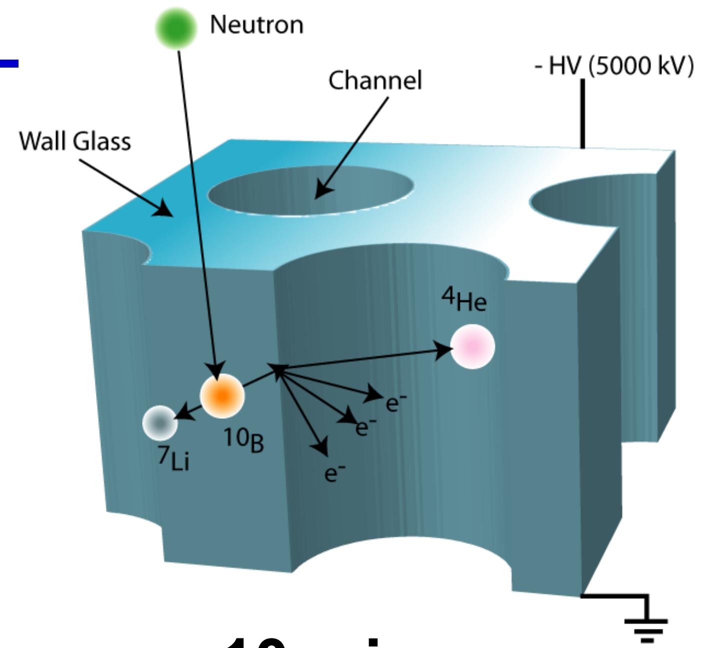


- **Wetting response is faster (10 – 30 sec) than the reciprocal drying response (~ minutes)**
  - **Wetting response is the result of water produced at cathode which quickly back diffuses to into the membrane.**
  - **Drying response requires water to move out of the MEA through wetted GDLs.**

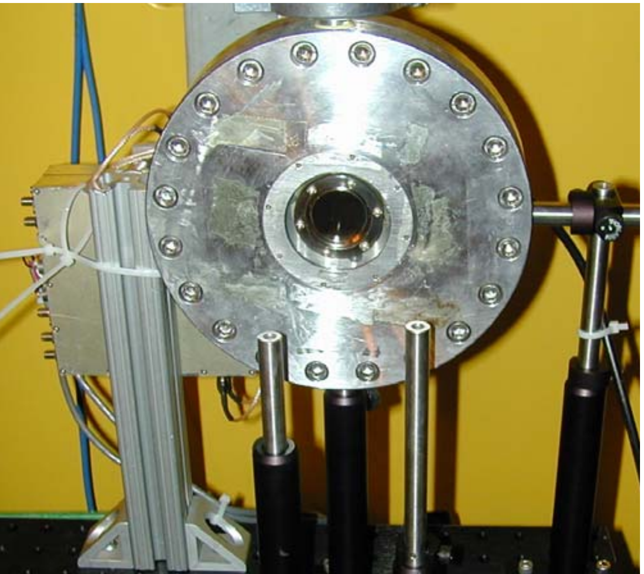
Neutron Imaging with MCPs

$^{10}B \rightarrow {}^{7}Li + {}^{4}He + Q\ (2.79\ MeV)$

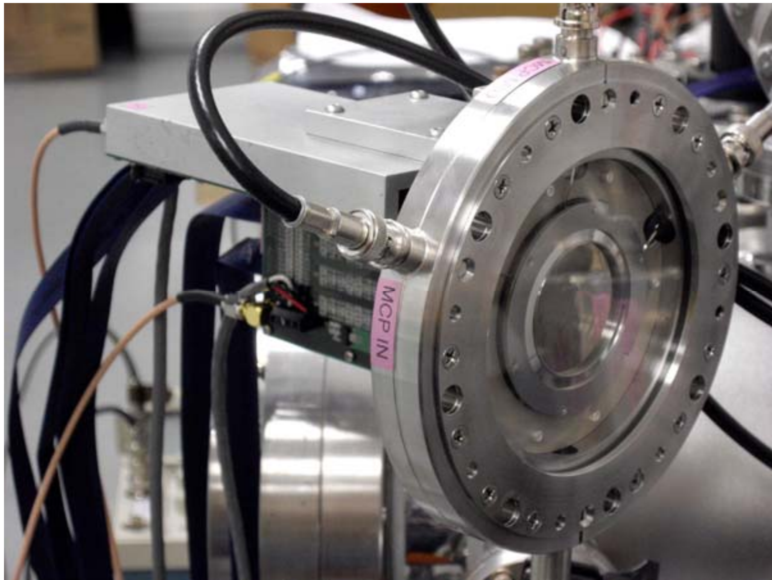
- ^{10}B or ^{nat}Gd in wall absorbs neutron
- Reaction particles initiate electron avalanche down channel
- Charge cloud detected with position sensitive anode
- Spatial resolution limited by channel size and range of charged particle
- Ultimate resolution about 1 micron



25 micron



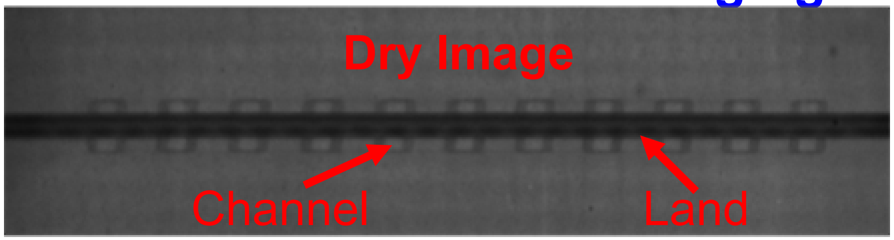
10 micron



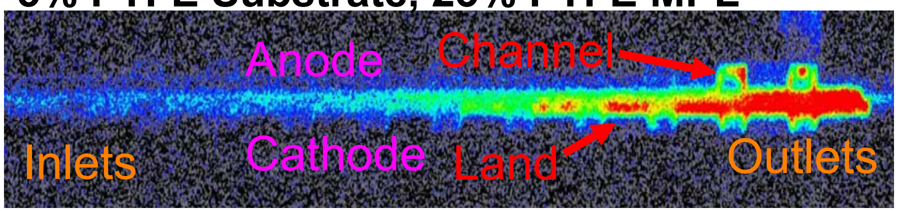
GDL Teflon Loading Effect on Water Content

Monitored by Neutron Imaging and AC Impedance

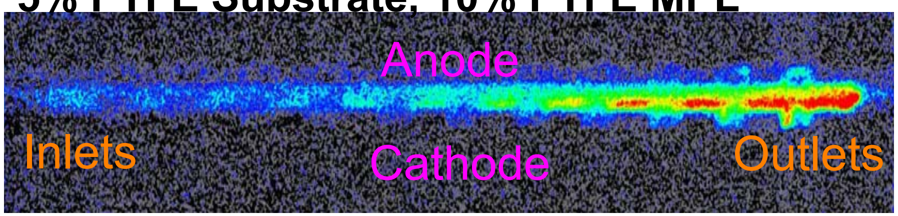
Cross-section Neutron Imaging

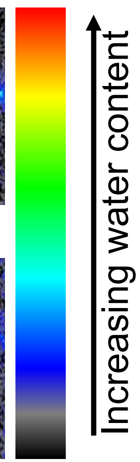


5% PTFE Substrate, 23% PTFE MPL



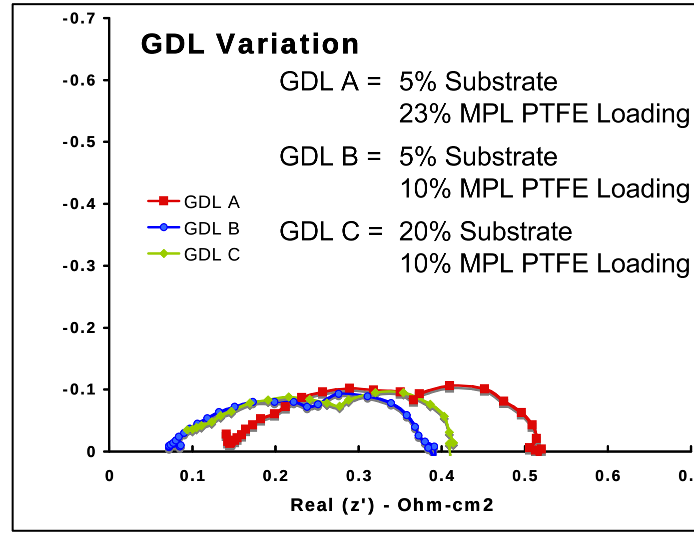
5% PTFE Substrate, 10% PTFE MPL





- 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

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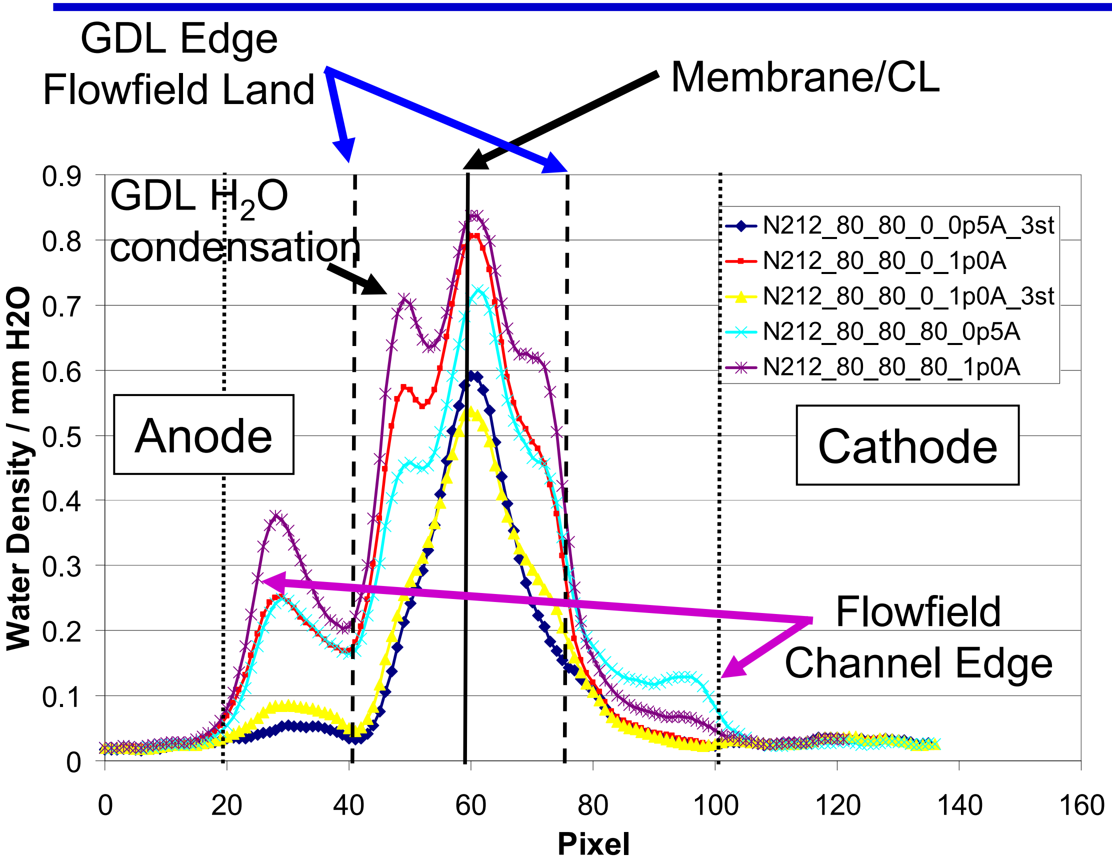
Water Profiles Nafion 212

Water content comparison for different operating conditions



- Low constant stoich (1.1/2.0)
- Simulating anode recycle (3.0)
- Flowfield co-flow

- Anode channel/GDL water:
  - With const. anode stoich ~ 1.1
  - Disappears with anode recycle
  - Anode GDL water may be water condensation (heat pipe effect)

- Membrane/Catalyst Layer is only ~ 5 pixels wide
- ~ 3 pixels for thinner MEAs
- 1 pixel = 14.7 microns

- Variation of water content as a function of current density/anode stoichiometry
  - Anode stoich = 3 (simulating anode recycle), dry cathode has lower water content
  - Anode stoich = 1.2, dry cathode similar water content to fully humidified cell
- Measured Water content in Nafion lower than expected

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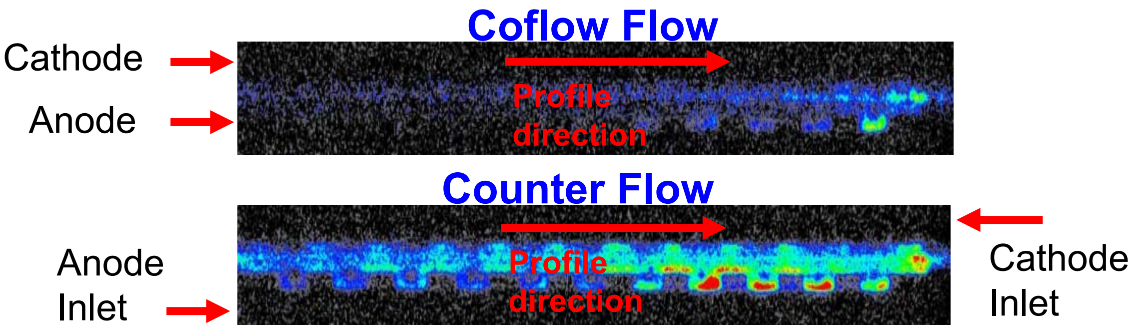
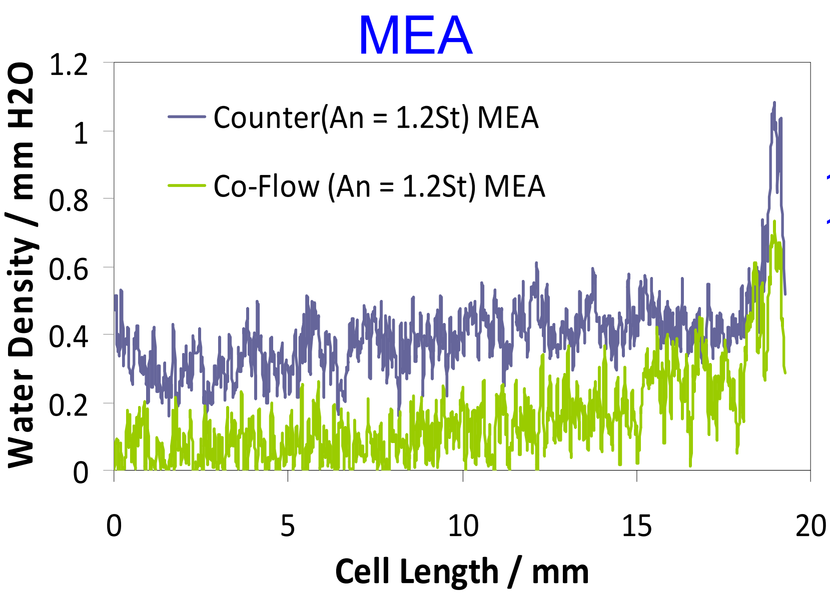
Cell Length Water Profiles

Co-flow vs. Counter flow

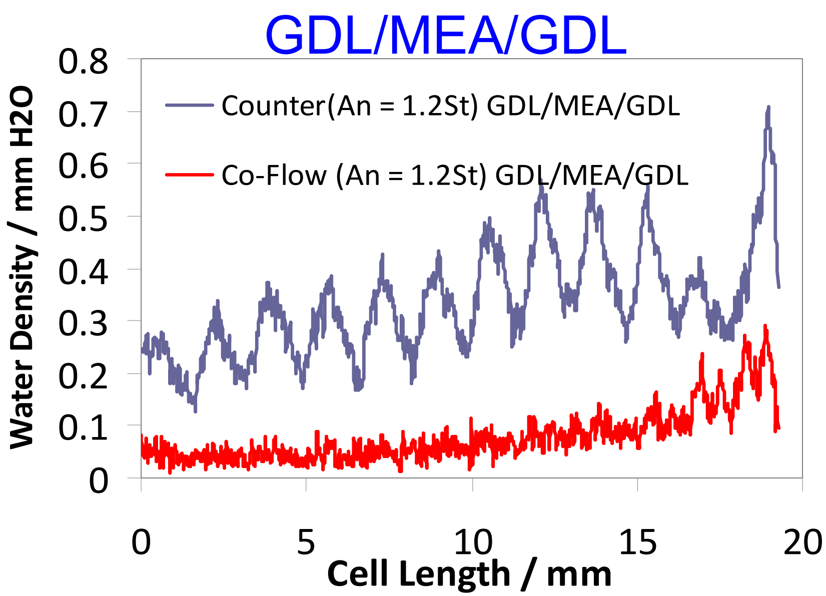


Co-flow :
I = 1.41 A/cm^2; V = 0.095 V
HFR = 0.10 Ohm.cm^2

Counter Flow :
I = 1.49 A/cm^2; V = 0.27 V
HFR = 0.064 Ohm.cm^2



100 / 0 % RH
1.2 / 2.0 St.



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

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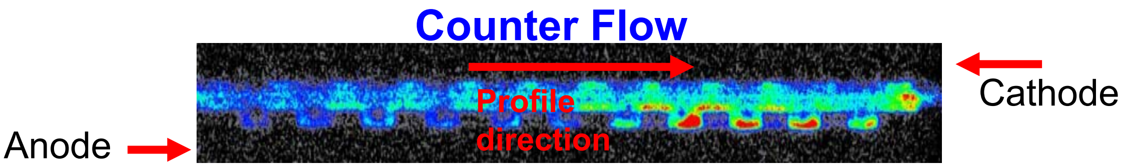
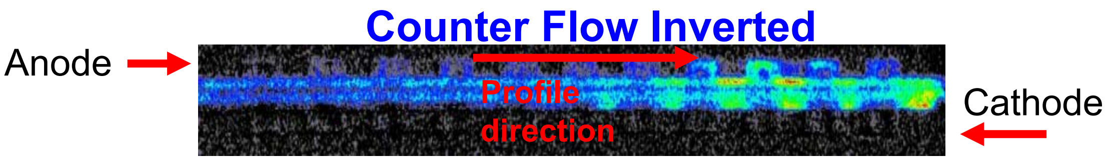
Cell Length Water Profiles

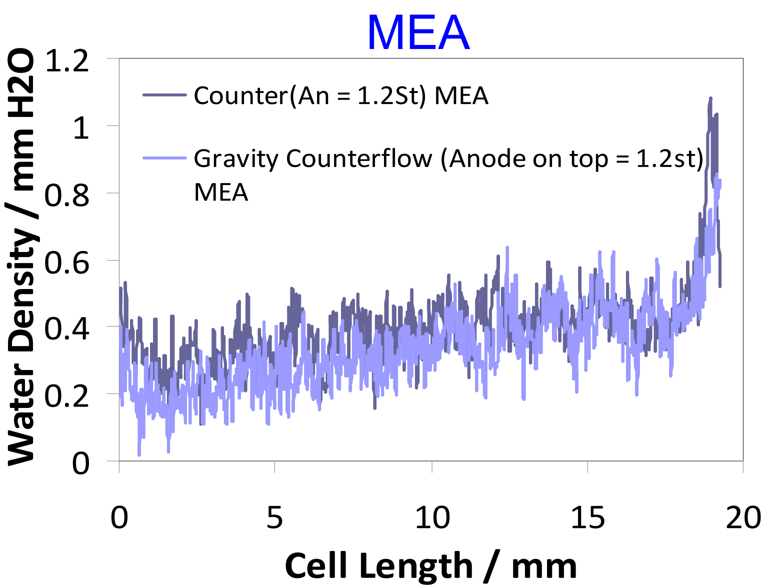
Orientation comparison



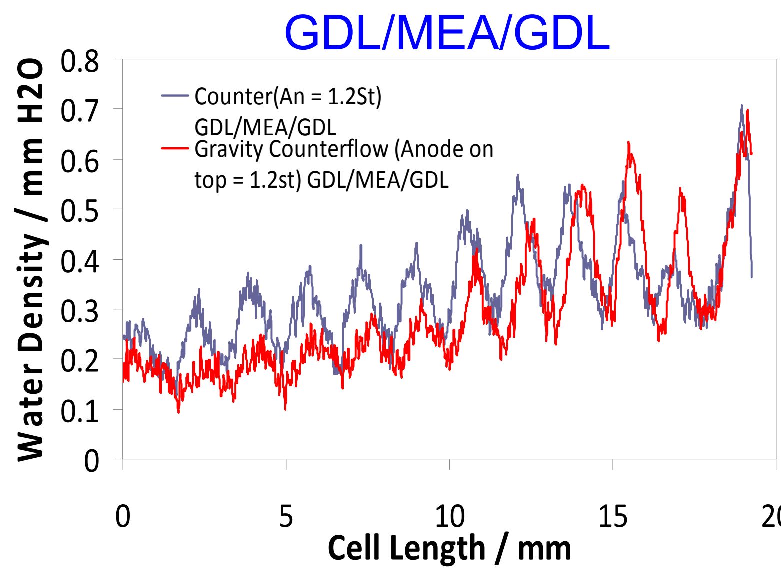
Counter Flow : 1.2St
I = 1.49; V = 0.27V; HFR = 0.064



Counter Flow Inverted: 1.2St
I = 1.39; V = 0.385; HFR = 0.067



100 / 0 % RH
1.2/2.0 St.
Orientation inverted



- Membrane water content similar
- Cathode on top shows flooding (gravity effect) and loss of performance
- Cathode on bottom GDL water lower water content

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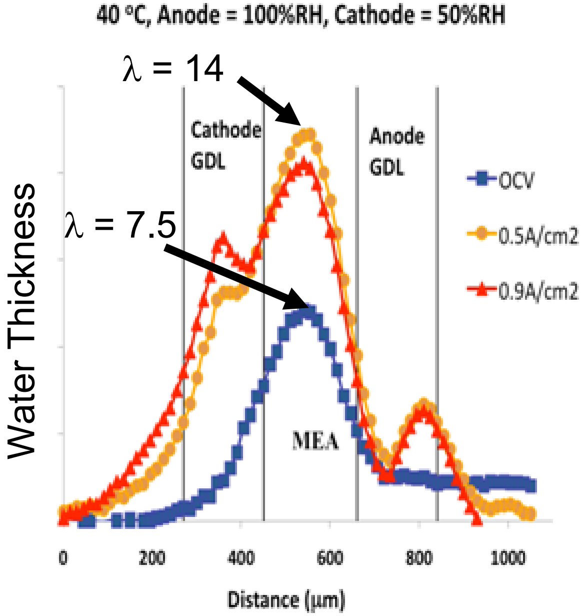
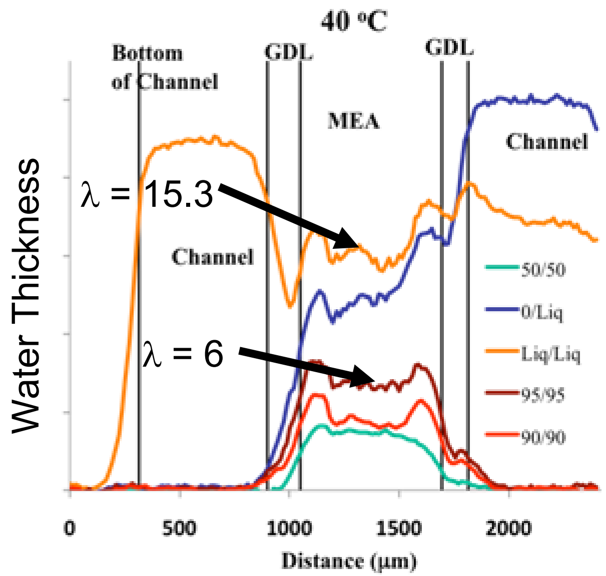
In situ Measurement of Membrane Water

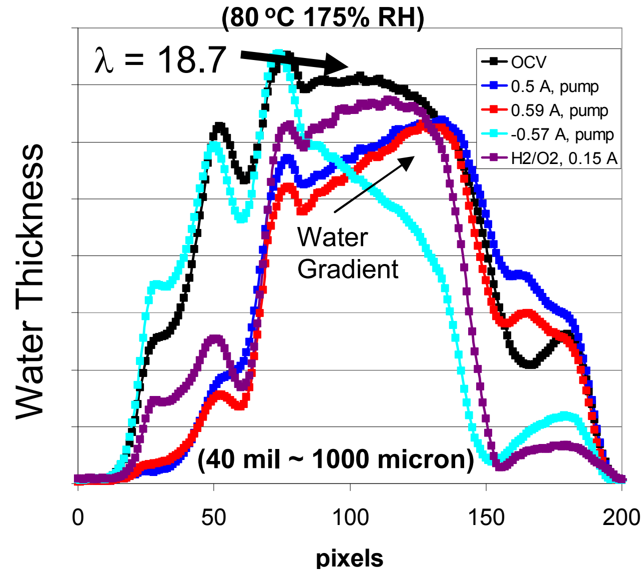
N117



3 x Nafion 117



40 Mil Nafion Membrane



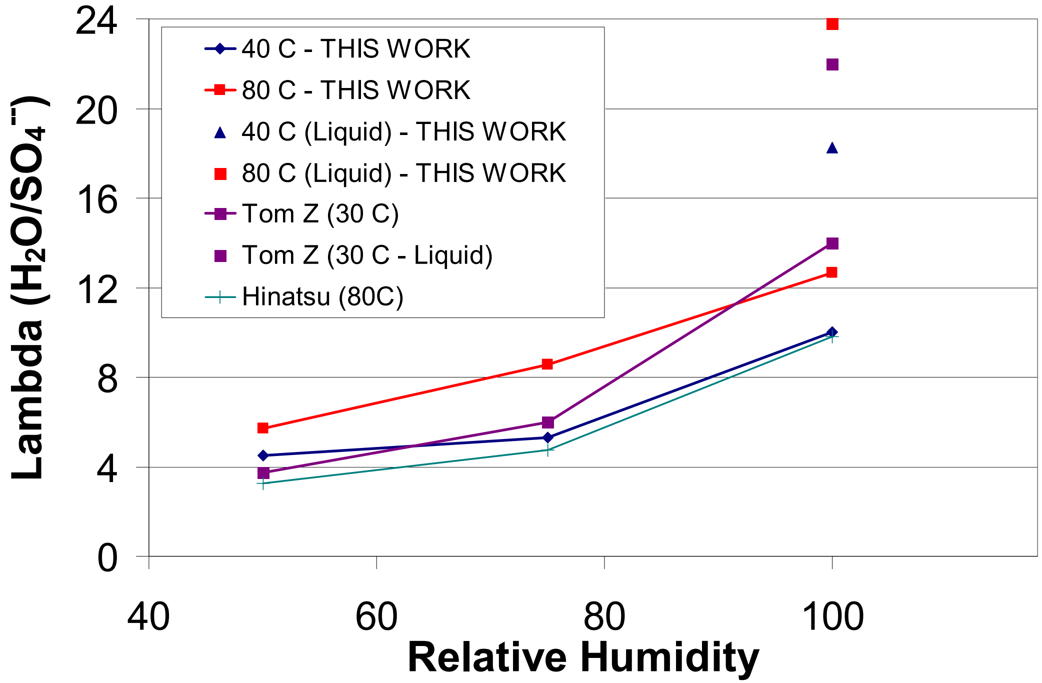
- Membrane conductivity is a f(water content)
  (λ = # of Water molecules per # of sulphonic acid sites)
  - Large literature base measuring water in Nafion
  - Vast majority of studies were conducted ex situ

- 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.

- 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 (≈ 100 µm) is much smaller than membrane thickness (≈ 585 – 1000 µm)
- Water gradient formed at saturated conditions by H_2 pump

λ Comparison



λ Measurement Summary:

λ ~ 10-12 at 100% RH
λ ~ 18-24 liquid H_2O
Fuel Cell current increases λ :
at 50/50 % RH's 5 → 8.8
at 100/100% 8.3 → 11.5
(depends upon current)

- Cathode under-saturated - Membrane water increases from λ ≈ 6 to λ ≈ 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:

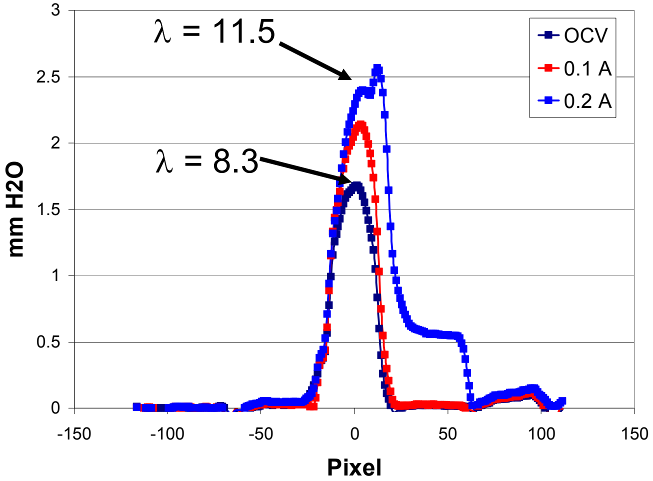
Tsushima, Shoji, **Water Transport Analysis by Magnetic Resonance Imaging**, LANL/AIST Meeting, San Diego, 2008

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

20 mil Nafion Membrane

(RH Equilibration, Fuel Cell and H_2 Pump Operation)

Fuel Cell Operation

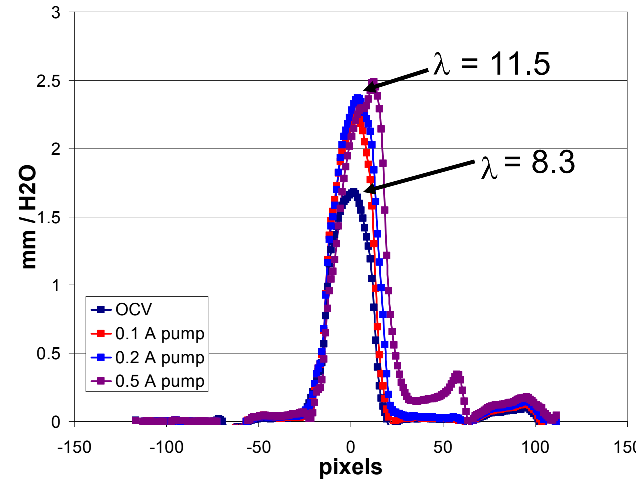


100/100 % RH 40 C

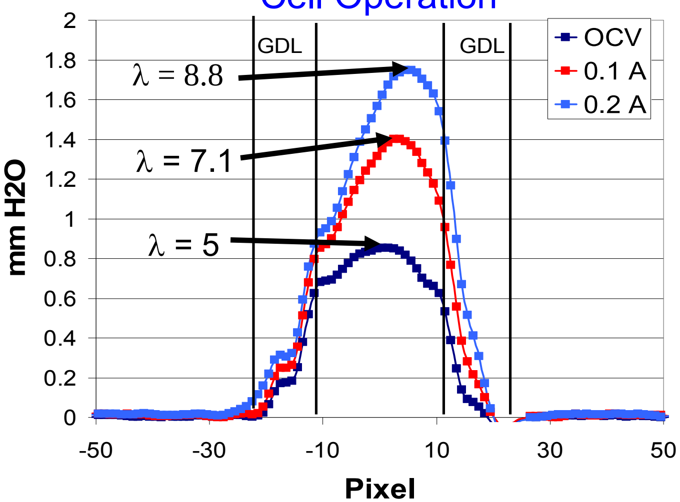
- Single Nafion® 20 mil electrolyte
- 6mg/cm^2 Pt on cathode and anode
- SGL Sigracet® 24 AA (Hydrophilic no MPL)
- Vertical setup

- 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

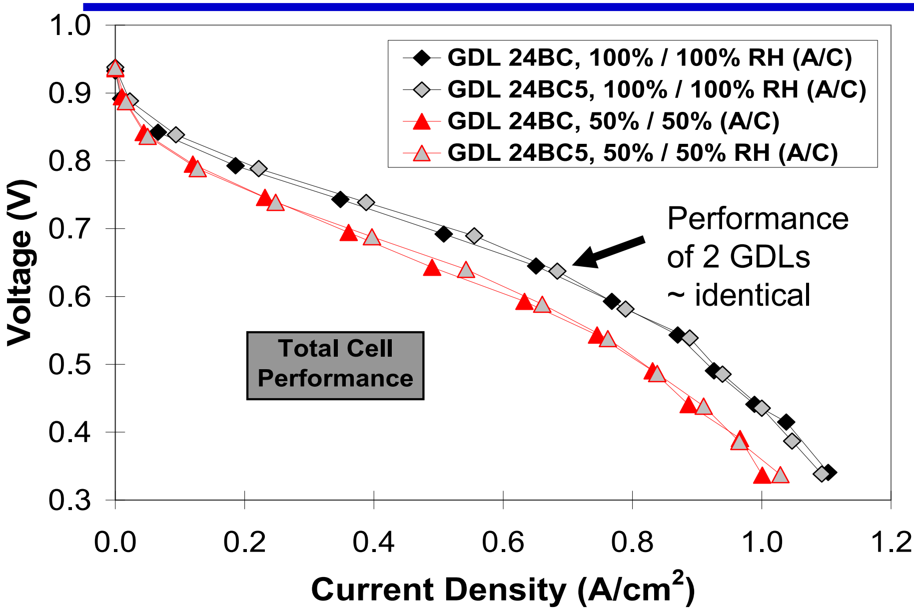


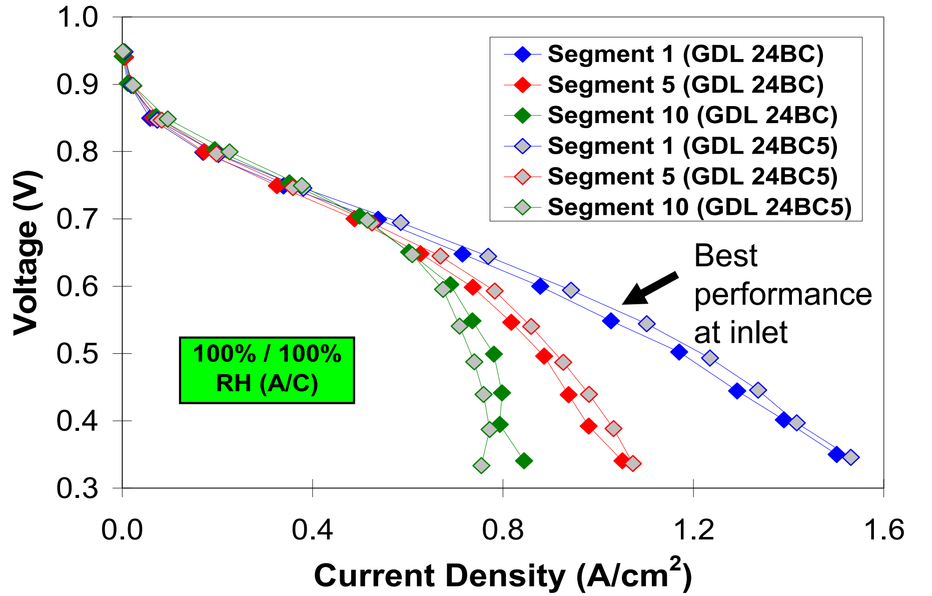
50/50 % RH, 40 C – Fuel Cell Operation



- Membrane hydration is observed to be
  - λ = 5.0 (50/50%) and 8.3 (100/100%)
  - λ increases with water production (Fuel Cell) and with H_2 pump (liquid water formation, electro-osmotic drag)
  - Observed differences with 40 mil membrane at 80 ^{o}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 H_2 pump mode
- Increasing pump current causes decreasing water on the anode and increasing water on the cathode side.

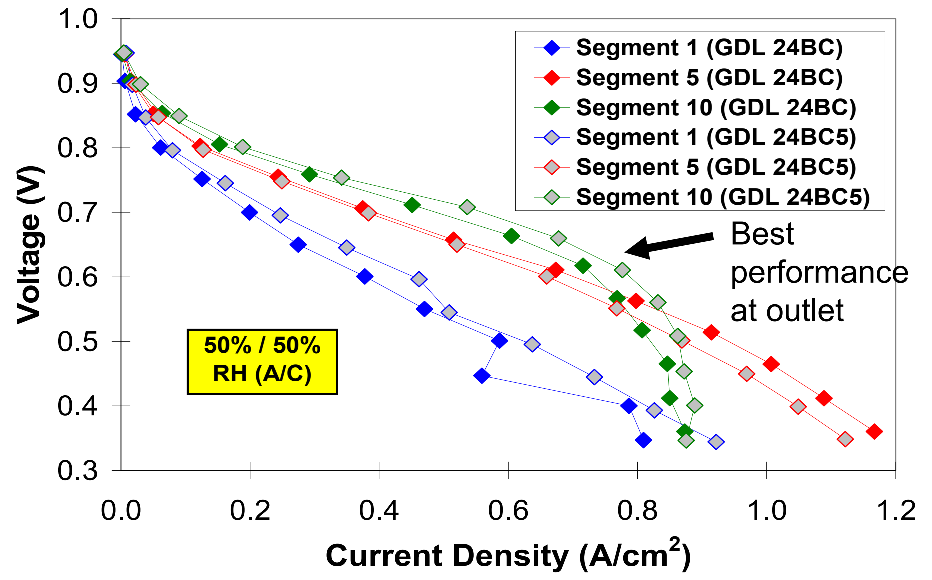
Segmented Polarization Data for Different ***Cathode*** GDLs



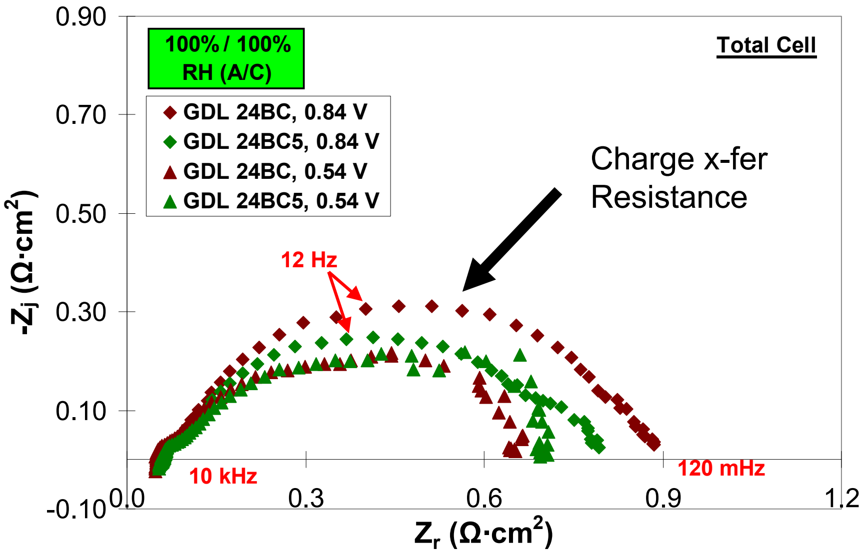


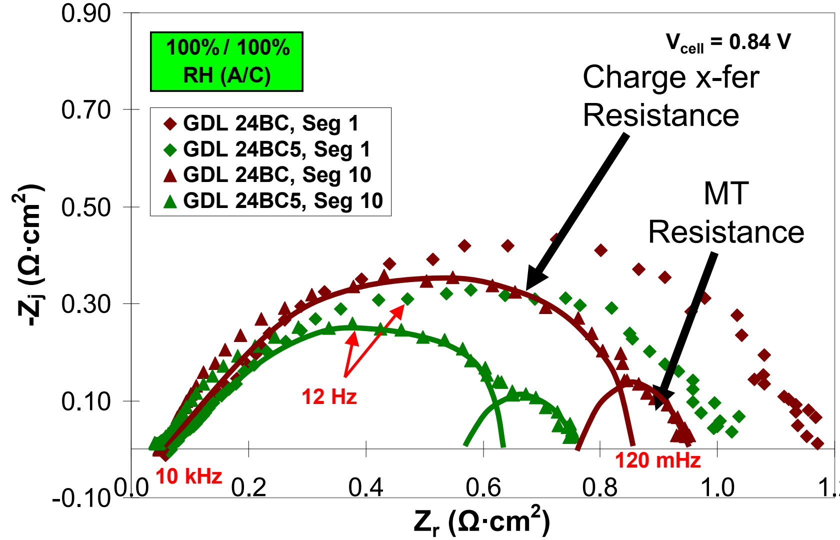
Segmented Cell Measurements show where Mass Transport losses dominate versus where IR losses, and kinetic occur

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

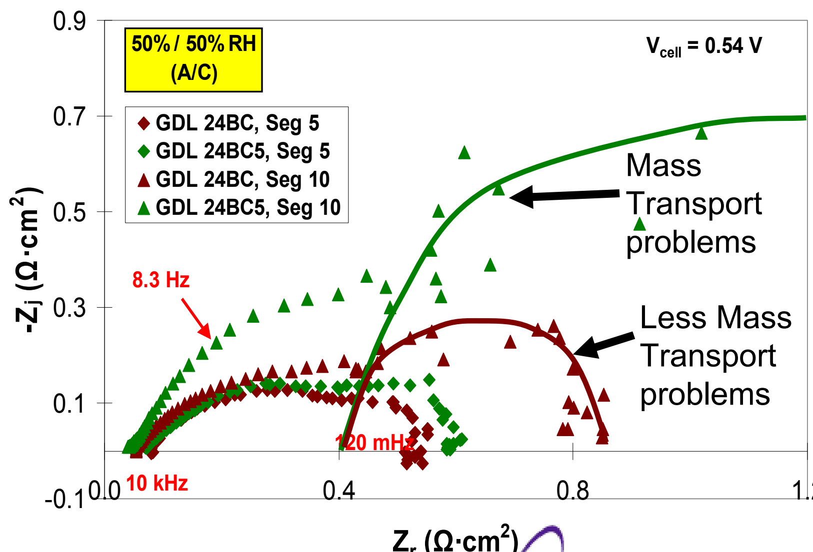


AC Impedance Data of Different Segments for Different Cathode *GDLs*





- 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.



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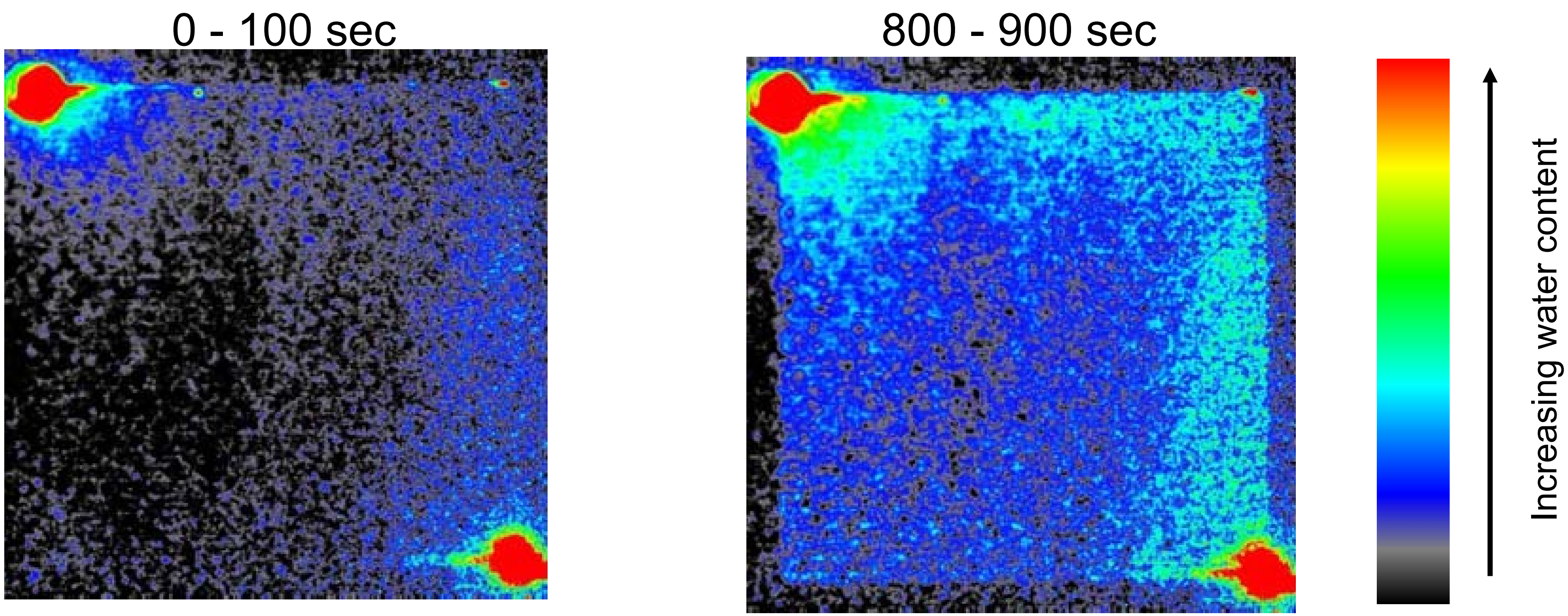
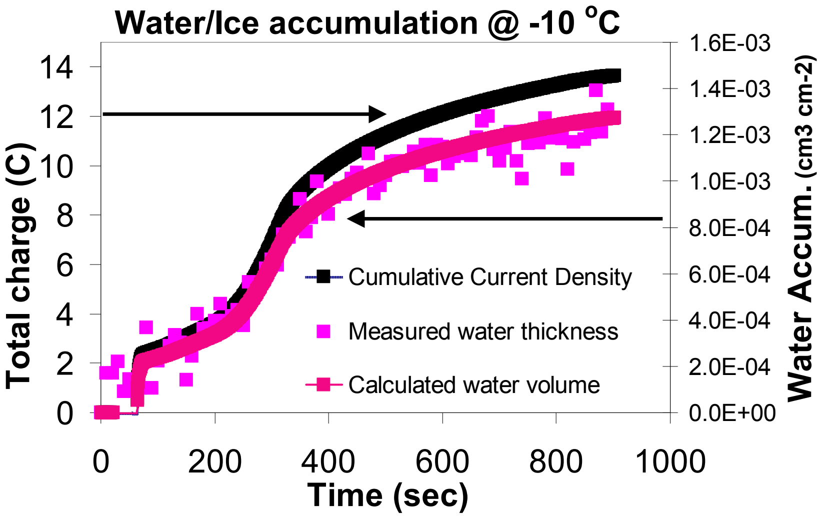
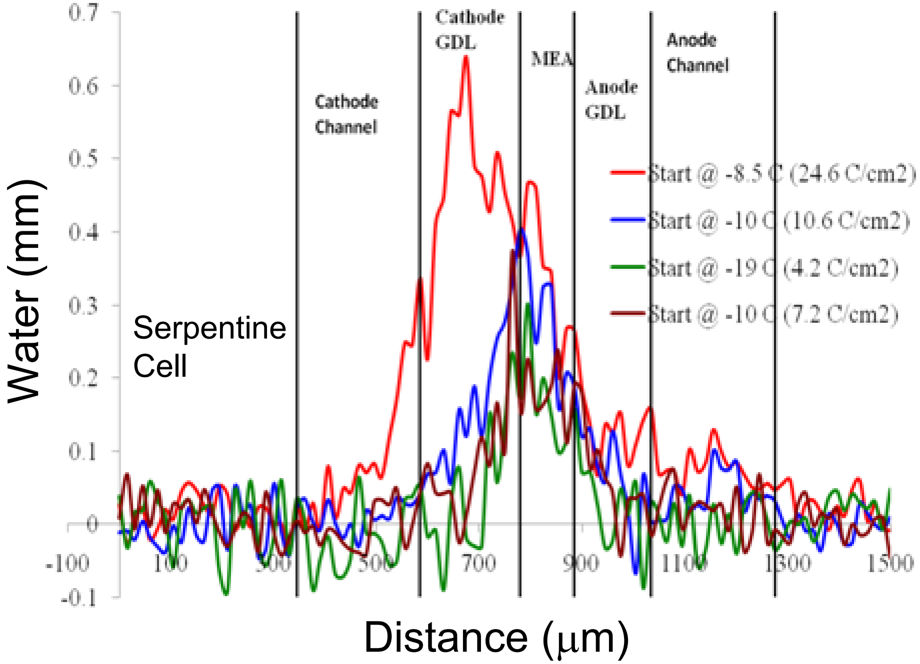
Neutron Imaging of Ice Formation During Operation at -10 ^oC

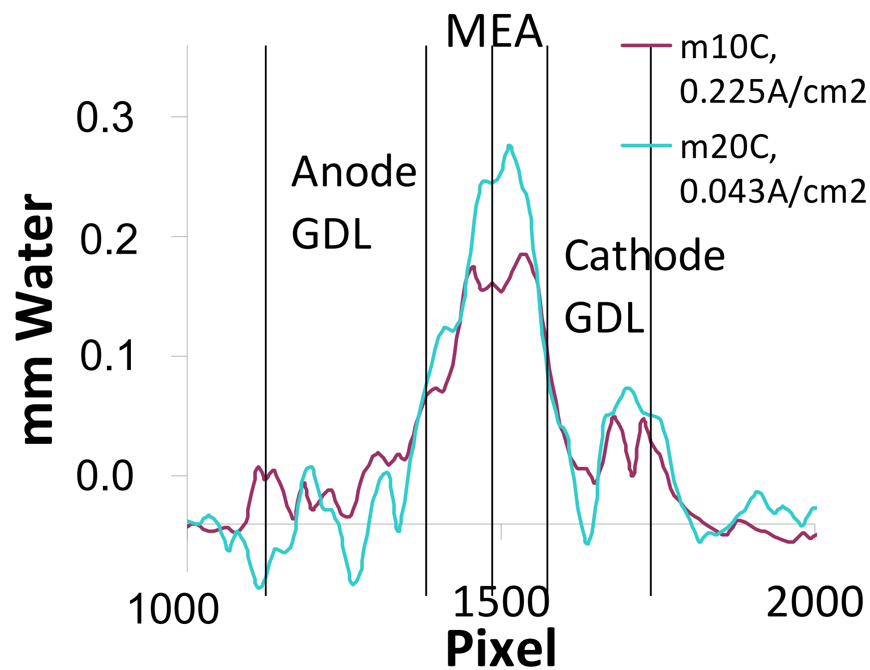




- Neutron imaging of ice formation in a 50 cm^2 fuel cell operated at 0.5 V at -10 ^oC.
- Calculated/measured water/ice accumulation from current and neutron imaging in the fuel cells track

Freeze: High resolution imaging

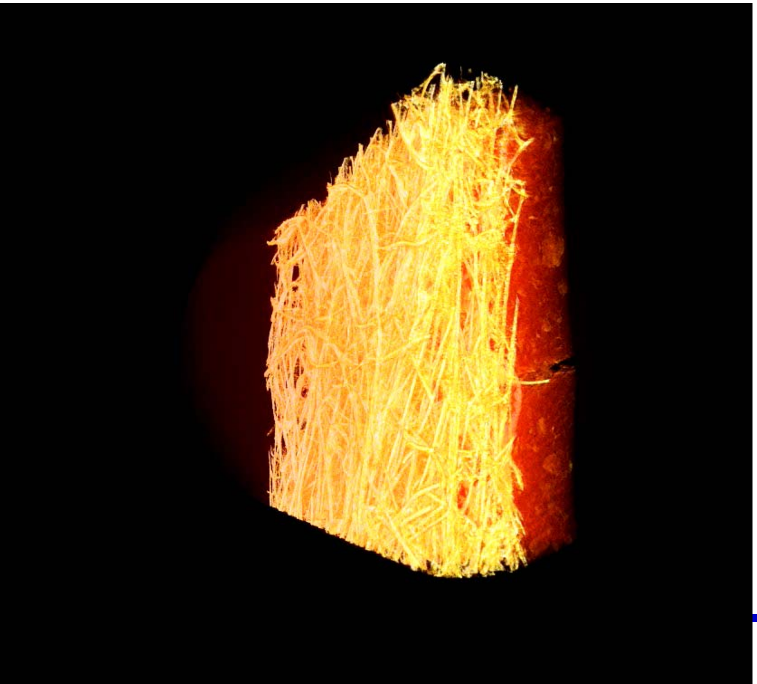


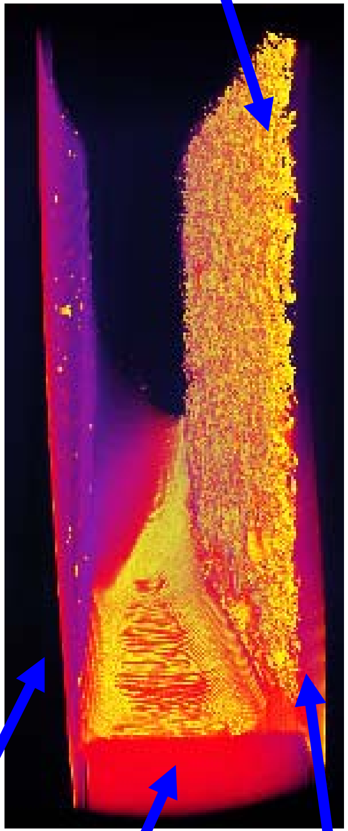


- Location of frozen water (ice) depends on operating temperature and current density
  - Water distribution closer to the cathode catalyst layer with:
    - Decreasing temperature
    - Increasing current
  - Greater water formation possible at higher temperatures and lower current densities

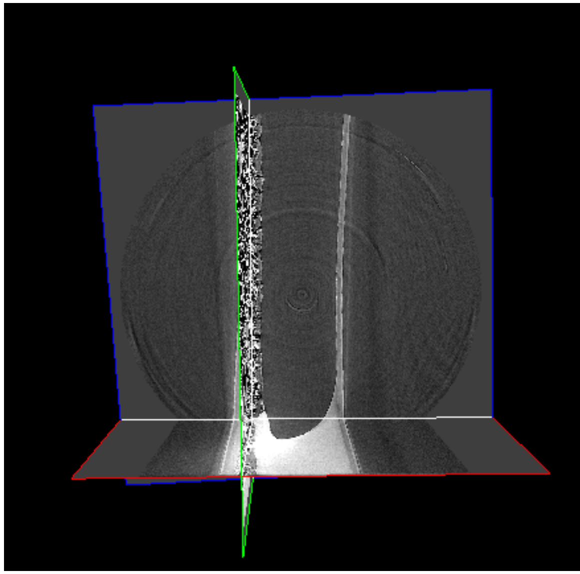
X-RAY Tomograph Image of water in GDL Pores

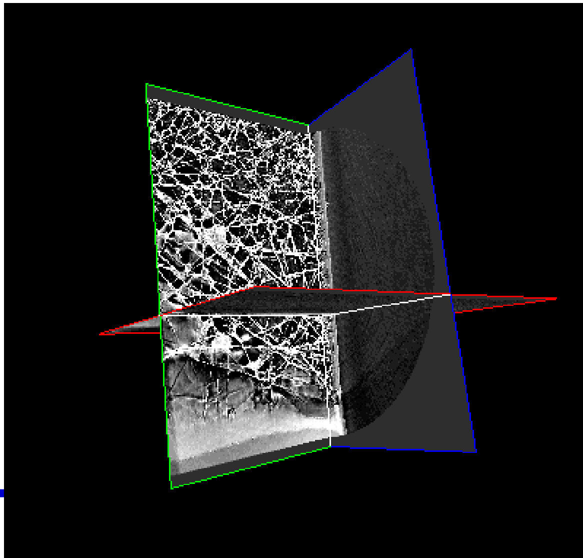
- Evaluate pore size density and distribution
- Observe GDL compression
- Observe/monitor water diffusion
- Evaluate water wetting and water diffusion pathways





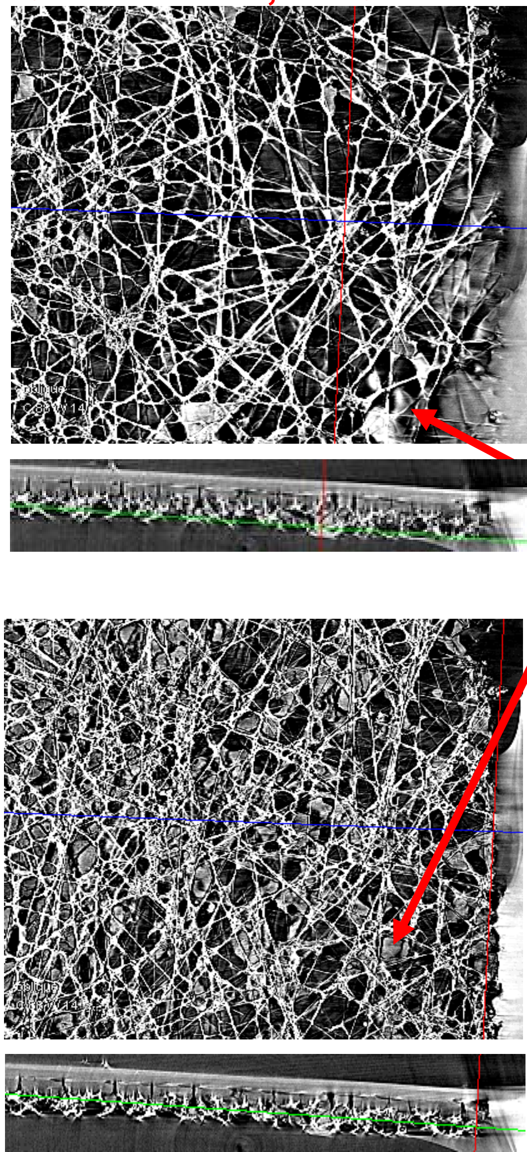
MPL side against Kapton





Water Inside SGL GDL Pores

(23% PTFE MPL, 20% Substrate)



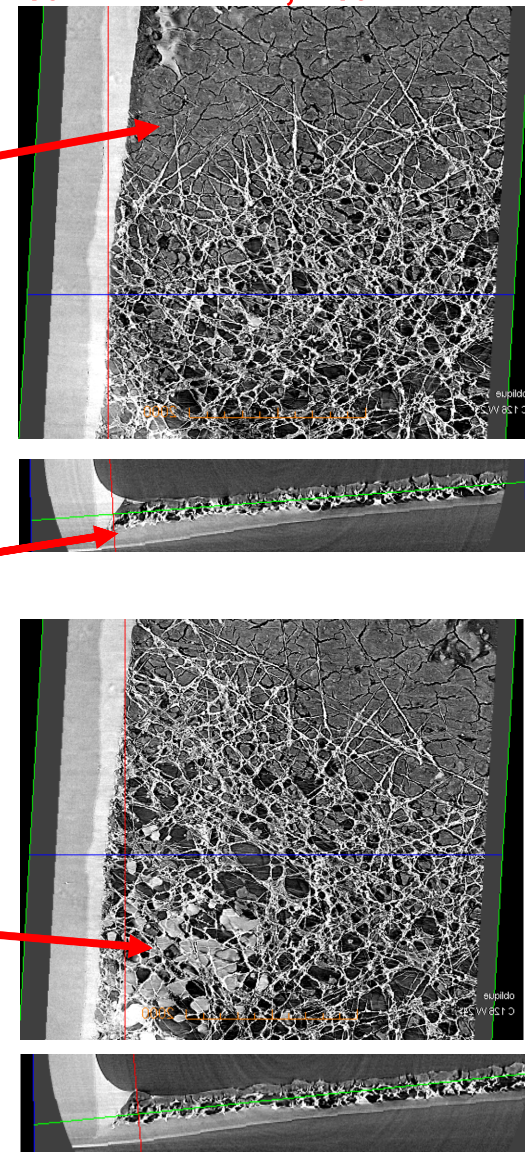
Water

(5% PTFE MPL, 5% Substrate)

MPL

Water

Water



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

Summary

- Varying MPL and substrate Teflon loadings and cell operating conditions
    - Neutron imaging, AC impedance, HFR, X-Ray Tomography
- Equilibrium water content in the membrane, how membrane water content changes with RH, T, current and water production
- Segmented cell operation
- Response of GDL and membrane water to transients
    - Fast membrane wetting
    - Slow GDL de-wetting, followed by membrane drying
- Freeze

Future Work

- **Experimental and Characterization**
- 3-D X-Ray tomography during operation observing water transport in GDL pores
    - Identify hydrophobic pores vs. hydrophillic pores
    - Identify liquid water pathways in GDLs
- Incorporate 3-D X-ray tomography PSD into Capillary Pressure Simulation

Thanks to

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