Neutron Imaging Study of the Water Transport in Operating Fuel Cells

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UNITED STATES DEPARTMENT OF COMMERCE
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Gaithersburg, Maryland 20899-8461

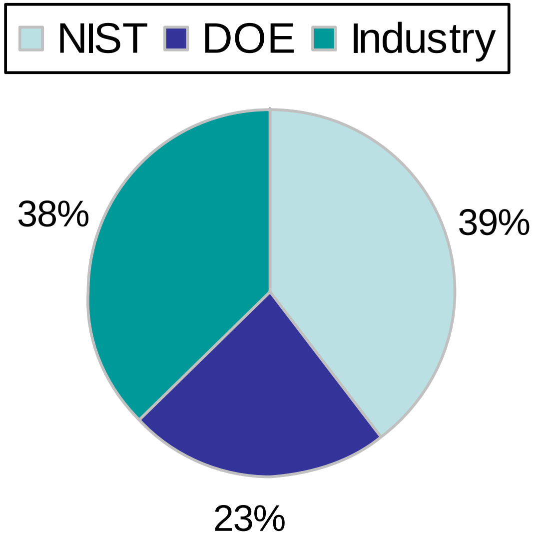
DOE Hydrogen Program

Overview

Timeline

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

Budget



Total: $1.4M

Barriers Addressed

Thermal and Water Management.

Water management techniques to address humidification requirements and maintain water balance.

2007 & 2008 Users/Collaborators

- Case Western Reserve University
- Ford
- General Motors
- Georgia Tech
- Illinois Institute of Technology
- Kansas University
- Korea Atomic Energy Research Institute
- Los Alamos National Laboratory
- NOVA Scientific
- Michigan Technological University
- Oak Ridge National Laboratory
- Pennsylvania State University
- Plug Power
- POSTECH
- Rensealar Polytechnic Institute
- Rochester Institute of Technology
- Sandia National Laboratory
- Sensor Sciences
- University of California, Berkeley
- University of California, Irvine
- University of Central Florida
- University of Connecticut
- University of Delaware
- University of Illinois
- University of Michigan
- University of Tennessee
- University of Waterloo
- Virginia Tech, NIST
- Wayne State University

Objectives of Fuel Cell Imaging at NIST

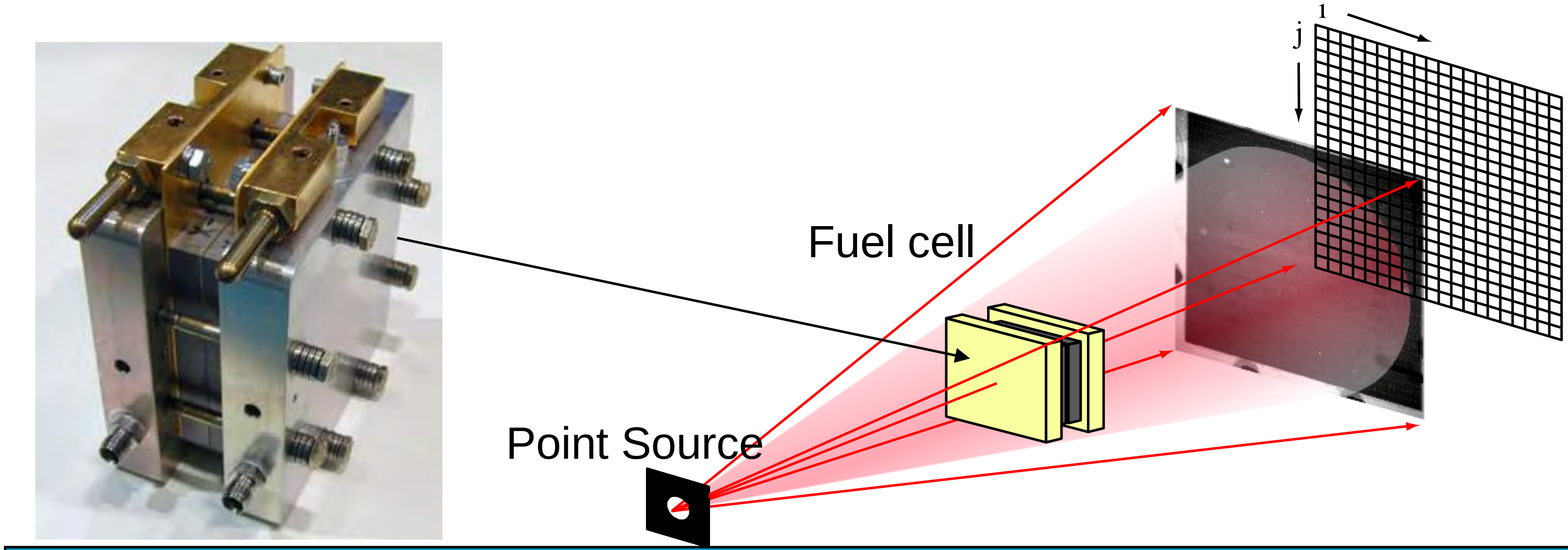
This National Institute of standards and Technology project aims to develop and employ an effective neutron imaging based, non-destructive diagnostics tool to characterize water transport in PEM fuel cells. Objectives include:

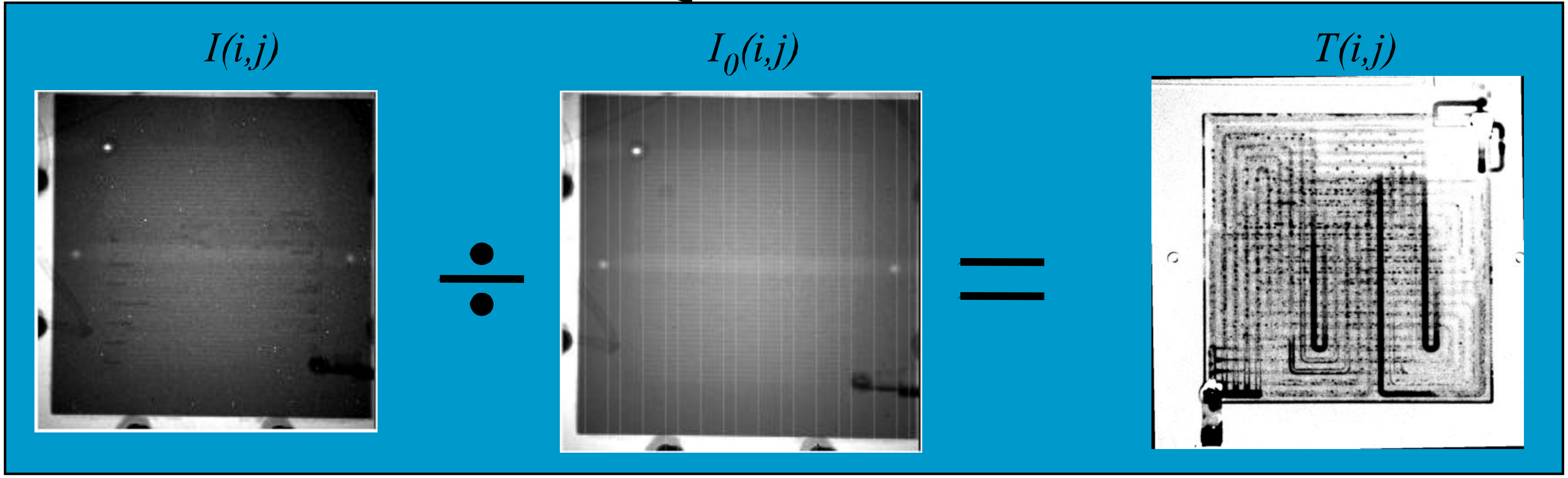
- **F**orm collaborations with industry, national lab, and academic researchers
- **P**rovide research and testing infrastructure to enable the fuel cell / hydrogen storage industry to design, test and optimize prototype to commercial grade fuel cells and hydrogen storage devices.
- **M**ake research 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

Facility Uses

- ***SEVEN NEW*** university research groups
- ***NO COST*** for open literature research
- ***20 Graduate Students*** have used the facility for their thesis research
- Typical data set size ***1 to 3 TB*** per week
- Facility is fully subscribed (about 50% proprietary use)
- Typically open beam time proposals exceed available time by 50%
- Proposals are externally peer reviewed for scientific merit and feasibility
- Beam time is awarded by a Beam Time Allocation Committee (BTAC) based on the reviews and available beam time
- Potential users submit proposals through NCNR Proposal system (see links from: www.ncnr.nist.gov)
- Contact David Jacobson or Daniel Hussey with any questions
- Freely available data analysis software written by NIST

Brief Review of Method





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

Methods Developed

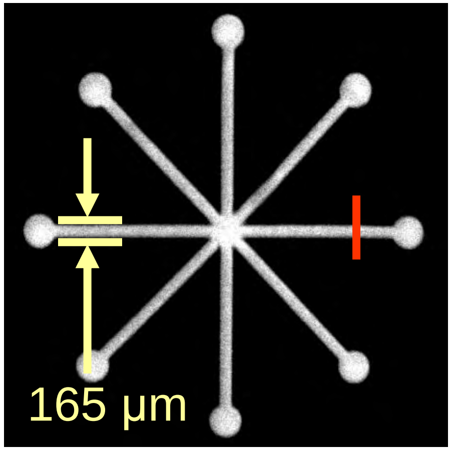
- **High Resolution** Imaging
  - Resolve Water distribution in GDL
  - Unambiguous discrimination of anode from cathode
  - 10 experiments in 2007 – several papers in publication and preparation

- **Environmental Chamber** for freeze testing
  - –40 C to +50 C with humidity control

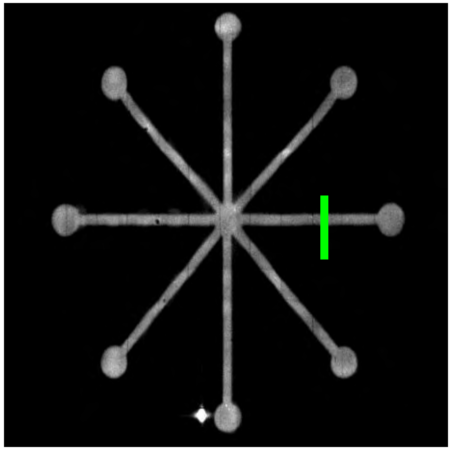
- **Radiography** is still the bread and butter
  - Only way to measure transient processes
  - One-dimensional cells can be made to validate simple edge on radiography

- **Measurement focus**
  - 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

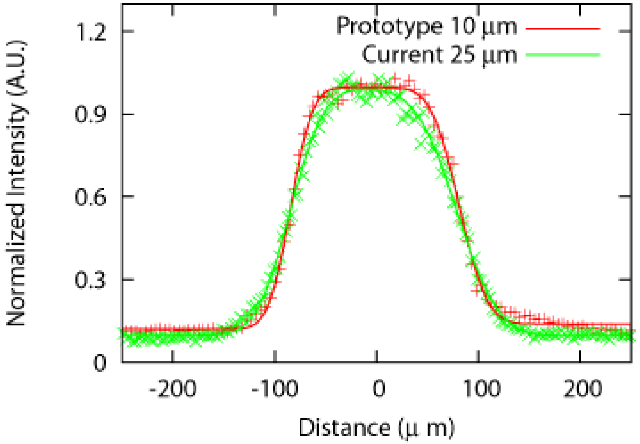
Improving Spatial Resolution



Current 25 µm detector



Prototype 10 µm detector



Prototype 10 µm detector shows 30 % improvement in spatial resolution compared to current 25 µm detector

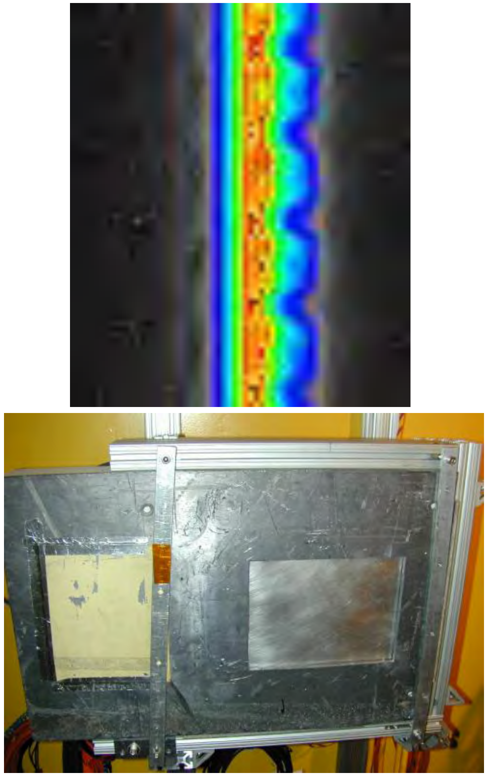
- Prototype 10 µm detector shows promise of the new technology with 30 % improvement in resolution
- Available for users in August, 2008
- Status of the time-of-flight, sub-micron position sensitive detector:
  - Time of flight encoders have been developed
  - Hardware for detector has been fabricated
  - Proceeding on challenging task of fabricating the 10 micron thick neutron converter foil

Collaborator work presented here

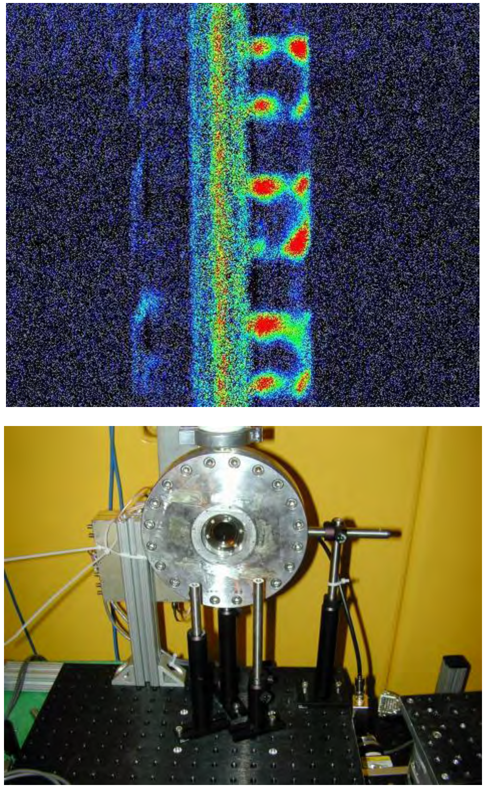
- M.A. Hickner, D. McBrayer, N.P. Siegel, K. Chen, Sandia National Laboratory
- S. Kandlikar, Rochester Institute of Technology
- J.J. Gagliardo, J.P. Owejan, T.A Trabold, General Motors
- J. Allen, Michigan Technological University
- A.K. Heller, M. C. Hatzell, M. M. Mench, Pennsylvania State University
- R.S. Fu, U. Pasaogullari, CT Global Fuel Cell Center, University of Connecticut
- J.B. Siegel, D.A. McKay, A.G. Stefanopoulou, University of Michigan
- R. Borup, R. Mukundan, J. Davey, Y. Kim, J. Spendelow, T. Rockward, Los Alamos National Laboratory
- T. Zawodzinski, V. Gurau, Case Western Reserve University

Neutron High Resolution Profile Imaging

Sandia National Laboratory, NIST , Pennsylvania State University



Amorphous Silicon panel with
250-300 µm Spatial Resolution

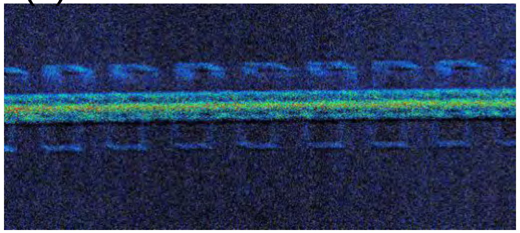


Micro-channel plate with
25 µm Spatial Resolution

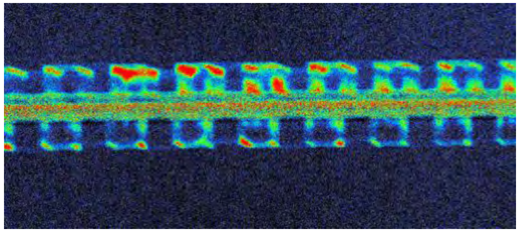
See M.A. Hickner, et al, *Journal of The Electrochemical Society,* **155** B427-B434 (2008)

Membrane Water content vs Current Density

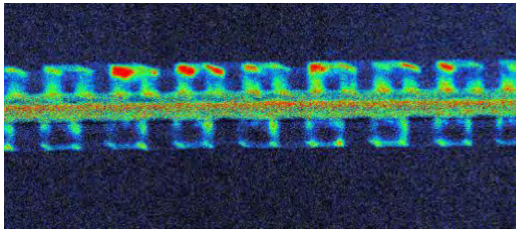
(♦) - 0 A/cm^2

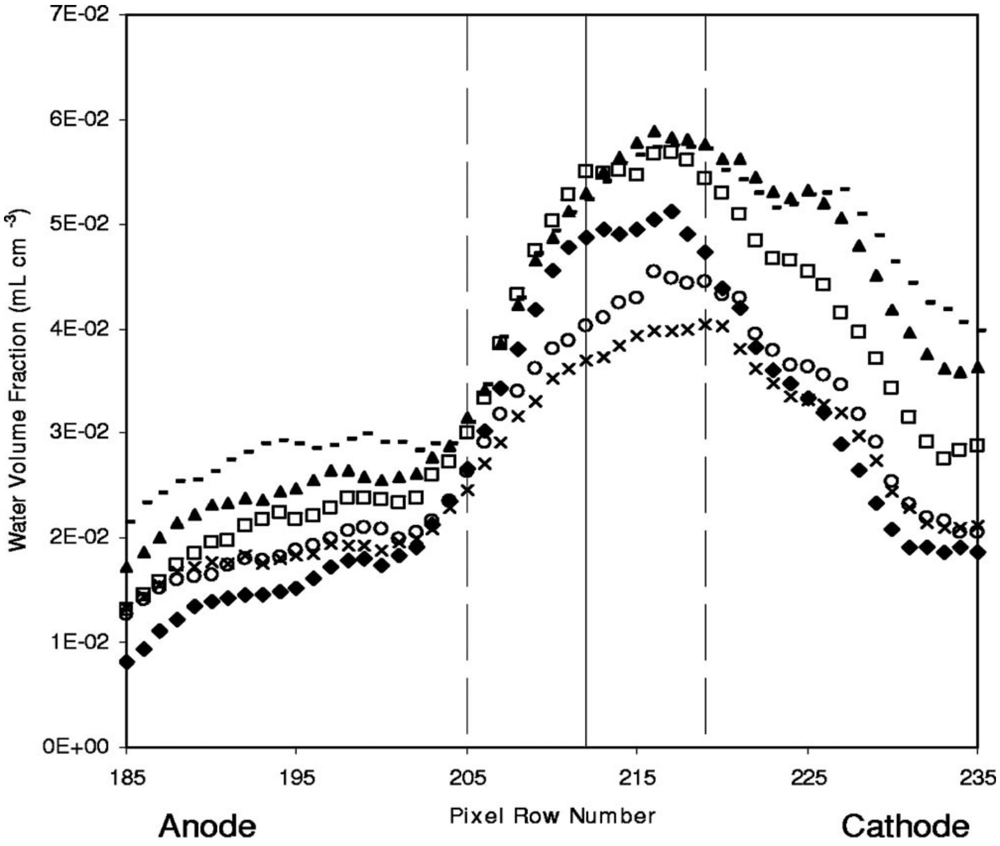


( ) - 0.25 A/cm^2

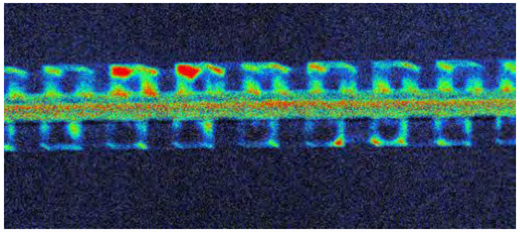


(▲) - 0.50 A/cm^2

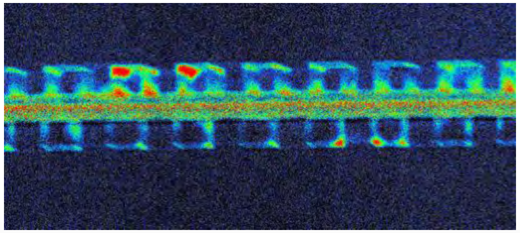




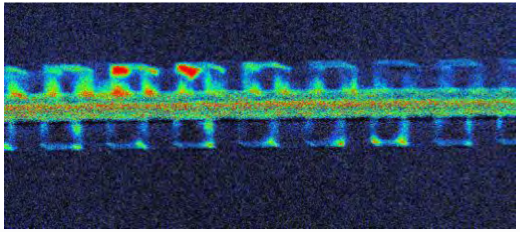
(-) - 0.75 A/cm^2



(○) - 1.00 A/cm^2

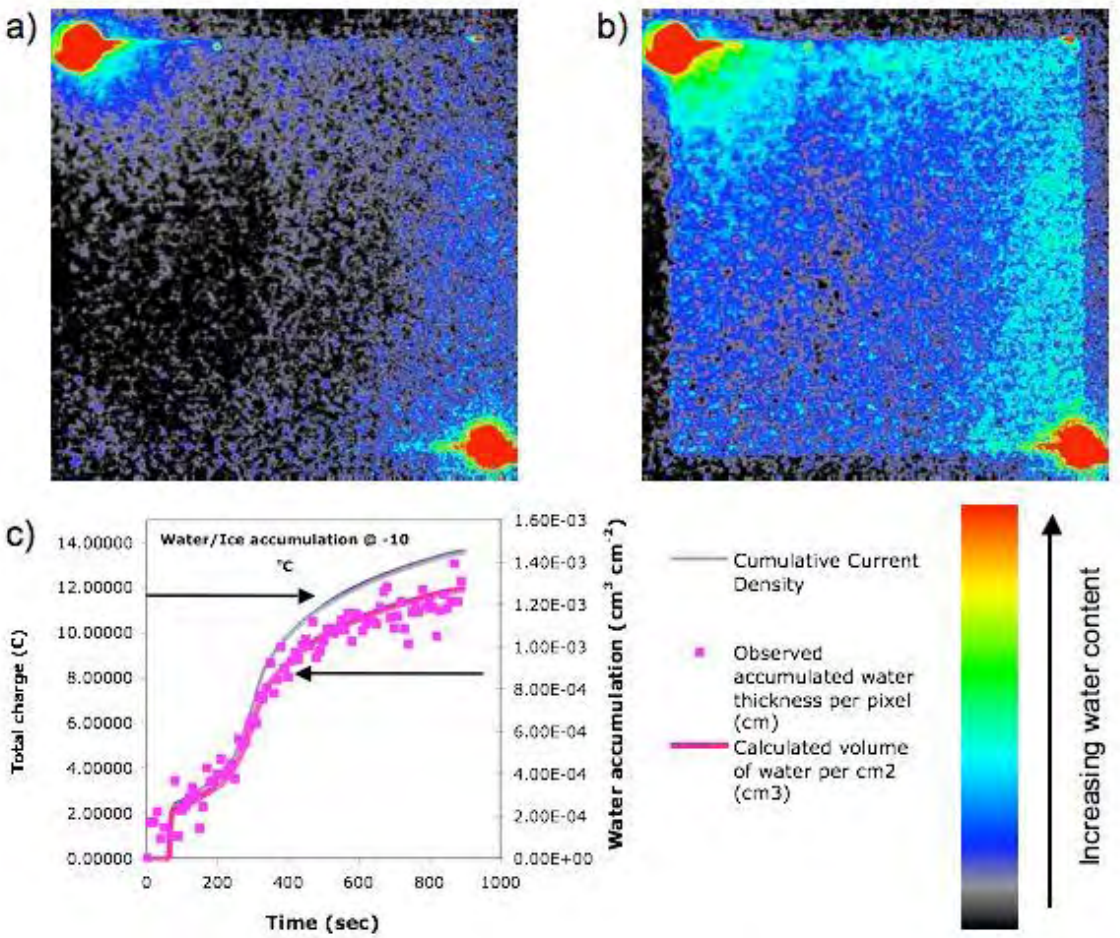


( ) -1.25 A/cm^2



First Freeze Data

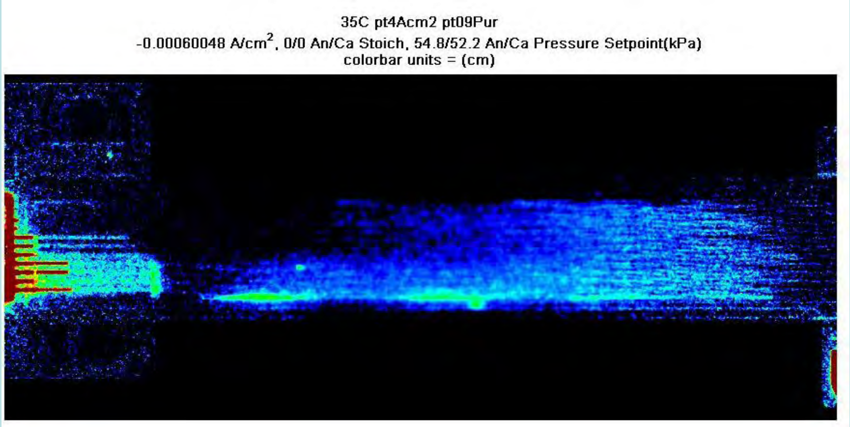
- Neutron imaging of ice formation in a 50 cm^2 fuel cell operated at 0.5 V at -10 ^{o}C.
- a) average water/ice density over the first 100 sec of the experiment,
- b)average water/ice density over the last 100 sec (800 – 900 sec) of the experiment, and
- c) calculated and measured water/ice accumulation in the fuel cells.
- **See FC 35 for more details**

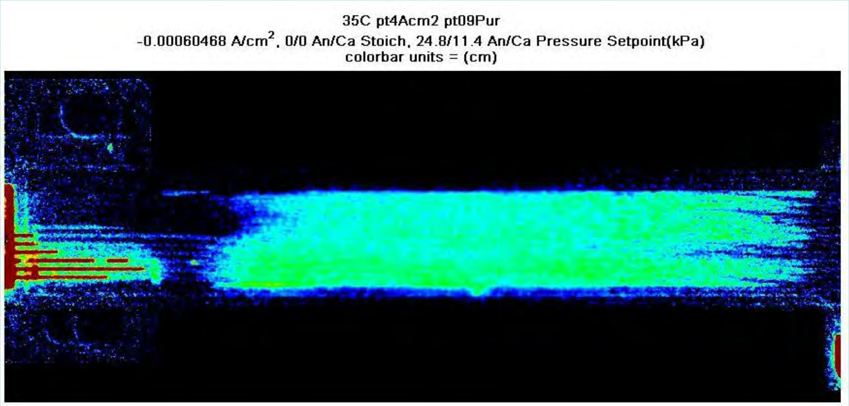


Neutron imaging can be used to quantitatively monitor ice formation in single fuel cells operated at sub-freezing temperatures.

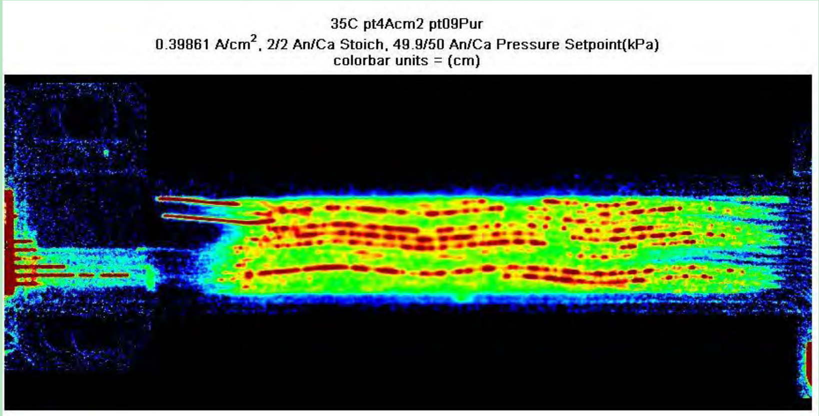
Freeze – Evaluating Purge Sequences

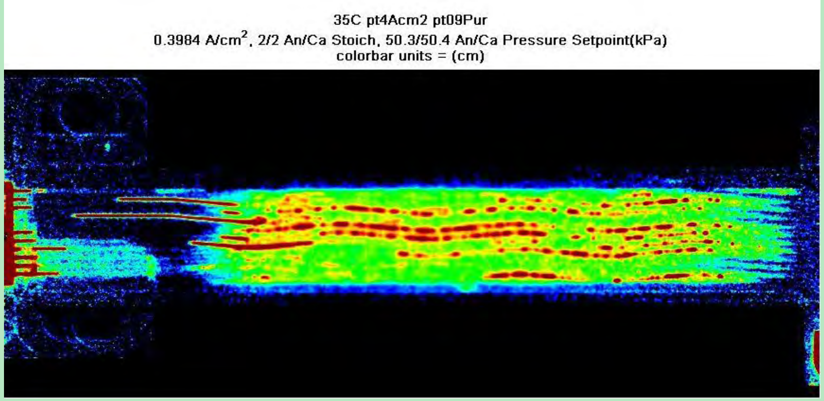
Water Content after a Purge



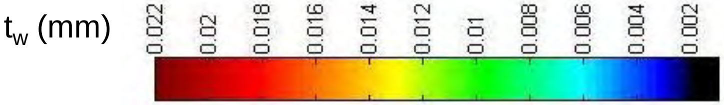


Water Content with 15 min precondition

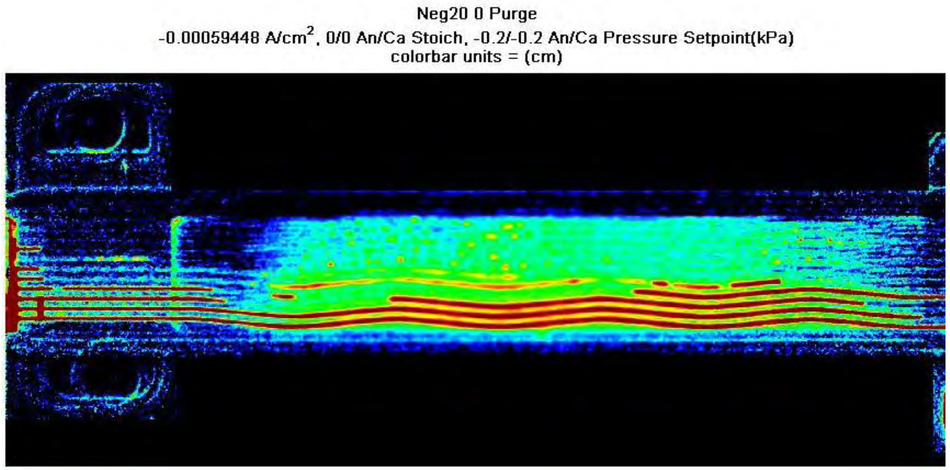




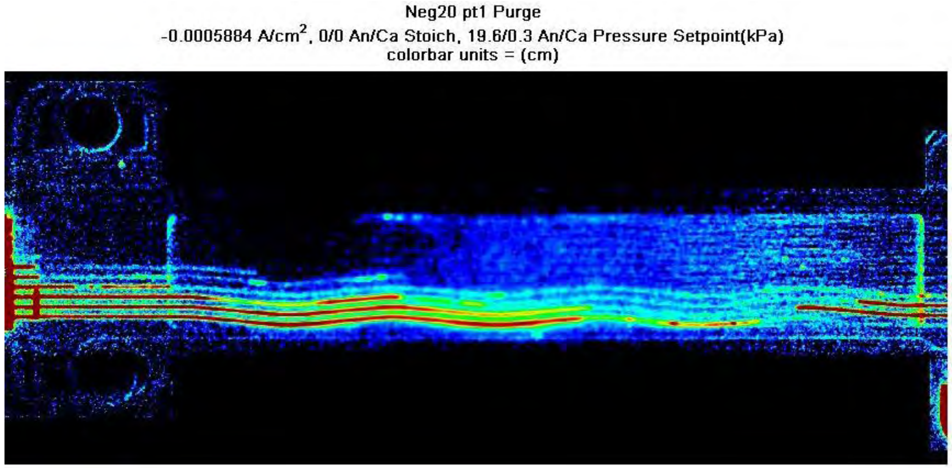
Neutron Imaging confirms repeatable precondition to avoid hysteresis



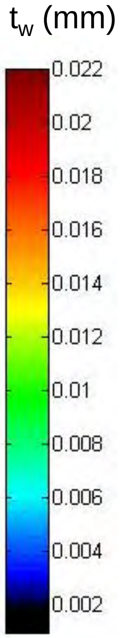
Freeze – Evaluating Purge Sequences



-20 C startup with no purge at shutdown



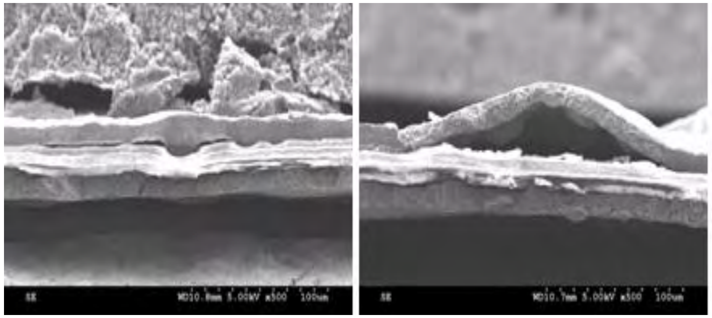
-20 C startup with 30s purge at shutdown



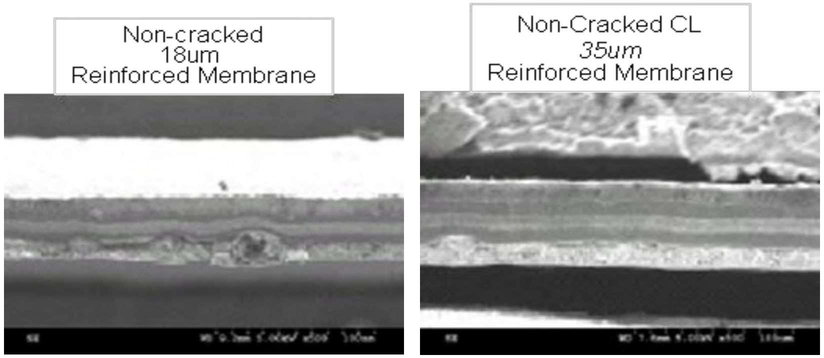
- Preconditioning cell for 15 minutes removes hysteresis in water content and cell performance
- Evaluate purge effect on water content in the channels and GDL
- 30 s purge shows reduced GDL water content
- **See FC 33 for more details**

Mechanisms to Transport Liquid Water on Shutdown

The key to avoid frozen damage and promote rapid startup is to remove liquid water from the catalyst layer on shutdown.



S. Kim and M. M. Mench, JPS 2007, 2008



Non-cracked 18um Reinforced Membrane

Non-Cracked CL *35um* Reinforced Membrane

S. Kim and M. M. Mench, JPS 2007, 2008

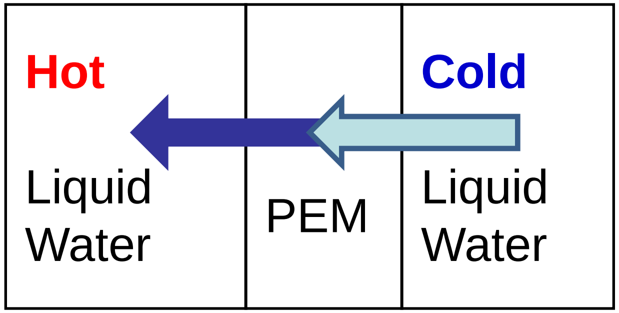
Key Question: What are the modes of transport that can be utilized to move water away from the catalyst layer with low energy input?

Capillary flow
Diffusion
Thermo-osmosis &
Heat Pipe Effect
Hydraulic Pressure

NIST facilities used to visualize and quantify these effects

Gas Phase Boundary Plays Critical Role in Water Direction

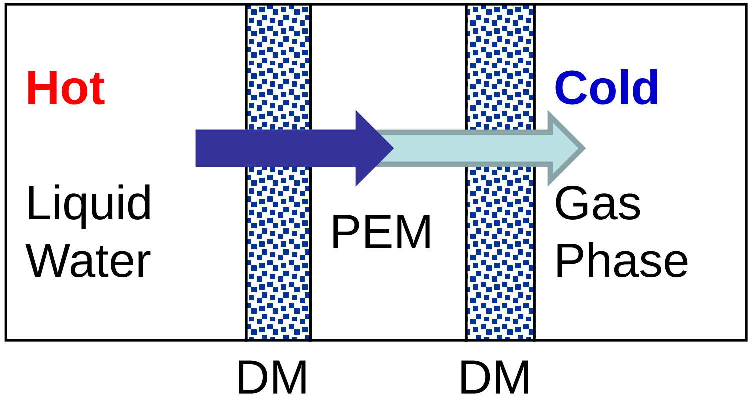
Case 1: Liquid Saturated on Both Sides of Membrane



<u>Thermo-osmosis</u> Tested at PSU FCDDL

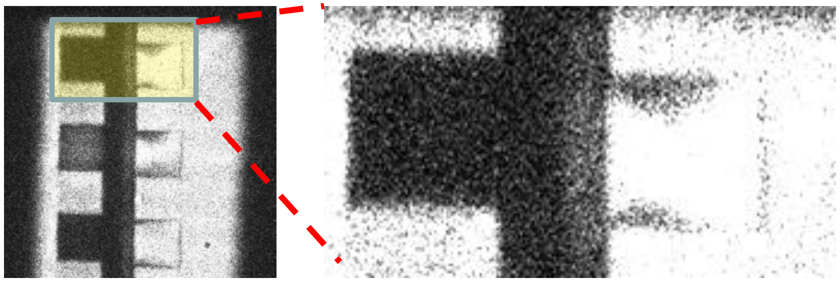
- **All tested membranes showed water flux from *cold to hot***
- **Water flux is significantly lower than the heat pipe effect.**

Case 2: Two Phase (Gas+Liquid)

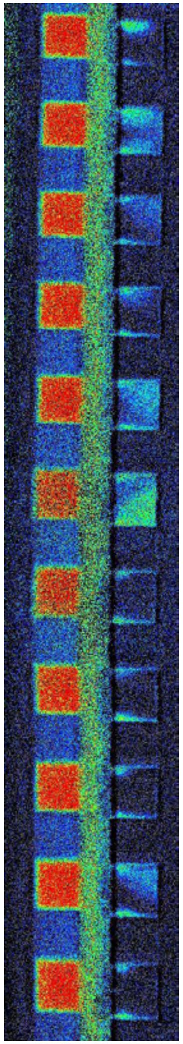


<u>Heat-Pipe Effect</u> Visualized at NIST

- **Water flows from *hot to cold***
- ***<u>Heat pipe effect</u>* is dominant**

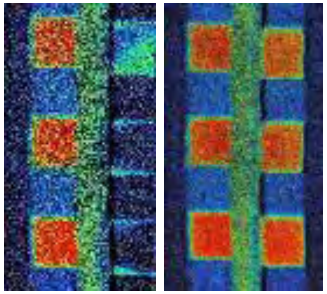


No MPL or Wetproofing

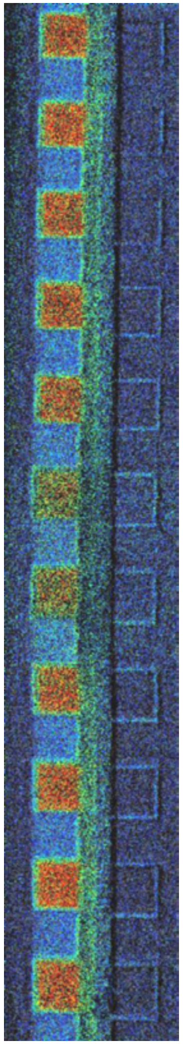


CASE A:
Anode/Cathode
= 65/65°C

Slow Leakage Flow

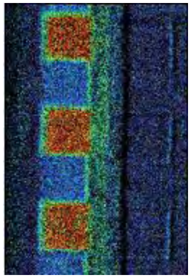


1 min 10 min

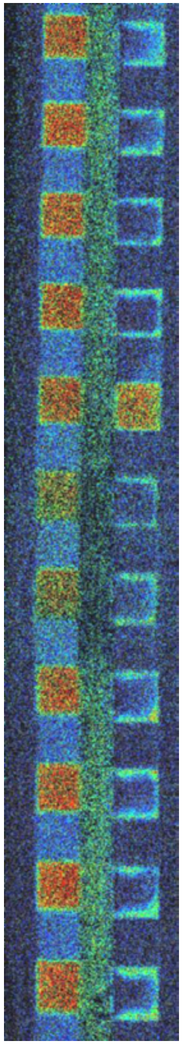


CASE B:
A/C = 60/70°C

Leakage Flow Prevented

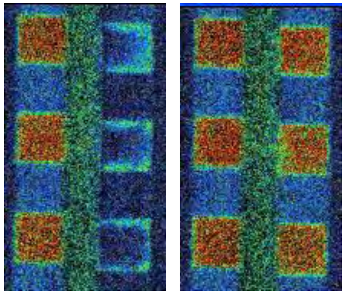


30 min



CASE C:
A/C = 70/60°C

Leakage Flow Accelerated

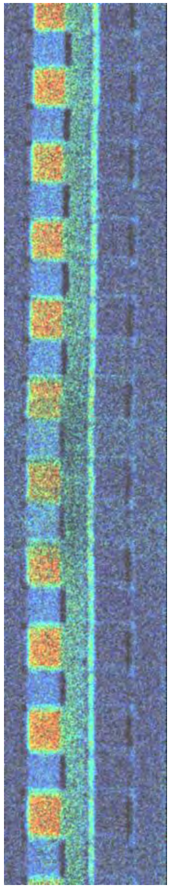


1 min 4 min

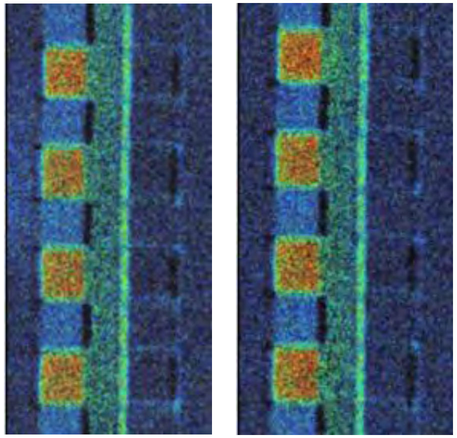
Videos represent approximately 30 minutes total time, images every minute

With MPL and 5% Wetproofing

CASE D:
A/C = 45/45^{o}C

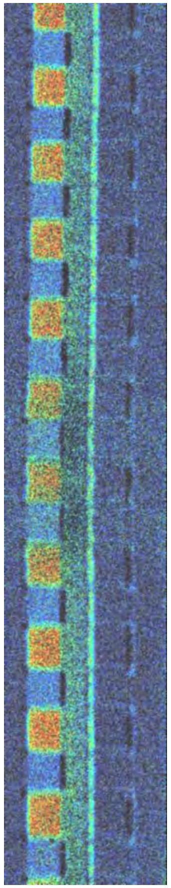


No Slow Leakage Flow – prevented by MPL

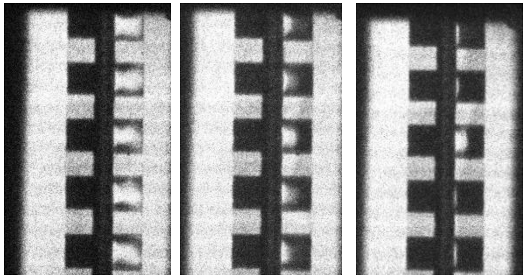


1 min 20 min

CASE E:
A/C = 40/50^{o}C



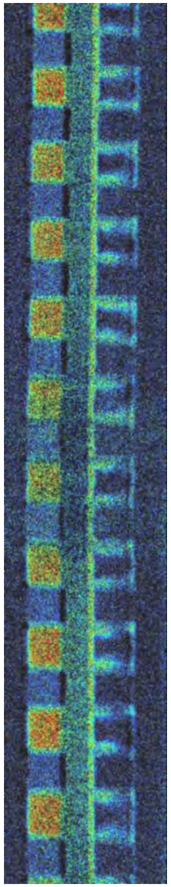
No Leakage Flow



1 min 5 min 10 min

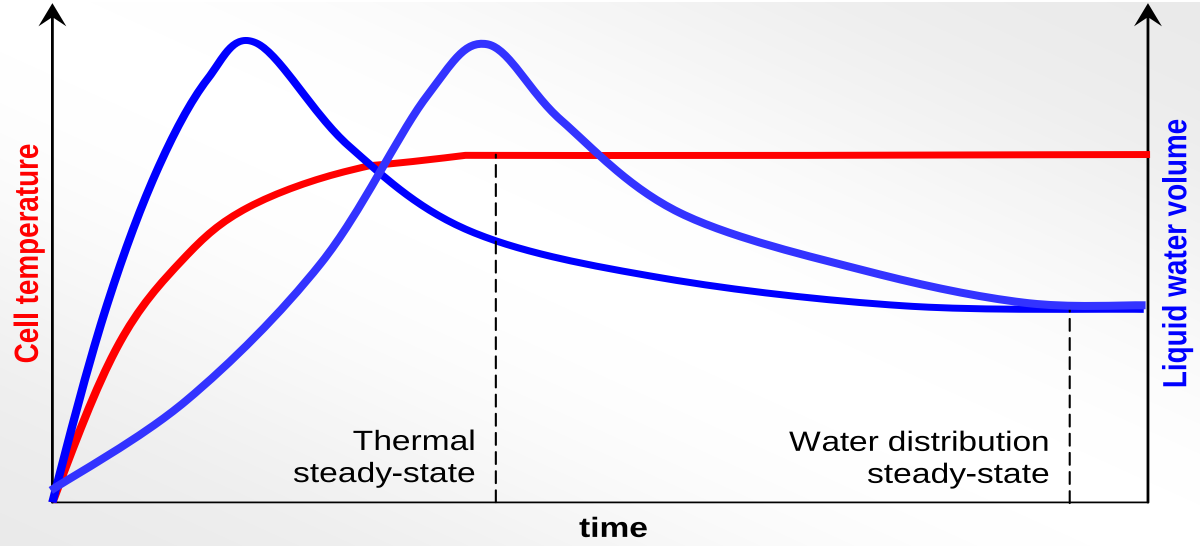
Accelerated Heat Pipe Flow to Cold Side

CASE F:
A/C = 50/40^{o}C



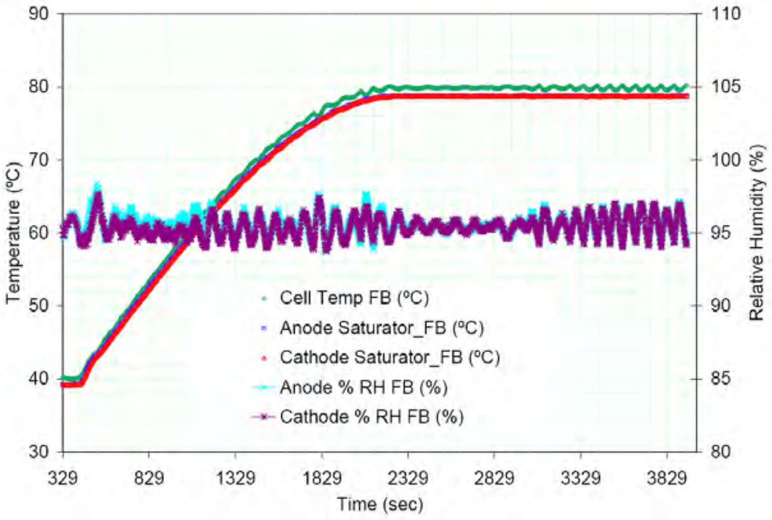
Simulated Non-Isothermal Start-up

- Investigation of non-isothermal start-up of PEFCs
  - Simulated self heat-up of a PEFC stack from ~room temperature
- 2-D NR visualization of liquid water profiles
  - Rate of liquid water build-up at different inlet humidities
  - Relation of liquid water and cell temperature
  - Expect cell temperature to equilibrate before water content

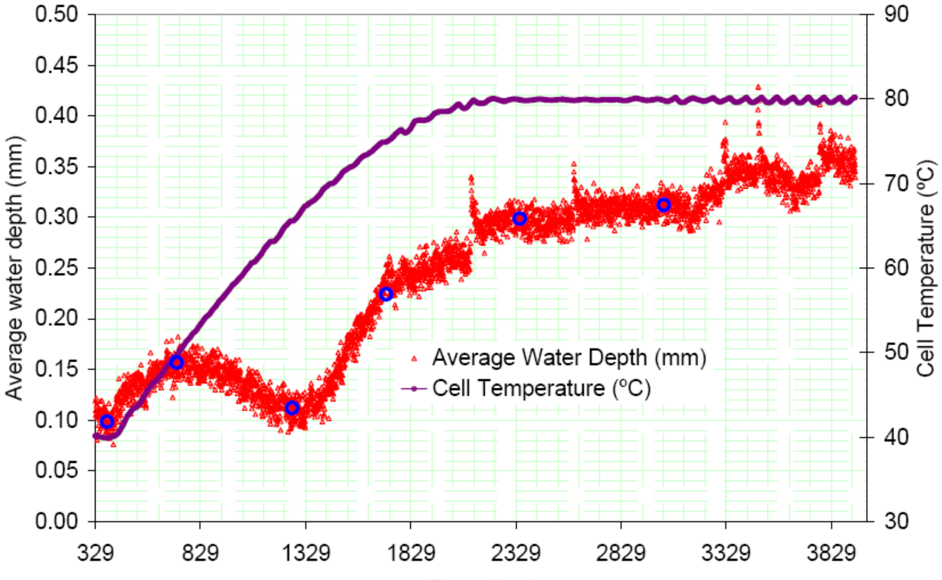


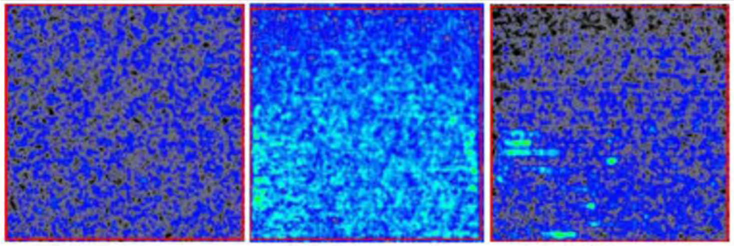
For more details see: R. Fu, U. Pasaogullari, D.S. Hussey, D.L. Jacobson, and M. Arif, ECS Trans. **11**, (1) 395 (2007)

Case 1: 95% Inlet Relative Humidity

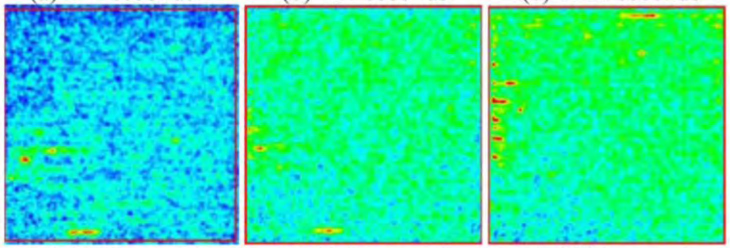


Cell and Humidifier Temperatures

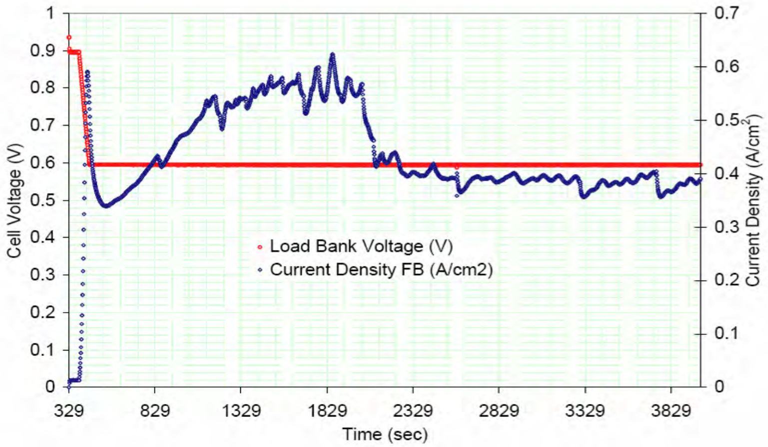




(a) 397 seconds (b) 721 seconds (c) 1326 seconds

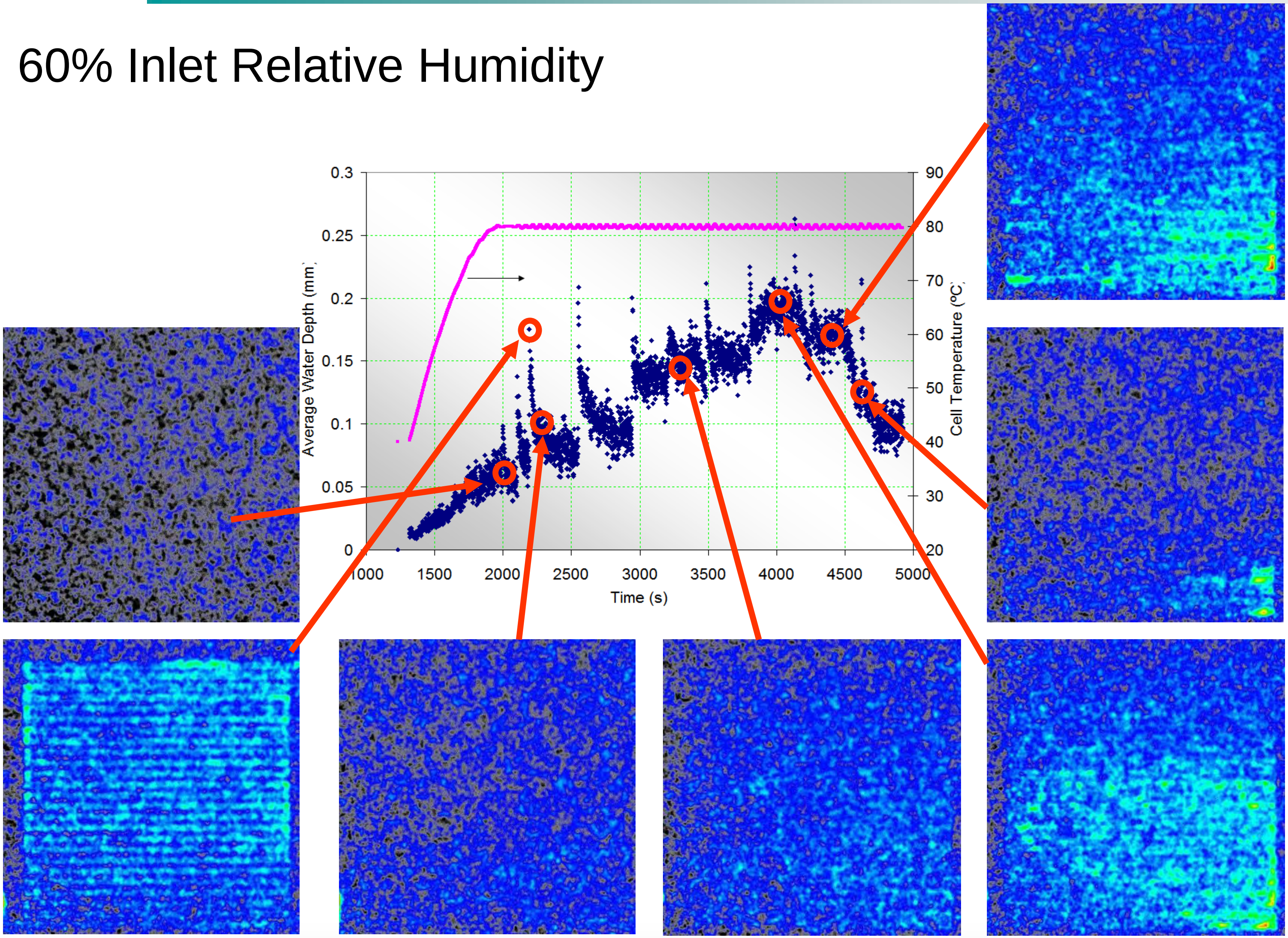


(d) 1723 seconds (e) 2345 seconds (f) 3034 seconds



Cell Performance

60% Inlet Relative Humidity



Fuel Cell Model Validation

Isothermal Boundary Value Problem for the anode

$$\left.\frac{\partial c_{H_2}}{\partial x}\right|_{x=0} = -\frac{N_{H_2,rct}}{D_{H_2}(s)|_{x=0}}$$

$$\left.\frac{\partial c_{v,an}}{\partial x}\right|_{x=0} = \frac{-N_{mb}}{D_v(s)}$$

$$\left.\frac{\partial s}{\partial x}\right|_{x=0} = 0$$

$$\frac{\partial c_{H_2}}{\partial t} = \frac{\partial}{\partial x}\left(D_{H_2}(s)\frac{\partial c_{H_2}}{\partial x}\right)$$

$$\frac{\partial c_{v,an}}{\partial t} = \frac{\partial}{\partial x}\left(D_v(s)\frac{\partial c_{v,an}}{\partial x}\right) + r_v(c_{v,an})$$

$$\frac{\partial s}{\partial t} = \frac{\partial}{\partial x}\left(\kappa_\mu(s)\frac{\partial s}{\partial x}\right) - \frac{M_v}{\rho_l} r_v(c_{v,an})$$

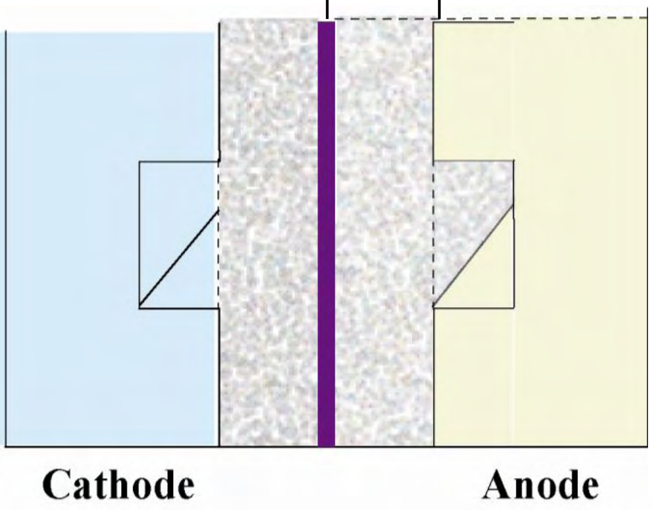
$$c_{H_2}|_{x=L} = c_{H_2,ch}$$

$$c_{v,an}|_{x=L} = c_{v,an,ch}$$

$$s(t,L) = s_{im}$$

Membrane BV

Channel BV



Conditions at Membrane

$$N_{H_2,rct} = \frac{i(t)}{2F}$$

$$N_{mb} = \beta_w(c_{v,ca} - c_{v,an})|_{x=0} - k_{v,0}\cdot i(t)$$

Conditions at Channel (cont.)

Model Calibration

1.1 Fuel Cell Stack

n .... Number of cells in the stack

V_{an} ...... Total anode volume (m^3)

V_{ca} ...... Total cathode volume (m^3)

k_{an} ...... Anode orifice constants

k_{ca} ...... Cathode orifice constant

1.2 Fuel Cell Membranes

A_{fc} .... Fuel cell active area (m^2)

$\rho_{m,dry}$ ... Membrane dry density (kg/m^3)

$M_{m,dry}$ .. Membrane dry equivalent weight (kg/mol)

t_{mb} .... Membrane thickness (m)

D_W K K ***Membrane water diffusion***

1.3 Fuel Cell GDL

t_{gdl} .... GDL thickness (m^3)

ϵ .... GDL porosity

$< D_{O_2} >$. Oxygen effective diffusivity (m^2/s)

$< D_v >$ ... Water vapor effective diffusivity (m^2/s)

$< D_{H_2} >$. Hydrogen effective diffusivity (m^2/s)

$$\langle D_i \rangle = D_i f_i(\varepsilon)(1-s)^2$$

K .... Absolute permeability (m^2)

$$K_{rl} = \left(\frac{s-s_{im}}{1-s_{im}}\right)^3$$

$$r_v(c_{v,an}) = \begin{cases} \gamma\,(c_{v,sat} - c_{v,an}) & \text{for } s > 0, \\ \min\{0, \gamma(c_{v,sat} - c_{v,an})\} & \text{for } s = 0 \end{cases}$$

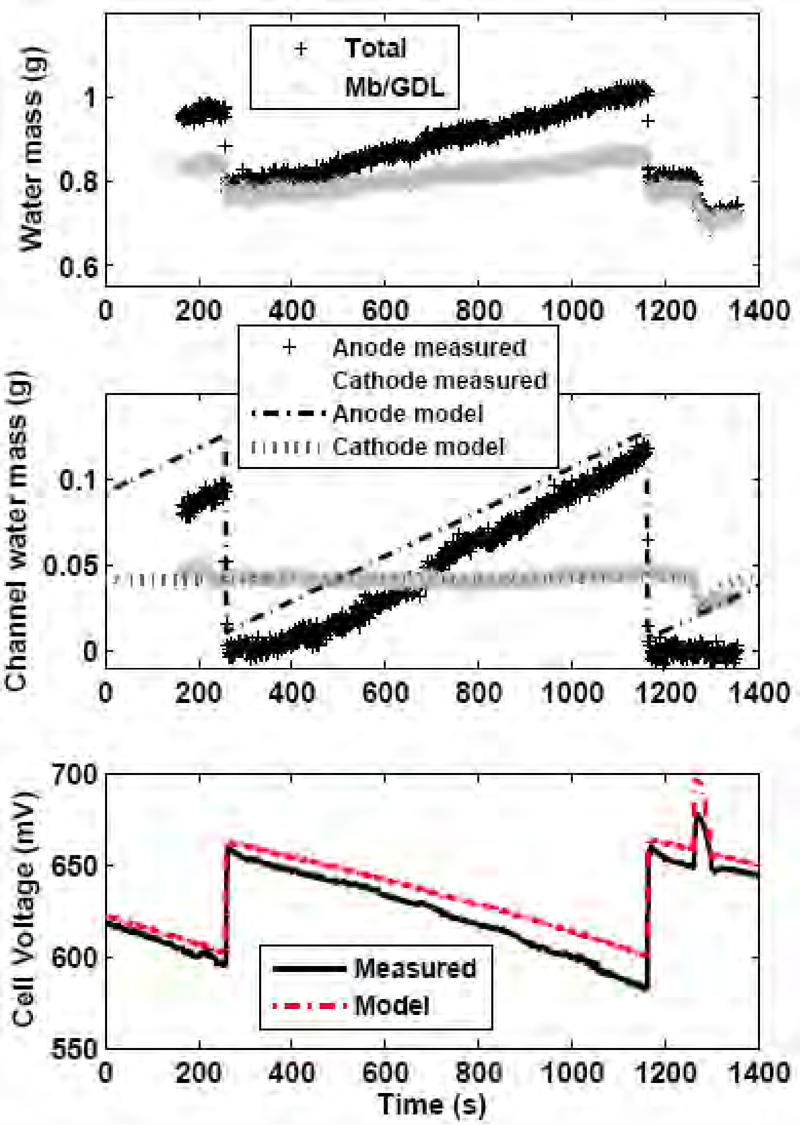
t_{wl} K K ***water film thickness (GDL/chan)***

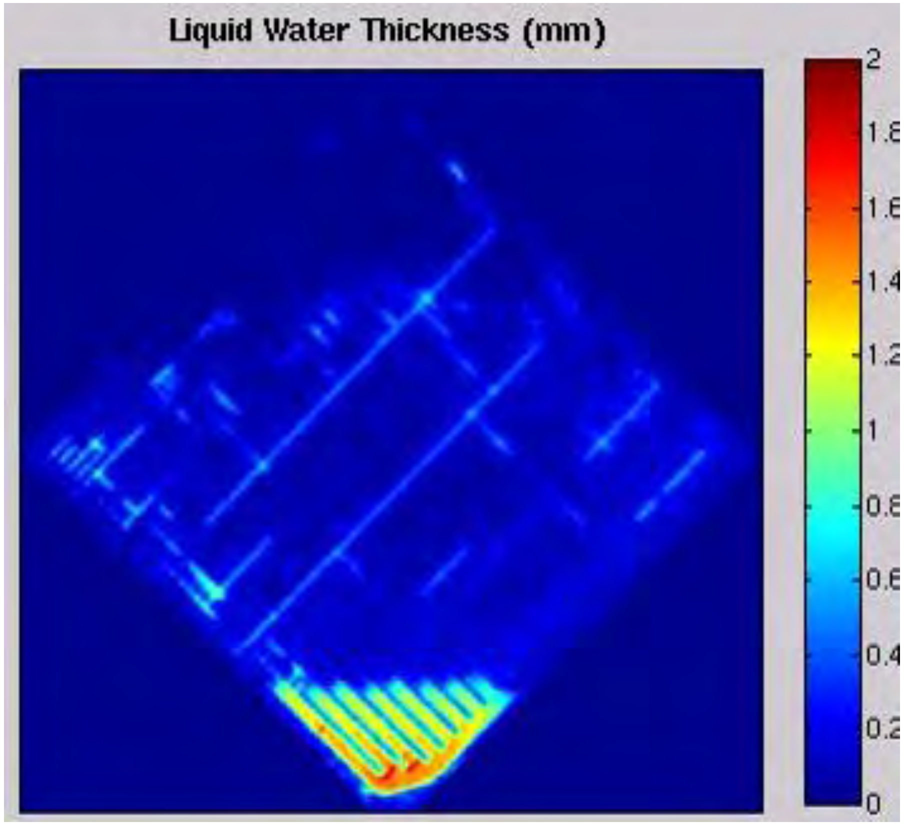
2.1 Cell Voltage Mapping

Four $k_{1:4}$ parameters (activation & resistive losses)

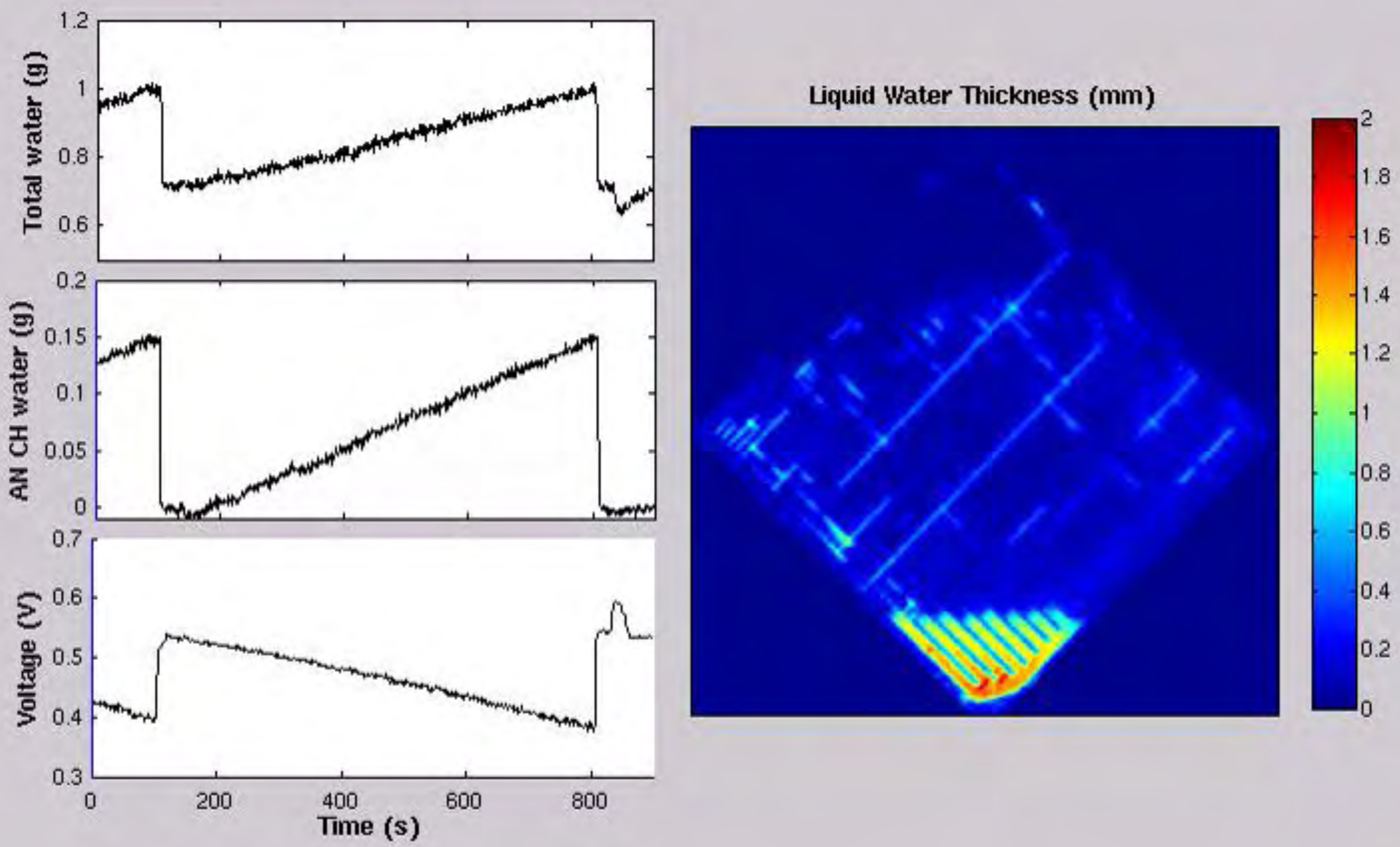
Six (6) unknown parameters

Data vs. Model Prediction



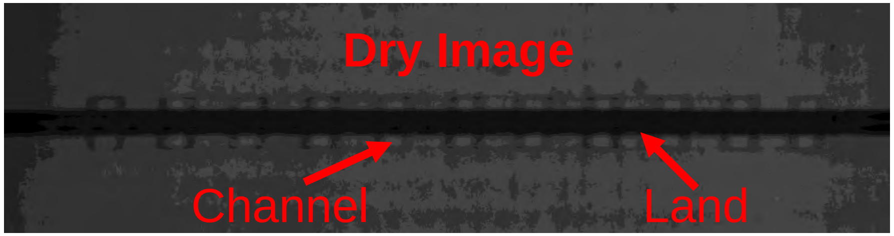


Data vs. Model Prediction

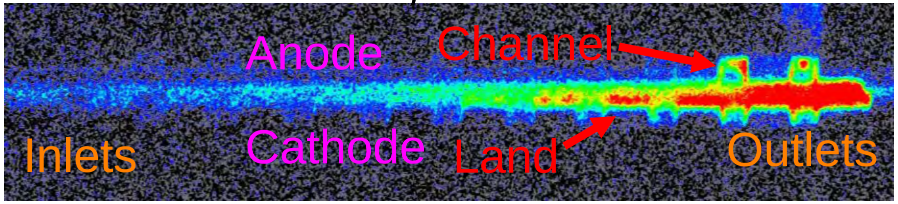


LANL High Resolution PEMFC to investigate GDL Teflon Loading Effect on Water Content

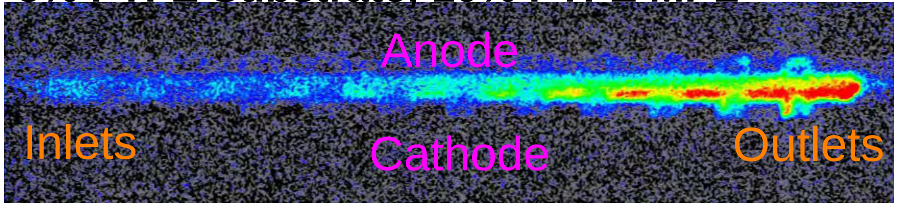
Cross-section Neutron Imaging

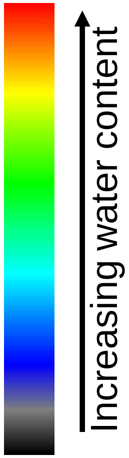


5% PTFE Substrate, 23% PTFE MPL

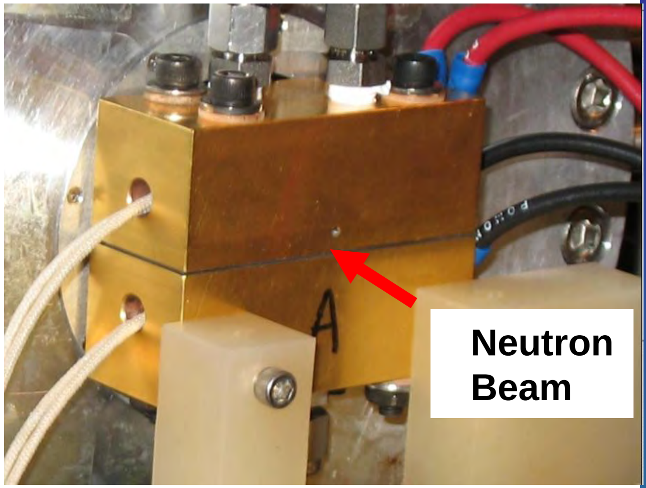


5% PTFE Substrate, 10% PTFE MPL





- 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

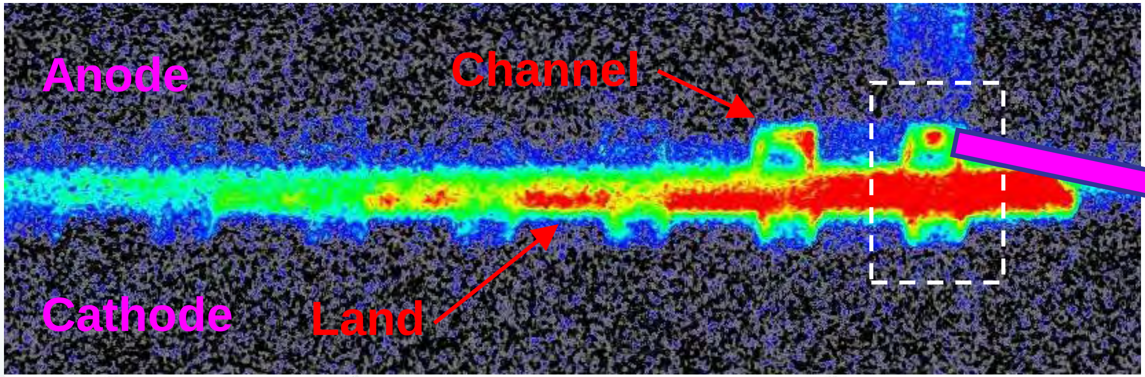


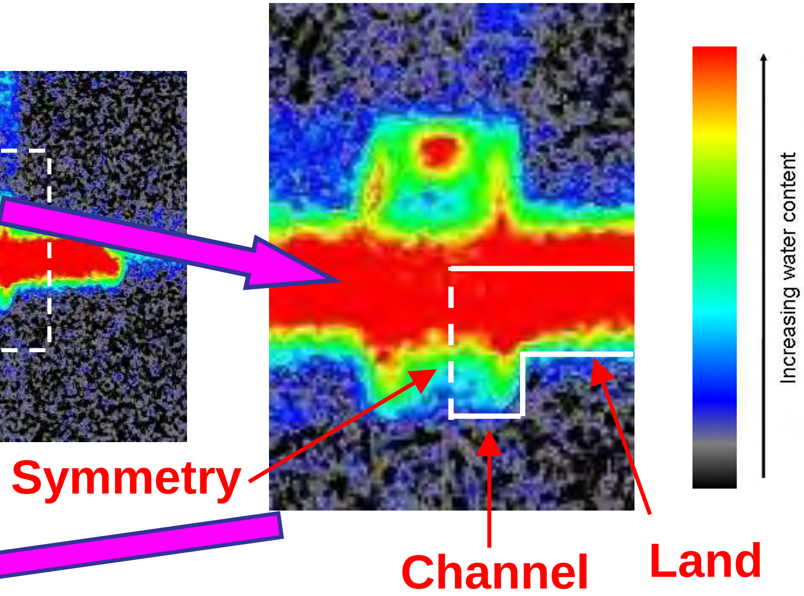
GDL A = 5% Substrate
23% MPL PTFE Loading

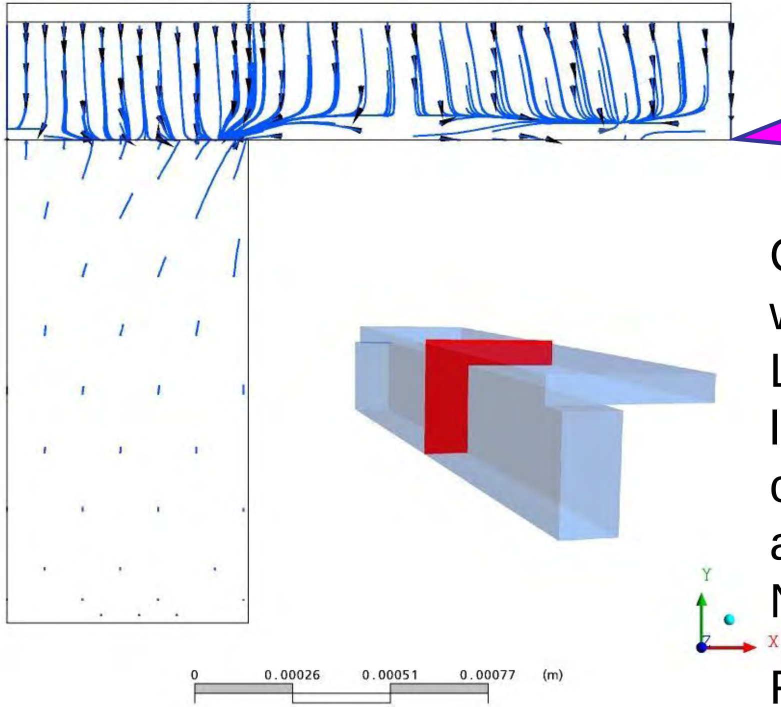
GDL B = 5% Substrate
10% MPL PTFE Loading

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

CFD Simulations of Channel vs Land Water







CFD simulations (left) representing liquid water streamlines in diffusion media. Liquid water accumulates above the lands before exiting the GDL in the channel. Area of maximum saturation is above the lands. CFD results agree with Neutron Images (above).

For more details see FC 35.

Future Work

- Anticipate receipt of 10 micron resolution detector in Summer 08
  - Highly resolved measurement of through-plane GDL water content and coarse measurement of MEA water content
  - Continue to develop sub-micron detection capability
- Electrical Impedance Spectroscopy
  - Correlate water content with impedance measurements
- Designing a new Cold Neutron Imaging Facility as part of the NIST Center for Neutron Research Expansion
  - Increased sensitivity to water and improved neutron detection efficiency
  - Enhanced capability for MEA related research
- Hydrogen Storage
  - Expanding imaging research to map hydrogen concentration gradients in prototype hydrogen storage devices

Summary

- The NIST Neutron Imaging Facility is the world’s premier national user facility for fuel cell neutron imaging, providing critical metrology capabilities in support of DOE goals for fuel cell development, performance and durability.
  - Freeze testing is routinely available
  - We continue to develop methods to improve image resolution
  - Fuel cell infrastructure is added, updated, and maintained to meet user needs and suggestions

- The number of participating groups using the NIST Neutron Imaging Facility continues to grow as well as range of water management research topics.

- Neutron imaging data is being used to validate and tune models of mass transport, advancing the fundamental understanding of fuel cell operation.

- Visit: http://physics.nist.gov/MajResFac/NIF/index.html

  for more details and facility access