Water Transport Exploratory Studies

2008 DOE Hydrogen Program Review

June 9-13, 2008

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, 3M Company, Nuvera Fuel Cells

FC35

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Project Overview

Timeline

- New Project for FY07
- 4 year Project Duration

Budget

- Total project funding
  - DOE Cost: $6,550,000 (over 4 yrs)
  - Cost Share: $290,811
- Funding for FY08

LANL	$1000k
Industrial Partners	$300k
Other National Labs	$350k
FY08 Total	1650

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

Organizations / Partners

- **Los Alamos National Lab: Rod Borup, Rangachary Mukundan, John Davey, Tom Springer, Yu Seung Kim, Jacob Spendelow, Tommy Rockward, Partha Mukherjee**
- **Sandia National Laboratory: Ken Chen & C.Y Wang (PSU)**
- **Oak Ridge National Lab: Karren More**
- **Case Western Reserve University** (sub-contract)**: Tom Zawodzinski, Vladimir Gurau**
- **SGL Carbon Group** (sub-contract in progress)**: Peter Wilde**
- **National Institute of Standards and Technology (no-cost): Daniel Hussey, David Jacobson, Muhammad Arif**
- **W. L. Gore and Associates, Inc.** (PR basis)**: Will Johnson, Simon Cleghorn**
- **Univ. Texas-Austin** (additional sub-contract)**: Jeremy Meyers**
- **3M: Mark Debe** (Technical Assistance – providing NSTF materials)
- **Nuvera: James Cross, Amedeo Conti, Olga Polevaya, Filippo Gambini** (Technical Assistance – low temperature conductivity)

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

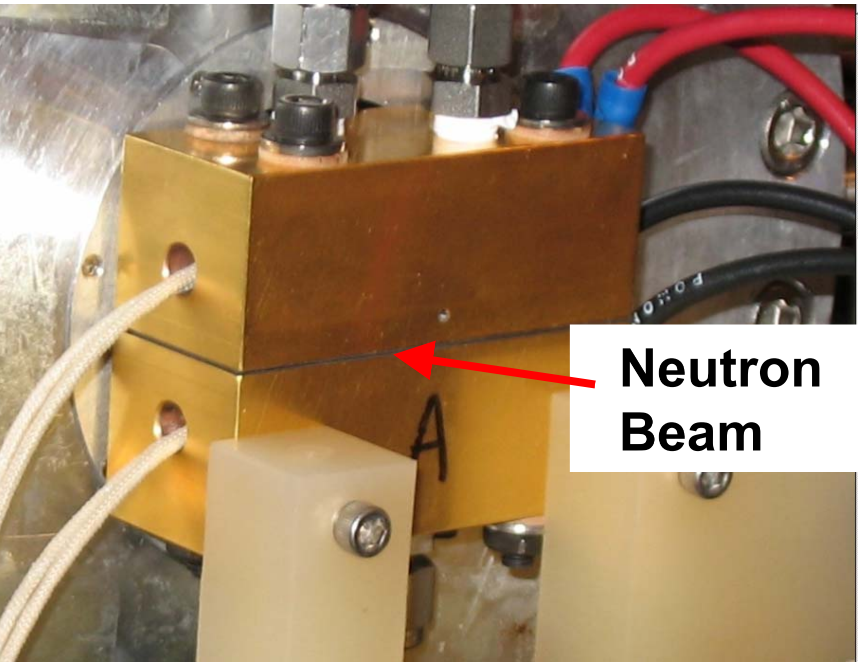
Approach

- **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 droplet detachment
  - 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

Neutron Imaging

Cross-Section Design for High Resolution Imaging

High resolution (~ 25 μm) cross-section cell



Design Considerations:

- Maximum field of view is 2 cm X 2 cm for the high resolution neutron detector.
  - Limits X dimension to 2 cm.
- Outermost edge to image = 3 cm from the detector for good focus.
  - Detector is 0.5 cm inset of the face plate,→ 2.5 cm available
- Active area 1.2 cm in width
  - Entire cell is < 3 cm from detector

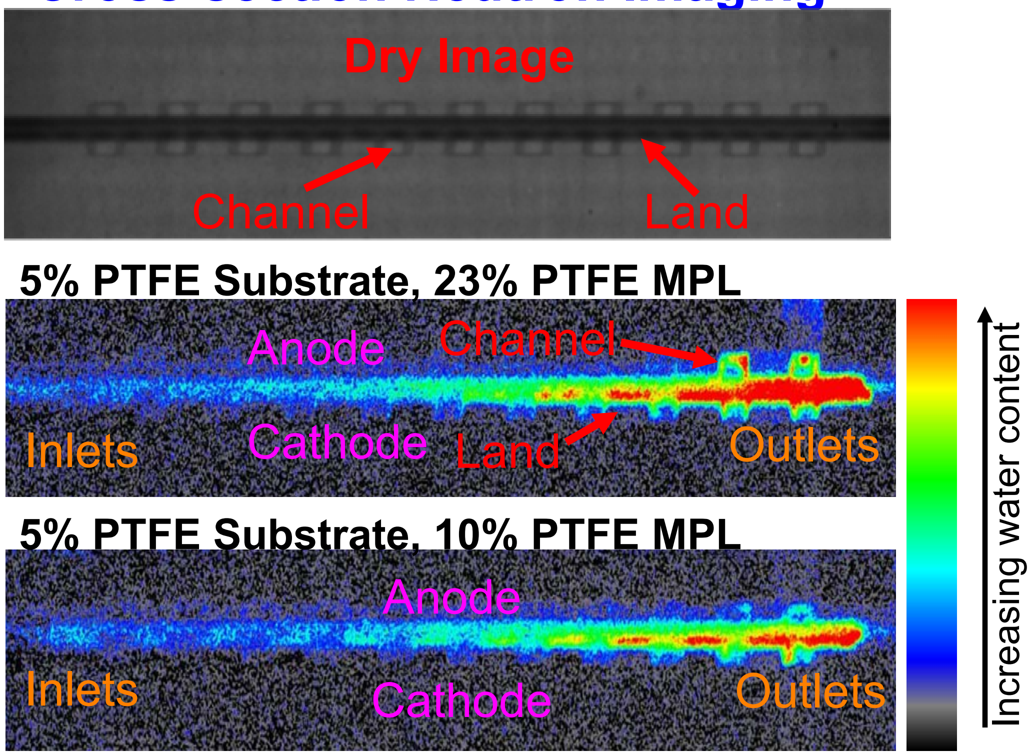
Design:

- 2.25 cm^2 active area
- No hydrocarbon materials
- Metal hardware
  - No plate porosity of hardware for water hold-up
- 1 cm linear water imaging length
- Shallow single serpentine flowfield
  - Attempt to simulate pressure drop of real flowfields

GDL Teflon Loading Effect on Water Content

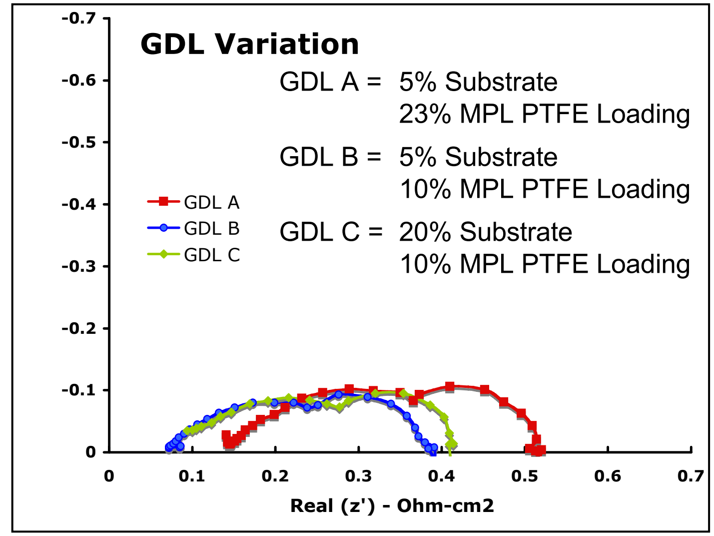
Monitored by Neutron Imaging and AC Impedance

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

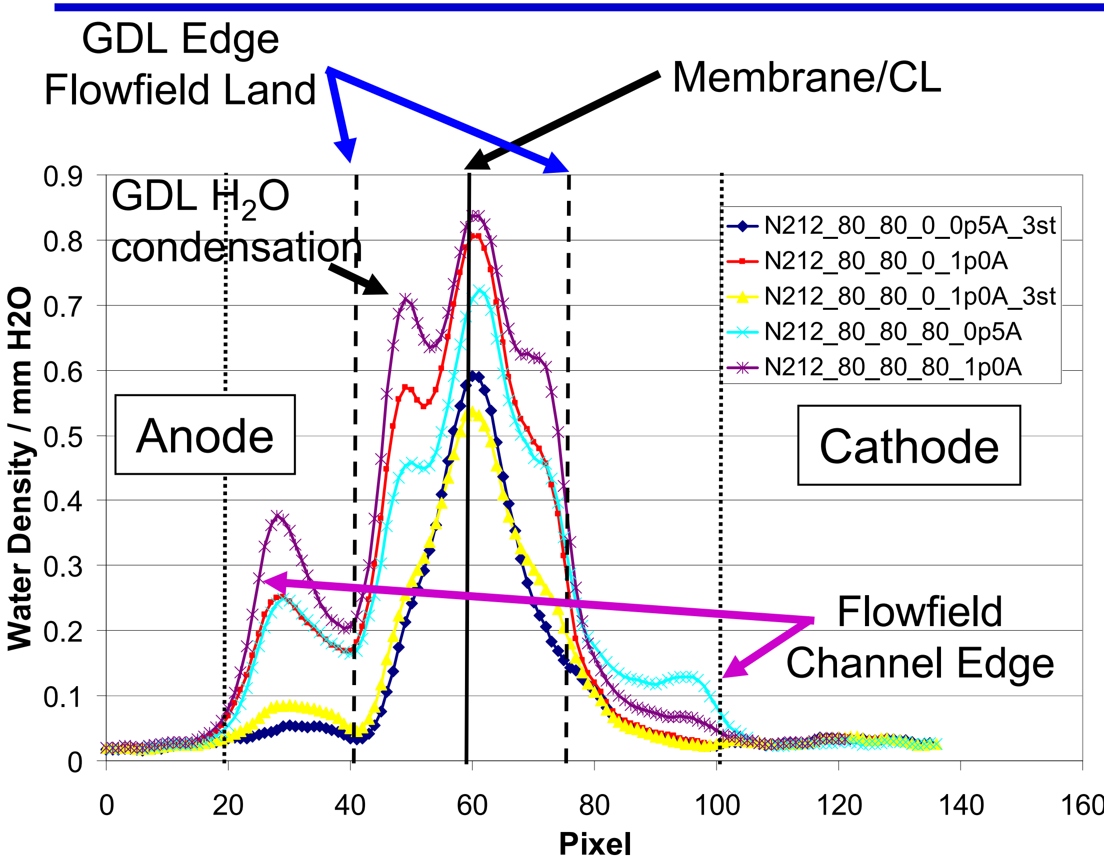


- Charge transfer resistance
  - Decreases with increasing current
  - Greater for GDL with 23% PTFE in MPL
- Mass transfer resistance
  - Increases with increasing current
  - Greater for GDL with 23% PTFE in MPL

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

Water Profiles Nafion 212

Water content comparison for different operating conditions



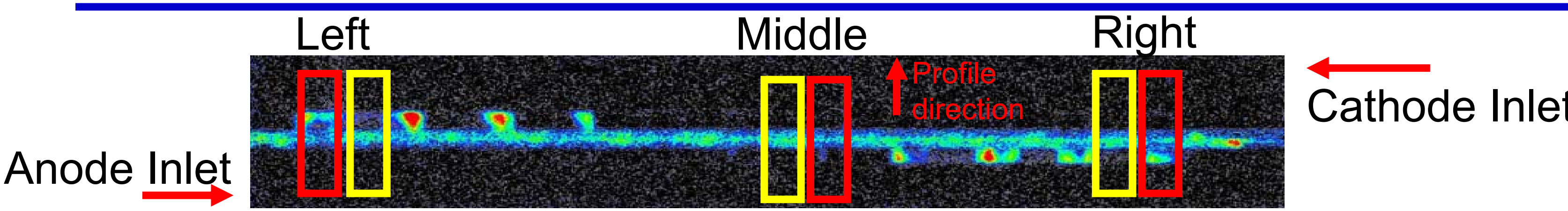
- Low constant stoich (1.1/2.0)
- Simulating anode recycle (3.0)
- Flowfield co-flow

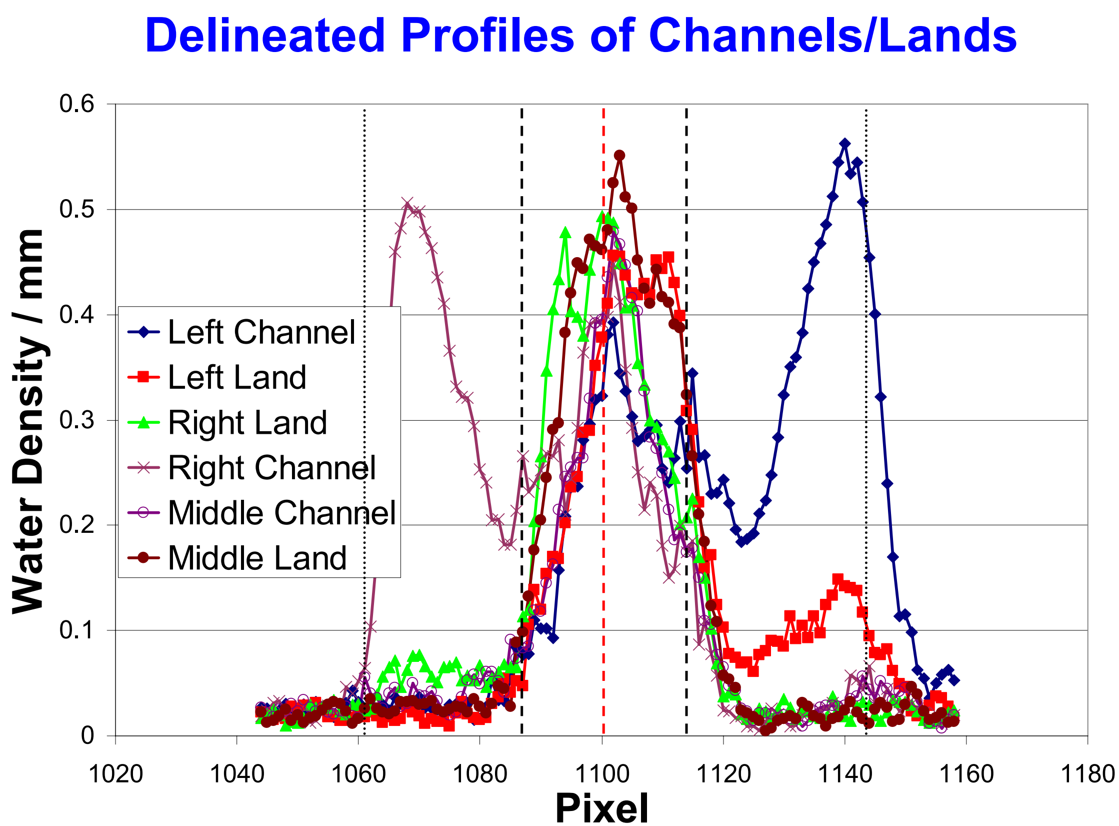
- Anode channel/GDL water:
  - With const. anode stoich ~ 1.1
  - Disappears with anode recycle
  - Anode GDL water may be water condensation (heat pipe effect)

- 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

Water Profiles Delineated in Counter-Flow Orientation

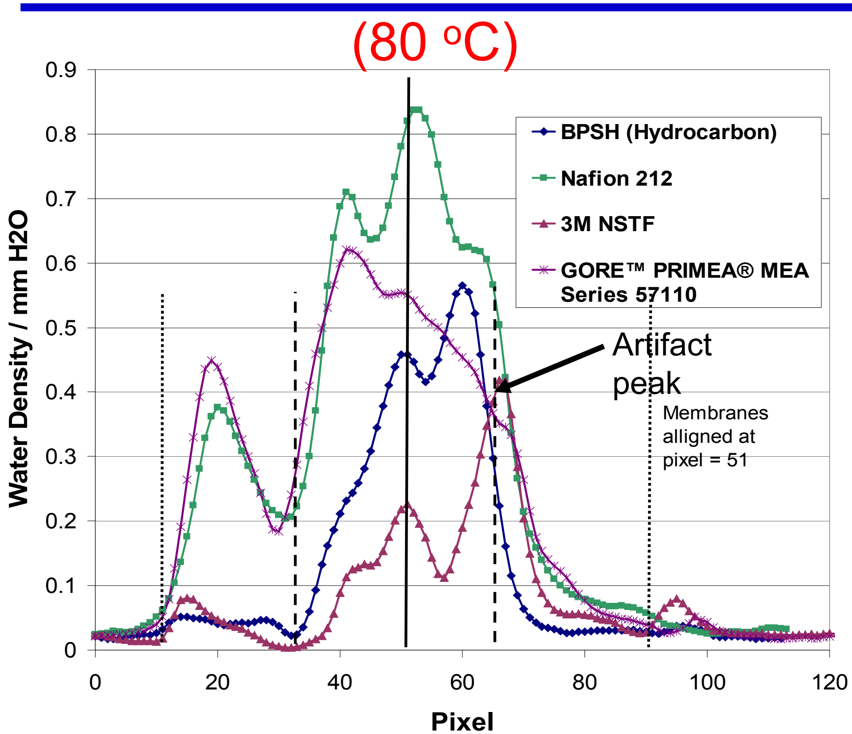


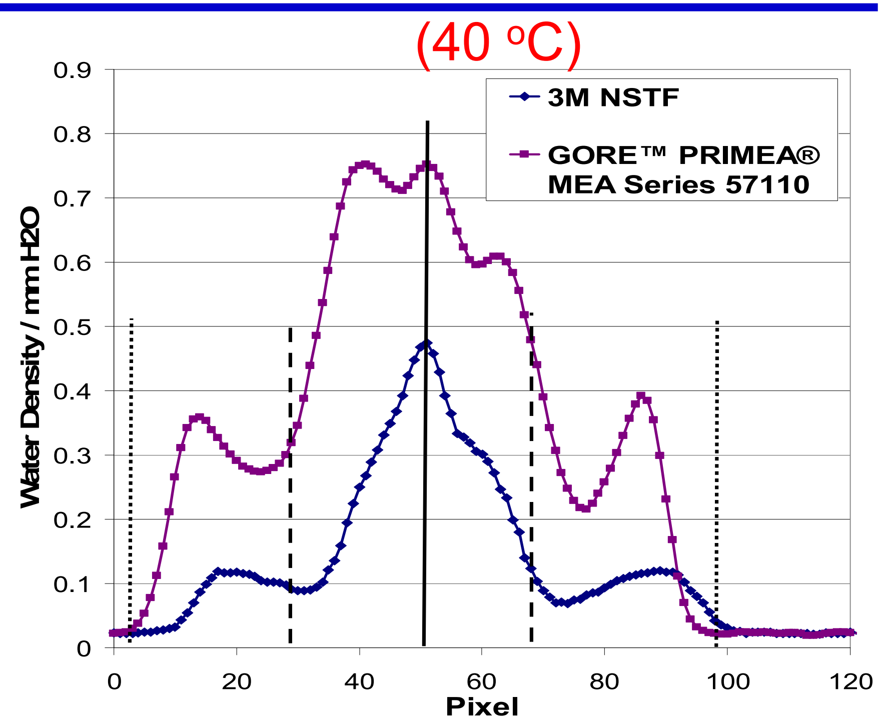


- MEA shows highest water content in middle of cell (land)
- Right Land / Channel (anode out)
- Low water content in cell (compared with other materials)
- Water in channels at outlets

3M NSTF, Counter Flow, 40 °C, 0.59 A/cm^2, T_a = 28, T_c = 28

Water Content Comparison with Various Materials

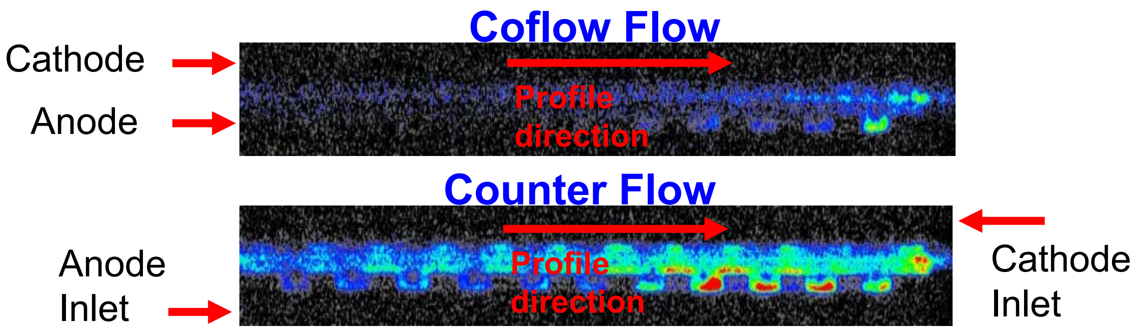




- High resolution neutron images of different MEA materials under similar operating conditions.
- N212 high water content, low water content for 3M NSTF materials
- Anode GDL water differs significantly
- Significantly more water in MEA/GDLs at lower temperatures

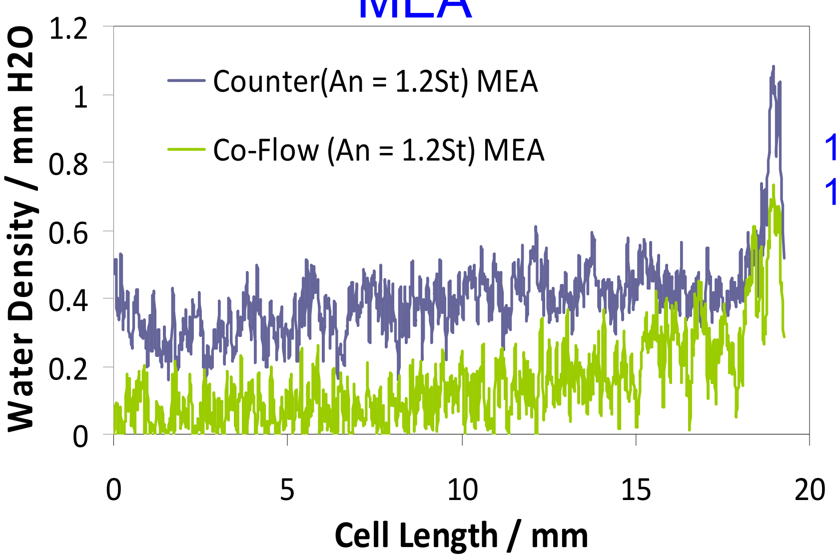
Cell Length Water Profiles

Co-flow vs. Counter flow

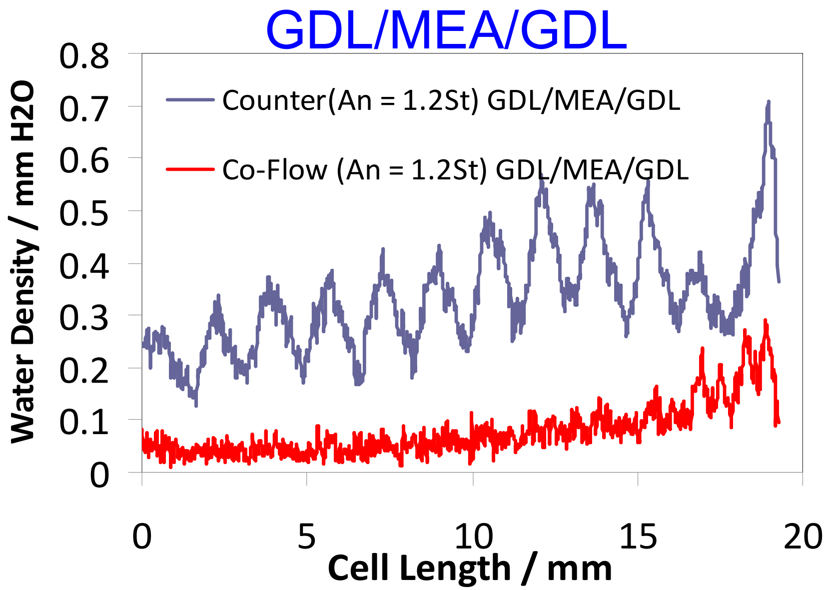


Co-flow :
I = 1.41 A/cm²; V = 0.095 V
HFR = 0.10 Ohm.cm²

Counter Flow :
I = 1.49 A/cm²; V = 0.27 V
HFR = 0.064 Ohm.cm²



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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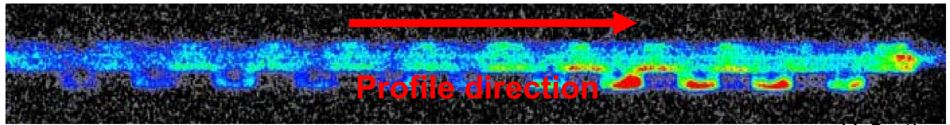
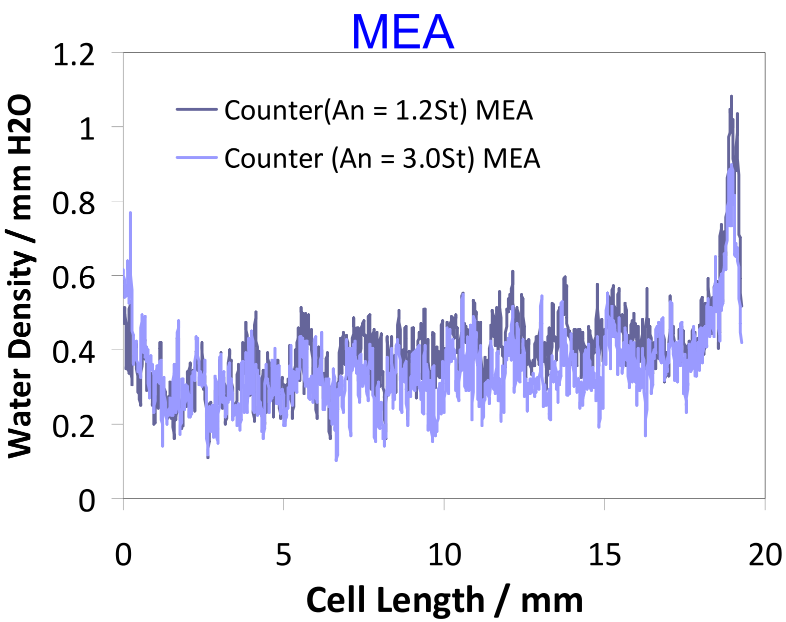
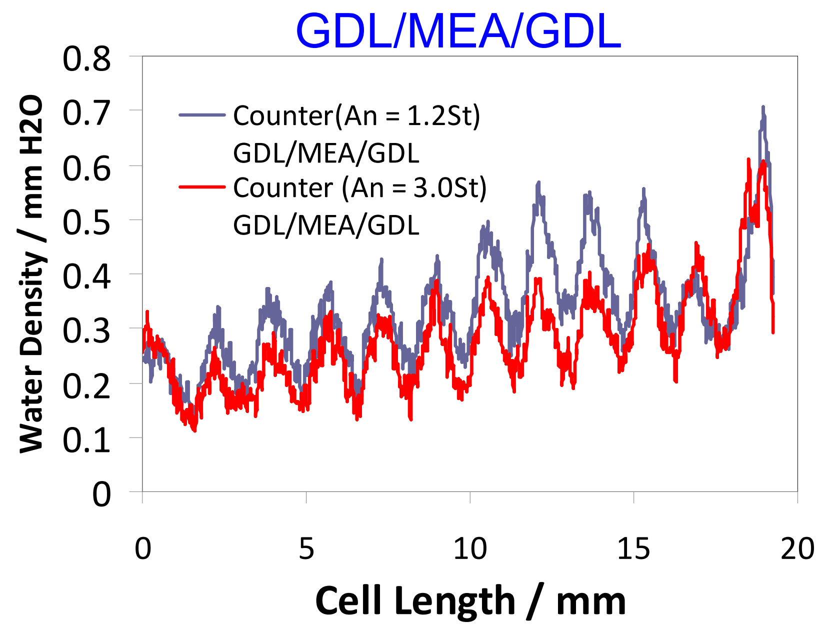
Cell Length Water Profiles

Anode Stoich comparison





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



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

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

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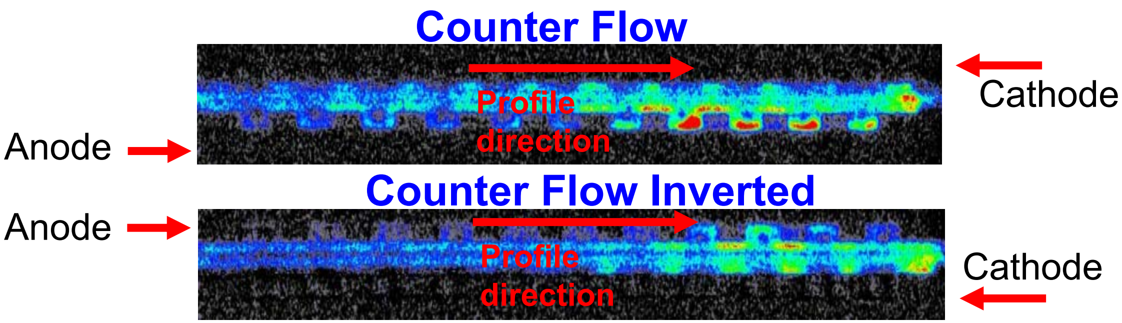
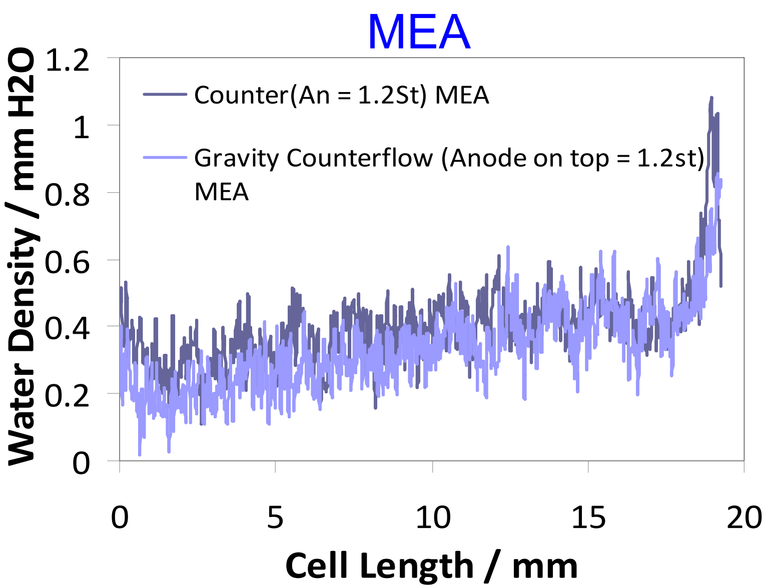
Cell Length Water Profiles

Orientation comparison

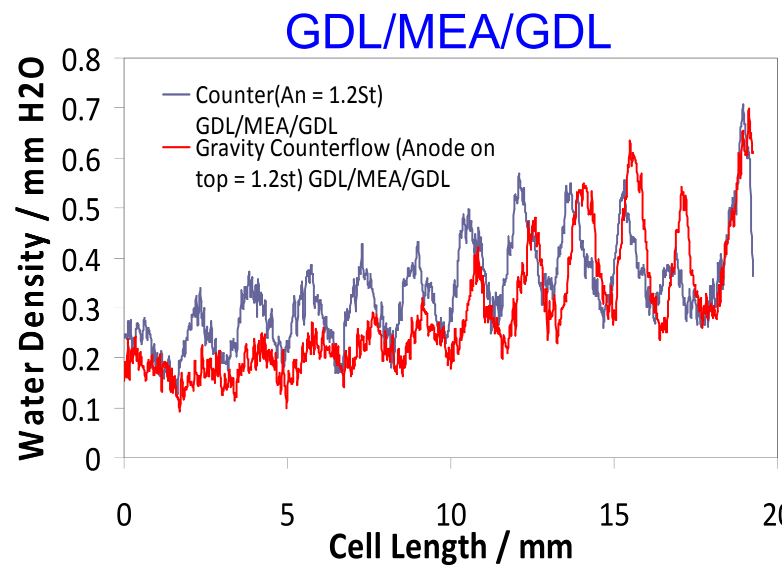


Counter Flow : 1.2St
I = 1.49; V = 0.27V; HFR = 0.064

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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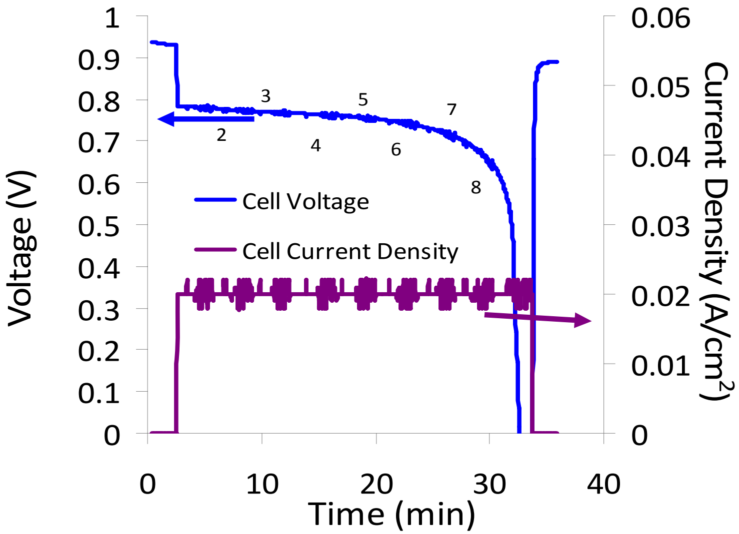
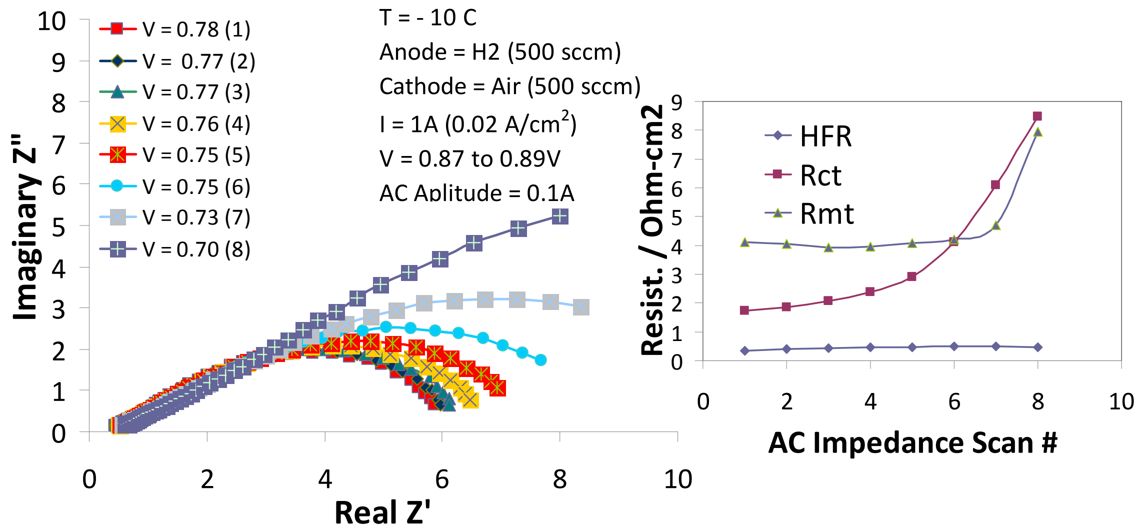
Freeze Operation

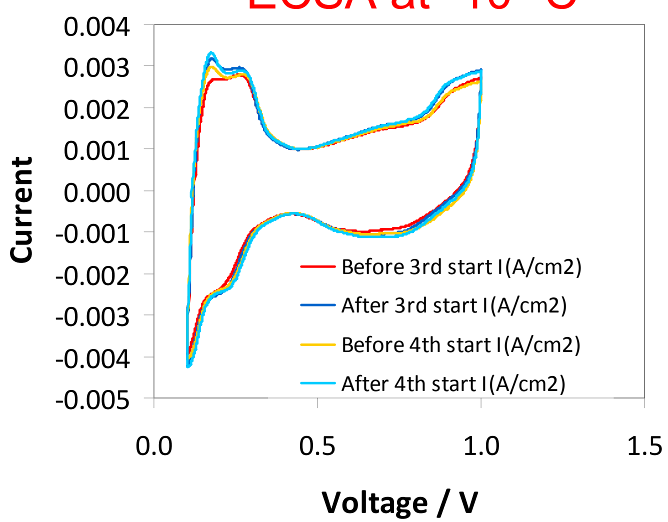
Fuel Cell Start-up at -10 °C



Impedance During Start-up at -10 °C



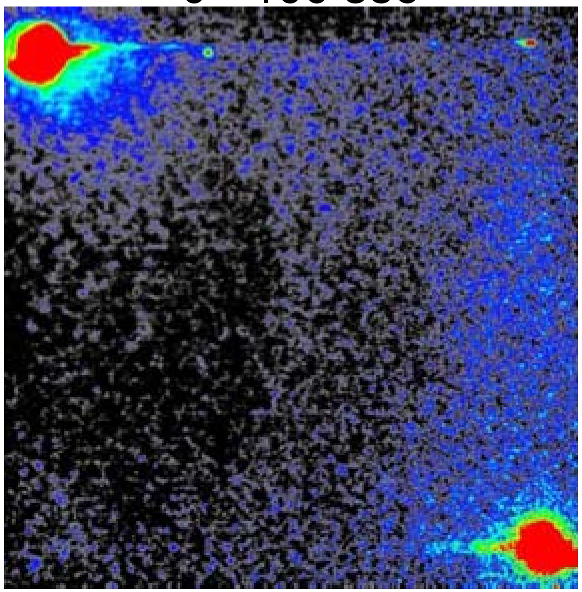
ECSA at -10 °C



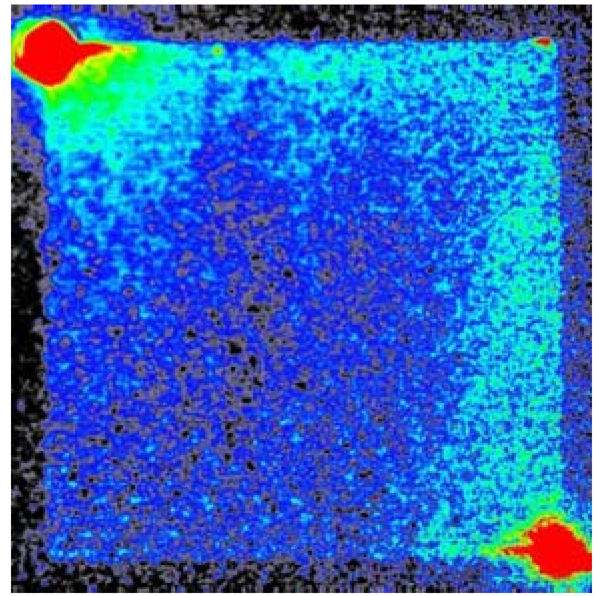
- Little change in HFR
- Steady increase of Charge Transfer Resistance
- Steep increase in Mass Transport Resistance when cell voltage drops
- Performance decays quickly at -10 °C
  - Ice formation leads to mass-transport limitations
  - No change in ECSA at low temperatures
  - As operating time increases, AC Impedance resistance shows mass-transport limitations
- ECSA slightly increases after multiple runs at -10 / 80 °C
  - Possible hydration of membrane or cell break-in

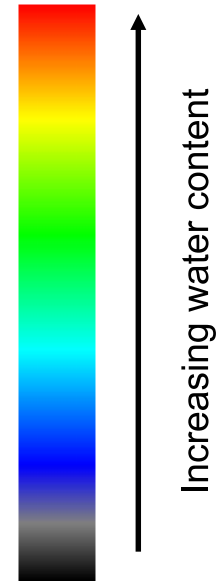
Neutron Imaging of Ice Formation During Operation at -10 ^oC

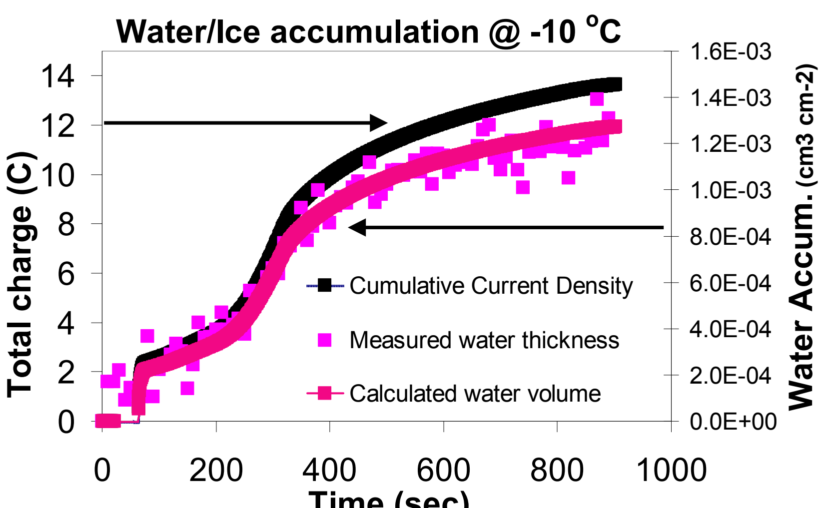
0 - 100 sec



800 - 900 sec

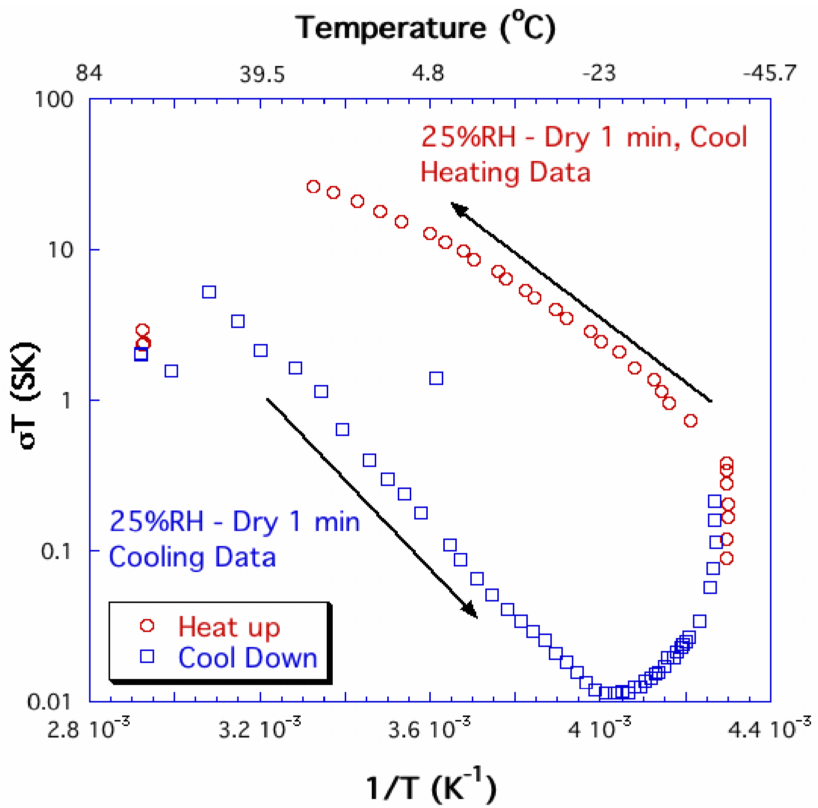


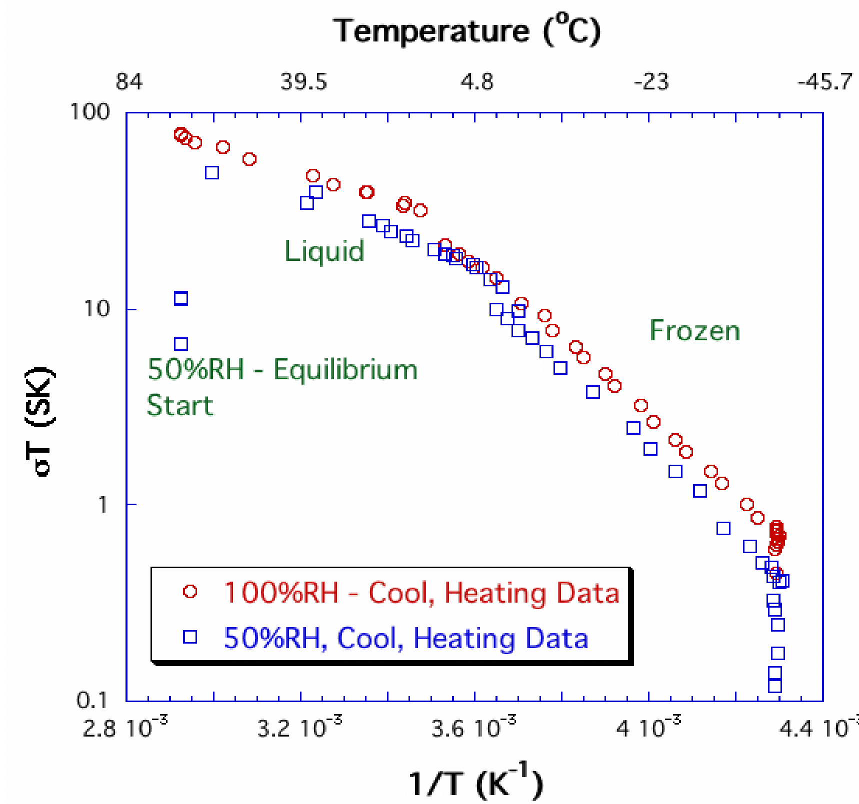




- Neutron imaging of ice formation in a 50 cm^2 fuel cell operated at 0.5 V at -10 ^oC.
- Calculated/measured water/ice accumulation from current and neutron imaging in the fuel cells track

MEA Freezing Conductivity



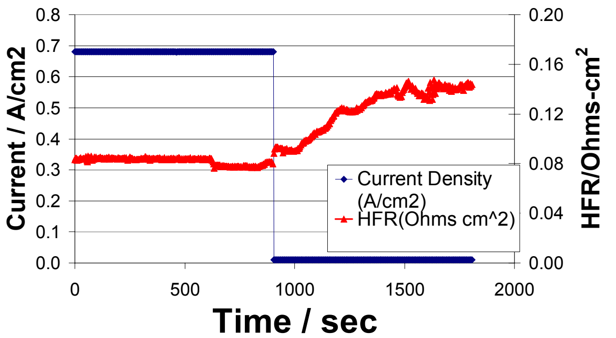


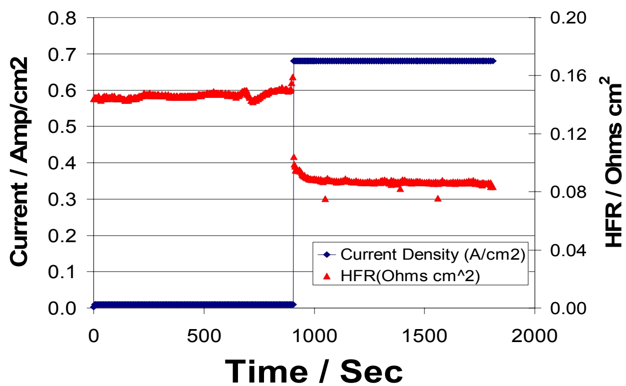
- At 25%RH @ 70 °C:
- Hysteresis is seen; Cooling (Lower λ); Heating (higher λ)
- If cell is left at cold temperatures: membrane will rehydrate

- At 100% RH @ 70 °C: Membrane fully hydrated; No hysteresis in conductivity
- At 50% RH @ 70 °C: Membrane λ is lower, Conductivity is lower
- However, membrane hydrates at low temperatures (higher RH)

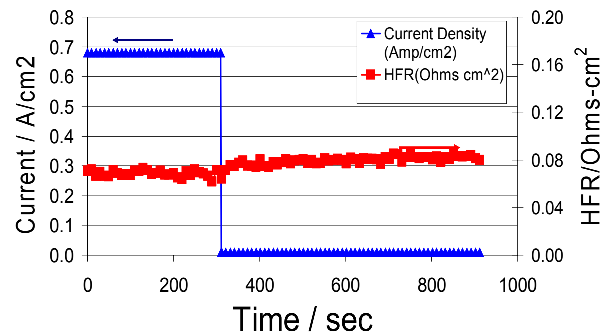
MEA HFR Response to Transients

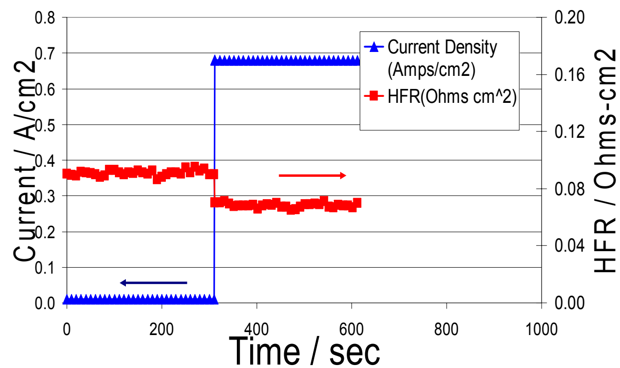
80 °C





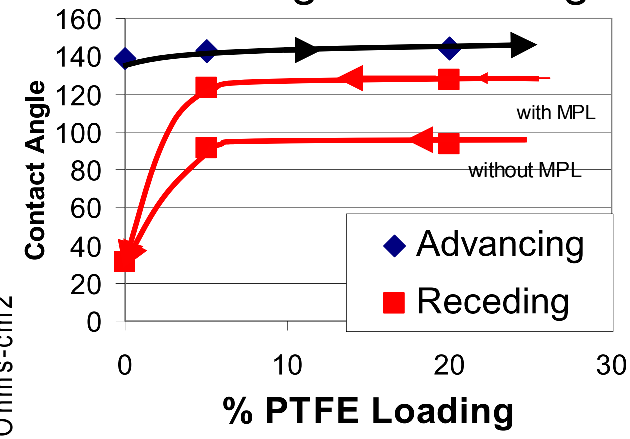
60 °C





Wilhelmy-Plate Contact Angle

advancing vs. receding



- Advancing more hydrophobic
  - Once wet; difficult to 'de-wet'

- Wetting / dewetting show very different time constants in response to transient inputs
  - MEA quickly hydrates / MEA slowly dehydrates
  - Contact angle characterization shows similar hysteresis

0.1/0.2 GORE™ PRIMEA® MEA Series 57110
100% RH Anode
50% RH Cathode

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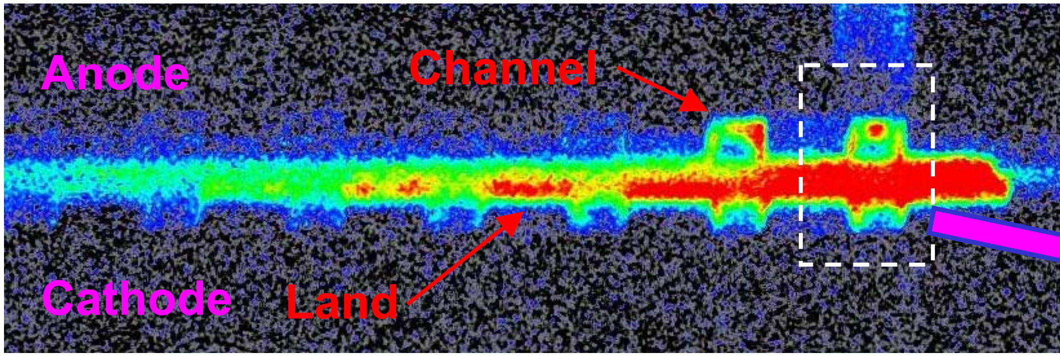
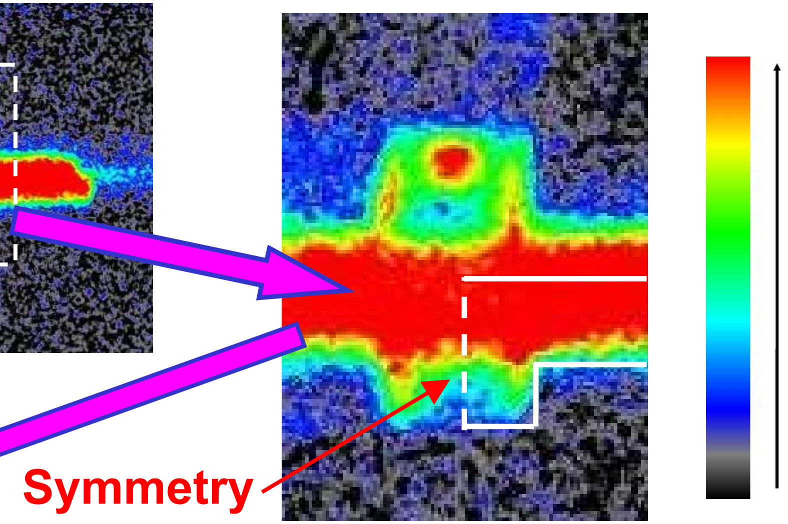
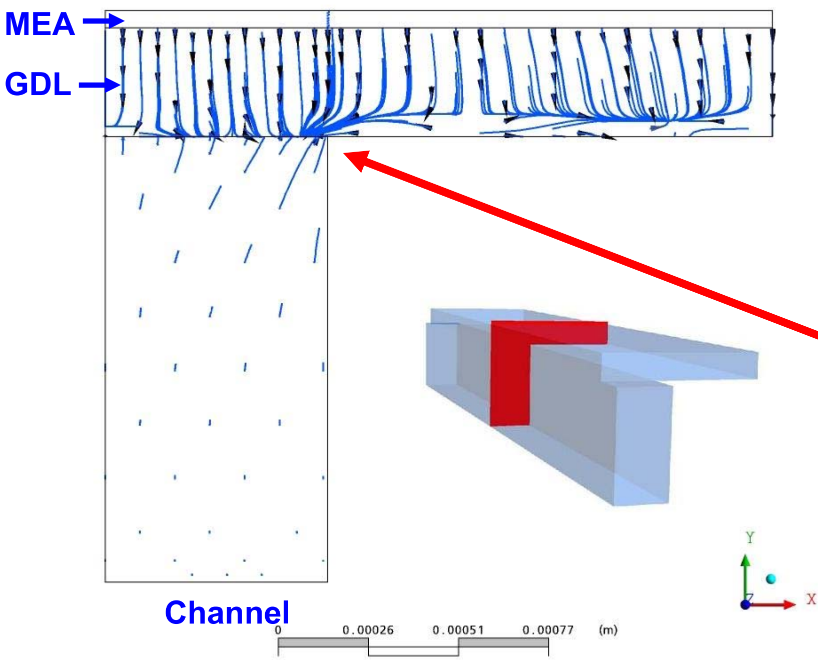
CFD Modeling of Water Removal from GDL





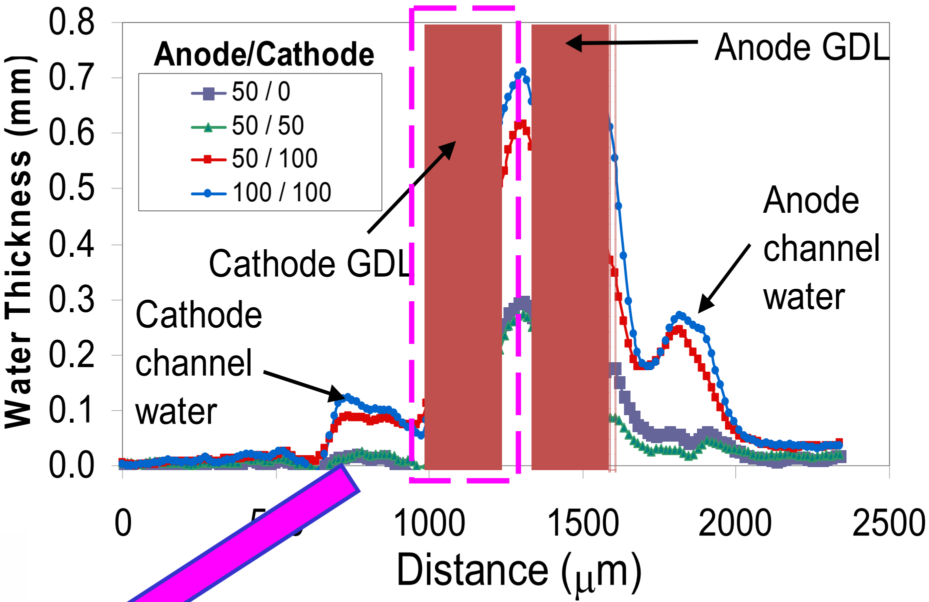
CFD simulations represent liquid water streamlines in diffusion media.

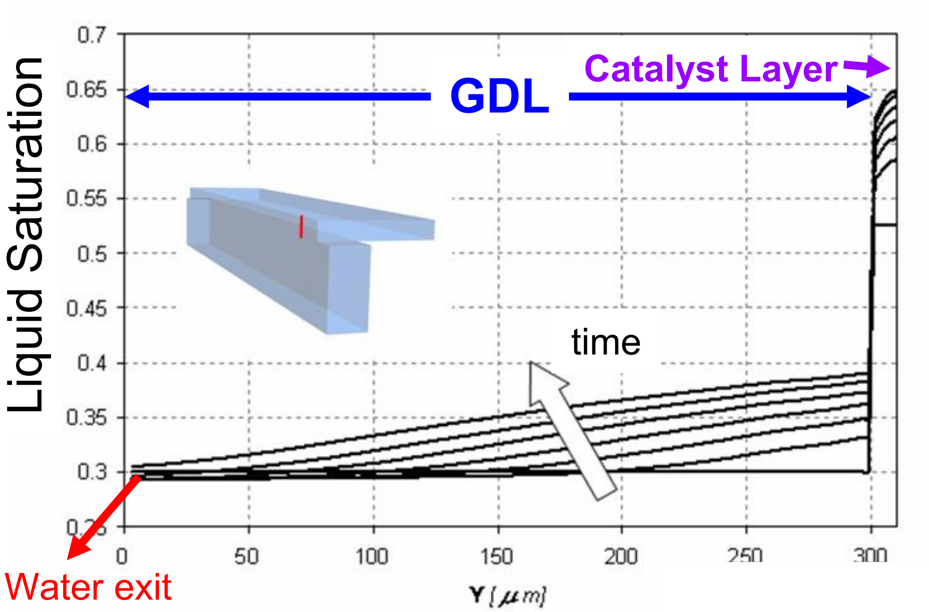


- Liquid water accumulates above the lands before exiting the GDL in the channel.
- Maximum saturation is above the lands.
- Liquid water streamlines converge towards the channel-land corners
  - Sessile/pendant droplets form and leak down the channel walls.
- CFD results agree with Neutron Images

CFD Simulation Results

- Liquid water saturation profiles modeled in the cathode GDL and catalyst layer.
- Liquid water accumulates in diffusion media over time
  - When liquid pressure at GDL-channel interface reaches a threshold value (Young-Laplace) it exits GDL via channel.

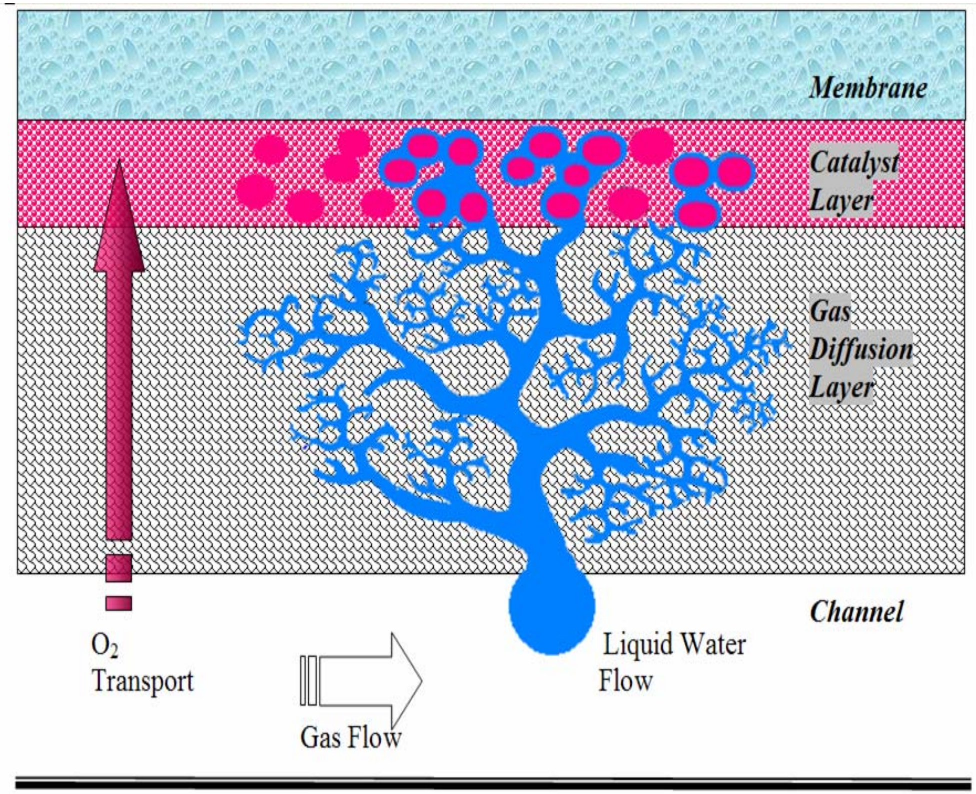




- CFD modeling profiles agree with experimental results (magenta frame above) obtained by neutron imaging.

Predicting Onset of Water-Droplet Detachment

Motivation: droplet detachment from GDL/channel interface is a key mechanism for liquid-water removal in PEM fuel cells. Elucidating water-droplet detachment from GDL/channel interface and being able to predict the critical air-flow velocity required to detach droplets can provide useful design and operational guidelines.



Schematic of water-droplet growing and being deformed by flowing air drag at the GDL/flow-channel interface

Channel/droplet/pore dimensions:

Channel height = 1 mm,
Droplet diameter = 0.6 mm,
Pore diameter = 100 μm

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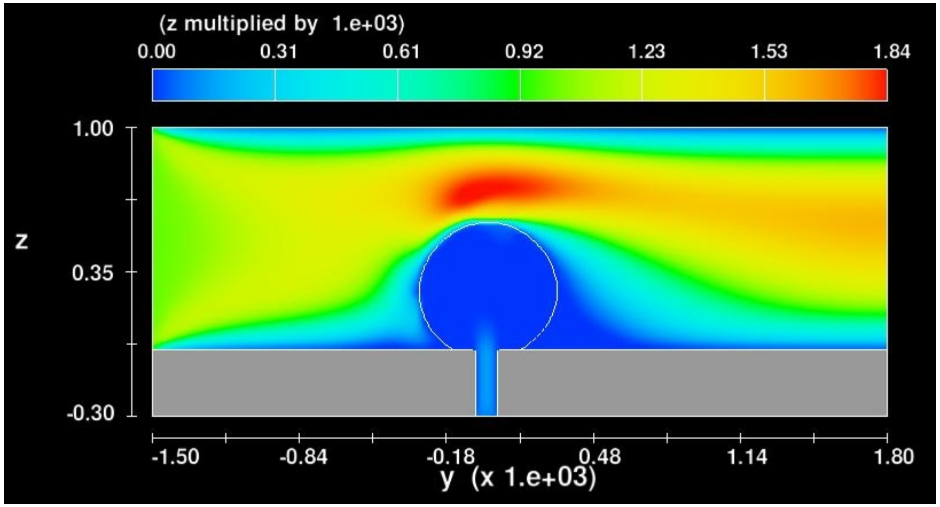
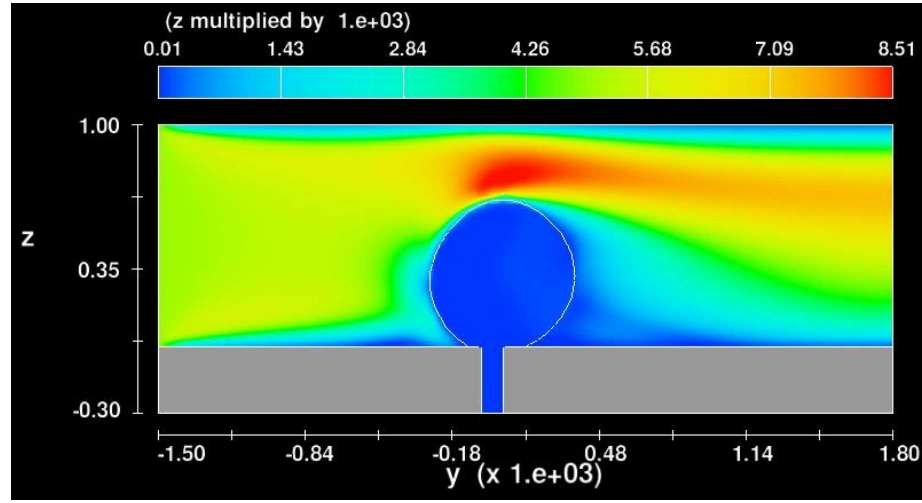
Sandia National Lab

Simulated 3-D water-droplet deformation and detachment from GDL/channel interface

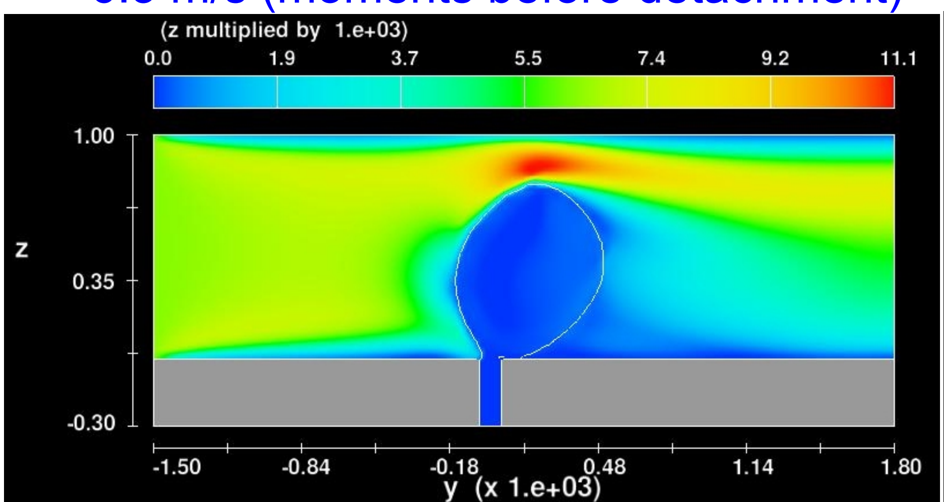
1 m/s (deformation not yet visible)



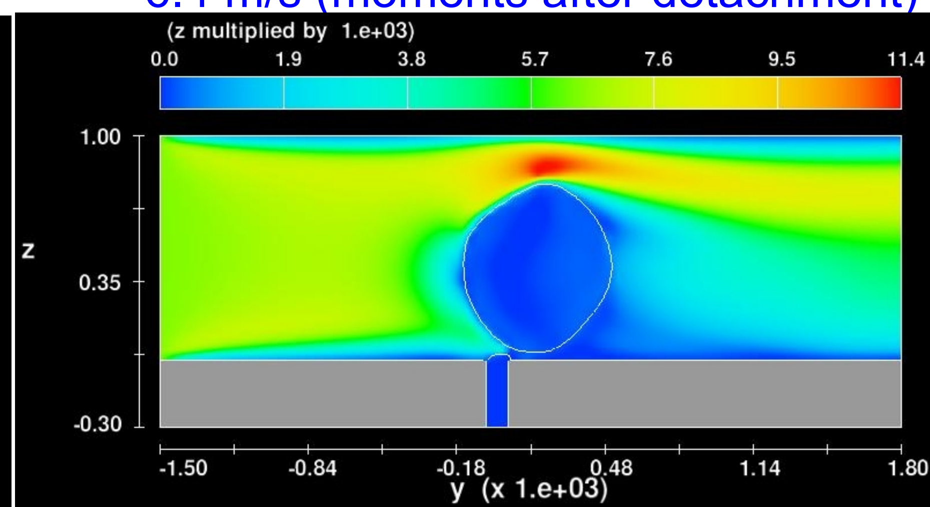
5 m/s (deformation visible)



6.3 m/s (moments before detachment)



6.4 m/s (moments after detachment)



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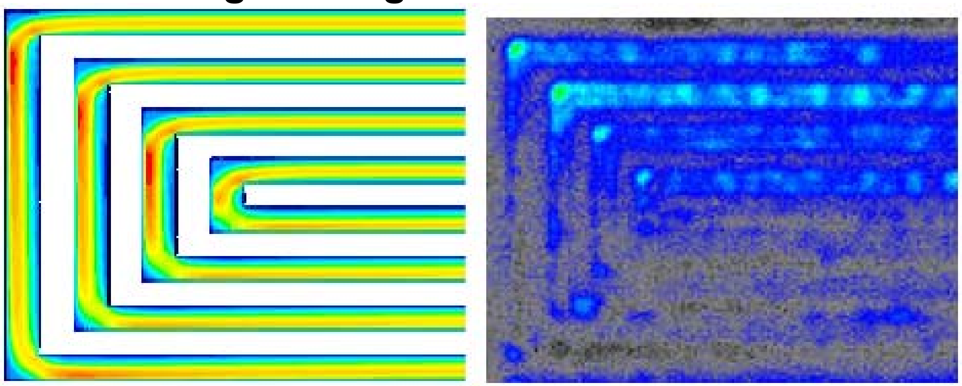
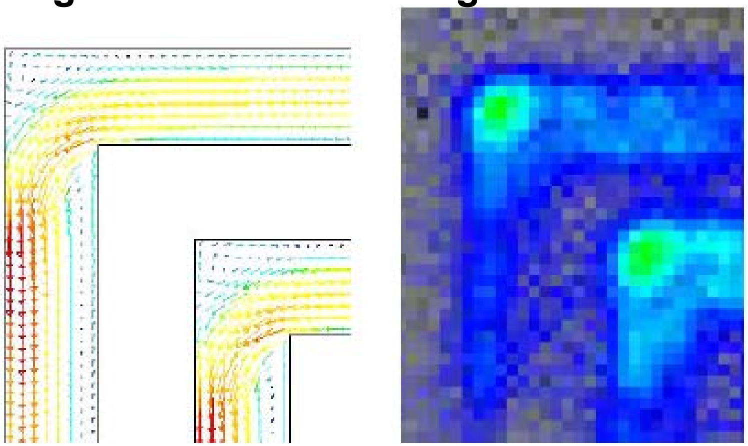
Sandia National Lab

Single-phase CFD model explaining neutron imaging patterns on water distribution*

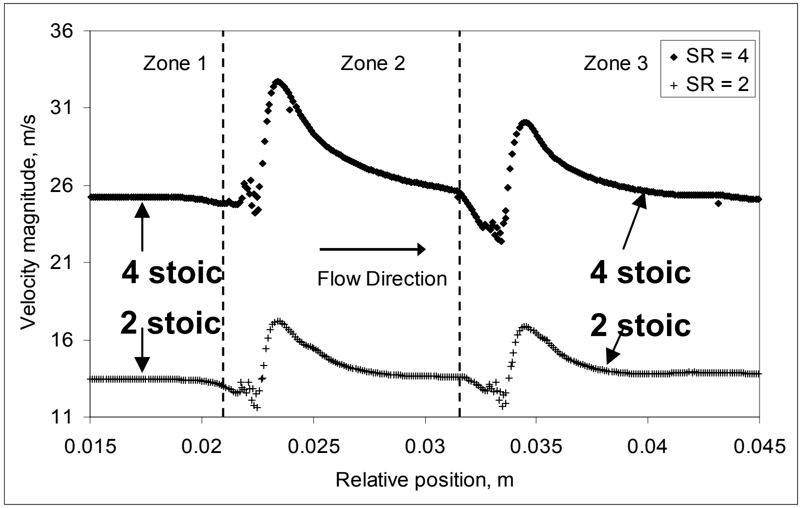
Computed along-channel velocity component and neutron image through a corner of flow channel



Computed velocity vector plot and neutron image in a corner of the gas flow channel



Computed along-channel velocity component through a corner of the gas flow channel



- Regions where liquid water content is reduced corresponds high gas velocity.
- Computed velocity field indicates the presence of recirculation zones in the 90° bends.
- Low flow speed and circular nature of gas flow lead to reduction in water removal driving force and corresponding increase in water content.

*Reference: M. A. Hickner, K. S. Chen, N. P. Siegel, to appear in *Journal of Fuel Cell Science and Technology* (2008)

Sandia National Lab

Future Work

- **NIST Neutron Imaging (June 12-18)**
  - NSTF Start-up, understand saturation water content of membrane, high resolution freeze, transients
- **Transient operation**
  - Simulate automotive operation, RH transients
- **Segmented Cell operation**
  - Measure water transport spatially in cell by HFR
- **Freeze Measurement**
  - *in situ* monitoring of ice formation
- **Characterization**
  - TEM characterization of aged GDL materials, surface spectroscopy of GDL surfaces
- **Model development**
  - Develop multi-dimensional (quasi-3D) model of water transport and removal
  - Incorporate sub-models of liquid-water removal via droplet detachment and evaporation

Milestones

Mon Yr	Milestone	
Dec 07	Quantify water content by HFR measurements in various cell components under steady-state operation	✓
Dec 07	Accurate water balance measurements during steady-state operation	In progress
Mar 08	100 freeze/thaw cycles to -40°C on fully humidified cells using paper GDL (completed FY07) New: Performance of fuel cells operated at –10°C	✓ ✓
Jun 08	Report surface properties of GDL and the effect of aging	✓
Sept 08	Direct observation of ice formation by neutron imaging (completed FY07)	✓

Summary of Technical Accomplishments

- Experimentally measure water *in situ* operating fuel cells
  - Direct water imaging at NIST by neutrons
    - High resolution (25 μm) imaging, Low resolution (150 μm) imaging
  - AC Impedance and HFR measurements
  - Freeze/Thaw
    - Ice results in performance loss associated with increasing low freq. resistance
      - Ice formation limits gas access to the reaction sites
- Characterization
  - Hydrophobicity characterization, microscopic characterization, elemental compositional
  - Varying GDL materials (MPL Teflon loading, GDL substrate Teflon loading)
    - GDL wetting/dewetting properties help explain fuel cell performance hysteresis.
- Modeling of water transport within fuel cells
  - Delineation of mass transport loss from IR, kinetics, etc.
  - Modeling of water-droplet detachment from the GDL/channel interface.
  - CFD modeling simulates liquid water saturation profiles