# Neutron Imaging Study of the Water Transport in Operating Fuel Cells

**Presented by: David Jacobson**

Daniel Hussey

Eli Baltic

Muhammad Arif, PI

Physics Laboratory

National Institute of Standards and Technology

Gaithersburg, MD 20899

Wednesday June 9, 2010

**UNITED STATES DEPARTMENT OF COMMERCE**
**National Institute of Standards and Technology**
Gaithersburg, Maryland 20899-8461

# FC021

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

# Overview

## Timeline

**Project Start :** 2001, continuing
**Percent Complete:** 100% for each year

## Barriers

**(A) Durability**
**(C) Performance**
**(D) Water Transport within the Stack**

## Budget

**Project funding FY 2009**

| | |
|---|---|
| DOE: | $ 300 k |
| NIST: | $ 550 k |
| Industry: | $ 550 k |
| **Total** | $ 1,400 k |

**Project funding FY 2010**

| | |
|---|---|
| DOE: | $ 584 k |
| NIST: | $ 550 k |
| Industry: | $ 266 k |
| **Total** | $ 1,400 k |

## Partners/Users/Collaborators

**Project Lead: National Institute of Standards and Technology**

- Ballard
- Ford
- General Motors
- Georgia Tech
- Lawrence Berkeley National Laboratory
- Los Alamos National Laboratory
- Michigan Technological University
- Nissan
- NOVA Scientific
- Nuvera
- Oak Ridge National Laboratory
- Pennsylvania State University
- Rochester Institute of Technology
- Sandia National Laboratory
- Sensor Sciences
- University of California, Berkeley
- University of Connecticut
- University of Kansas
- University of Michigan
- University of Tennessee
- Wayne State University

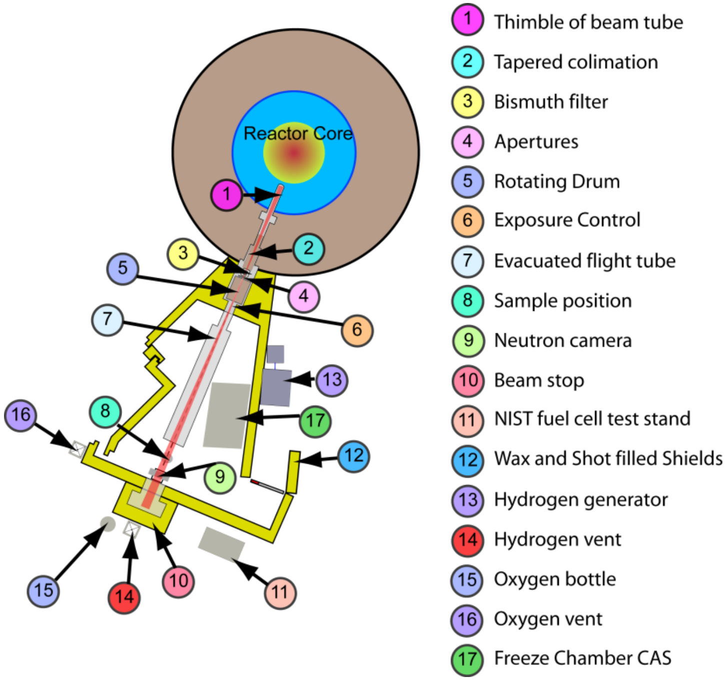
# Relevance/Objectives

This National Institute of Standards and Technology project aims to develop and employ an effective neutron imaging based, non-destructive diagnostics tool to characterize water transport in PEM fuel cells. Objectives include:

- **F**orm collaborations with industry, national lab, and academic researchers
- **P**rovide research and testing infrastructure to enable the fuel cell / hydrogen storage industry to design, test and optimize prototype to commercial grade fuel cells and hydrogen storage devices.
- **M**ake research data available for beneficial use by the fuel cell community
- **P**rovide secure facility for proprietary research by Industry
- **T**ransfer data interpretation and analysis algorithms techniques to industry to enable them to use research information more effectively and independently.
- **C**ontinually develop methods and technology to accommodate rapidly changing industry/academia need

# Approach

- **NIST Neutron Imaging Facility**
  - National user facility access to beam time through peer reviewed proposal system
  - Experiments published in open peer reviewed literature
  - State-of-the-art imaging technology
  - High flux neutron source
  - Proprietary access provided to fuel cell industry
- **Fuel cell testing infrastructure**
  - State-of-the-art small scale fuel cell test stand and EIS fully supported (details in supplementary slides) .
  - **Environmental Chamber for freeze testing** -40 C to +50 C
- **Radiography**
  - New image acquisition software developed by NIST and tailored to facility users
  - Dramatic improvement of resolution anode vs. cathode using slit apertures
  - Only way to measure transient processes
  - One-dimensional cells can be made to validate simple edge on radiography
- **Improving imaging technology**
  - **High resolution neutron imaging 13 μm resolution**
    - *Resolve Water distribution in GDL and thick MEAs*
    - *Unambiguous discrimination of anode from cathode*
  - **High resolution CCD/gadox scintillator < 20 μm**
- **Measurement focus**
  - Membrane water uptake
  - Through-plane water distribution to understand water transport in the GDL
  - Freeze studies
  - Capillary properties of GDL and Catalyst materials
  - In-Plane Water transport in MEA/Flow channels



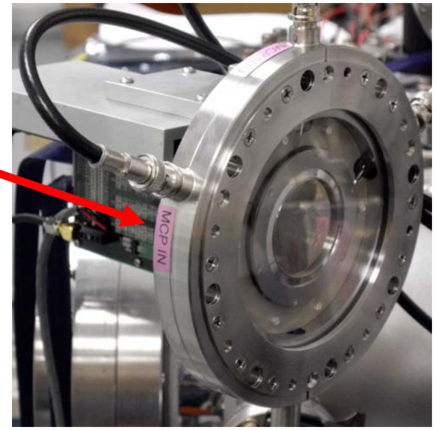

NIST Neutron Imaging Facility. Full facility capabilities provided in supplemental slides.

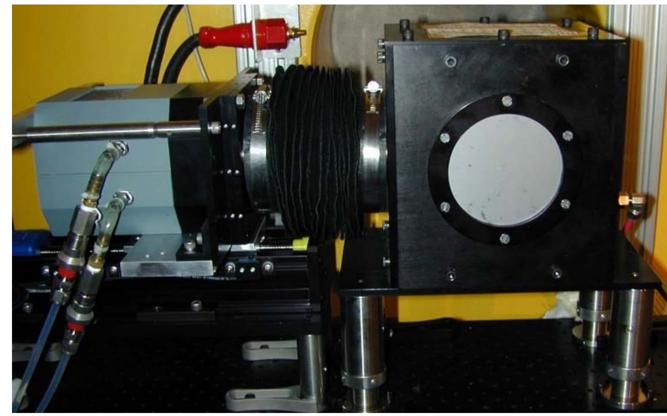
# Collaborator work presented here

- T.A Trabold, S. Kandlikar, Rochester Institute of Technology
- J.J. Gagliardo, J.P. Owejan, General Motors
- J. Allen, Michigan Technological University
- A. Turhan, S. Kim, M. Hatzell, M. M. Mench, Pennsylvania State University
- R.S. Fu, U. Pasaogullari, CT Global Fuel Cell Center, University of Connecticut
- R. Borup, R. Mukundan, J. Davey, Y. Kim, J. Spendelow, T. Rockward, Los Alamos National Laboratory

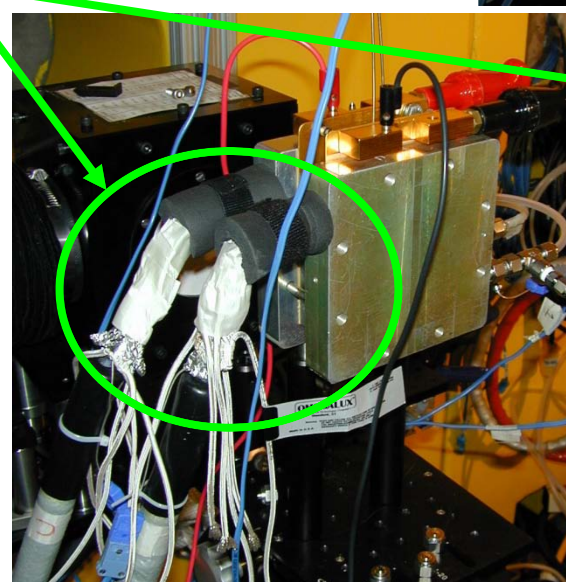
# Instrument Development

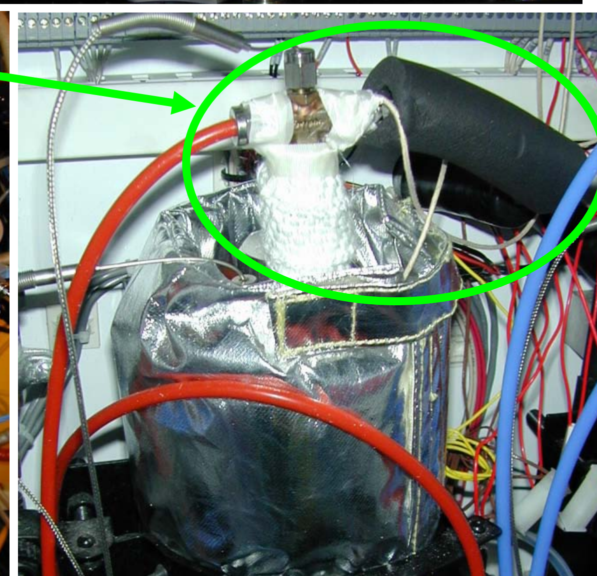
- ***New MCP detector with 13μm spatial resolution!!***
- New High Resolution CCD/GadOx Scintillator detector
  - Resolution <20 μm limited by pixel pitch
- Updates to NIST image analysis code
  - Address systematic effects due to counting statistics, spatial resolution, and beam hardening
- Improved humidity control by eliminating all cold spots and introducing check valve in the bypass
- New closed bath chiller to expedite freeze testing
- 2 Planned large format high resolution detectors
  - MCP with 15 μm resolution, 10 cm x 10 cm FOV
  - Large format CCD, 10k x10k, with 9 μm pixel pitch
  - Backup plates for existing MCP detectors



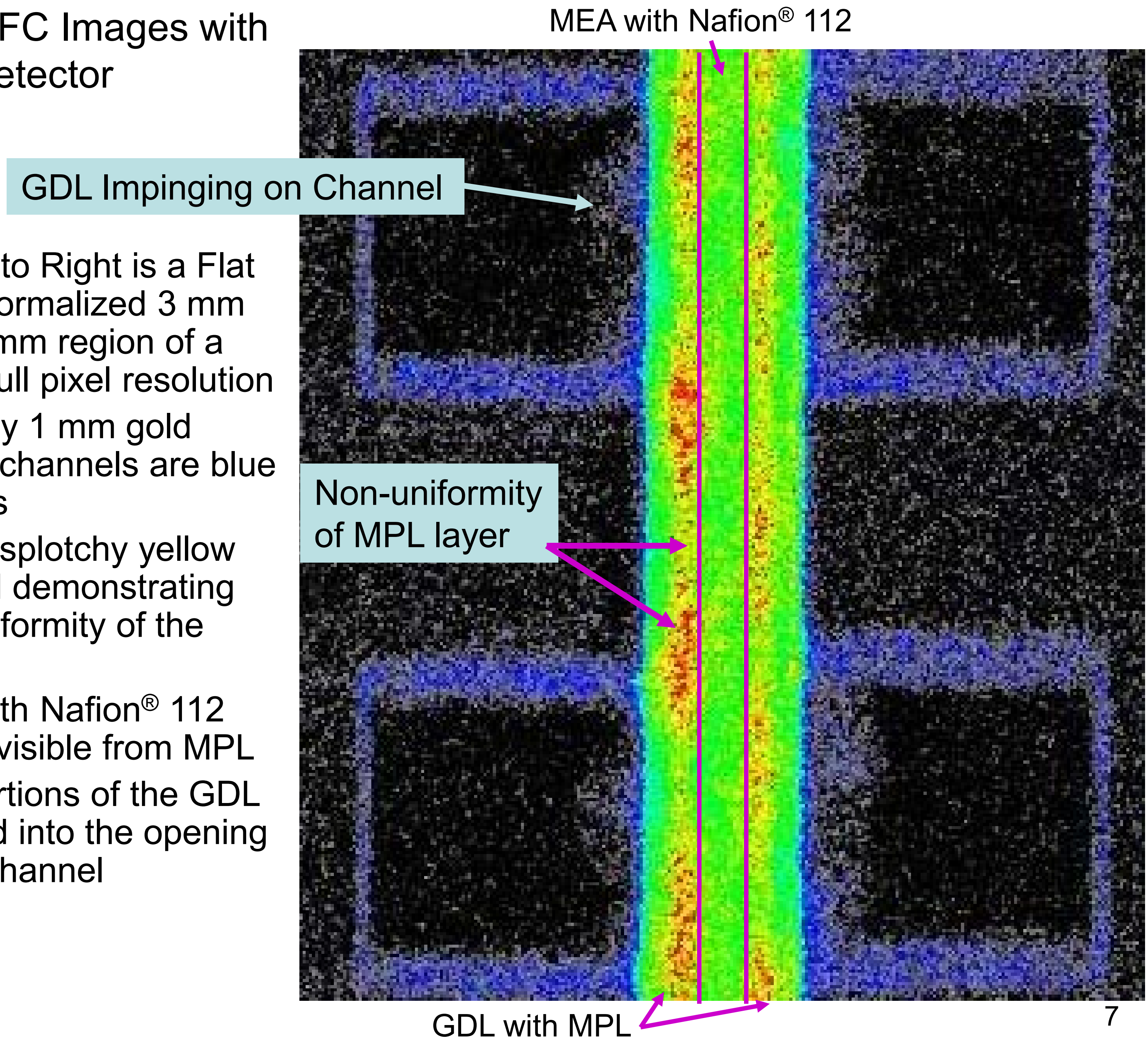



CCD/GadOx Detector System with <20 μm spatial resolution will enable high resolution imaging of in-plane water content



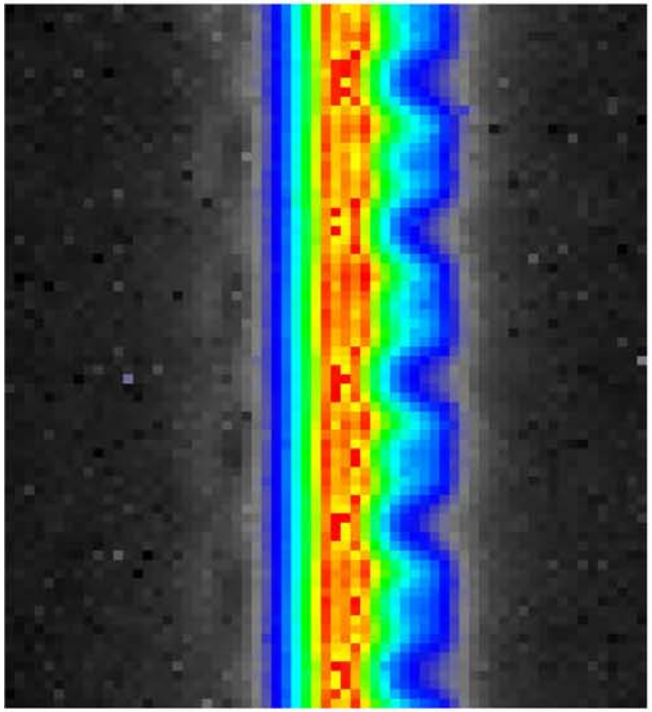


# First PEMFC Images with “10 µm” detector

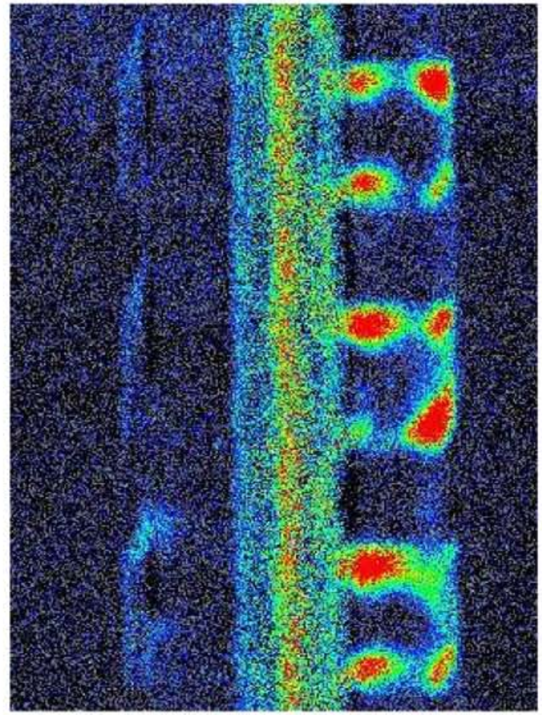



- Shown to Right is a Flat Field Normalized 3 mm by 2.5 mm region of a cell at full pixel resolution
- 1 mm by 1 mm gold coated channels are blue squares
- MPL is splotchy yellow and red demonstrating non-uniformity of the layer
- MEA with Nafion® 112 clearly visible from MPL
- See portions of the GDL crushed into the opening of the channel

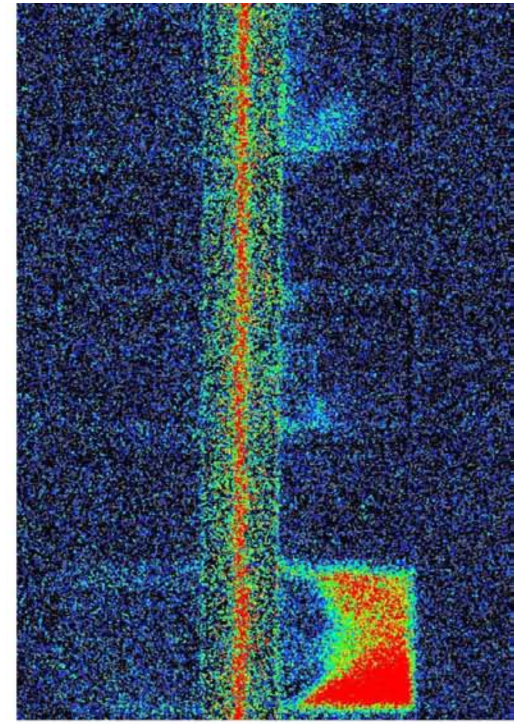
# Progress of higher spatial resolution



Scintillator 250 µm



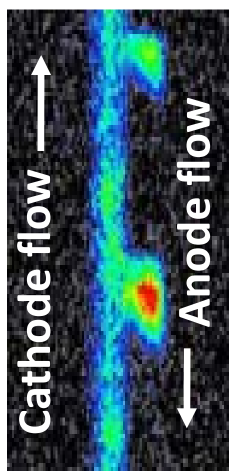
MCP 25 µm



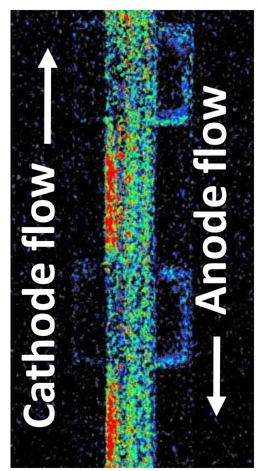
MCP 13 µm

Detectors:
Pixel pitch 14.7 µm vs. 5 µm
Resolution 25 µm vs. 13 µm

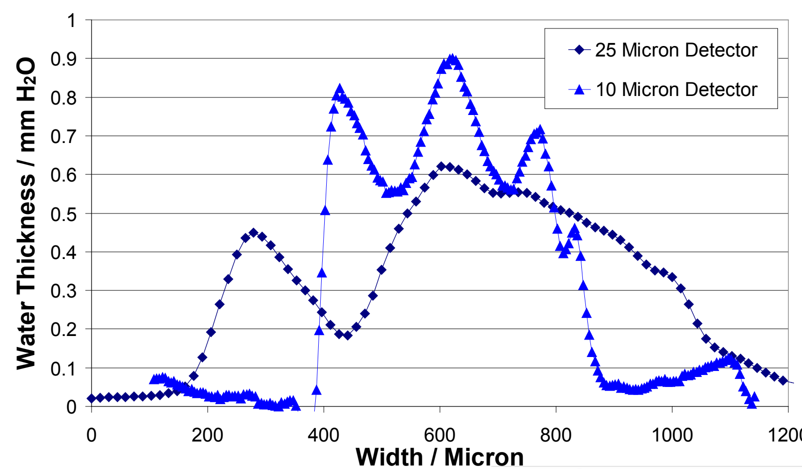
Cell details
Gore Primea




25 µm Detector



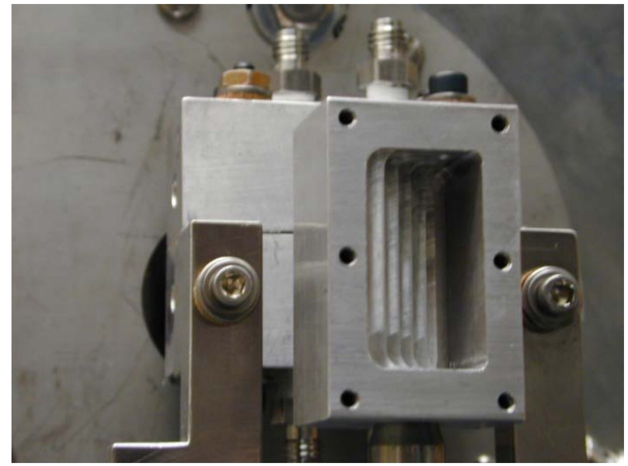

10 µm Detector

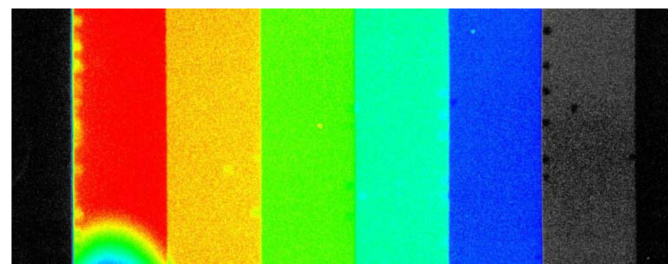



Los Alamos

# Effects of residual water and beam hardening

- Water attenuation increases as neutron kinetic energy decreases – lower energy neutrons are preferentially scattered
- Neutron beam is polyenergetic; neutron beam transmitted through a section of water has a more energetic spectrum (harder) and penetrates deeper through material
  - ***Sections of water appear to be thinner***
- Can accurately measure beam hardening to obtain correct water contents; modeled as a quadriatic:
  - $OD = \mu t_w + \beta t_w^2$
- However, membrane never fully dries for *in situ* testing; *ex situ* tests show $\boldsymbol{\lambda_{res} \approx 2}$
- When normalizing by the dry image, the effect of residual water causes a change in Optical Density vs. water thickness:
  - $OD(t_w + t_{res}) = (\mu\mathbf{+2\beta t_{res}})\, t_w + \beta t_w^2$
- Clear shift in attenuation due to the MEA of a cell in front of the cuvet is shown in figures to right
- Also checked carbon, which showed no beam hardening effects, will soon investigate common gasket materials

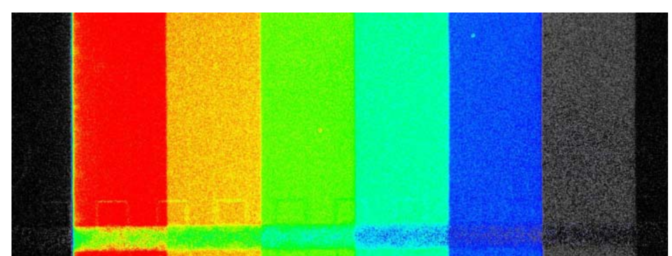




Without a PEMFC

5.5 4.4 3.4 2.4 1.3 0.3

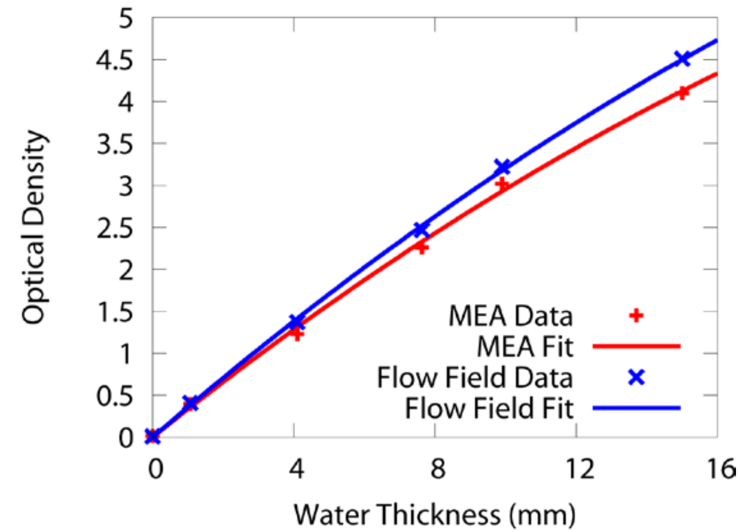
Water depth (mm)

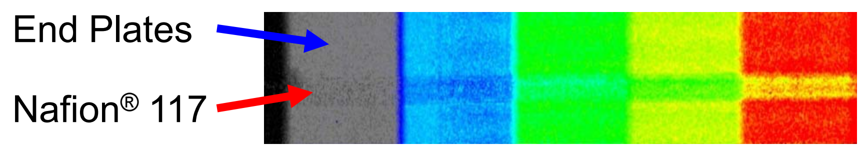


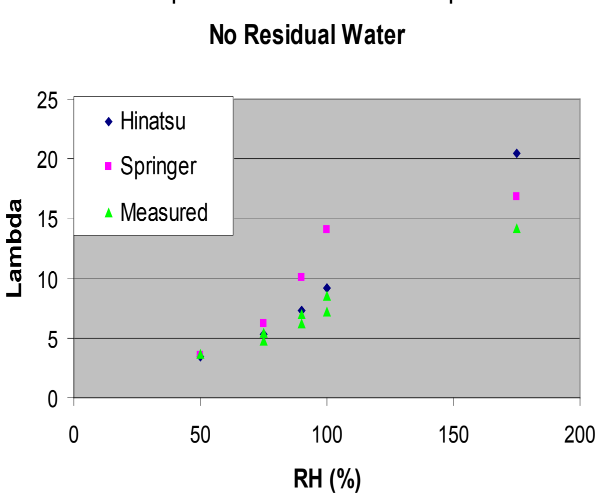
With a PEMFC

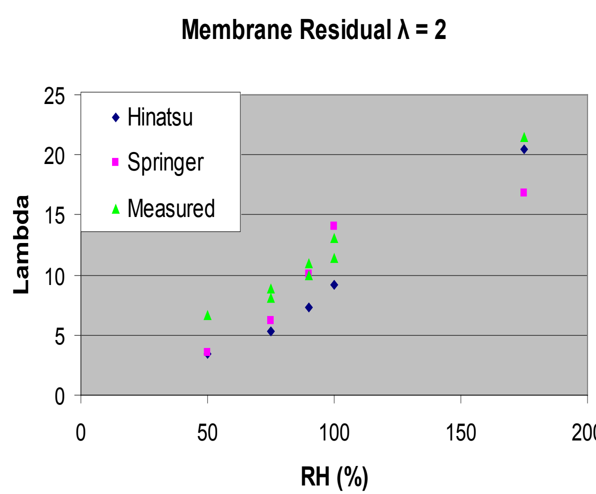
# Verifying the effect of residual water

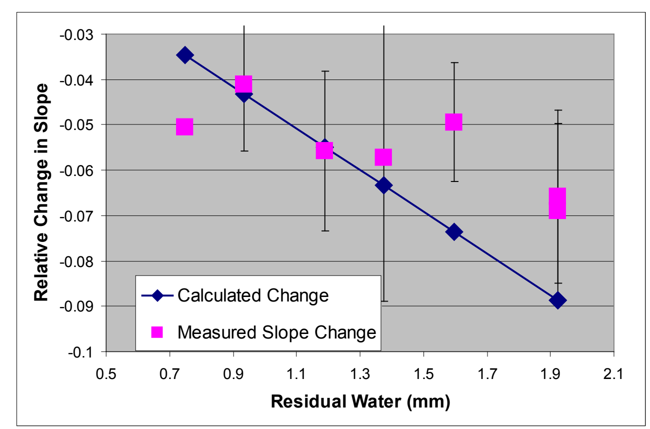
- LANL fabricated 3 sets of hardware with N117 active widths of 8 mm, 12 mm and 20 mm, along with scanning the RH, this enables varying the residual water content
- Place a cell between detector and water cuvet, taking two sets of images with the cuvet empty and filled with water
- Measure water attenuation in MEA and Flow Field End Plates; clear difference in the linear behavior attributed to membrane water content
- Membrane water content estimated using λ(RH) from literature; its assumed λ=1.5 under gaskets, λ=1.5 in the active area for dry inlet gases
- Residual water was measured by:
  - Obtain $OD(t_w)$ in flow fields to fix μ & β
  - Fit MEA region allowing only $t_{res}$ to vary in:
    $OD(t_w + t_{res}) = (\mu + 2\beta t_{res})\, t_w + \beta t_w^2$
- Reasonably good agreement between estimated and measured slope change
- ***New Data Acquisition and Analysis Strategy***:
  - Perform calibration measurement for each cell in the dry state to measure residual water content
  - Historic data must rely on estimates from *ex situ* drying experiments
  - Applied correction to constrained membrane data, which shows the need to incorporate the residual water into the analysis
  - Working with LANL to complete a survey of membrane water uptake experiments that will incorporate the correction



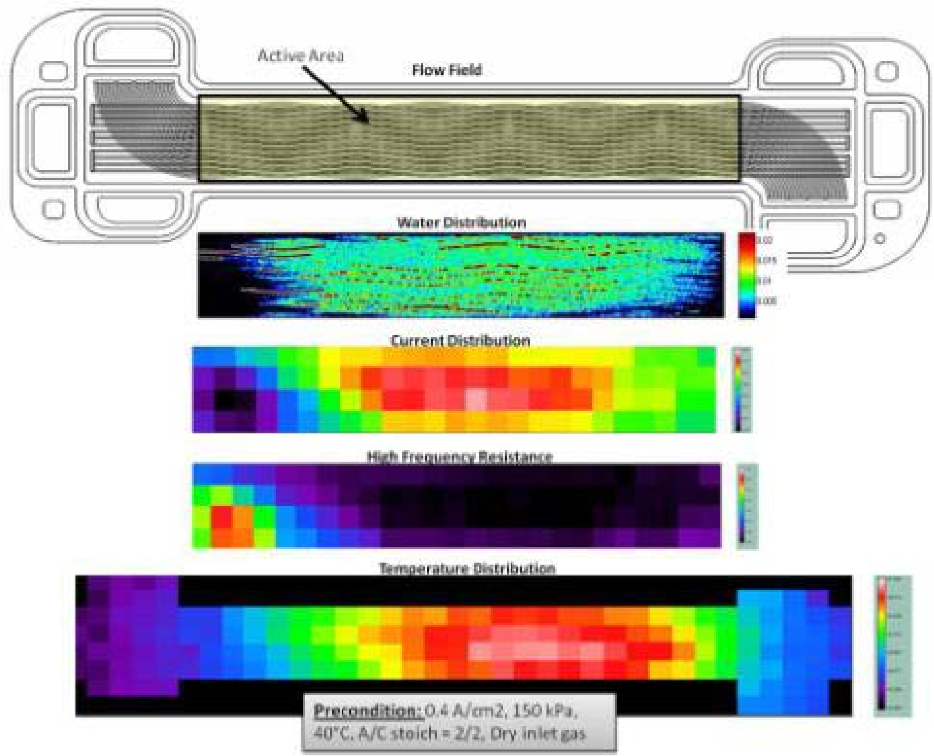



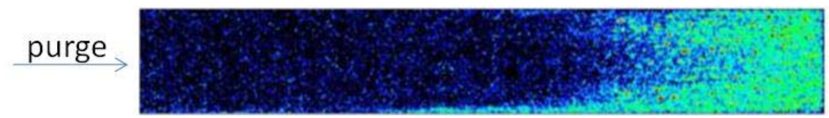
# Simultaneous Water, Current, HFR, and Temperature Measurement

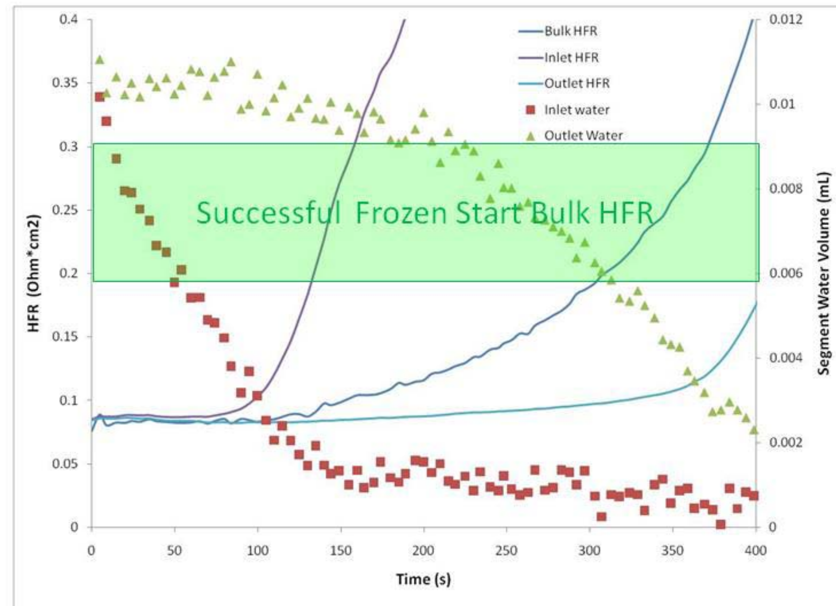
Correlate temperature effects to ionomer and GDL water content, down-the-channel model validation

Owejan, et al., J. Electrochem. Soc., 156, B1475-B1483 (2009).




Local temperature, current density and HFR vary significantly for a given precondition

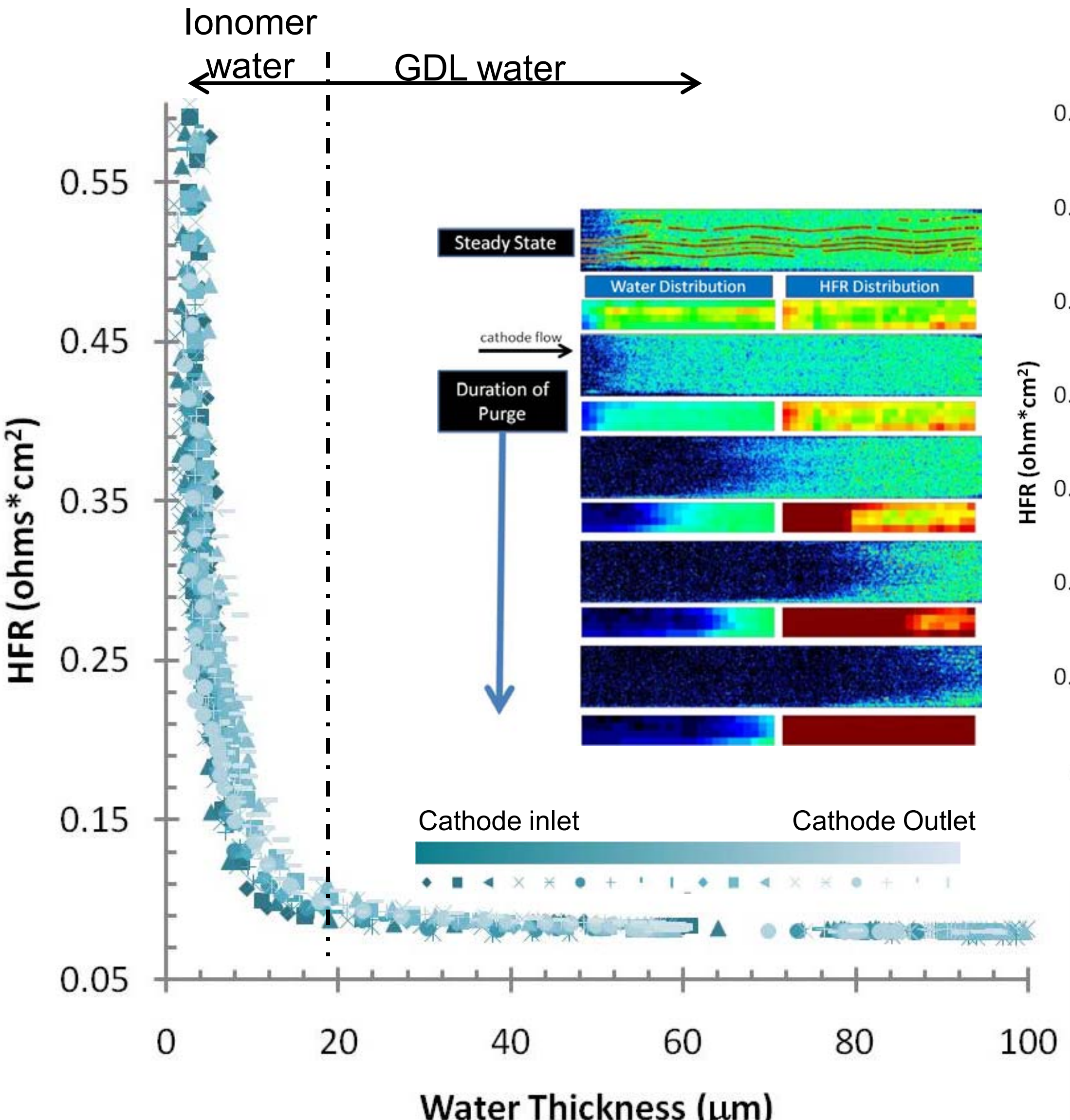


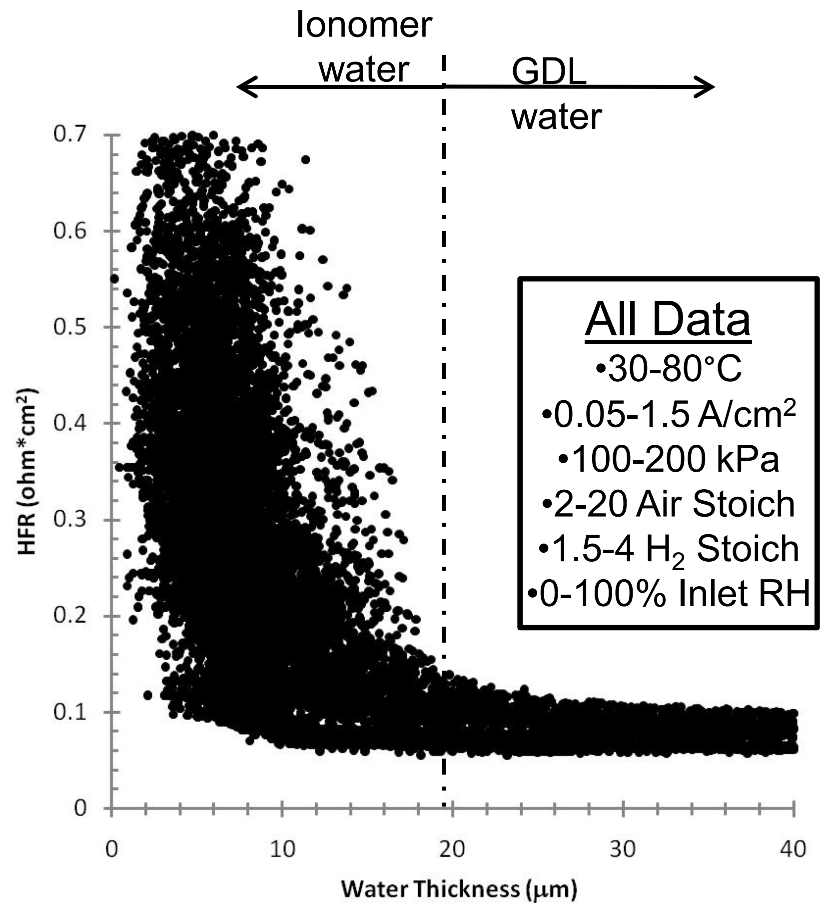

Once the saturation state for a precondition is understood, the relationship of local HFR increase with drying must be known to optimize purge conditions and materials for successful starts that have an even current distribution. Bulk HFR measurement is not sufficient.

Is there a direct correlation between local HFR and liquid water content in the GDL? After liquid water is removed from the GDL how quickly does HFR respond?

# Relationship between liquid water content and HFR




**Purge condition:** 100 kPa, 33°C, 1 SLPM N2, Dry inlet gas




Direct correlation between HFR rise and water removal from GDL. Liquid water required in GDL to minimize HFR as transition is very sensitive.

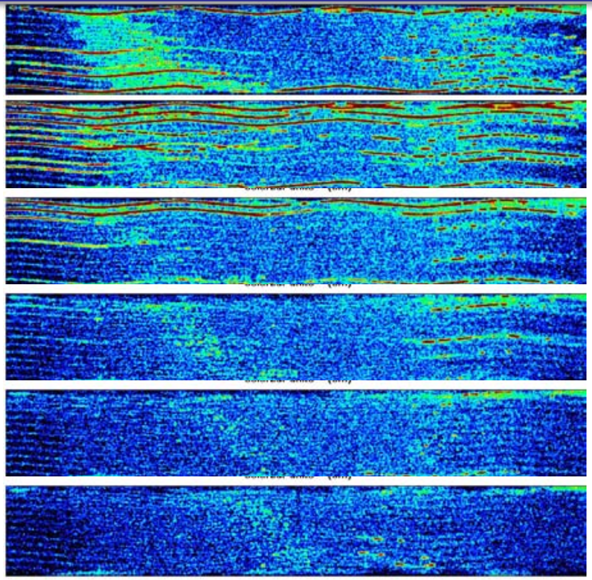
R·I·T GM MichiganTech

# GDL thermal conductivity impact on water accumulation

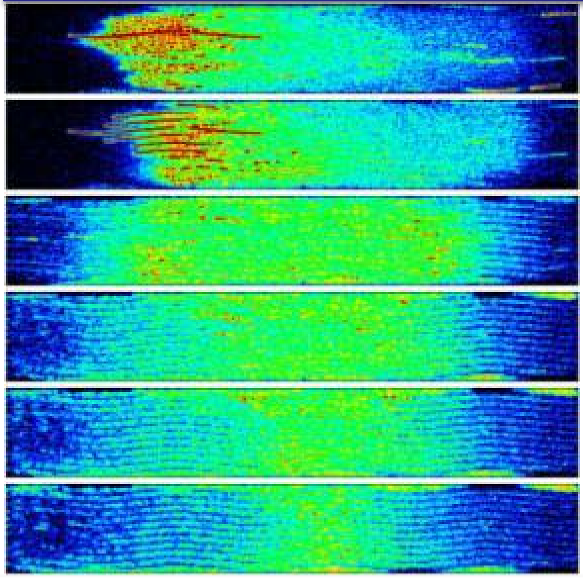
cathode flow → ← anode flow

**Pol Curve Condition:**
200 kPa, 80°C
A/C stoich = 1.5/2 100% RH inlet gas

## Baseline ($k_{sub}$ = 0.3 W/mK)



## GDL B ($k_{sub}$ = 0.9 W/mK)



0.05 A/cm$^2$

0.2 A/cm$^2$

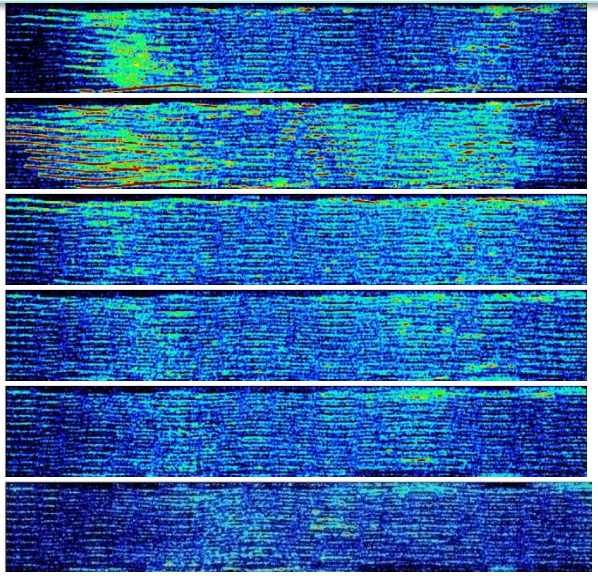
0.6 A/cm$^2$

1.0 A/cm$^2$

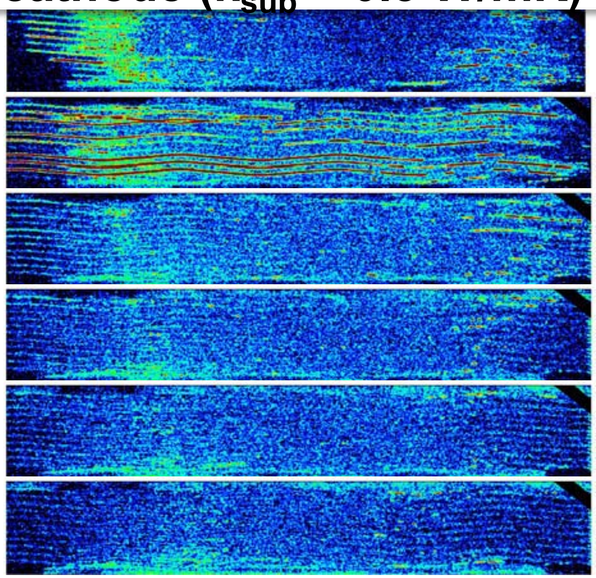
1.2 A/cm$^2$

1.5 A/cm$^2$


## GDL A ($k_{sub}$ = 0.3 W/mK)



## GDL A anode, Baseline cathode ($k_{sub}$ = 0.3 W/mK)



0.05 A/cm$^2$

0.2 A/cm$^2$

0.6 A/cm$^2$

1.0 A/cm$^2$

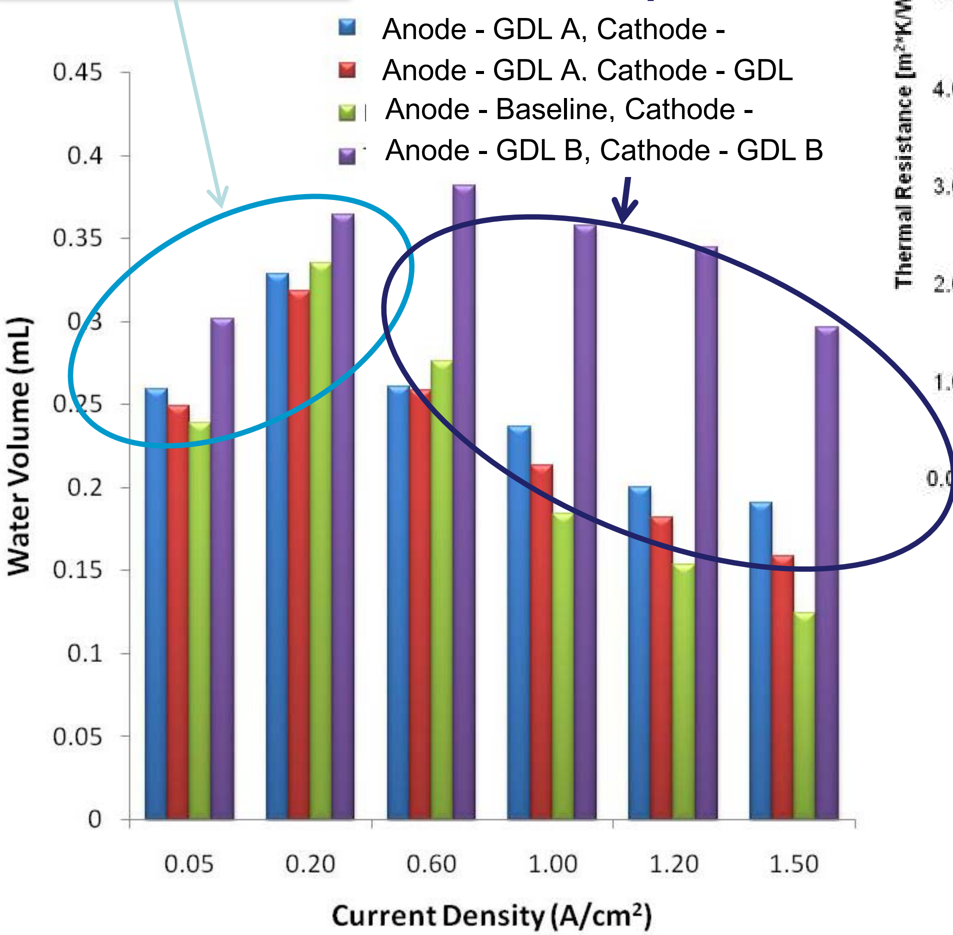
1.2 A/cm$^2$

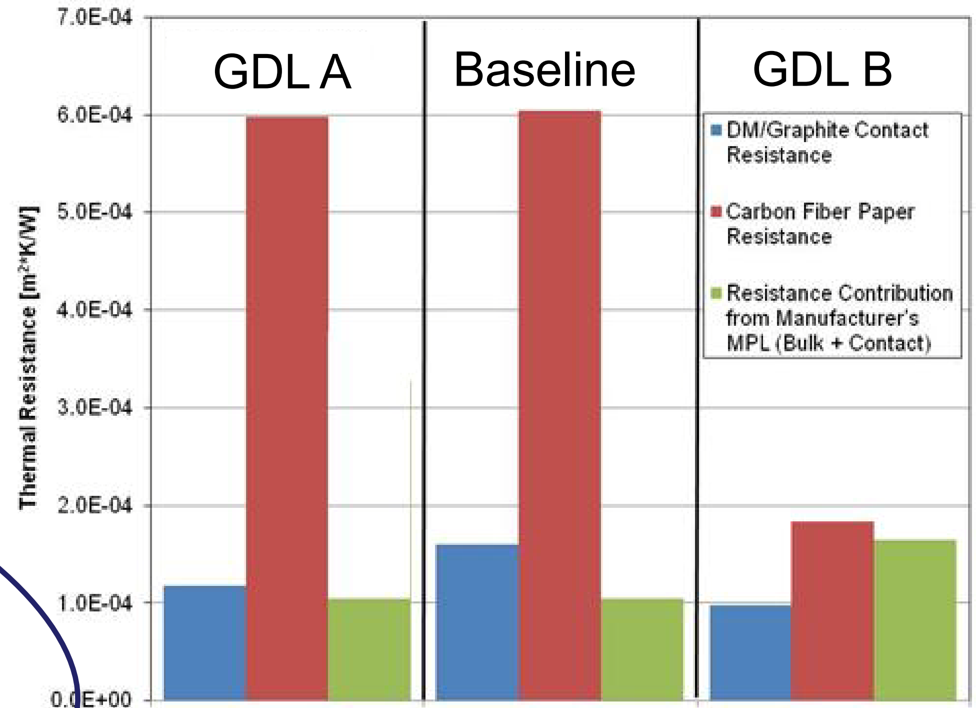
1.5 A/cm$^2$

# What impacts the initial saturation state – GDL thermal conductivity?

Low heat flux = small temperature gradient, values should be similar

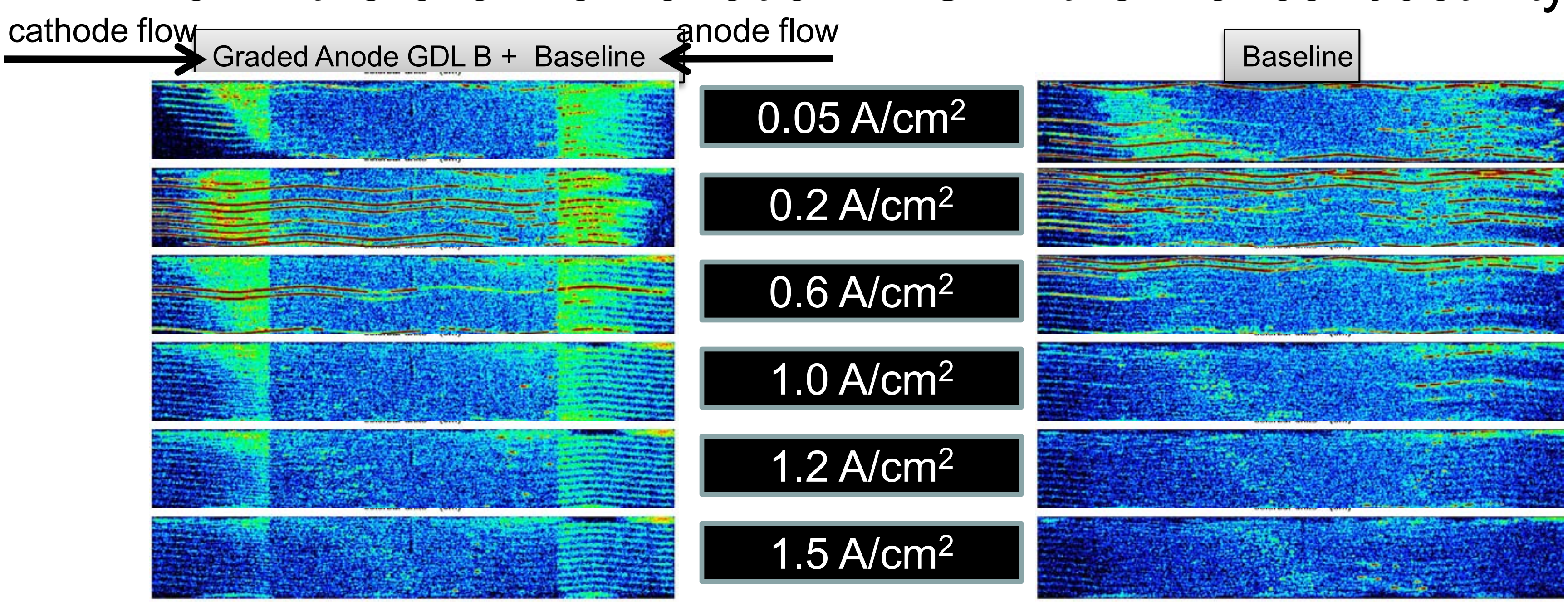
As heat flux increases, more conductive substrates have lower dT and more water condenses

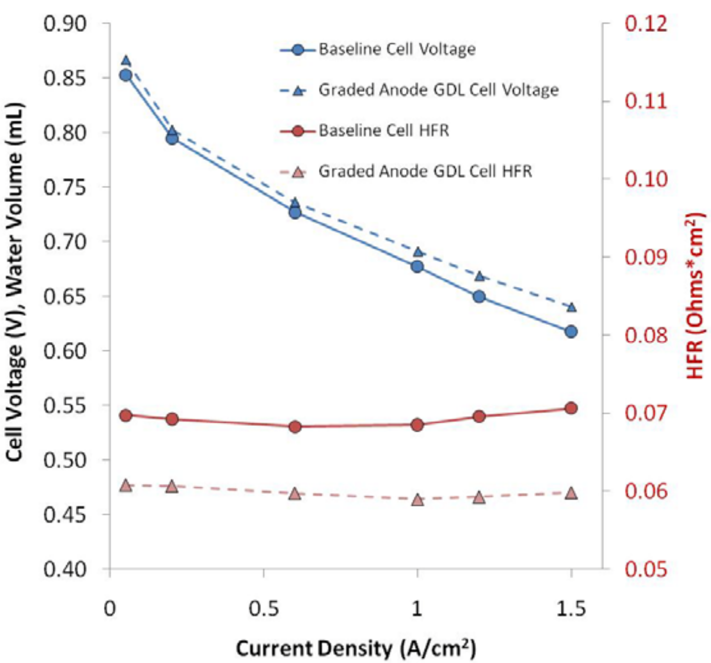


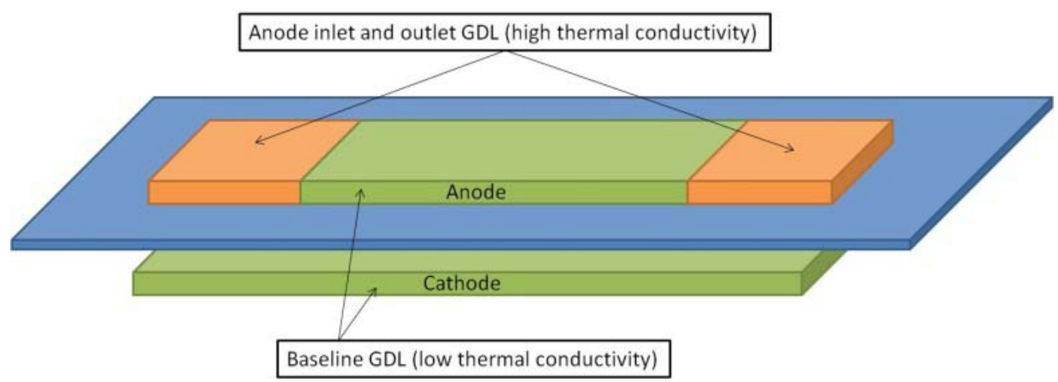




Higher thermal conductivity effectively lowers the saturation pressure near the MEA and more condensation in the bulk substrate results.

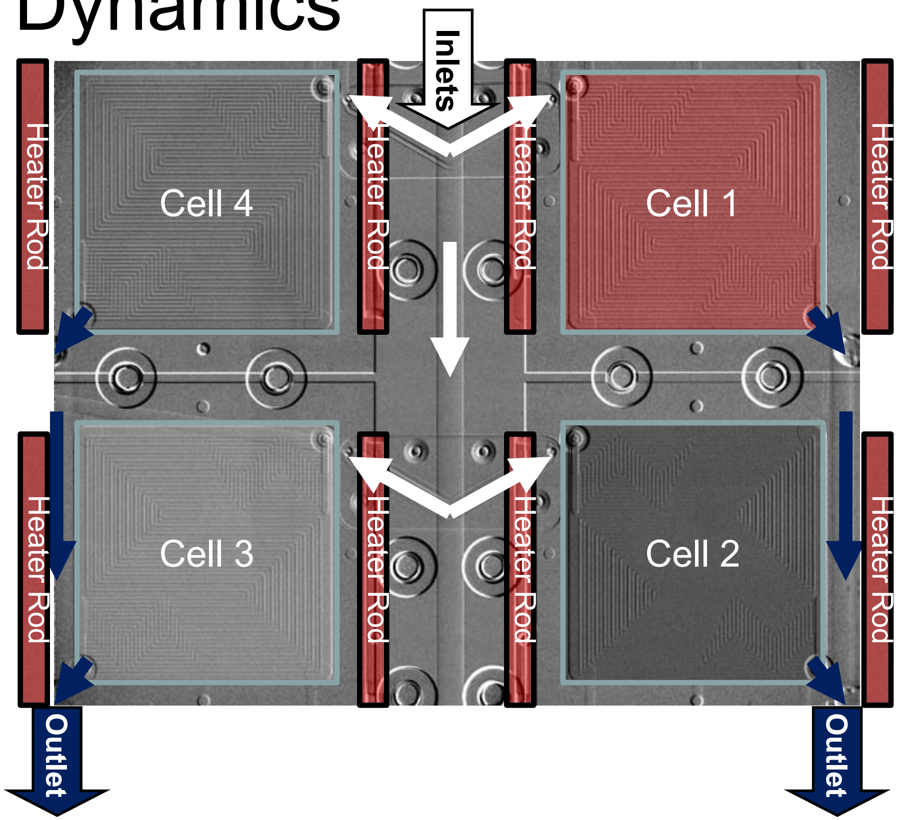
# Down-the-channel variation in GDL thermal conductivity

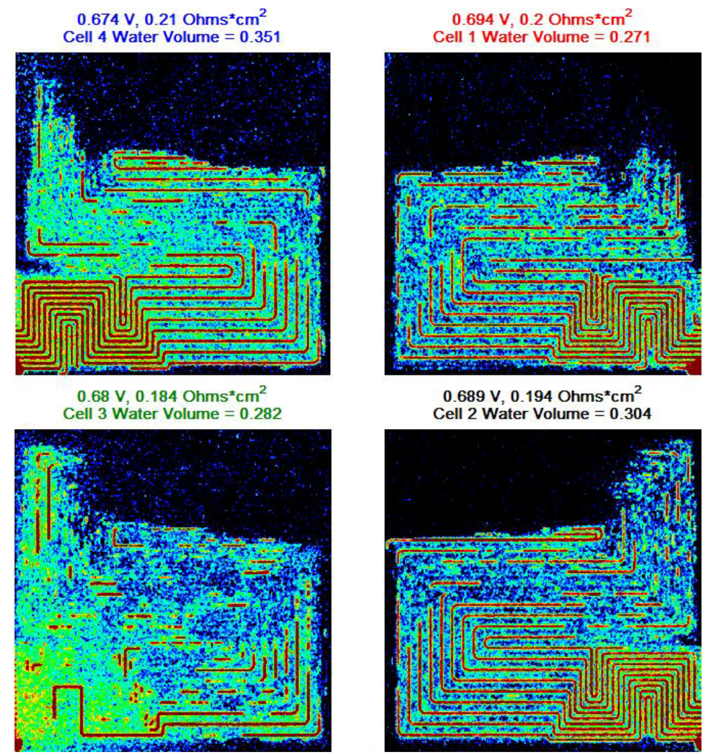


# Individual Cell Diagnostic for Stack Transport Dynamics



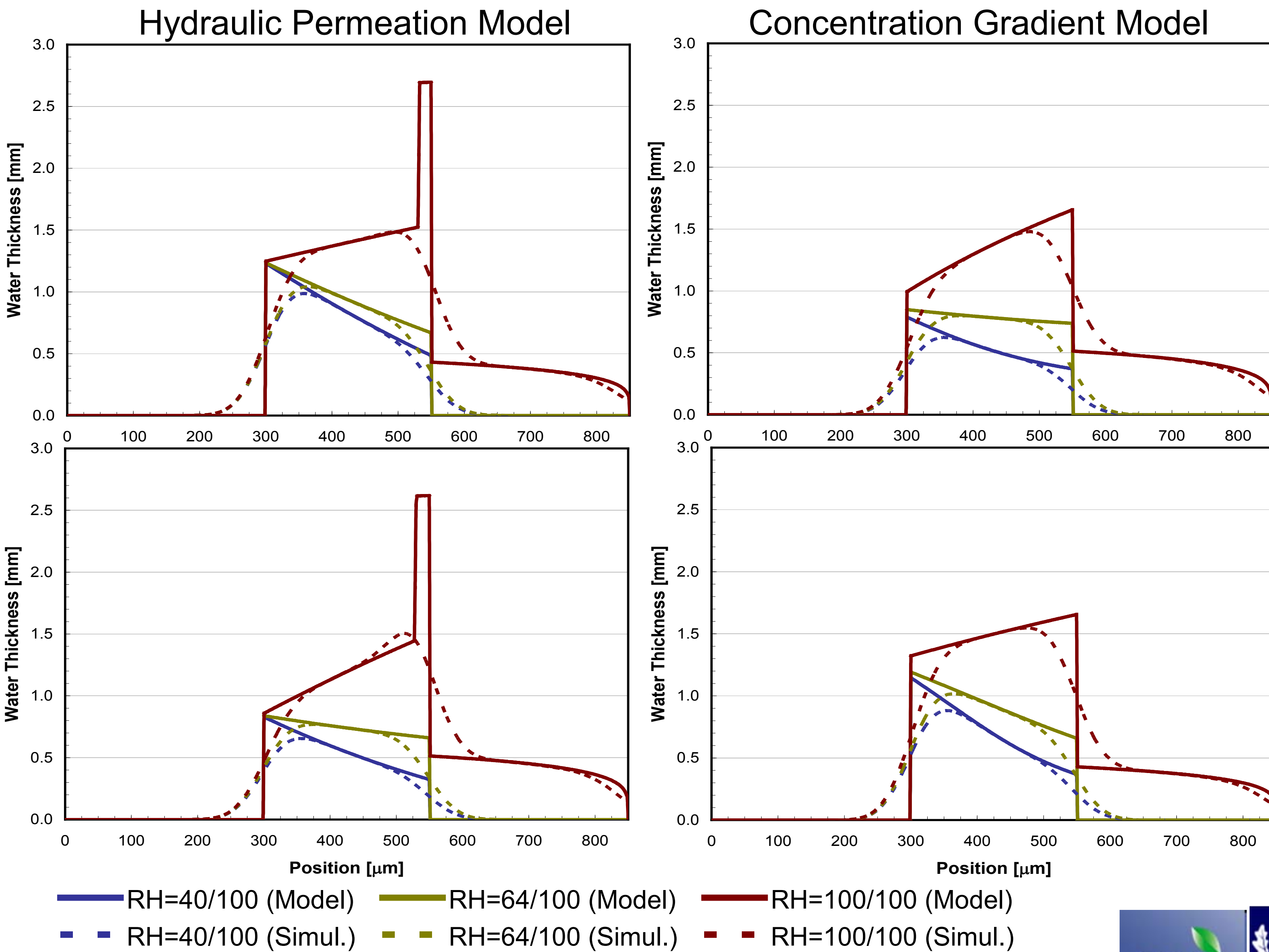




- Planar 4 cell stack to observe liquid stack-level water transport in individual cells during polarization, stoichiometric ratio sensitivity, purge and start-up experiments.
- Enables one to directly observe relationship between liquid water accumulation and performance with precise control of flow and temperature.
- Cells are 50 cm$^2$ active area with co-flow reactant gas flows. All four cells in stack share the same active area plane electrically connected in series by external bus bars.
- Details in Poster FC056, Satish Kandlikar

# Numerical Modeling Results: Blurred for 25 µm Spatial Resolution

Case A:
T=70ºC/62ºC
T=8ºC

Case B:
T=70ºC/50ºC
T=20ºC



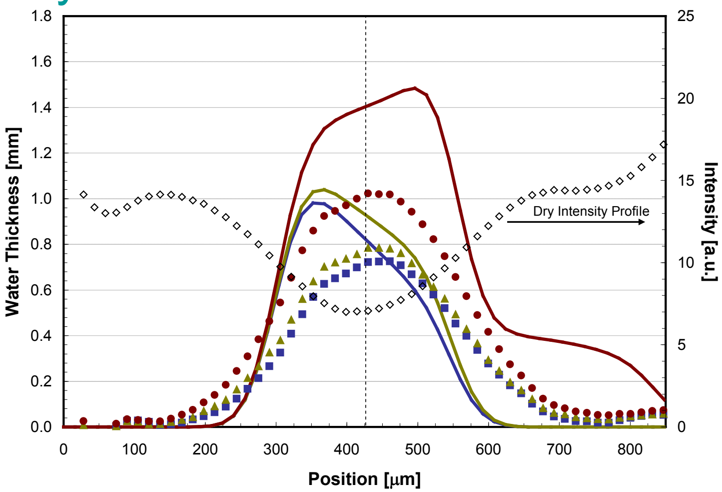
# Comparing Blurred Numerical Modeling Results to Experiment

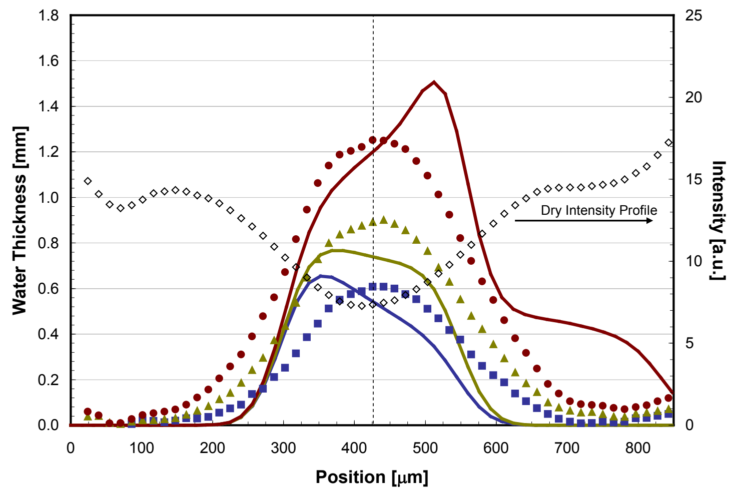
RH=40/100 (Model) RH=40/100 (NR Exp.)
RH=64/100 (Model) RH=64/100 (NR Exp.)
RH=100/100 (Model) RH=100/100 (NR Exp.)

Case A: T=70 ºC /62 ºC, ΔT=8 ºC

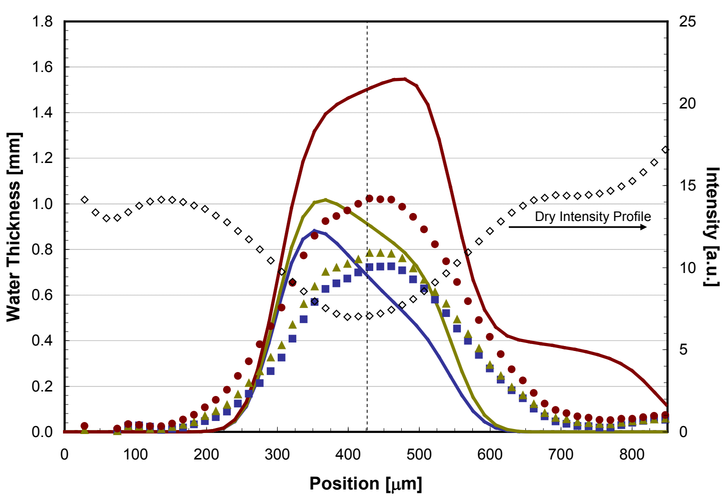
Case B: T=70 ºC /50 ºC, ΔT=20 ºC

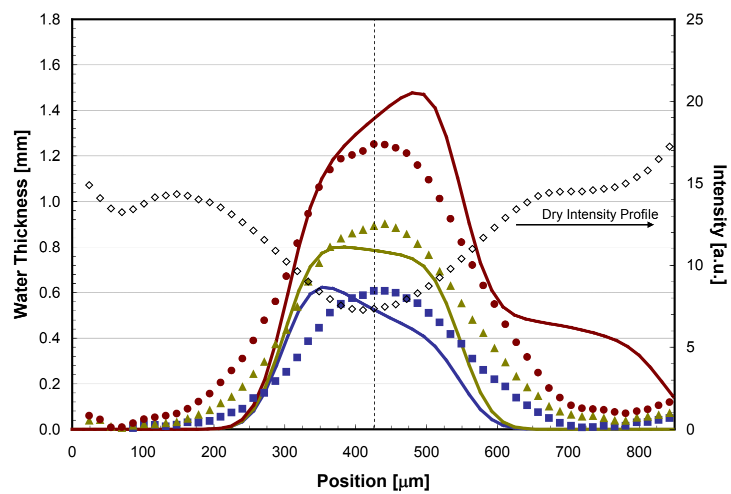
## Hydraulic Permeation Model



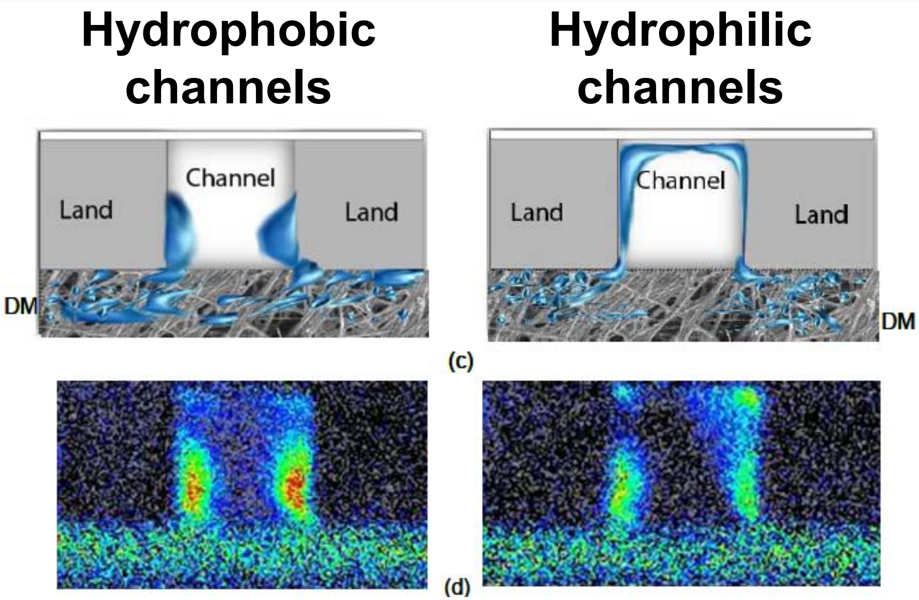



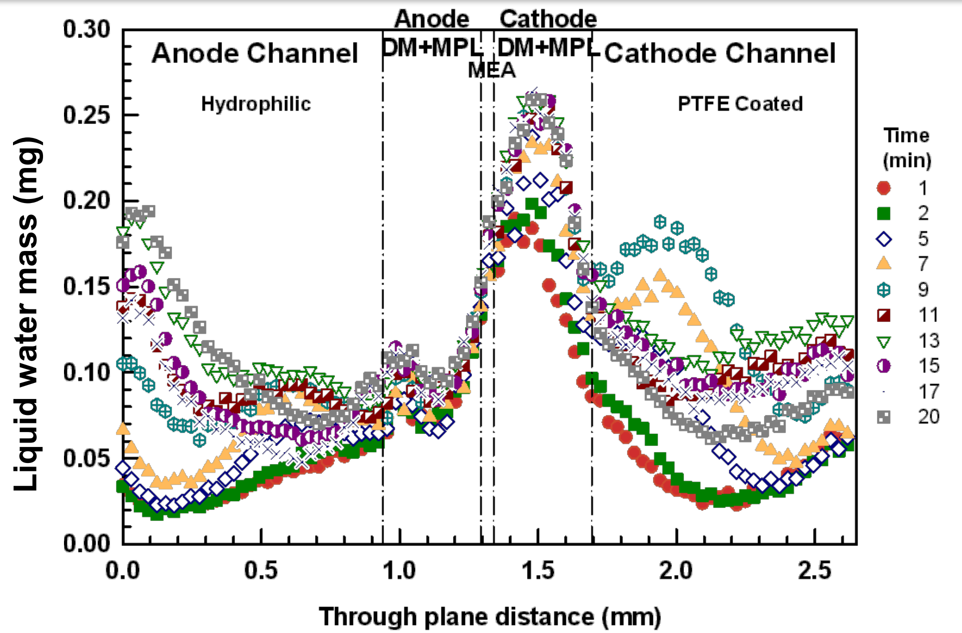

## Concentration Gradient Model



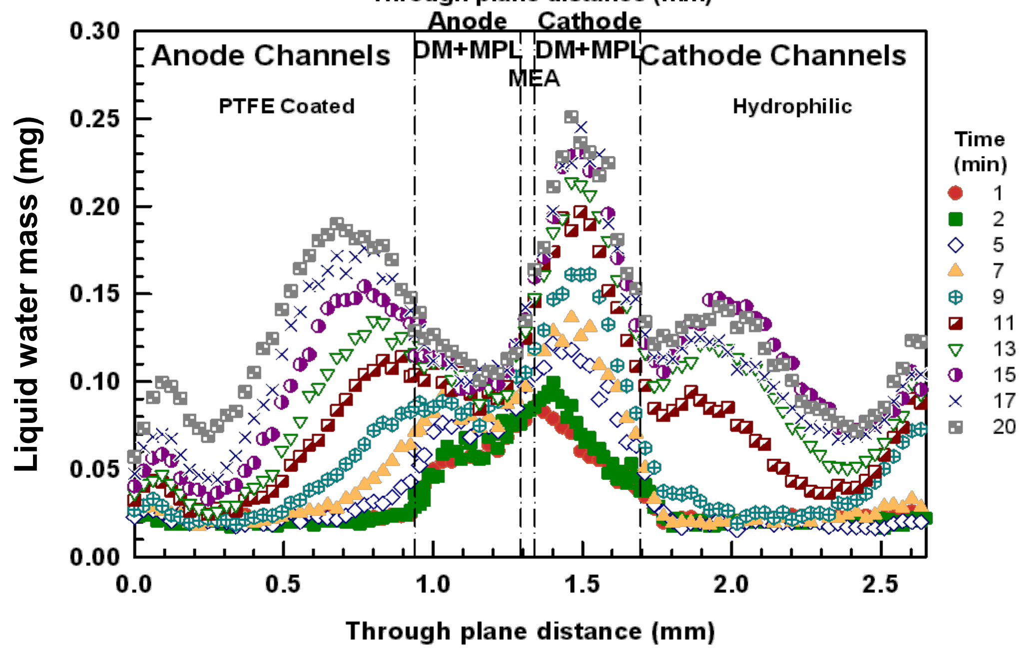



# PSU FCDDL Investigated Role of DM|Land Interface



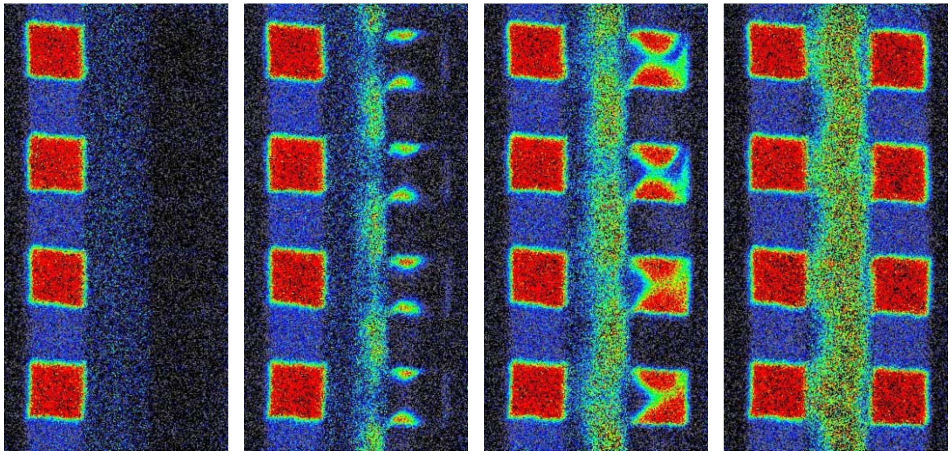

**Data show channel wall|DM interface plays a critical role in water drainage and overhead in DM and can be better engineered**



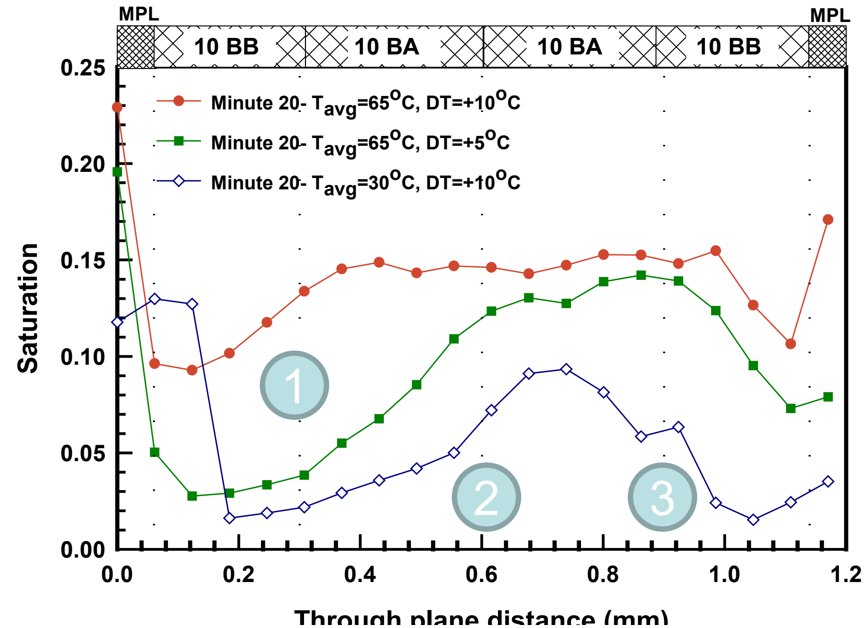

A. Turhan, S. Kim, M. Hatzell, M. M. Mench, Impact of channel wall hydrophobicity on through-plane water distribution and flooding behavior in a polymer electrolyte fuel cell, *Electrochim. Acta,* **55** (8) (2010) 2734-2745.

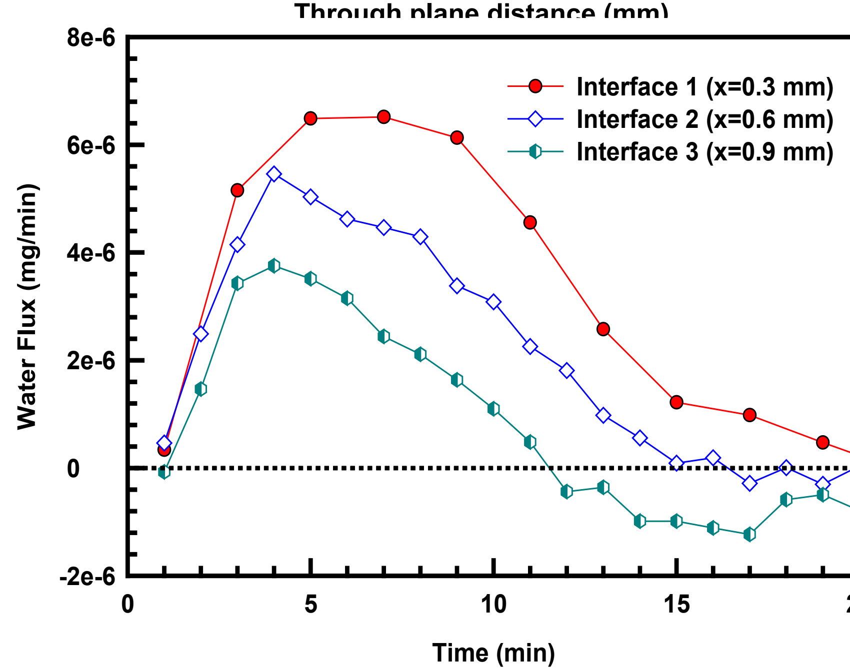
# PSU Measured Temperature Gradient Driven Flow in DM

NR images (Minute 20)



| | | | |
|---|---|---|---|
| Δt=0 °C | Δt=10 °C | Δt=5 °C | Δt=10 °C |
| $T_{avg}$=65 °C | $T_{avg}$=30 °C | $T_{avg}$=65 °C | $T_{avg}$=65 °C |




**4 layer DM stack was bound by MPL on outside edges, with liquid initially on left side only and temperature gradient induced by coolant.**

**Water flux data calculated across the indicated interfaces shows dynamic balance between phase change induced flux and capillary action.**

Hatzell et al., *In preparation*

# Future Work

- Continue to develop advanced imaging methods for fuel cell research
  - Improve accuracy of water content measurements by implementing new *in situ* measurement of residual water in dry cells
- Continued advancement of imaging technology and capabilities at the facility
  - Improve field of view while maintaining spatial resolution to look at larger fuel cells
  - New large format detectors will be incorporated into the facility to improve acquisition capabilities.
- Add new cold imaging capabilities using new facility to be built for expansion of the NCNR

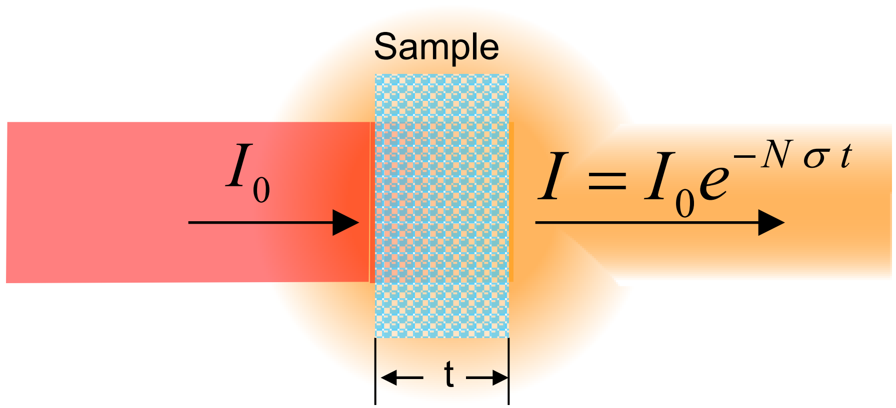
# Summary of Technical Accomplishments

- High Resolution Neutron Imaging
  - New high resolution neutron imaging system deployed and in use.
  - Measured spatial resolution is 13 μm.
  - High resolution system using scintillator coupled to CCD achieves sub 20 μm spatial resolution
- Search for systematic errors in neutron radiography
  - Determined systematic underestimation of water content
    - Due to unaccounted residual water in dry membrane images
    - With beam hardening this results in underestimation of water content
    - Can experimentally measure this effect and obtain true water content of cell
  - Improved humidity control
    - Installed check valve to ensure dry gas at low flow rates and freeze studies
    - Heating all exposed sections of humidified gas lines to eliminate condensation
    - Changed from 0.25” to 0.125” gas lines to improve flow consistency for small scale cells
- Study of water hydration of membranes
  - In collaboration with LANL have studied a range of membrane histories and compositions, anticipate completing the analysis in summer 2010
- Freeze and Purge studies are ongoing
  - Research will benefit from closed-bath chiller with -45 °C to 100 °C range

# Supplemental Slides

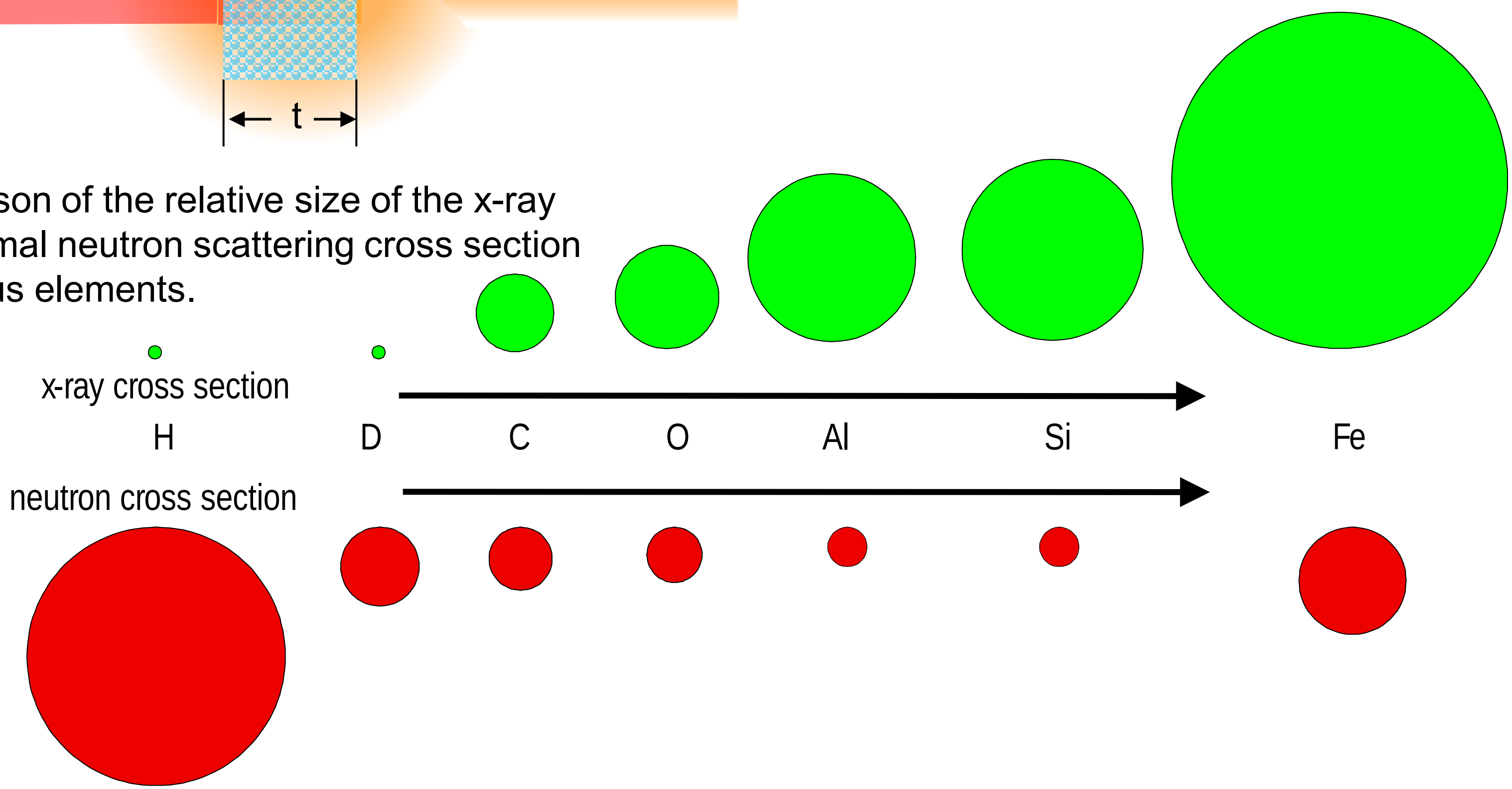
# Why Neutrons

Neutrons are an excellent probe for hydrogen in metal since metals can have a much smaller cross section to thermal neutrons than hydrogen does.

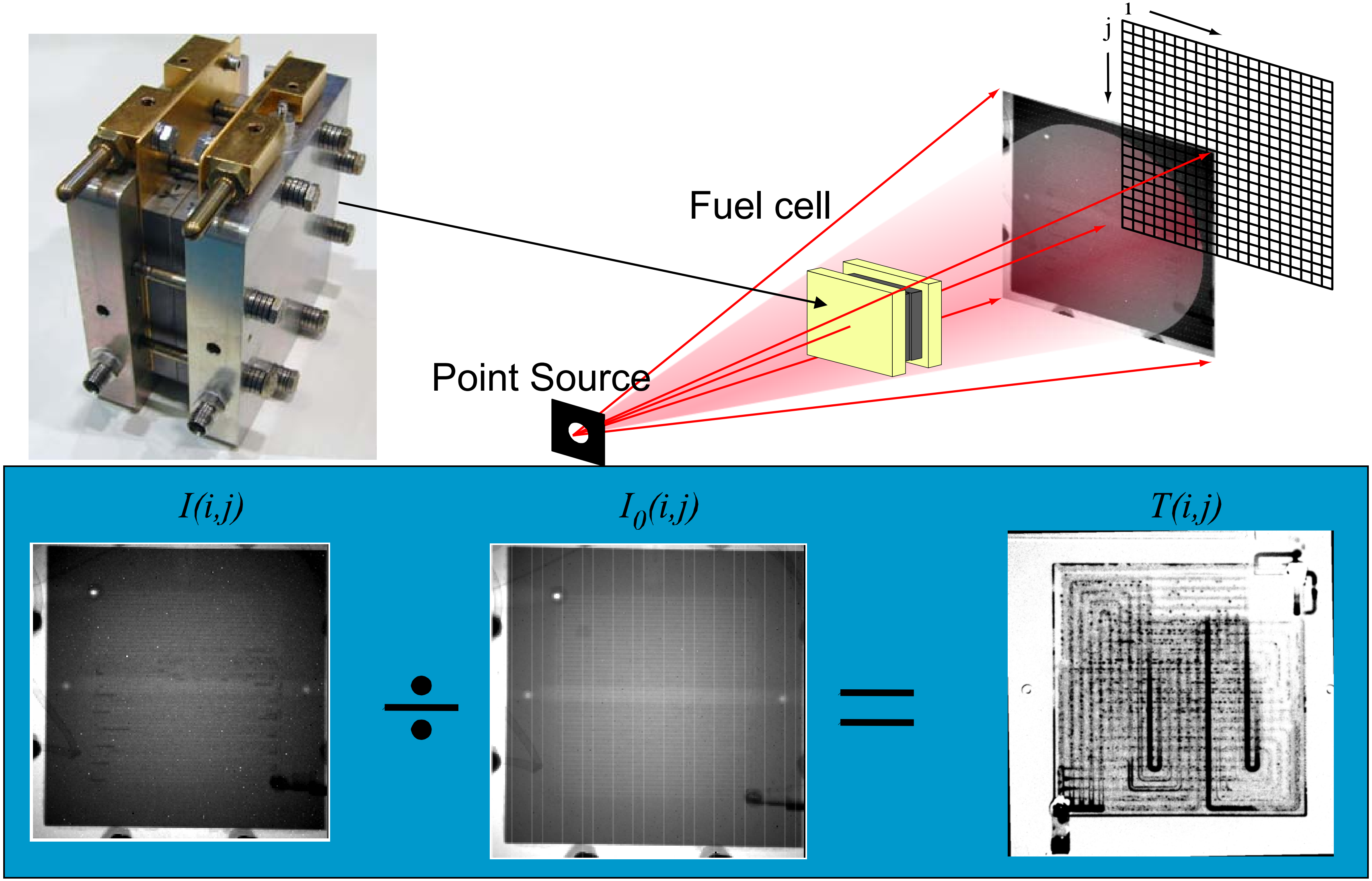



- N – numerical density of sample atoms per $cm^3$
- $I_0$ - incident neutrons per second per $cm^2$
- $\sigma$ - neutron cross section in ~ $10^{-24}$ $cm^2$
- t - sample thickness

Comparison of the relative size of the x-ray and thermal neutron scattering cross section for various elements.



Brief Review of Method

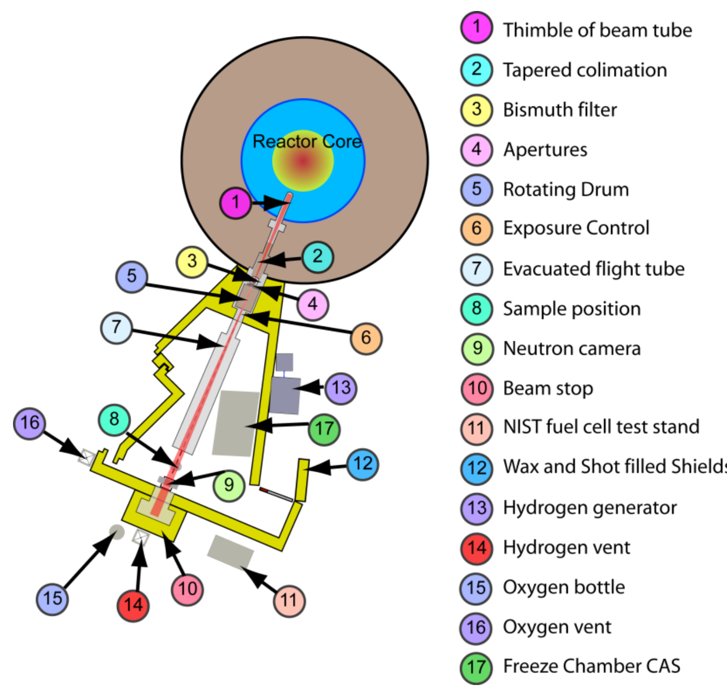



Water thickness ($t_w$) simply found from: $\mu \, t_w(i,j) = -\ln\{ T(i,j) \}$

# The NIST Neutron Imaging Facility at BT2

## Current Beam Characteristics

| Aperture # | Aperture Dimension | Beam | ≈ L/D (x,y) | Fluence Rate |
|---|---|---|---|---|
| 5 | 15 mm | 1 | 600 | 6.36E+06 |
| 5 | 15 mm | 2 | 450 | 1.38E+07 |
| 4 | 10 mm | 1 | 600 | 4.97E+06 |
| 4 | 10 mm | 2 | 600 | 6.14E+06 |
| 3 | 3 mm | 1 | 2000 | 5.23E+05 |
| 3 | 3 mm | 2 | 2000 | 5.94E+05 |
| 2 | 10 x 1 mm | 1 | 600, 6000 | 6.54E+05 |
| 2 | 10 x 1 mm | 2 | 600 ,6000 | 8.00E+05 |
| 1 | 1 x 10 mm | 1 | 6000, 600 | 7.17E+05 |
| 1 | 1 x 10 mm | 2 | 6000, 600 | 8.13E+05 |



# NIST Fuel Cell Infrastructure

- Hydrogen Generator, max flow 18.8 slpm
- State of the art Fuel Cell test stand, with graphical User Interface
- Flow control over H2, Air, N2, He, O2:
  - H2: 0-50, 0-500 and 0-3000 sccm
  - N2: 0-2000 sccm
  - Air: 0-50, 0-100, 0-500, 0-2000, 0-8000 sccm
  - O2: 0-500, 0-5000 sccm
  - He: 0-600, 0-6000 sccm
- 1.5 kW boost power supply allowing Voltage control of the cell to a minimum of 0.01V
- Heated Inlet gas lines, Built-in humidification
- 8 T-type thermocouple inputs
- 2 Viasala dew point sensors available
- Interfaced with facility hydrogen safety system
- Freeze Chamber Available to All Users
  - **-40 C to +50 C, 1000 kW cooling at -40 C**
  - **32” W, 24” H, 18” D sample volume**
  - Explosion-proof, and Hydrogen safe
- **Zahner IM6eX Electrochemical Workstation available**
- ***All users of the NIST NIF have full access to all fuel cell infrastructure***

Fuel Cell Stand

Freeze Chamber Installed inside the Imaging Facility

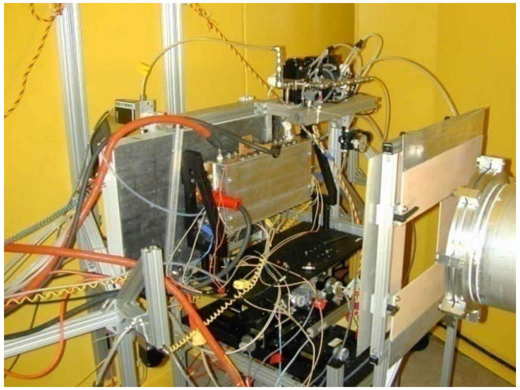
# Current Neutron detectors: a-Si and MCP

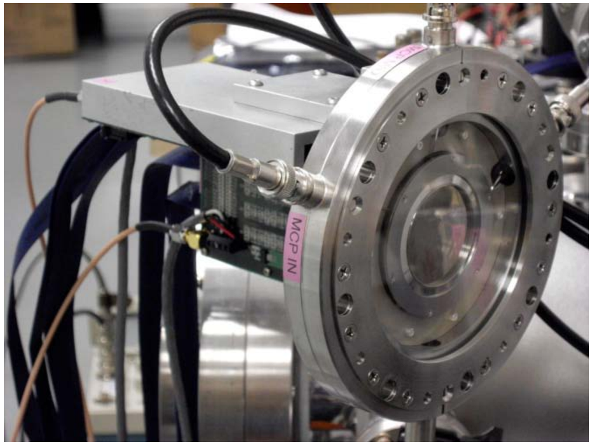
**a-Si Panel with ZnS**

- **250-300 µm** Spatial Resolution
- 127 µm Pixel Pitch
- 25 cm x 20 cm Field of View
- 30 Hz max frame rate
- 1 Hz min frame rate
- 10 µm water thickness resolution in about 10 seconds
- Automatic dark image removal simplifies processing

**MCP Detector with XDL**

- **13 µm** Spatial Resolution
- 5 µm Pixel Pitch
- 4 cm diameter Field of View
- ≈ 0.1 Hz max frame rate - Noisy
- 30 µm water thickness resolution per pixel in about 1 h
- Gamma sensitive glass, requires taking dark image





# Numerical Modeling

## Water Uptake (Zawodzinski et al., 1993)