Neutron Imaging Study of the Water Transport in Operating Fuel Cells

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

FC021

Overview

Timeline

Project Start Date: Fiscal Year (FY) 2001
Project End Date: Project continuation and direction determined annually by DOE
Percent Complete: 100% for each year

Budget

Project funding FY 2011

DOE:	$ 590 k
NIST:	$ 2100 k
Industry:	$ 275 k

Project funding FY 2012

DOE:	$ 300 k
NIST :	$ 600 k
Industry:	$ 250 k
Total	**$ 1,175 k**

Barriers

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

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 Laboratories
- Sensor Sciences
- University of California, Berkeley
- University of Connecticut
- University of Kansas
- University of Michigan
- University of Tennessee
- Wayne State University

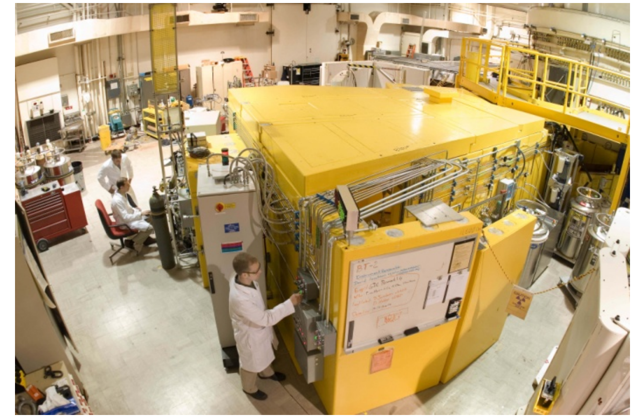
Relevance/Objectives

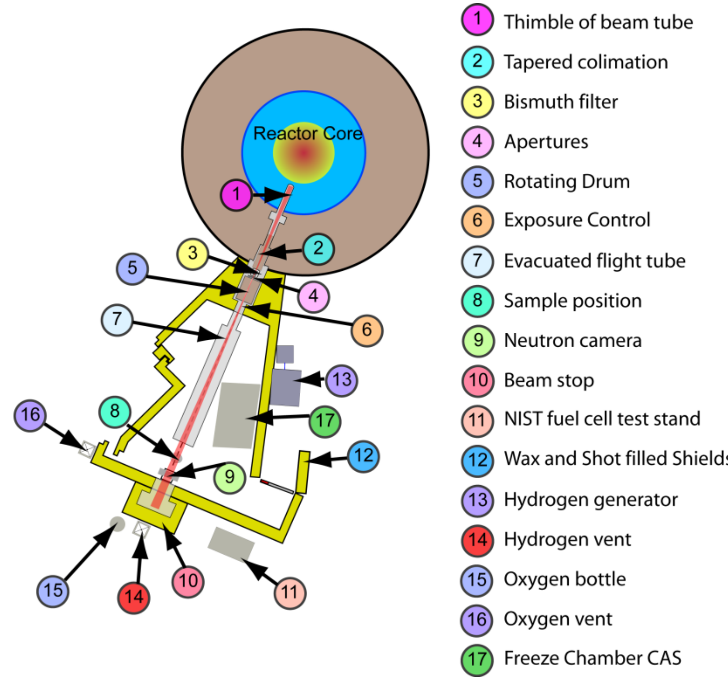
This National Institute of Standards and Technology project aims to develop and employ an effective neutron imaging based, non-destructive diagnostics tool to characterize water transport in PEM fuel cells. Objectives include:

- **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/Milestones

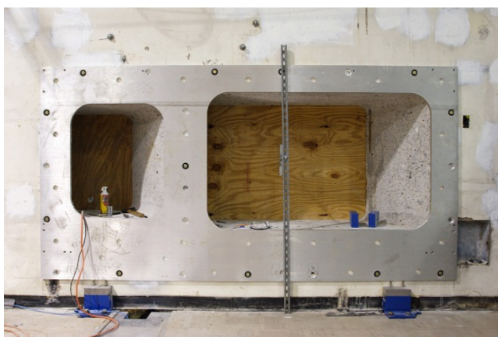
- **NIST Neutron Imaging Facility**
  - Maintain a national user facility; access to beam time through independent peer reviewed proposal system
  - Develop state-of-the-art imaging technology and analysis
  - Publish user experiments in peer-reviewed literature
  - Provide proprietary access provided 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
  - **Full scale hardware test stand added to user program.**
- **Radiography**
  - Only way to measure transient processes
  - One-dimensional cells can be made to validate simple edge on radiography
- **Improving imaging technology**
  - **New methods developed show promise for sub 10 μm resolution**
  - **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**
- **Milestones 2011 - 2012**
  - Performed in situ corrosion studies on the beamline
  - Large area detectors for fuel cell imaging currently being fabricated
  - Studies of flooding phenomena in non-precious metal catalyst layers using high resolution neutron imaging recently performed and data currently being analyzed
  - Gratings for sub 10 micron resolution designed and manufactured. Incorporation into detector systems is in progress.





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

NCNR Expansion/Shutdown
April 2010 – April 2011



New facility infrastructure

Full Scale Hardware Test Stand

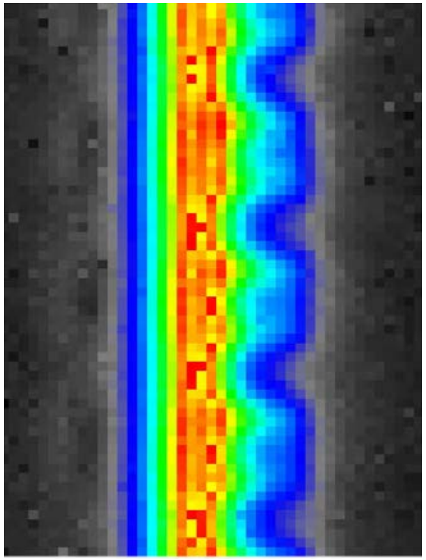
- Allows testing full scale hardware
- Hydrogenics G300
- Full scale hardware
- 800 W
- Hydrogen: 0.065 slpm – 11.31 slpm
- Air: 0.239 slpm – 26.92 slpm
- Load bank:
  - Current: 6 A -1000 A @ 0.2 V
  - Voltage: 0 V – 50 V
  - Liquid cell coolant D_2O or DI-water
- Temperature: 20 ºC – 85 ºC
- Pressure: 0 – 400 kPaA
- Contact humidification:
  - Dewpoint: 35 ºC – 85 ºC
  - Gas Temp: 95 ºC

Micro test stand upgrades

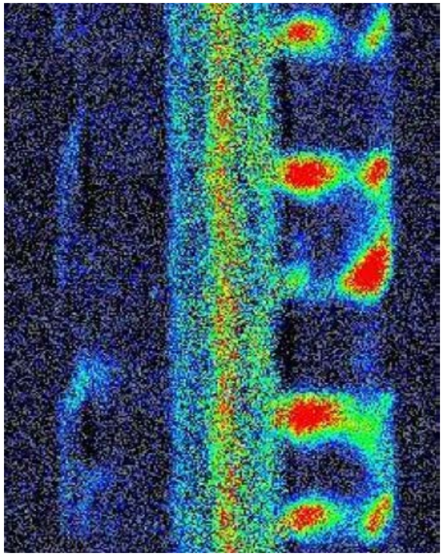
- Dual liquid coolant control
- Upgraded pressure transducers allows for running sub atmospheric pressure

Approach: High Resolution

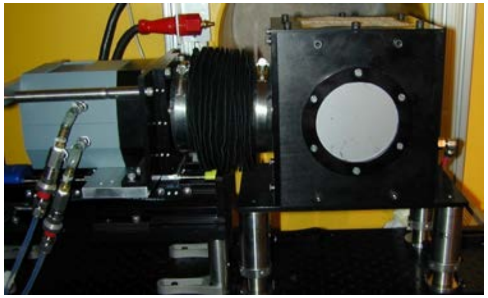
Current Neutron Imaging Capabilities

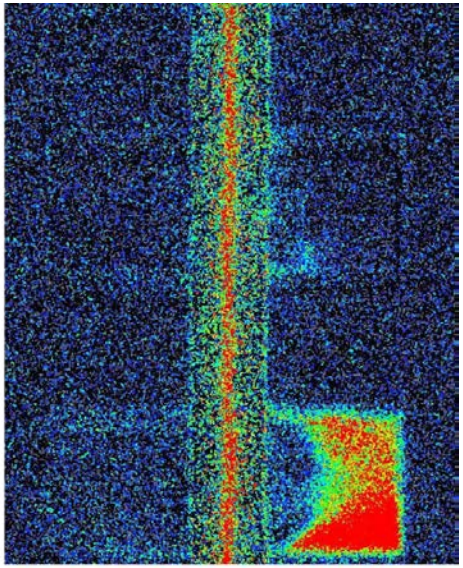


Amorphous silicon
Spatial Resolution: 250 µm
Field of View: 25 cm x 20 cm
Frame Rate: 30 frame/s

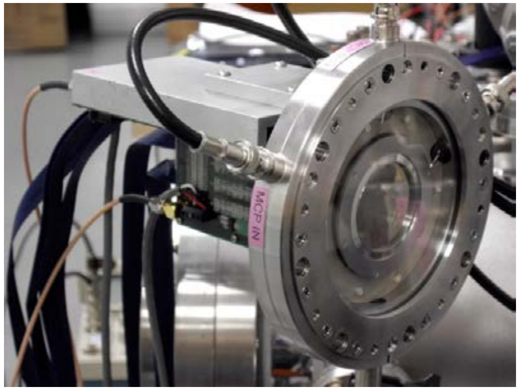


CCD
Spatial Resolution: 18 µm
Field of View: 1 cm x 1 cm
Frame Rate: 0.5 frame/s



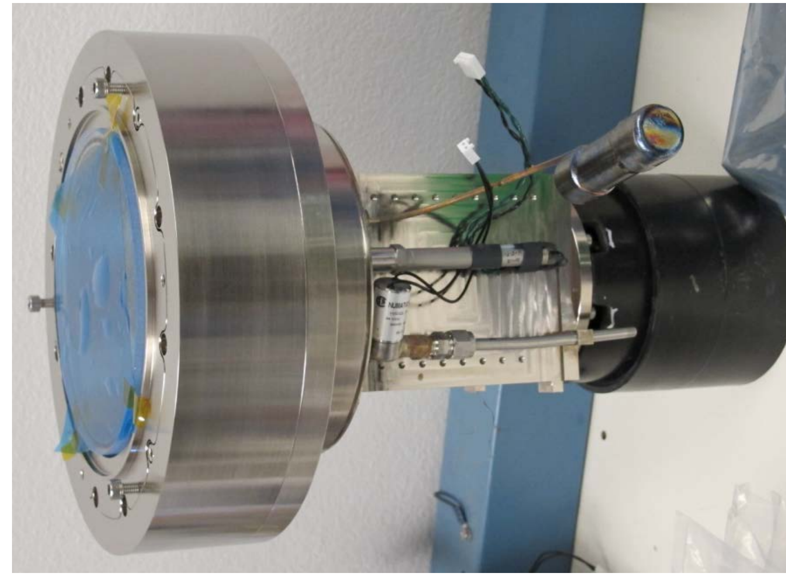


MCP
Spatial Resolution : 13 µm
Field of View: 3.5 cm x 3.5 cm
Frame Rate: 10 s – 20 min

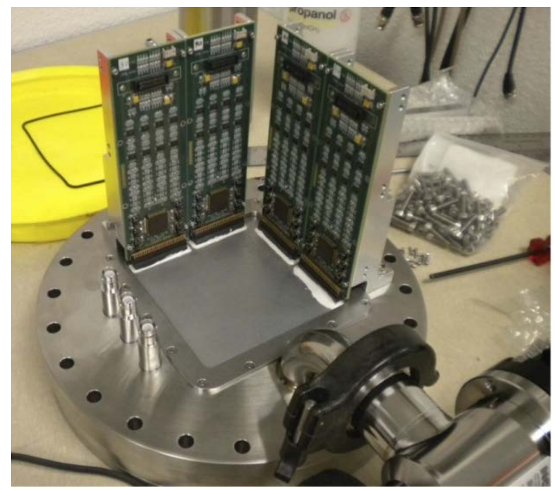


NIST

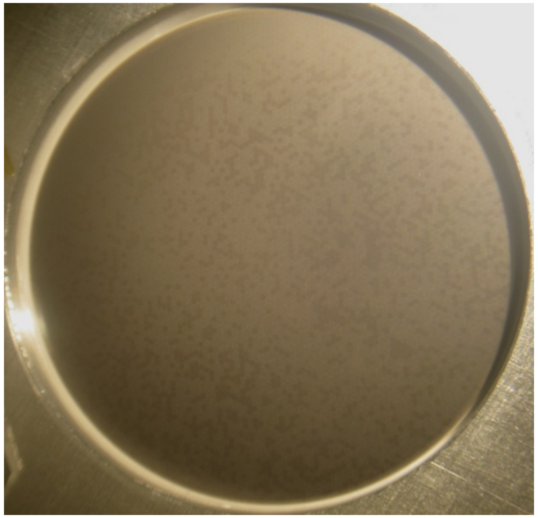
Technical Accomplishments

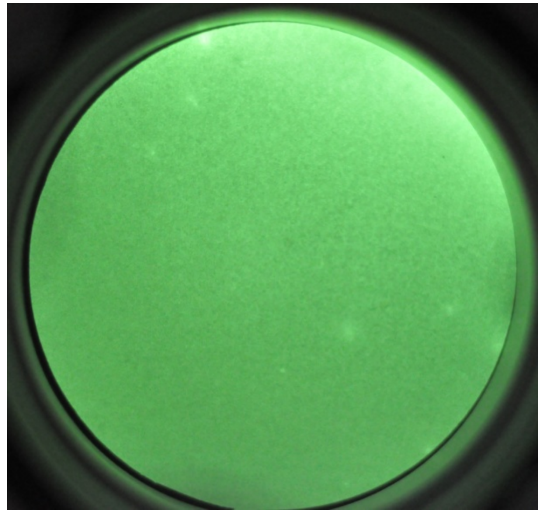


- Large Format CCD Camera
  - Big CCD: 100 MP (10k x 10k) two readout modes, 10 s, 120 s,
  - 4 e- read noise.
  - 9 um pixel pitch
- Large Format MCP
  - 10 cm field of view
  - 15 micron resolution
- sCMOS
  - 5 MP camera,
  - 6.5 um pixel pitch,
  - 100 fps (rolling) 1 e- read noise,
  - cools to -40°C

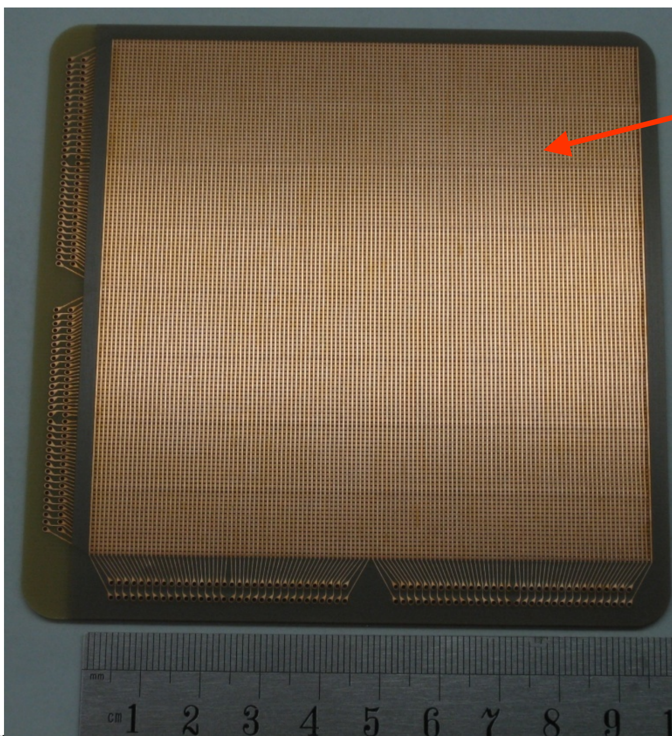


New 10 cm x 10 cm MCP Detector making progress



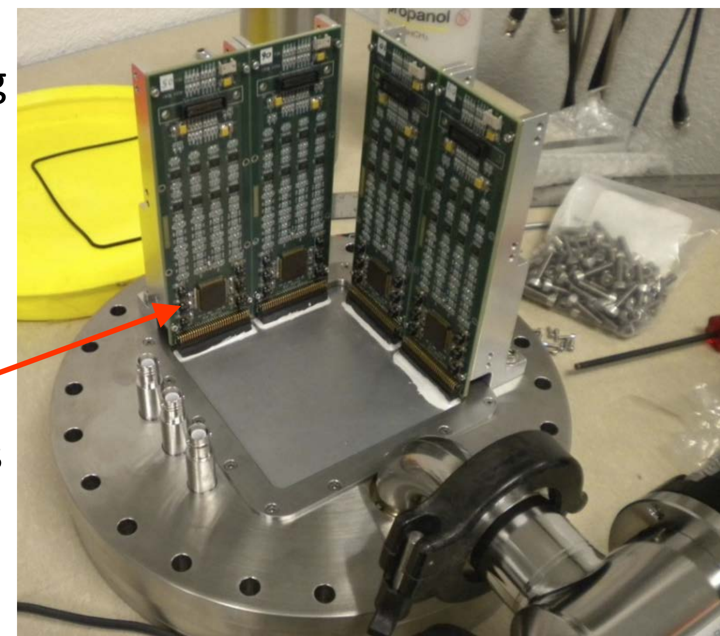


New improved micro-channel plate coatings were tested and show enhanced performance and almost no loss in performance with use. Left is a photo of a plate and right shows the uniform gain map of the new plate. New coating technology results in better tuned plates and increases the lifetime of the system.



Left shows new electron centroiding grid.

Right shows new readout electronics mounted on detector.



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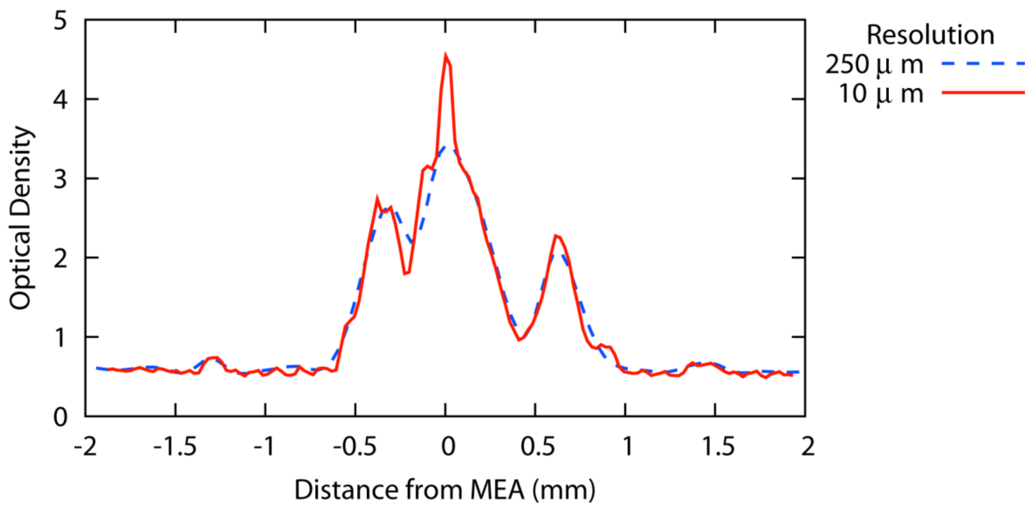
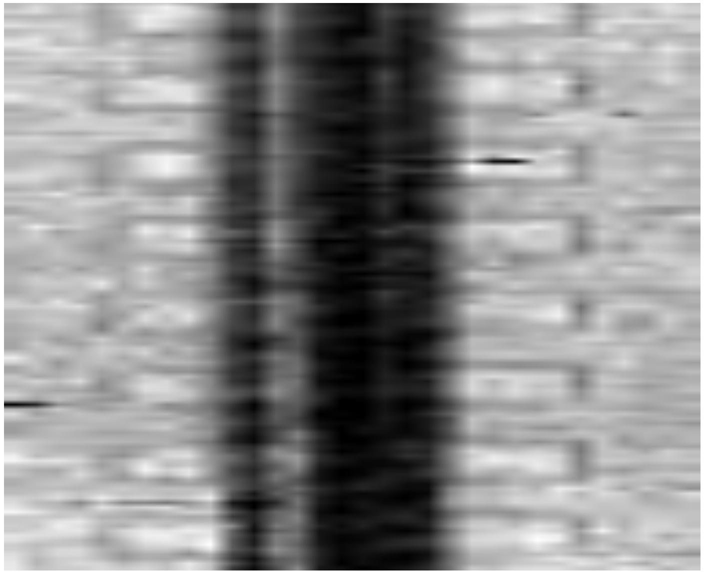
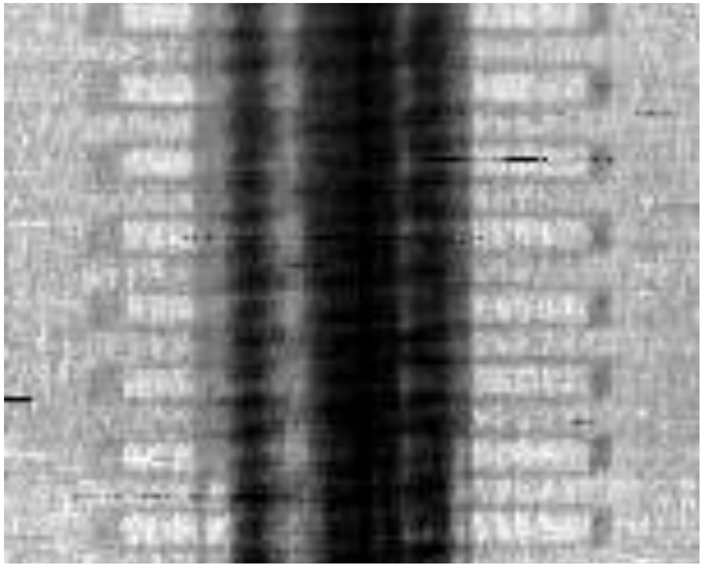
Early results proof of principle



- Original detector spatial resolution 250 microns (image top right)
- Scanning a grating of 10 micron slits results in 10 micron resolution (factor of 25 improvement) (image reconstructed bottom right)
- Noticeably improved feature resolution in histogram profile shown above.
- Improvements to the design of this method will be pursued to achieve **~1 µm** resolution to enable measurement of water distribution within commercial MEAs



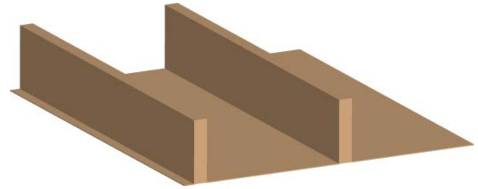
Original 250 µm image with a-Si detector

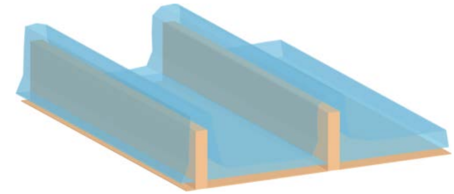


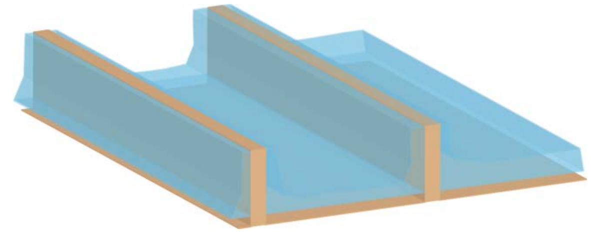
10 µm image taken with a-Si detector

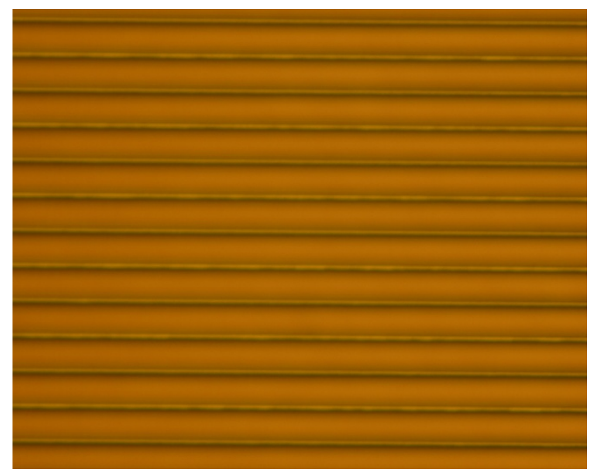
Path towards 2 µm spatial resolution…

- Spatial resolution is limited by physics to approximately 10 µm.
- However a sub 10 µm neutron absorbing mask can overcome this limitation.
- Mask must be scanned in order to form an image.
- Optimized mask is a series of slits know as a grating.
- NIST Nanofab lab is a national user facility that is being used to fabricate gratings.
- Gadolinium has a very neutron large cross section and is ideal for grating fabrication.


Create 1-2 µm wide combs in Si on 25 µm -50 µm periods


Coat surface with thick Gd film (5 µm -10 µm)


Use chemical-mechanical polishing to expose silicon resulting in a 1 µm -2 µm wide neutron slit


Gadolinium grating: Optical microscope image of Gd-coated 2 µm wide combs on 25 µm period.

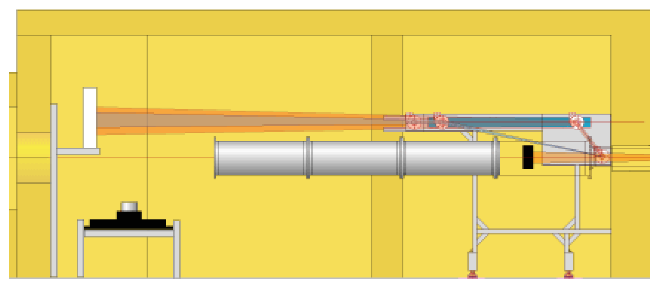
New Energy Selective Neutron Imaging Feature

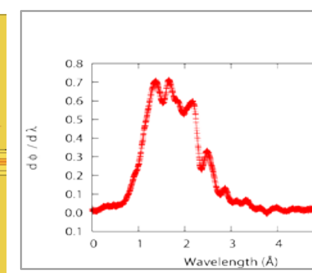
Thermal Neutron Imaging

Max Beam = 26 cm in diameter (at sample)
L/d Ratio = 6000 - 300
Fluence = 7.5×10^{5} - 3.0×10^{7}
Resolution = < 15 micrometer
Detectors = CCD, MCP, aSi, sCMOS
Low Temp. = - 40 ^{O}C (Fuel Cells)
= Cryostat for hydrogen storage

Energy Selective Neutron Imaging

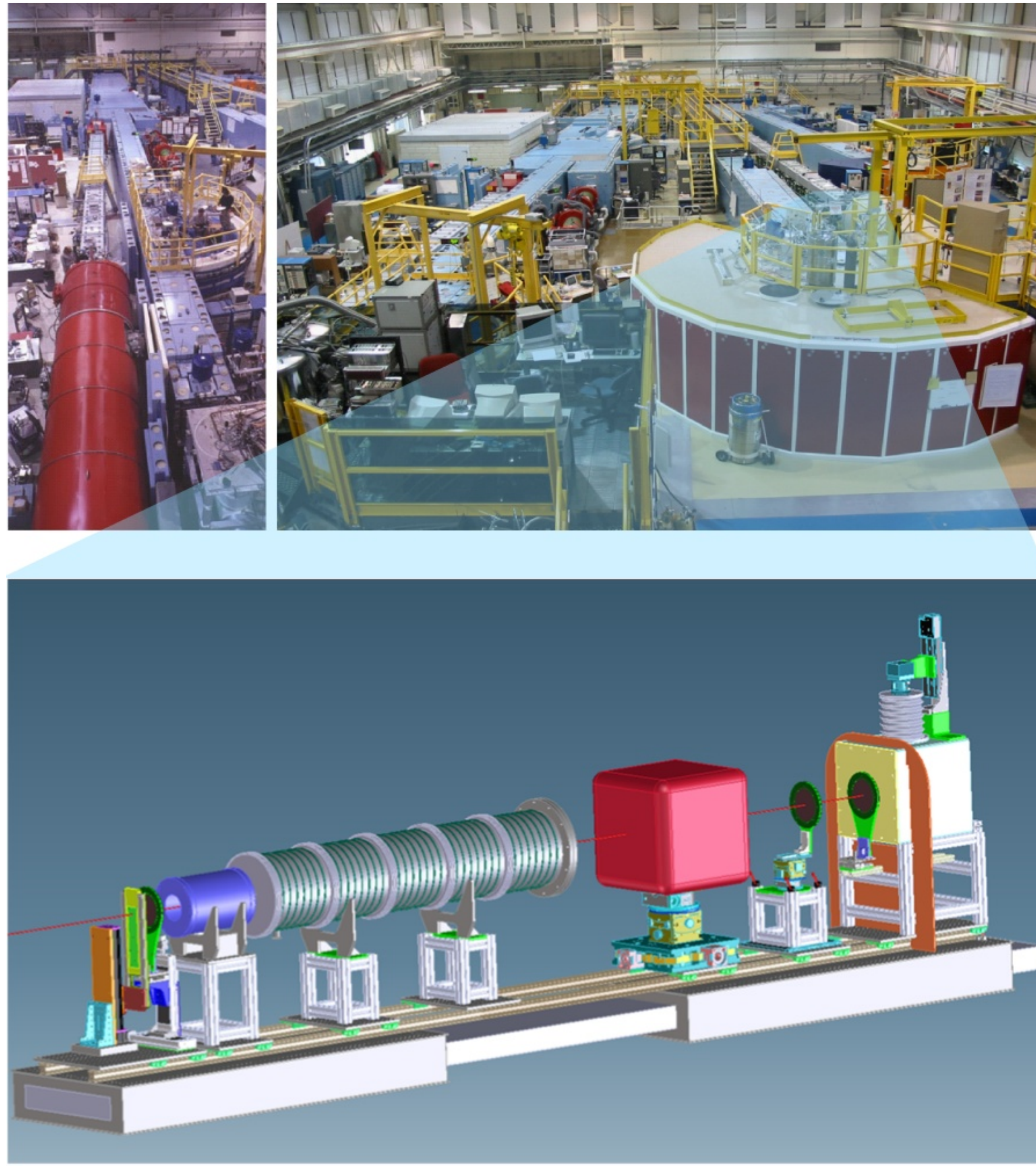
- Vertical Double Crystal PG(002) Monochromator Assembly
- Range 0.075 nm – 0.35 nm
- Refined Quantification of Polychromatic Images





Imaging with cold neutrons

- In the process of designing a beamline for cold neutron imaging
- Multi-purpose facility
- Fuel cell applications:
  - Determine volume fraction of ice and water by tuning wavelengths
  - High resolution imaging may realize better counting statistics through use of new optics
- Anticipate design complete summer 2012
- Begin testing 2013



New: Standardized High Resolution Test Cell

- Interchangeable flow distributor is included in the design.
- Using a flow field carrier or locator plate, different plates can be inserted.
- There are provisions to manipulate the direction of the inlet gas through header valves within the locator plate along the edges of the flow field.
- The header valves can be arranged to allow lengthwise flows or widthwise flows depending on the needs of the experimentalist.
- The replaceable flow field can be designed with a minimum of constraints, thus giving designer latitude to choose if the channels in the flow field are entirely straight, serpentine, or composed of a metal foam or mesh.
- Optimized for independent thermal control.
  - The thermal boundary conditions of the cell are critical when studying the water distributions in a two phase system .
  - The boundary conditions must be accurately defined but also precisely controlled with a liquid cooling system.
  - Low thermal mass systems such as those used for through plane neutron imaging using localized resistive heating have transient thermal profiles and non-ideal temperature distributions that have been shown to impact the liquid water distribution within the cell [3].
  - The coolant layer in the proposed design consists of channels created by bonding the coolant plate to the adjacent backing plate.
  - The two coolant flow fields are independent of each other thus allowing separate control to support research where temperature gradients orthogonal to the active area are desired.
- Test cell will be adjustable between horizontal or vertical orientations.

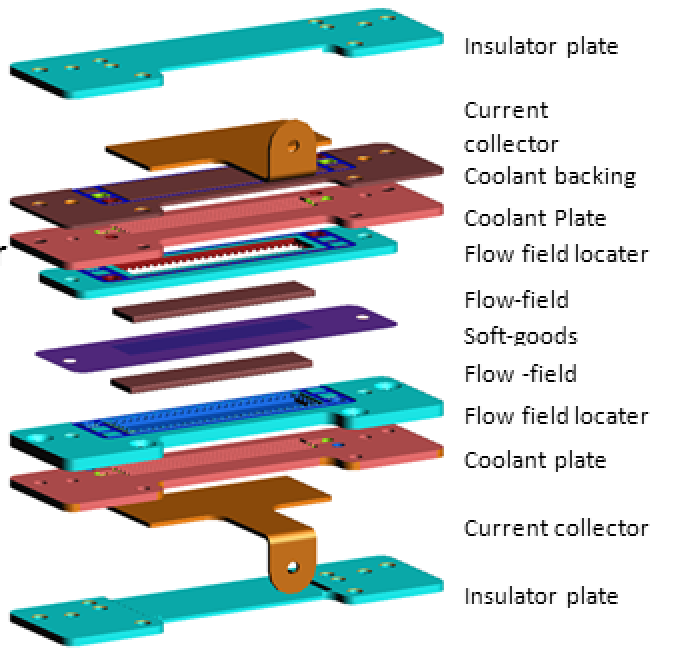
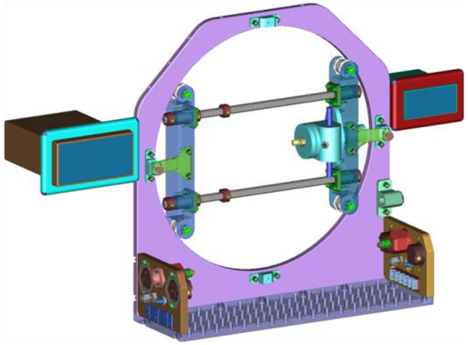


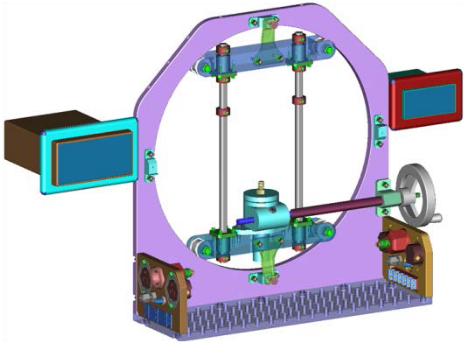
Figure 1.1 - Exploded drawing of the proposed fuel cell design showing the layers involved. User responsibility is limited to the flow fields and soft goods.

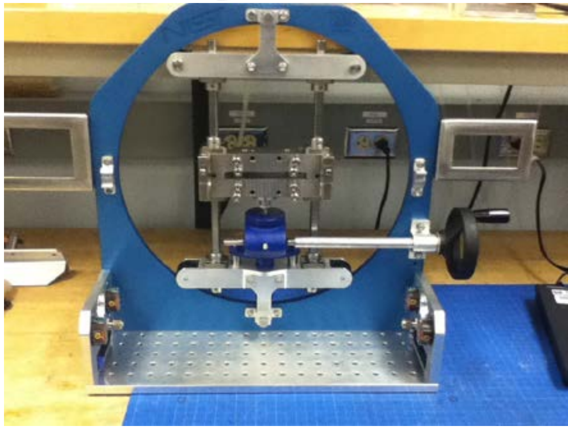
NIST GM

New: Standardized High Resolution Test Cell Fixture

- The cell fixture shown with the cell carriage oriented in the two directions.
- The adjustment process is simple but rigid and gives the user the opportunity to quickly re-build the cell in place regardless of experimental configuration.
- To ensure repeatable and well controlled build conditions for material studies, two measurement systems related to displacement are included in the cell fixture.
- Users can choose either fixed displacement or load compression by using the load cell and/or the linear variable differential transformer (LVDT) measuring systems that are fully integrated into the fixture.
  - The load and displacement measured by the transducers will be displayed on digital interfaces mounted onto the fixture.
  - A precision screw jack is used to provide displacement and its shaft is mated to a load cell attached to the fuel cell.
  - The LVDTs measure the relative distance between the compression plates at both ends to ensure the correct compression.
  - The end plates, bearings and guide rails are all sized to ensure uniform compression in the cell.
- These interfaces will sever two purposes, first the complex experimental set-up will be more organized, and second the test fixture can be installed and removed from the beamline quickly.
- Status:
  - Built.
  - Documentation and validation in progress.
- Demo video:
  - http://www.pemfcdata.org
  - http://www.youtube.com/watch?v=E9VRnb1_qKg







Collaborator work presented here

- J.J. Gagliardo, J.P. Owejan, General Motors
- R. Borup, R. Mukundan, J. Davey, J. Spendelow, T. Rockward, D. Spernjak, J. Fairweather, G. Wu, B. Li, P. Zelenay, Los Alamos National Laboratory
- William A. Rigdon, Xinyu Huang, University of South Carolina
- Kyu Taek Cho, Lawrence Berkeley National Laboratory
- Ahmet Turhan, and Matthew M. Mench Electrochemical Energy Storage and Conversion Laboratory, Mechanical, Aerospace, and Biomedical Engineering, The University of Tennessee/Oak Ridge National Laboratory

University of South Carolina

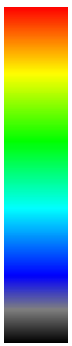
Flooding in non-precious metal cathode catalysts

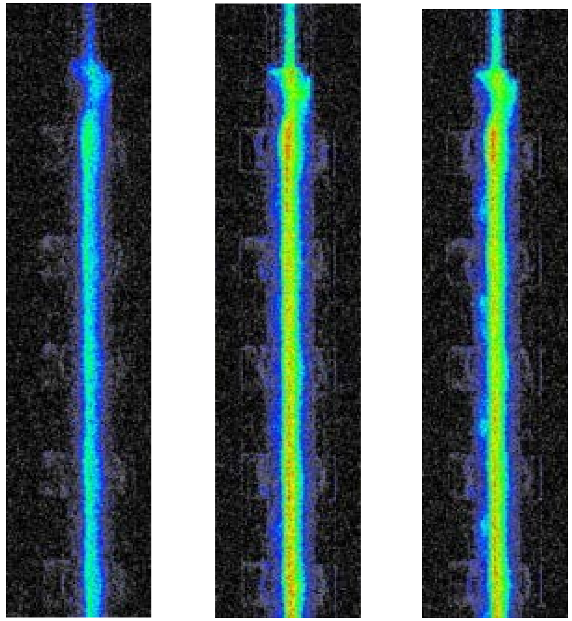
Cathode: NPMC (PANI)
70-80 µm thick

RH100, 206 kPa, 80°C

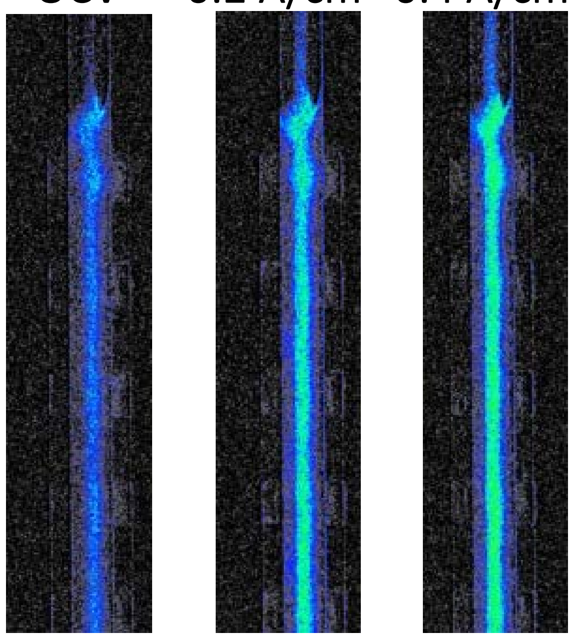
Nafion ®117, Cloth GDL

Water thickness





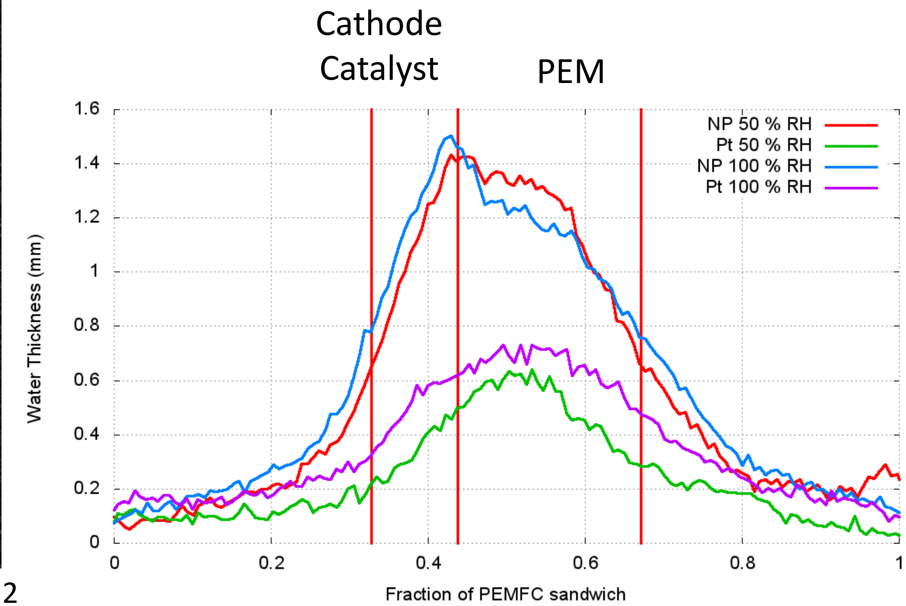
OCV | 0.2 A/cm² | 0.4 A/cm²



Cathode: Pt/C
50-55 µm thick

RH100, 206 kPa, 80°C

Nafion ®117, Cloth GDL

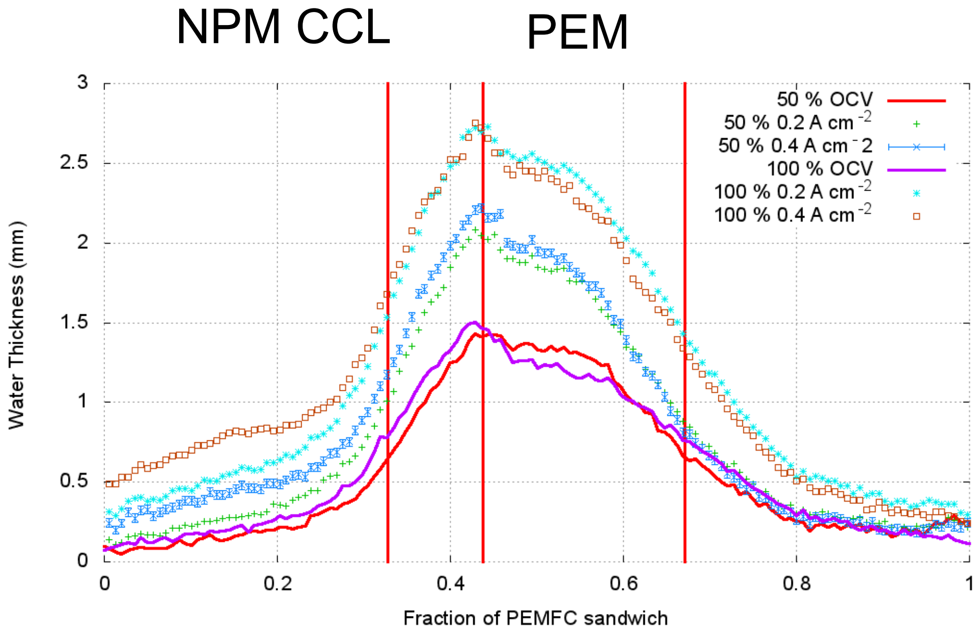


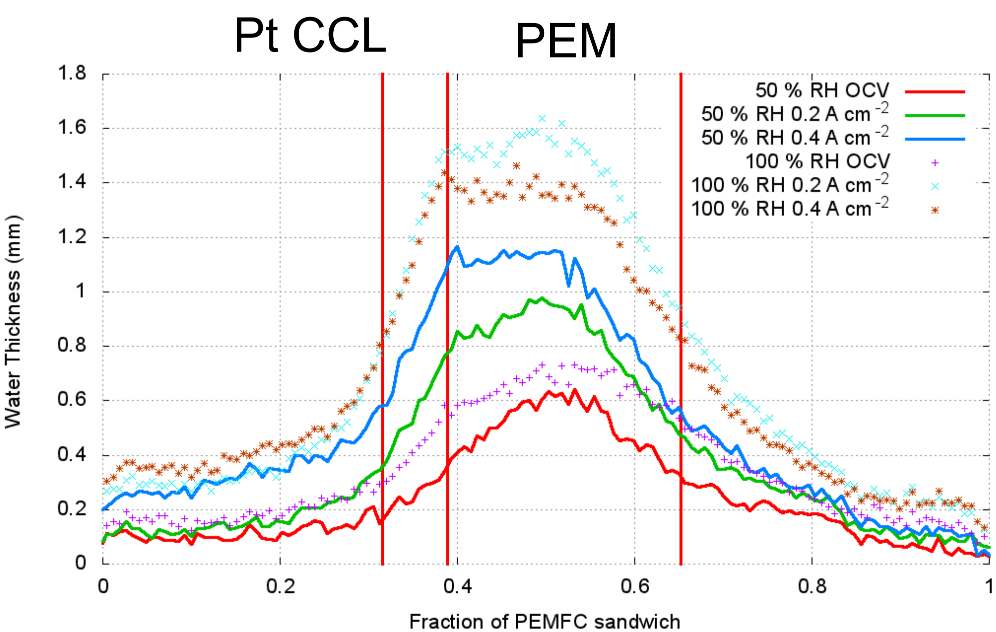
The OCV data suggests that the NPMC / PEM interface maybe hygroscopic.
The component demarcations are for the NPMC and not exact for the Pt.
In general, the NPMC has ~2x the water holdup as the Pt/C catalyst.

D. Spernjak, J. Fairweather, P. Zelenay, G. Wu, M. Rangachary, R. Borup, LANL

NIST

NPMC & Pt Water content (RH) at 206 kPa backpressure



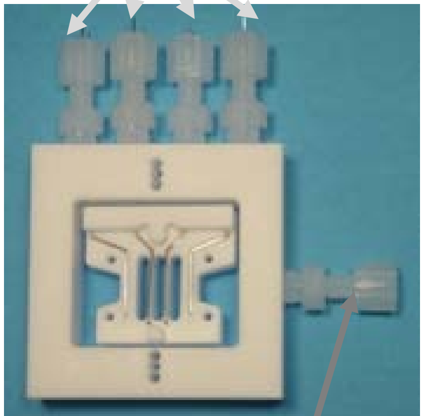


- Catalyst coated on cloth GDL, resulting in large back-pressure
- There is a layer of water at the NPM CCL/PEM interface – there is flooding
  - *Need to explore ionomer concentration, contact with GDE and membrane, etc.*
- The Pt catalyst shows no evidence of flooding, rather a “typical” water content
  - The water content of the PEM is flat near the cathode
  - With thick membrane, back diffusion in thick PEM is slow and the anode dries out, even at 100% RH (symbols).

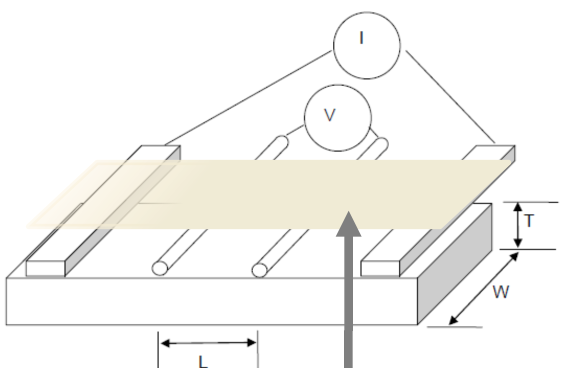
Transient relationship between log conductivity and water content vs. time

University of South Carolina

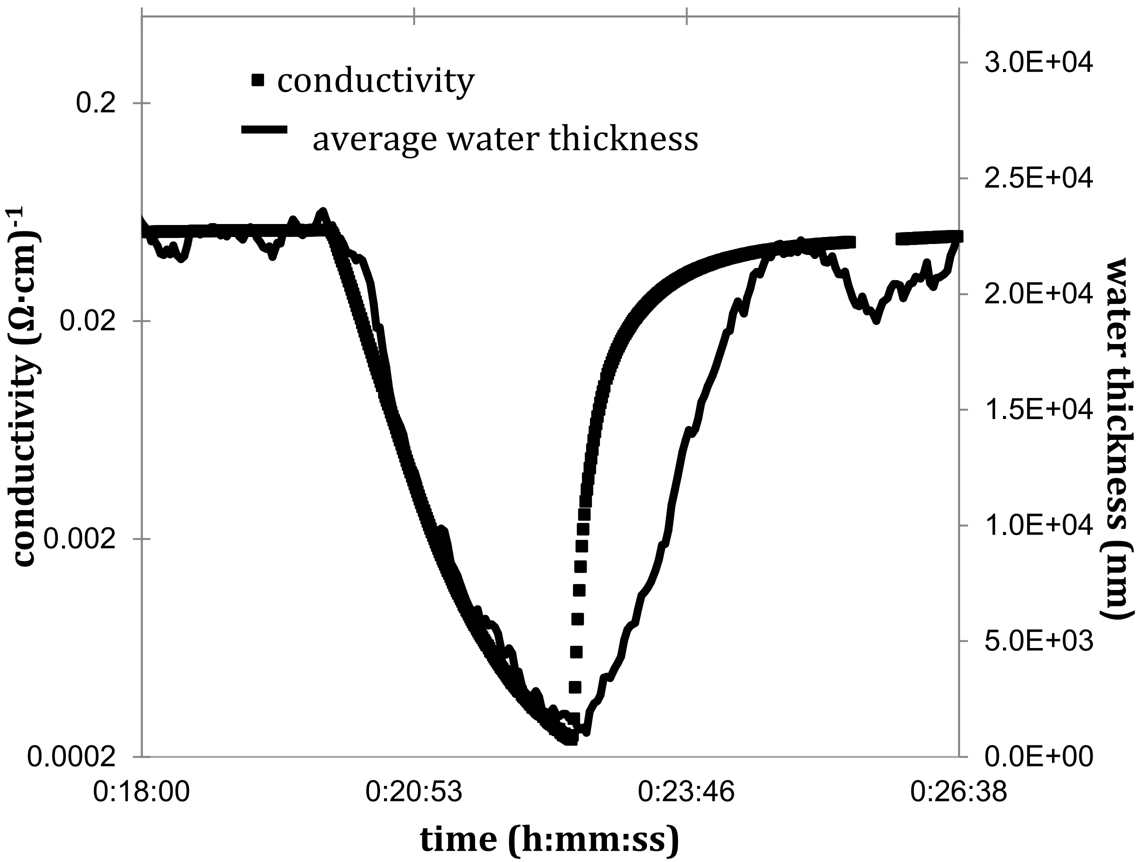
Pt electrodes



thermocouple port



Nafion® sample strip



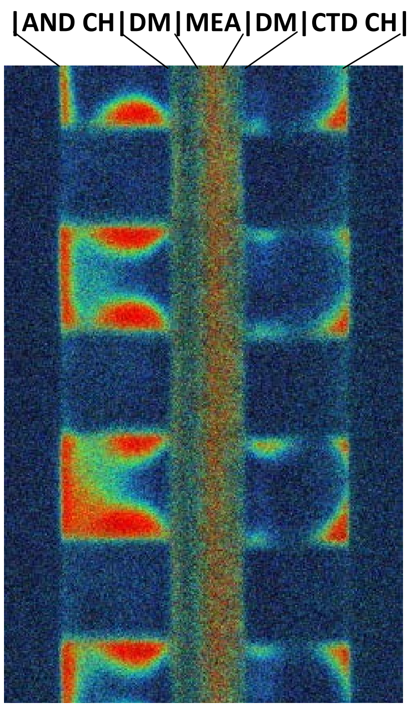
Conductivity and water thickness vs. time shows symmetric water contents, but asymmetric conductivity relationship during the wetting/drying cycle at 200 sccm for Nafion®117

H_2-D_2 contrast NR

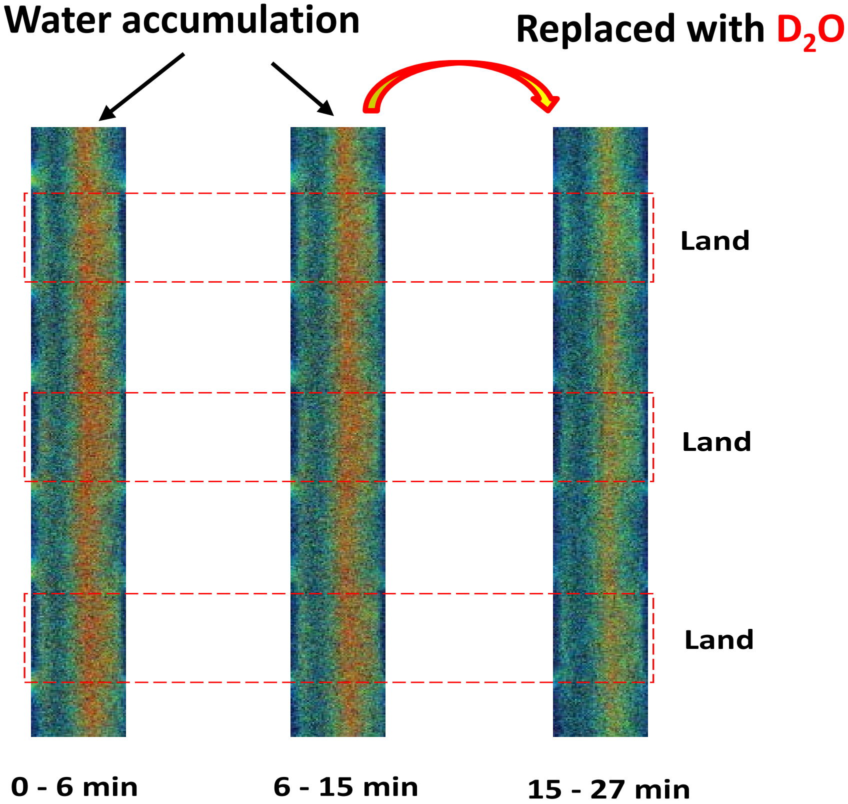
❖ Basic principle

- Light water (H_2O) is a strong attenuator for neutron beams in comparison to heavy water (D_2O) which is almost transparent.

Large difference in neutron attenuation of the D_2O produced at the cathode
→ used to track the movement of the product water



Switch
To D_2



DM: SGL 10BA W/O MPL
0.2A/cm^2 with H_2/Air(2/2)
60°C (RH80%)

NIST

BERKELEY LAB
Mechanical Aerospace Biomedical Engineering
OAK RIDGE National Laboratory

H_2-D_2 contrast NR: DM W/O MPL

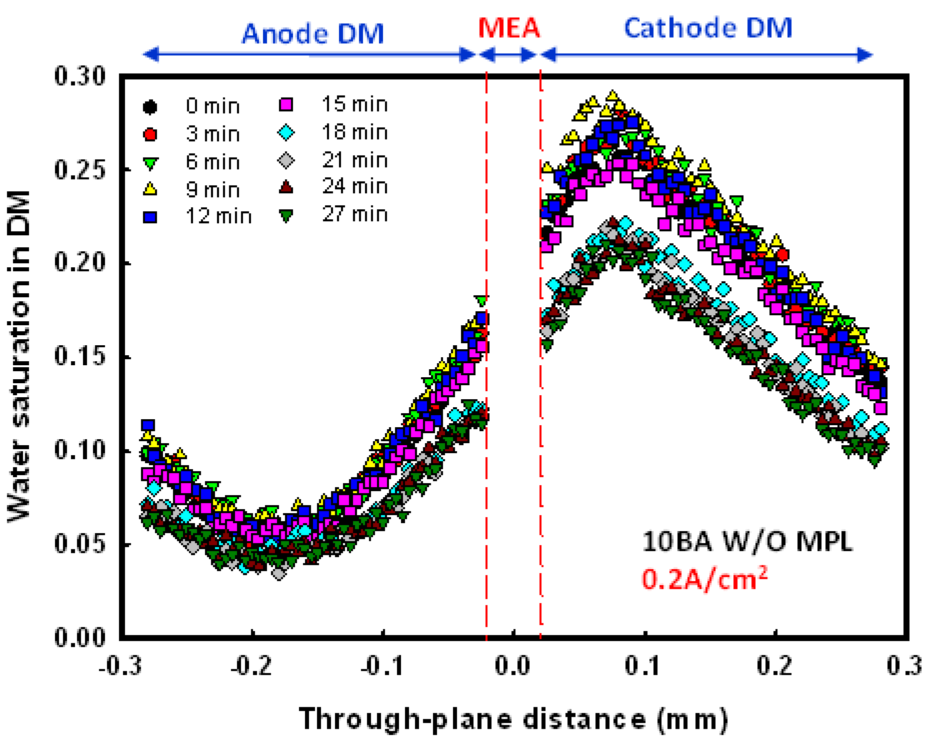
- **Water amount variation with D_2O generation**

  - **Water decreased in cathode DM**

    : generated D_2O mainly moves to cathode DM, whereas its moving to anode DM is negligible

  - **Significant fraction of water remained in DM at the steady condition**

    : immobile water was different for location.



NIST

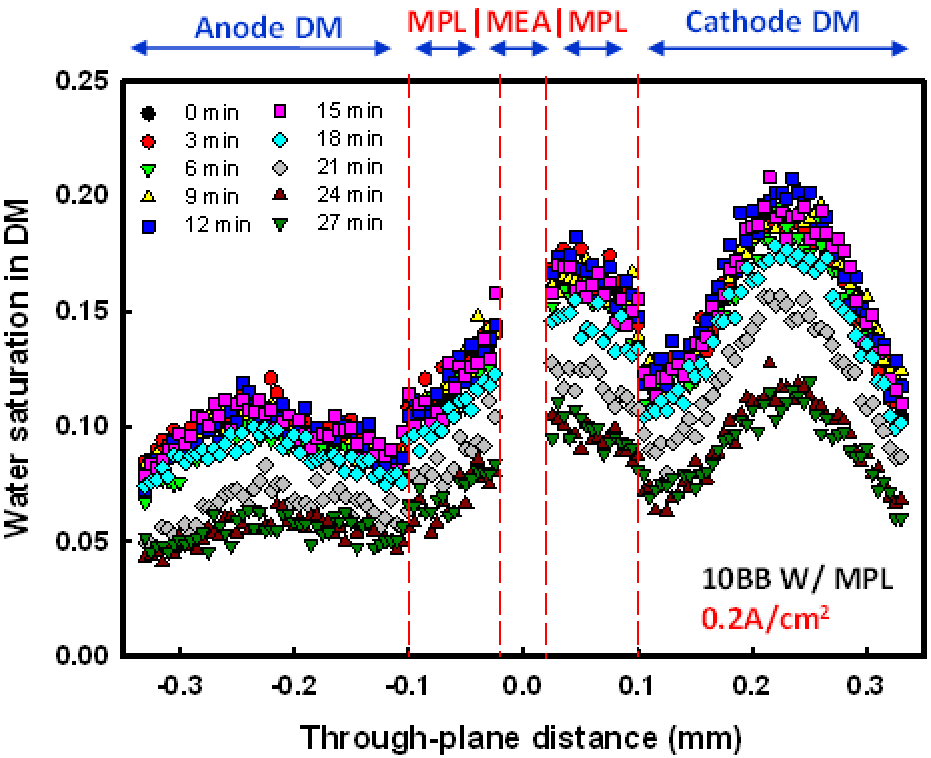
H_2-D_2 contrast NR: DM W/ MPL

- **Redistribution of generated water**

: Water amount decreased in anode DM as well as cathode DM

→ generated D_2O moves to anode DM as well as cathode DM.

→ validate the capillary barrier to pressurize and force liquid water away from cathode DM to anode



Main role of MPL: redistribution of generated water

BERKELEY LAB Mechanical Aerospace Biomedical Engineering OAK RIDGE National Laboratory NIST

H_2-D_2 contrast: Conclusion

- Role of MPL was understood
  - Redistribute the generated water through porous cell components
  → mitigate flooding in the cathode side and increase tolerance to drier gas condition on the anode side

- Effect of operating current on water content
  - At low current, water resides in disconnected and randomly distributed form (pendular regime). As current increases, the water state changes to the correlated distribution (or funicular regime), promoting water transport out of the pores by capillary action and accordingly decreasing water content

- Immobile liquid water
  - Significant fraction of water was found to be immobile during operation
  - Amount was changed with operating condition and application of MPL

NIST

BERKELEY LAB Lawrence Berkeley National Laboratory

Mechanical Aerospace Biomedical Engineering

OAK RIDGE National Laboratory

Future Work

- Continue to develop advanced imaging methods for fuel cell research
  - Apply encouraging new high resolution techniques to improve the spatial resolution to sub 10 micrometers with a **goal of 1-2 micrometer**
  - Can be applied to large scale fuel cell stacks.
- Continued advancement of imaging technology and capabilities at the facility
  - Improve field of view while maintaining spatial resolution to look at larger fuel cells
  - Measure the water content in an operating fuel cell membrane electrode assembly with a resolution of at least 5 micrometers.
  - Correction algorithms for systematic uncertainties in the measurement of the in-plane water content of fuel cells are demonstrated and published.
- Add new cold neutron imaging capabilities by designing new facility to be built for expansion of the NCNR

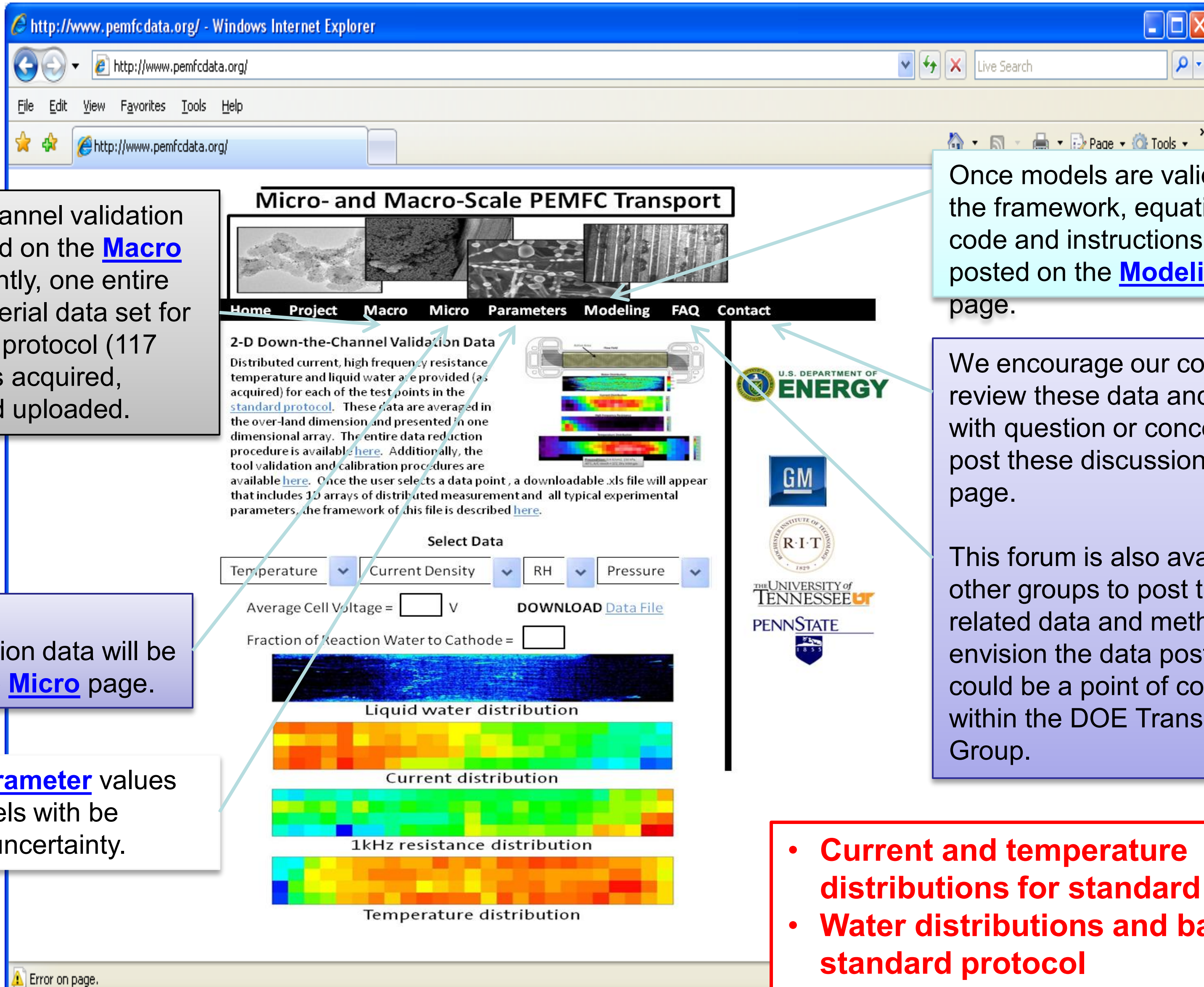
Summary of Technical Accomplishments/Results Presented

- Ultra-High Resolution Experiments
  - Developed illumination system to achieve ~1 micrometer spatial resolution to overcome conventionally accepted 10 micrometer resolution limit for MEA imaging.
  - Demonstrated method by improving a detector with 250 micrometer resolution to a spatial resolution of 10 μm; **a 25 fold improvement**.
- LANL Study of non-precious metal catalysts
  - Neutron imaging showed that the PANI-derived catalyst is hygroscopic
  - Fabrication methods can be modified to reduce pressure drop and boost performance
- USC Transient Membrane Hydration & Conductivity
  - On wetting, conductivity rises more quickly than steady-state correlation with λ
  - On drying, conductivity follows steady-state correlation with λ
- U Tenn D_2/H_2 contrast radiography
  - MPL is seen to distribute generated water throughout the PEMFC sandwich
  - Without an MPL, generated water is primarily in the cathode GDL

Technical Back-Up Slides

Database: www.PEMFCdata.org

Down-the-channel validation data is posted on the **Macro** page. Currently, one entire baseline material data set for the standard protocol (117 test points) is acquired, analyzed and uploaded.



Once models are validated, the framework, equations, code and instructions will be posted on the **Modeling** page.

We encourage our colleagues to review these data and **Contact** us with question or concerns. We will post these discussions to the **FAQ** page.

This forum is also available for other groups to post transport related data and methods. We envision the data posted here could be a point of consensus within the DOE Transport Working Group.

Component characterization data will be posted to the **Micro** page.

All single **Parameter** values used in models with be posted with uncertainty.

- **Current and temperature distributions for standard protocol**
- **Water distributions and balance for standard protocol**
- **Upload data to project database**

Standardized High Resolution Test Cell and Mounting Fixture

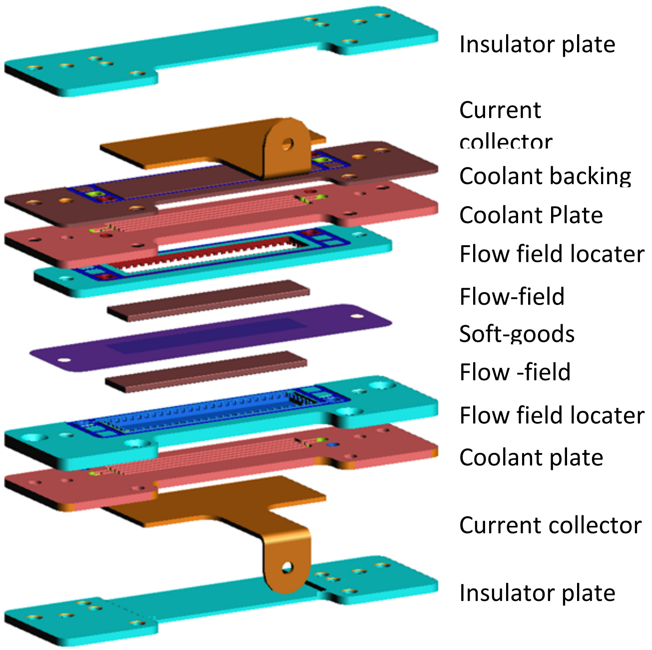
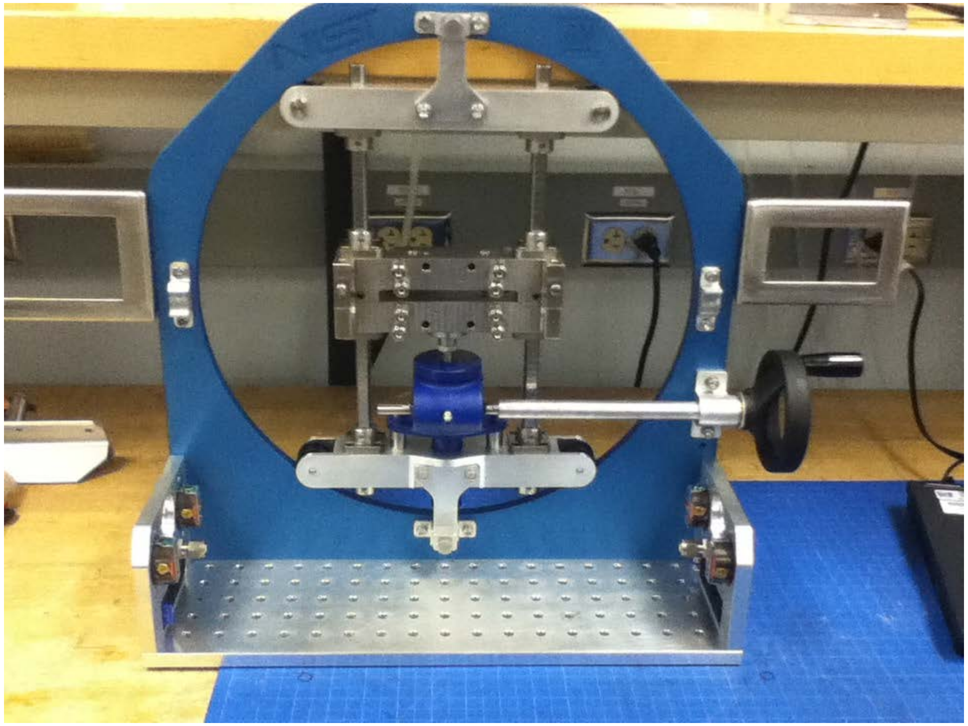
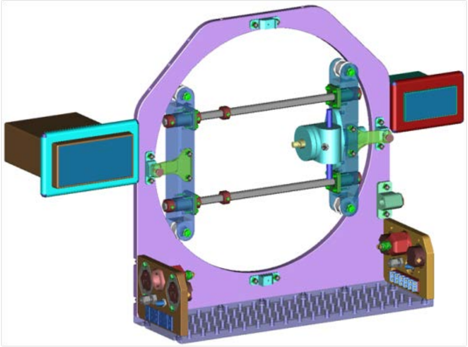
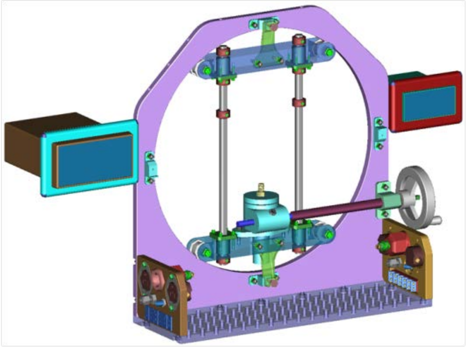


Figure 1.1 - Exploded drawing of the proposed fuel cell design showing the layers involved. User responsibility is limited to the flow fields and soft goods.





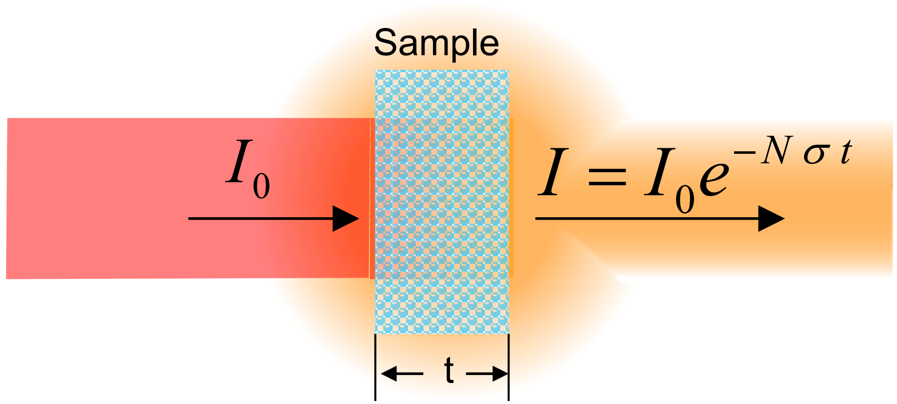


Engineered with multiple flow fields so that users only need to bring soft goods. Soft goods can be exchanged in situ. Additional details in backup slides Demo video:
http://www.pemfcdata.org
http://www.youtube.com/watch?v=E9VRnb1_qKg

NIST GM

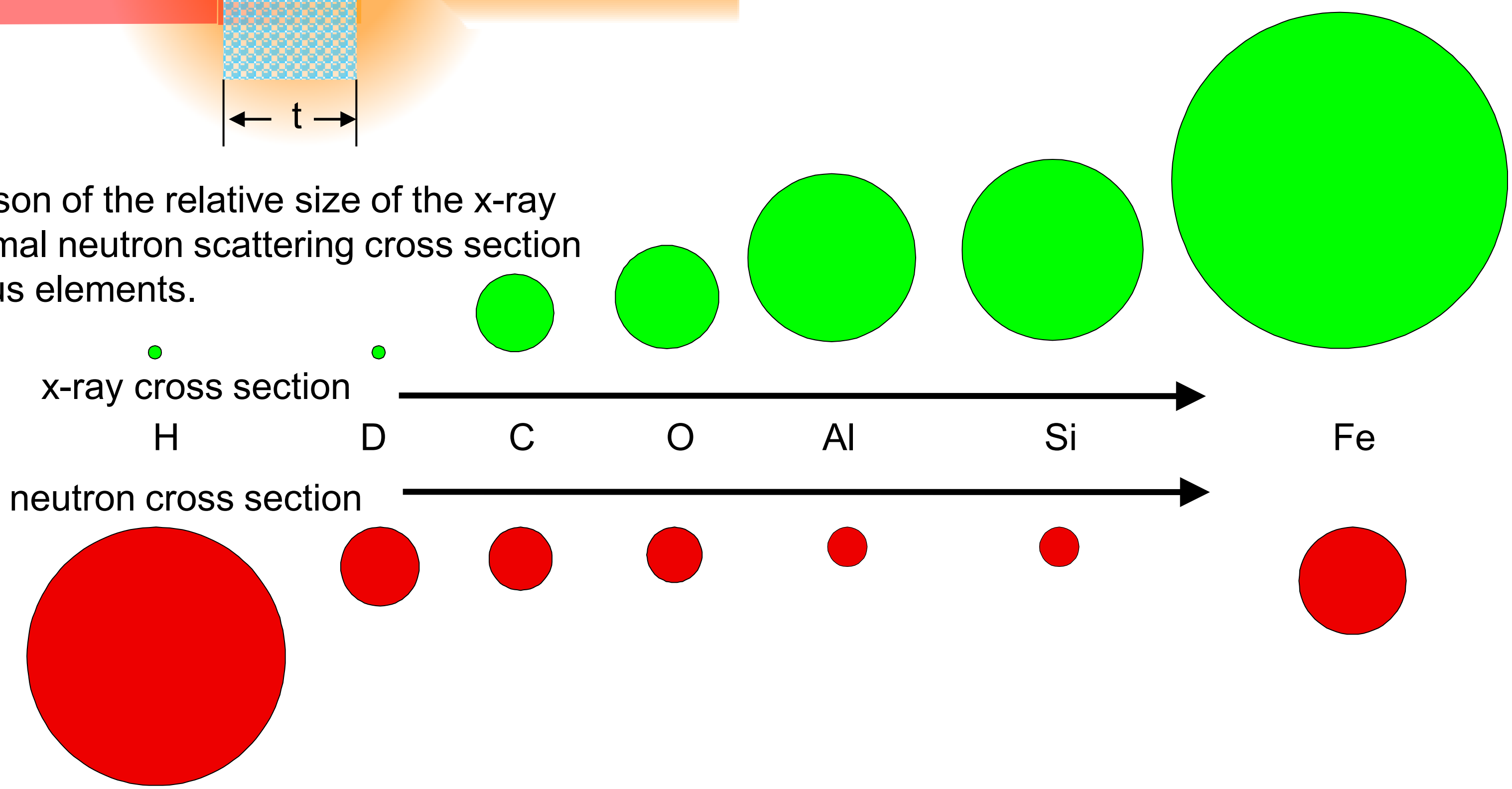
Why Neutrons

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
- σ - 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.



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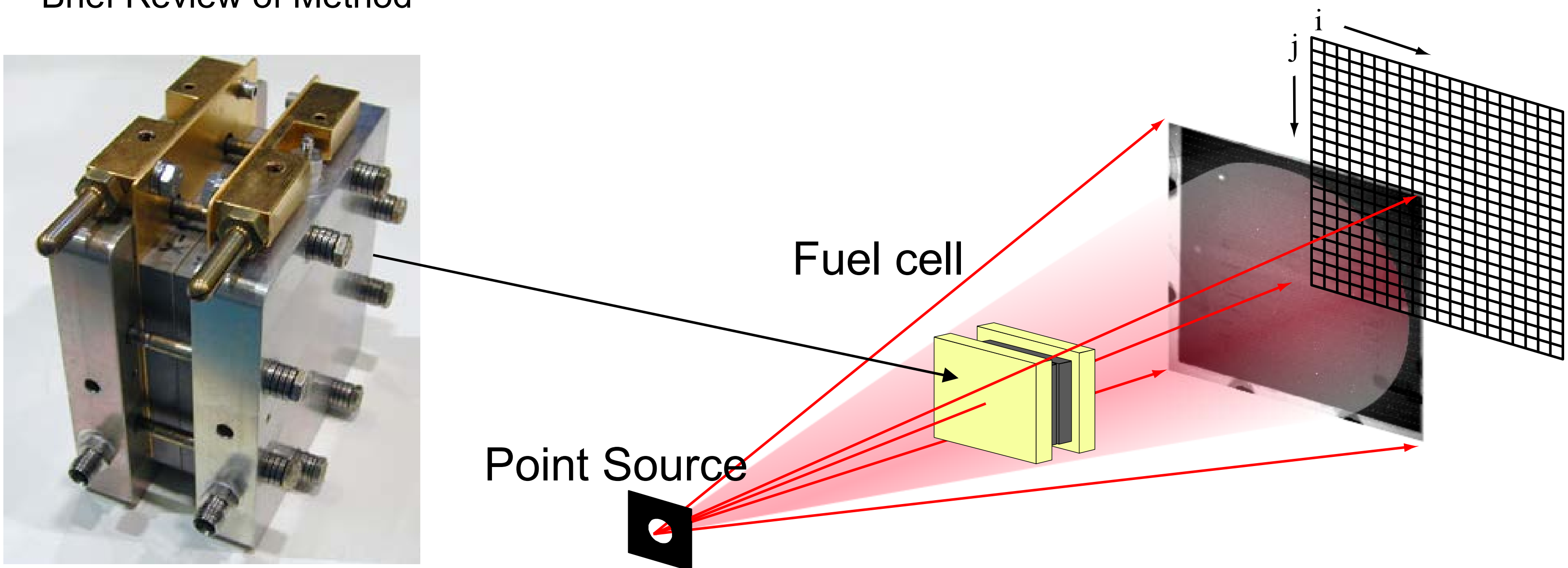
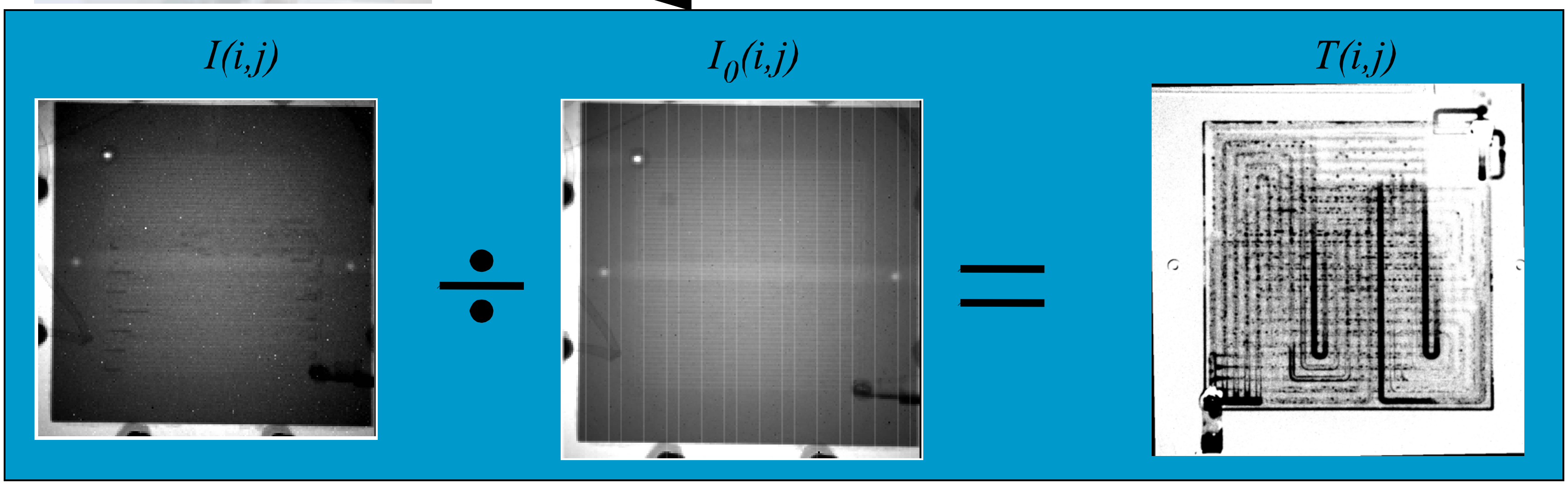
Brief Review of Method





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

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 H_2, Air, N_2, He, O_2:
  - H_2: 0-50, 0-500 and 0-3000 sccm
  - N_2: 0-2000 sccm
  - Air: 0-50, 0-100, 0-500, 0-2000, 0-8000 sccm
  - O_2: 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