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

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

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NIST

Overview

Timeline

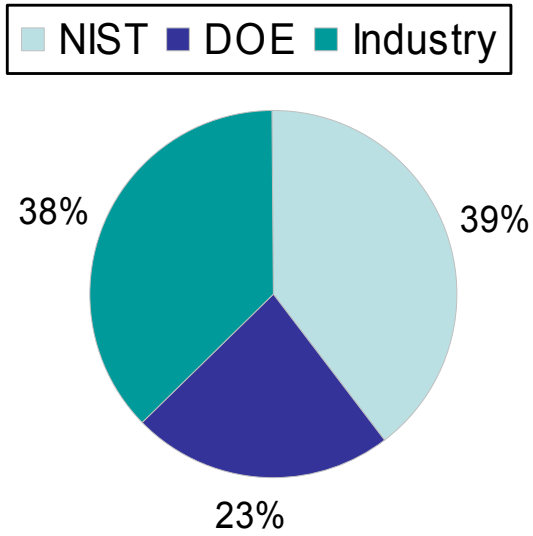
Project Start : 2001, continuing
Percent Complete:100% for each year

Barriers

Thermal and Water Management.

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

Budget



Total: $1.4M

Partners/Users/Collaborators

Project Lead: National Institute of Standards and Technology

- General Motors
- Ford
- Plug Power
- Los Alamos National Laboratory
- Georgia Tech
- Oak Ridge National Laboratory
- Illinois Institute of Technology
- Korea Atomic Energy Research Institute
- NOVA Scientific
- Michigan Technological University
- Pennsylvania State University
- 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
- Wayne State University

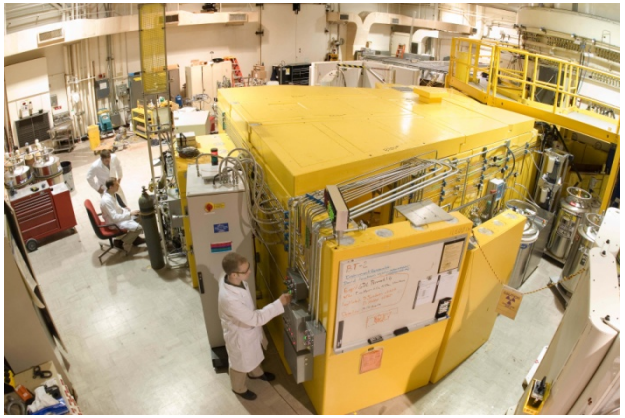
Relevance/Objectives

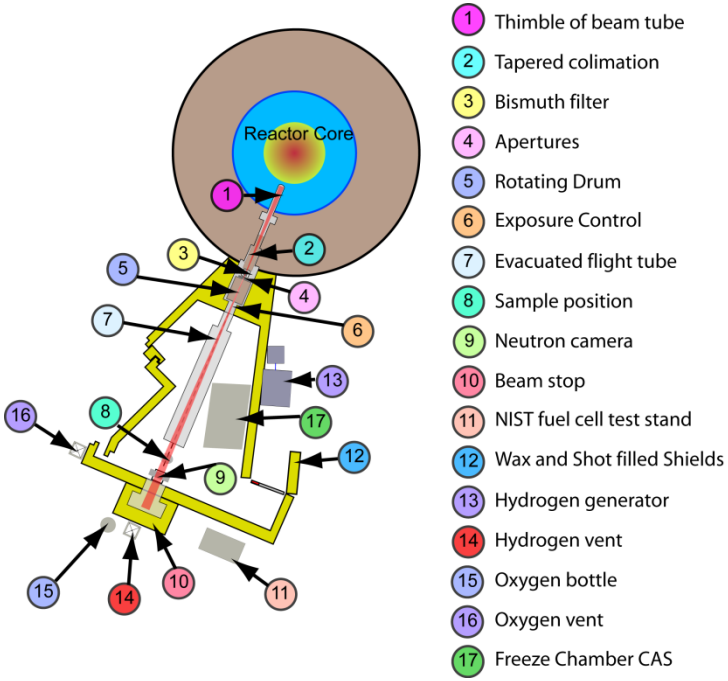
This National Institute of standards and Technology project aims to develop and employ an effective neutron imaging based, non-destructive diagnostics tool to characterize water transport in PEM fuel cells. Objectives include:

- **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
  - Users provided open 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 fully supported (details in supplementary slides)
  - **Environmental Chamber for freeze testing** -40 C to +50 C with humidity control
  - **EIS-Zahner IM6eX Electrochemical Workstation**
- **Radiography**
  - **New image acquisition software developed by NIST and tailored to facility users**
  - **Dramatic improvement of resolution anode v.s. cathode using slit appertures**
  - 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
  - Resolve Water distribution in GDL
  - Unambiguous discrimination of anode from cathode
- **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



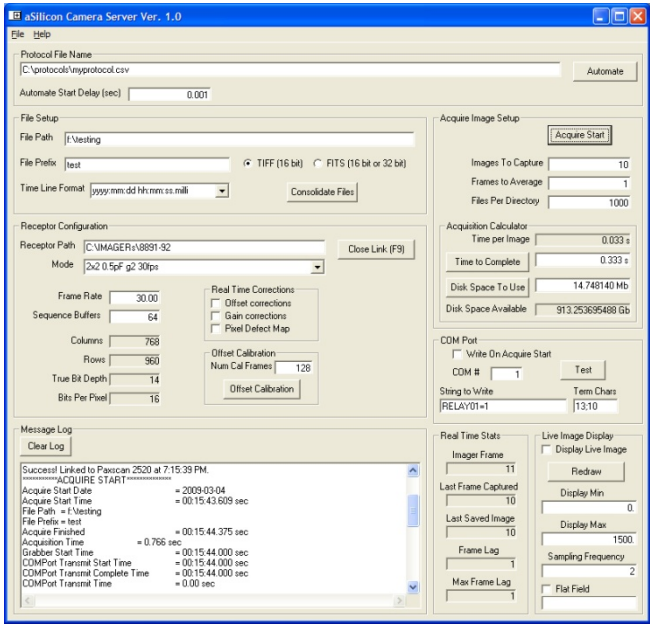


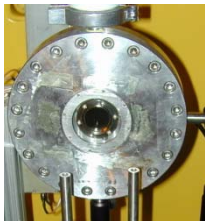
NIST Neutron Imaging Facility. Full facility capabilities provided in supplemental slides.

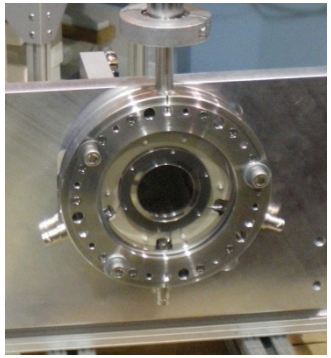
NIST

Detectors and Software

- 2 new flat panel systems have been acquired
  - Provides for new primary and backup system for low resolution radiography
  - New imaging software developed by NIST
    - Eliminates frame dropping
    - Reduces data set size
    - Improved ability to integrate protocols with fuel cell test stand
- New XDL detector
  - Backup to existing detector
- New XS detector
  - 10 x greater rate
  - Larger field of view available
  - Greater that factor of 2 improvement in spatial resolution
- Planned large format high resolution detector
  - Performance of the XS detector
  - Active area 100 mm x 100 mm
- Backup hardware for existing MCP detectors
- Sub-micron detector prototype for testing by September 2010



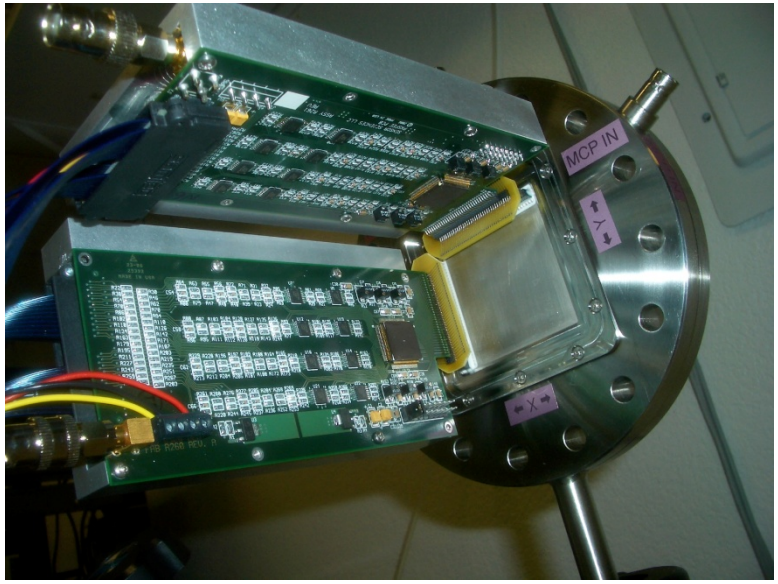




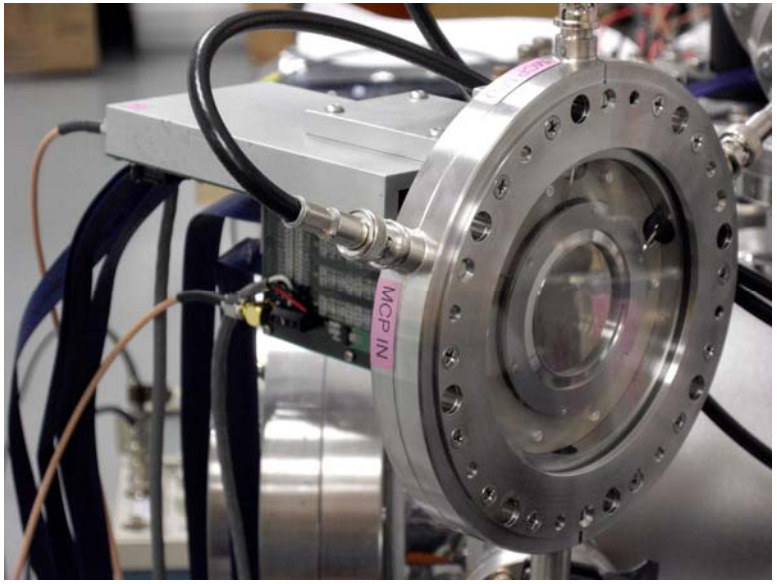
Advanced High Resolution Neutron Imaging System at the Facility

- Faster – handles 10x the previous rates
- Better – ~10 μm improves resolution by factor of 2
- But much more complex!

40mm Cross Strip (XS) neutron detector



40mm XS anode neutron detector showing the back of the detector with the amplifier boards for X and Y axis event position encoding.

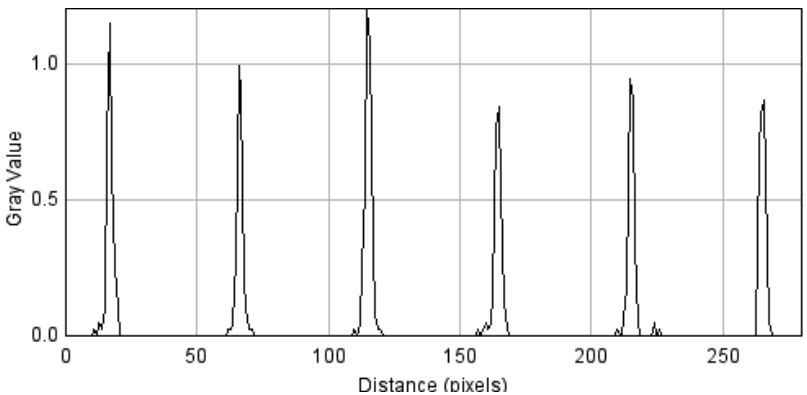


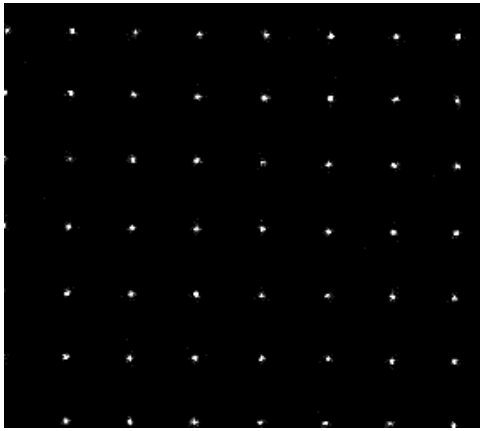
40mm XS anode neutron detector showing the front of the detector on the 6” conflat flange, and the HV connections.

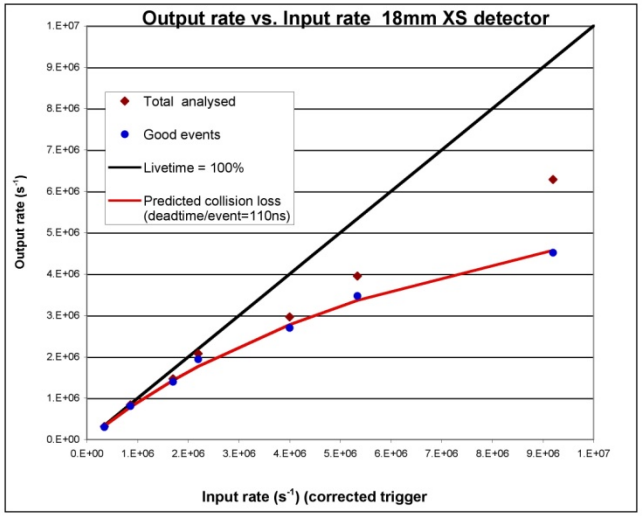
•Berkley Space Sciences Laboratory
•Sensor Sciences, LLC.
•NOVA Scientific

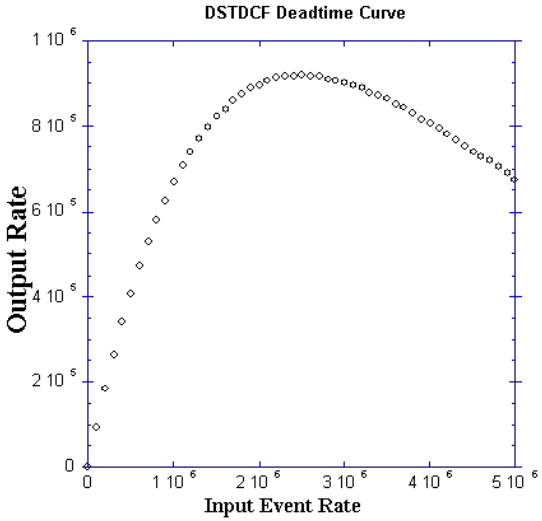
Characterization Tests of New High Resolution Detector System

- Imaging 10 μm pinholes with UV light demonstrates spatial resolution approaching 8 μm.
- New detector readout increases detection rate by 10x allowing a 10x increase in image field of view







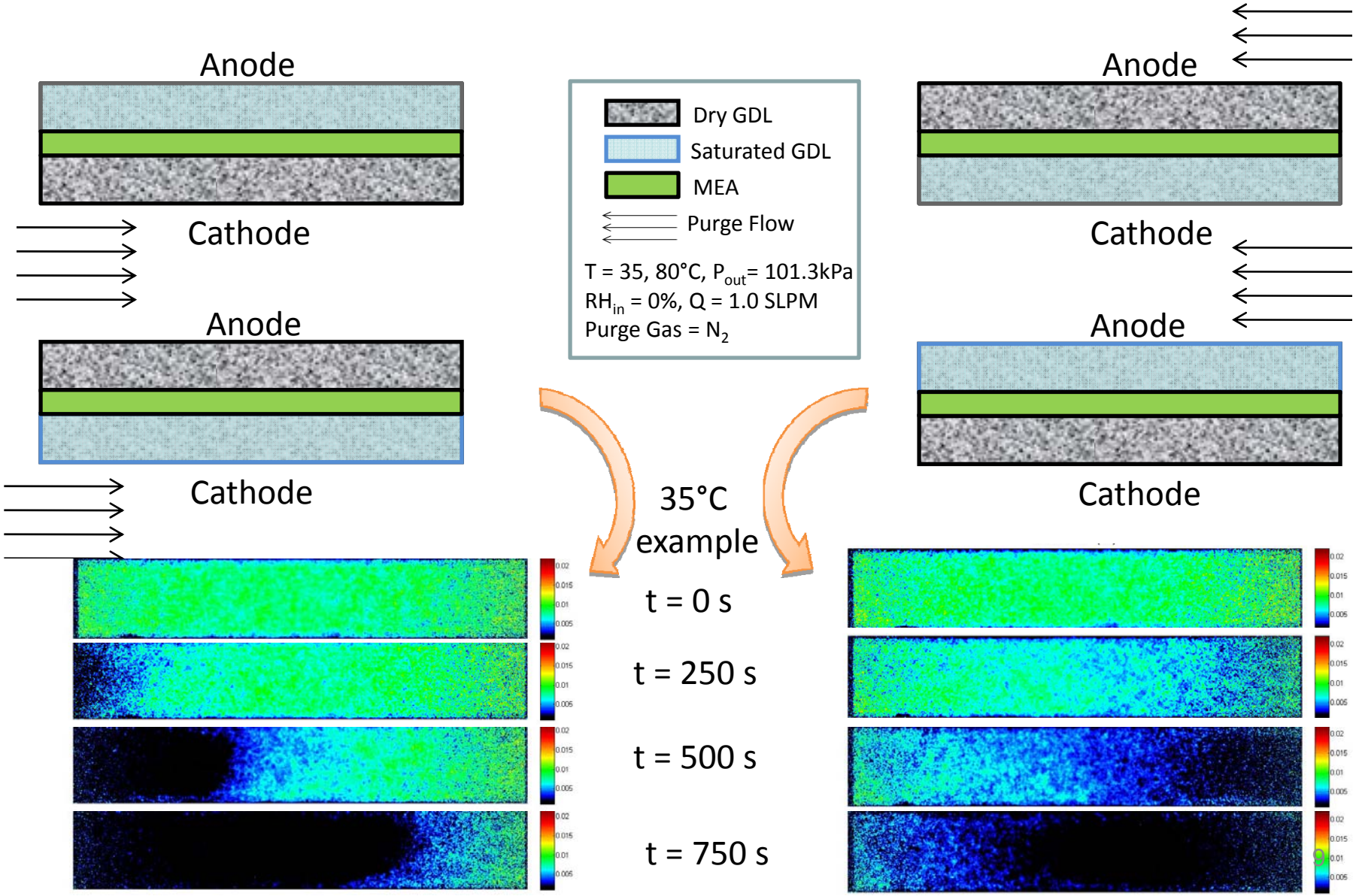


Artificially Saturated GDL Purge Experiments

- J.J. Gagliardo, J.P. Owejan, T.A Trabold, General Motors
- S. Kandlikar, Rochester Institute of Technology
- J. Allen, Michigan Technological University

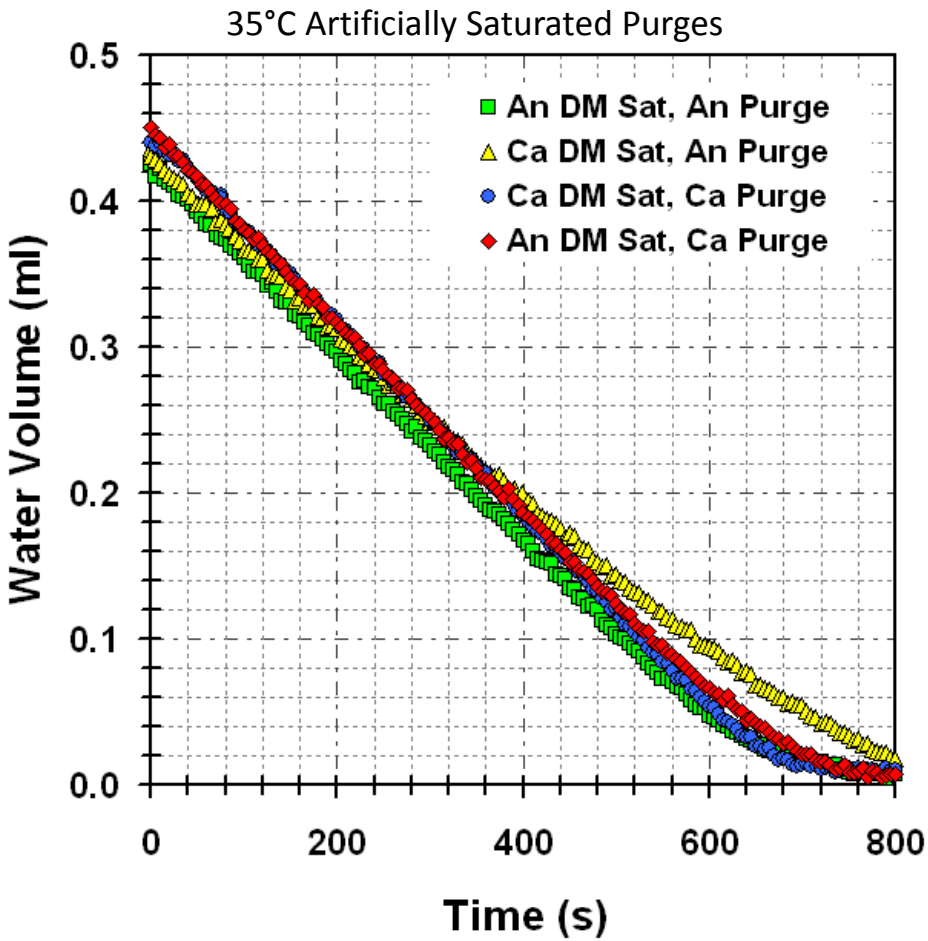
Artificially Saturated GDL Purge Experiments

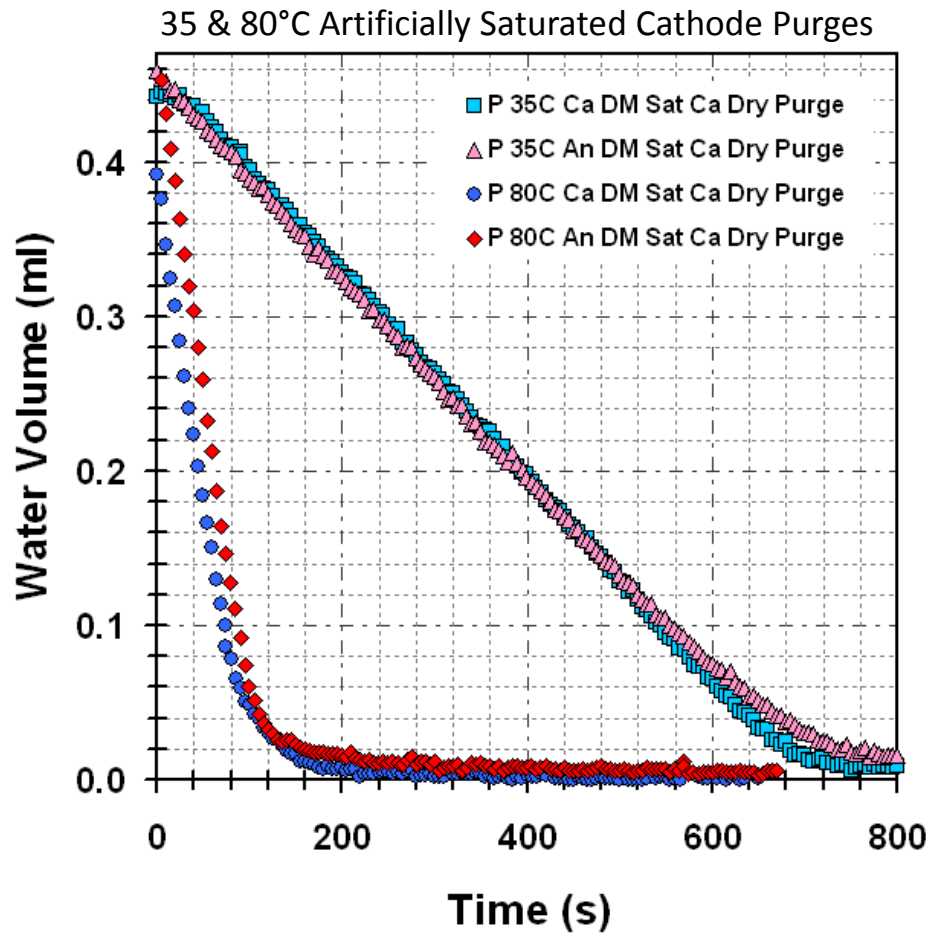
Measurement of removal rates for liquid water in known locations



Bulk Water Removal Results

$$\frac{\text{total water removed}}{\text{time}}$$



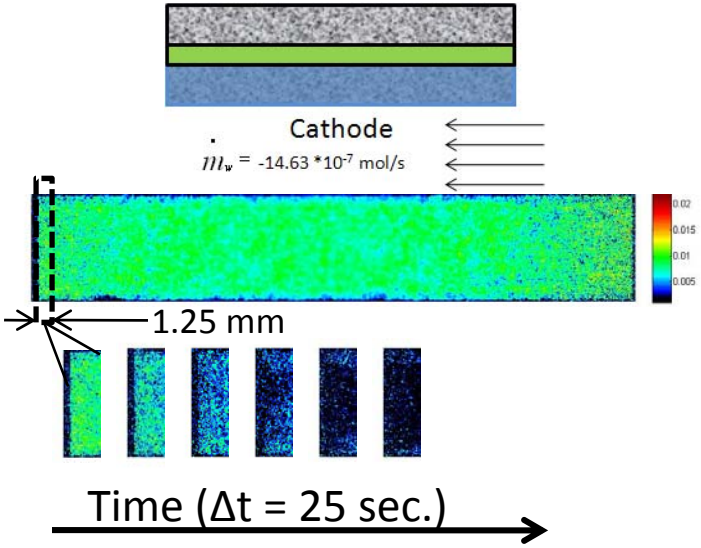


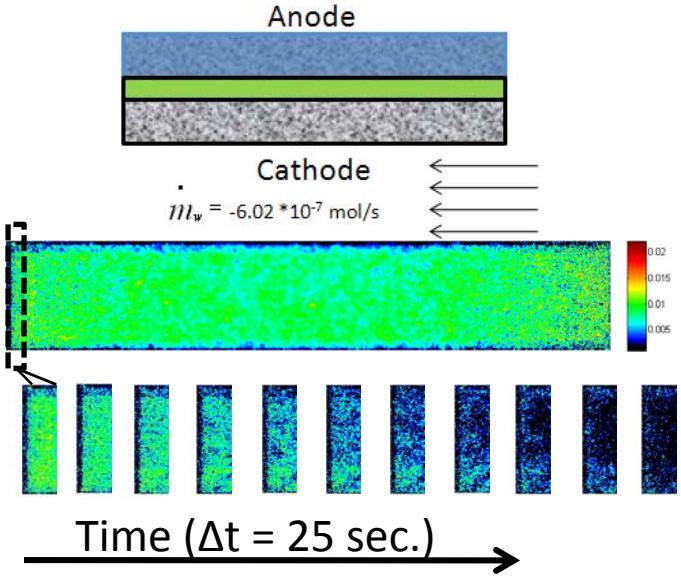
Key Observations

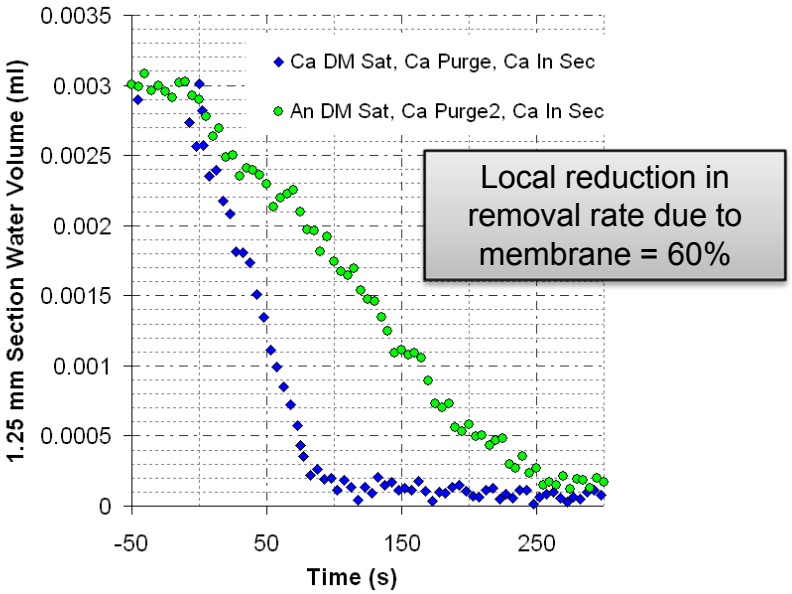
- Evaporative mechanism (constant removal rate)
- Total removal rate weakly dependent on location in anode or cathode GDL

Mass Transfer Evaluation

Differential evaluation reveals membrane transport resistance during purge



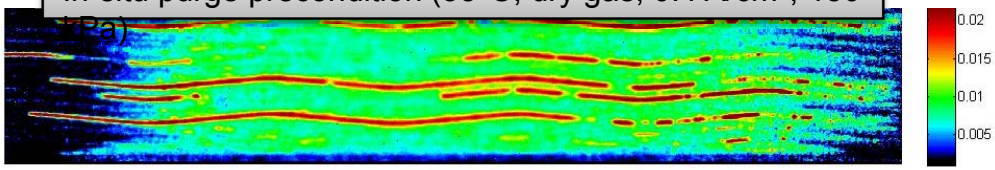




Local reduction in removal rate due to membrane = 60%

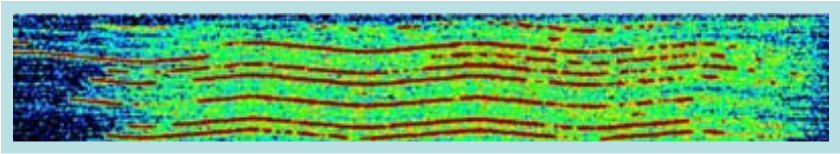
Use ex-situ measured parameters to locate in-situ water

In-situ purge precondition (35°C, dry gas, 0.4 A/cm^2, 150 kPa)

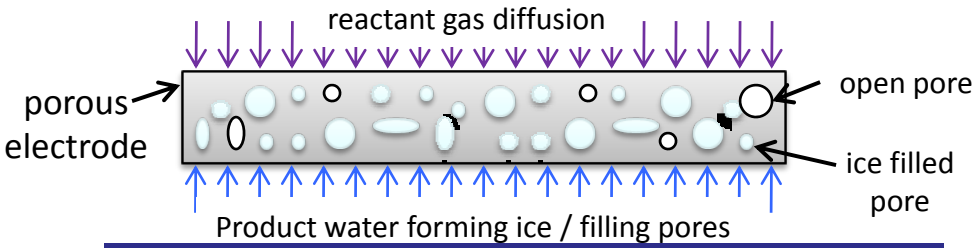


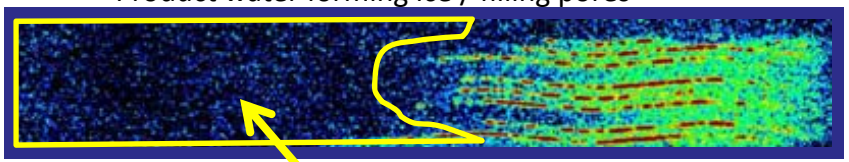
Diagnosis of Two Freeze Failure Mechanisms

Complete Ice Blockage of Flow Field (Primary)

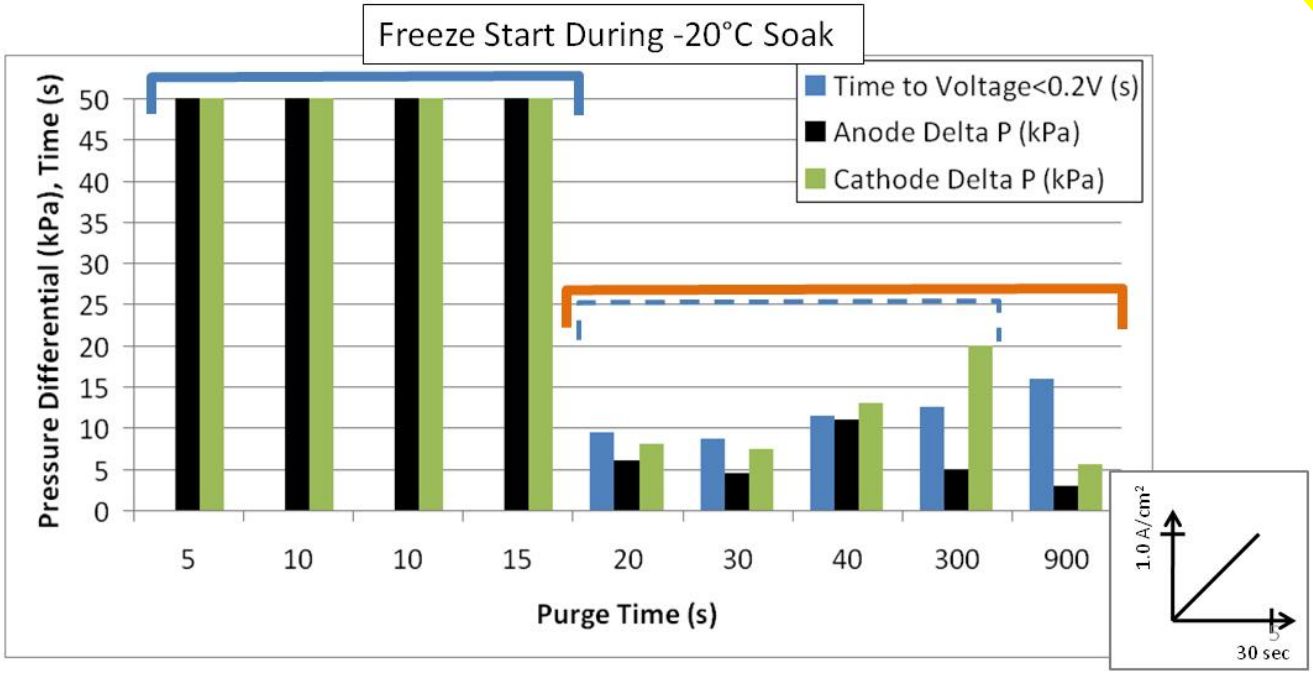


Ice Formation Capacity (Secondary)





Evaporating water from porous layers extends run time while frozen by providing volume for additional ice formation



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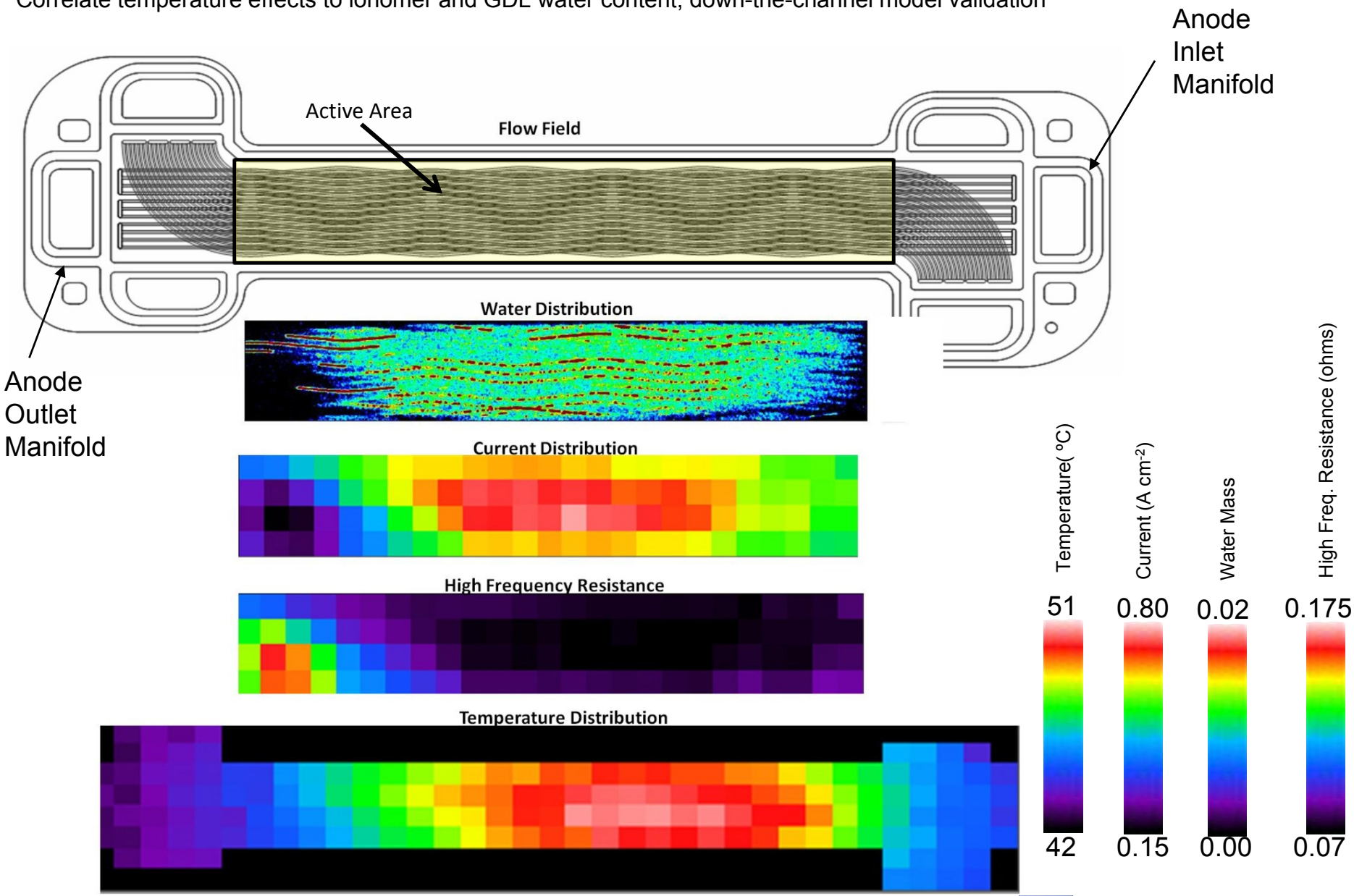
Simultaneous Water, Current, HFR, and Temperature Measurement

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



NIST GM R·I·T MichiganTech

Systematic uncertainties in neutron imaging of proton exchange membrane fuel cells

Daniel S. Hussey and
D.L. Jacobson
National Institute of Standards and Technology

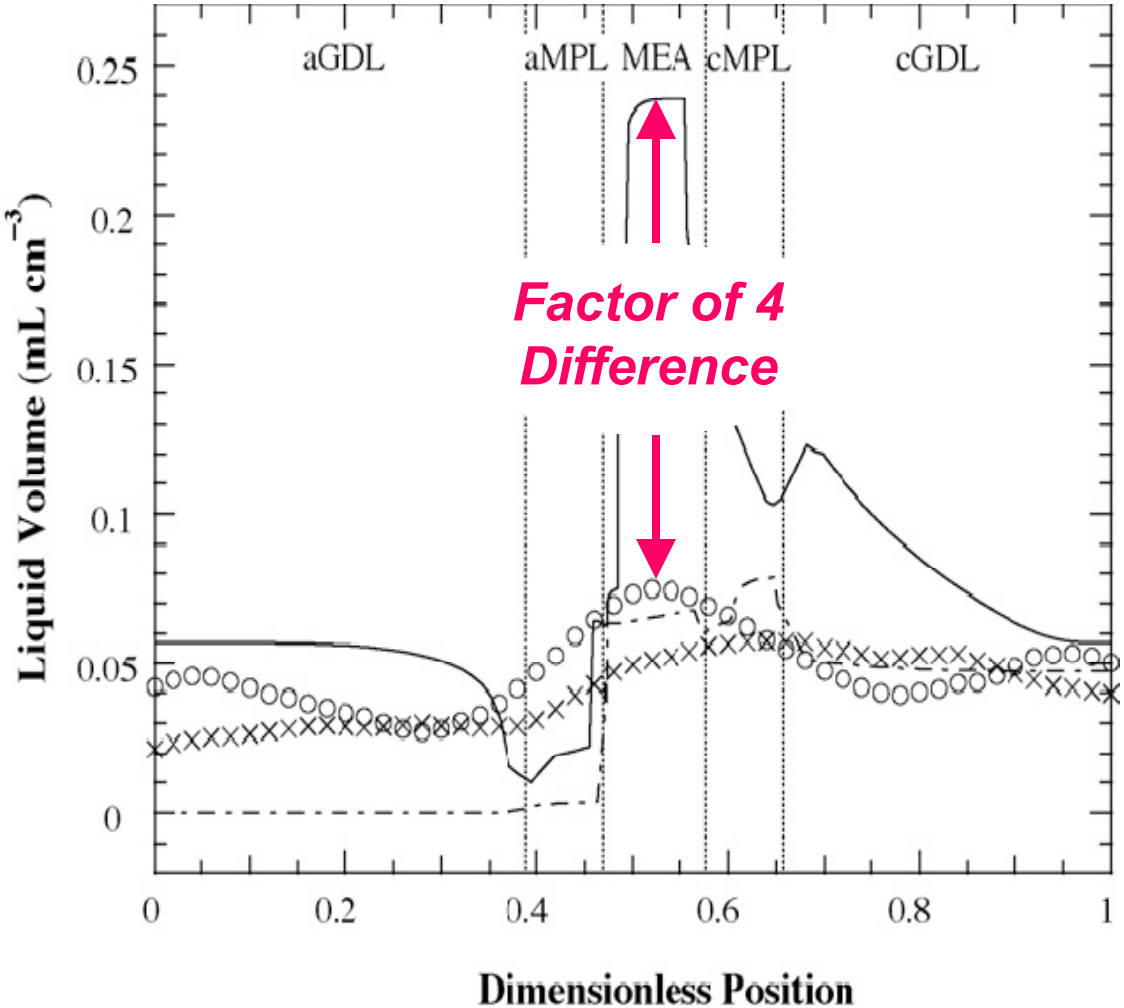
M. Rangachary, R. Borup,
and J. Spendlow
Los Alamos National Laboratory

National Institute of Standards and Technology
U.S. Department of Commerce

Los Alamos

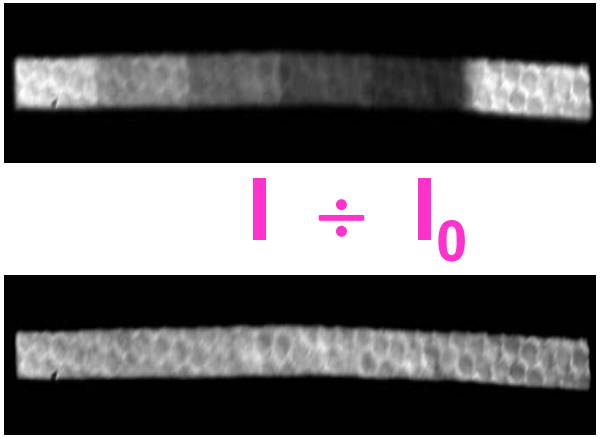
Through-Plane Water Content: Data vs. Model

- Measured the through-plane water content at several operating points
- For some conditions, model predictions and data disagree on membrane water content by a factor of ≈4
- **Check measurement systematic effects:**
  - ***Departure from Lambert-Beer Law behavior***
  - ***Finite resolution***
  - ***Change in Neutron scattering from water due to Nafion®***

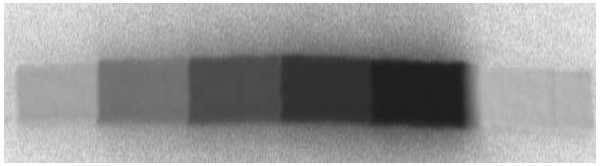


A.Z.Weber, M.A. Hickner, Electrochimica Acta 53 (2008) 7668–7674

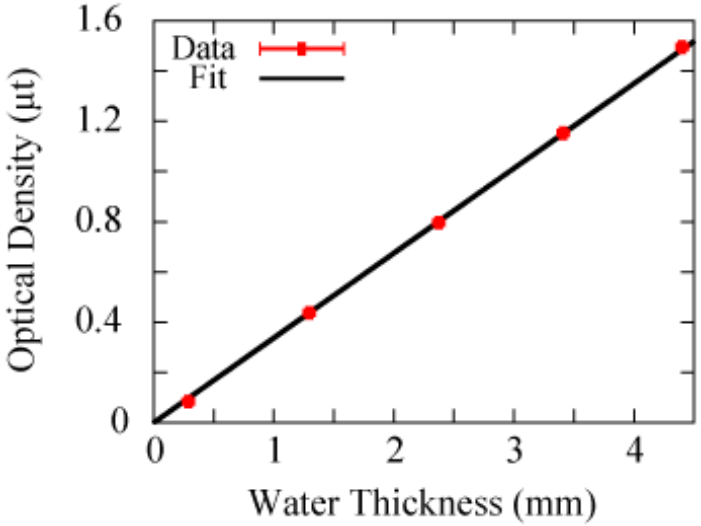
Measurement of μ – Check for Beer Law Deviation



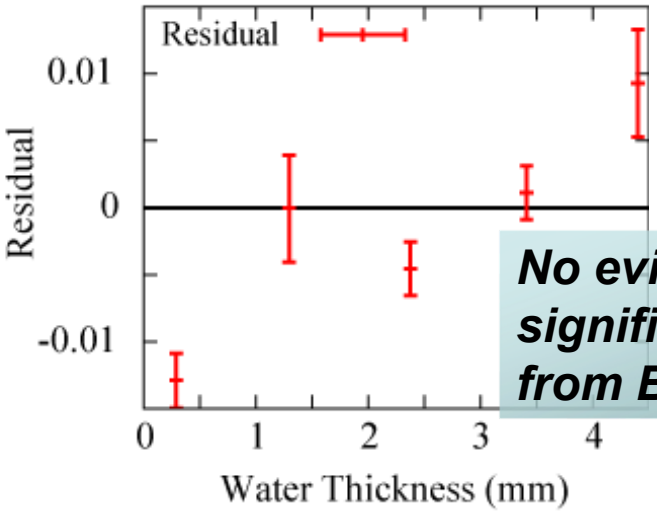
$I \div I_0 = T = e^{-\mu t}$



Al step wedge. Step depths measured optically to ± 1 μm



μ = 0.338 ± 0.001



No evidence for a significant deviation from Beer Law

Uncertainty dominated by machining tolerances of 2 – 4 μm

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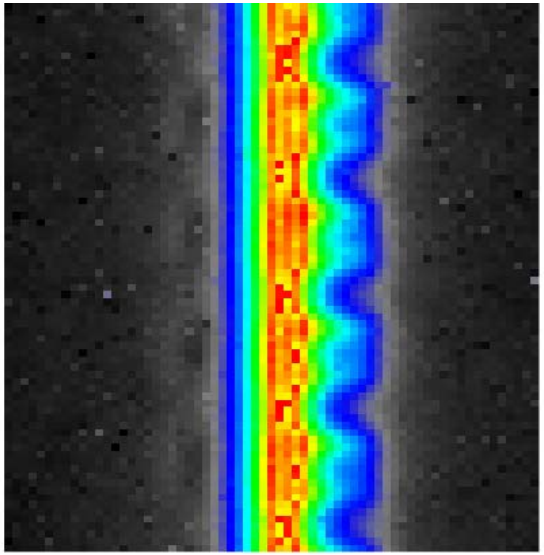
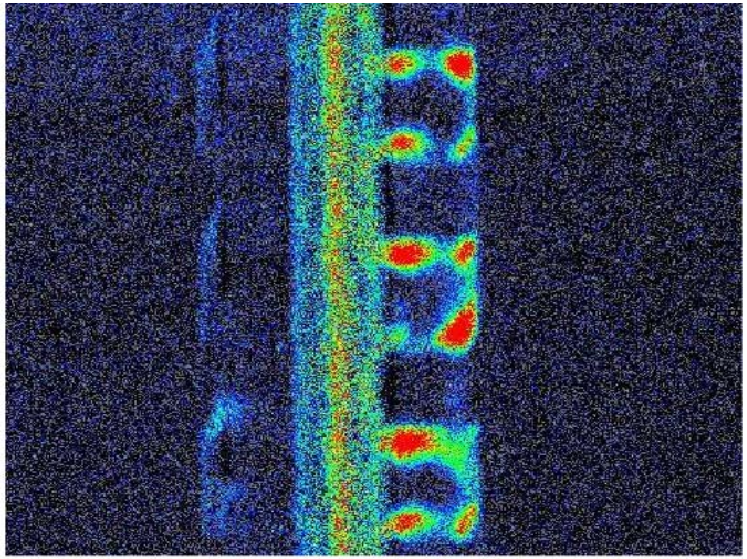
Image Spatial Resolution



Scintillator – 250 µm

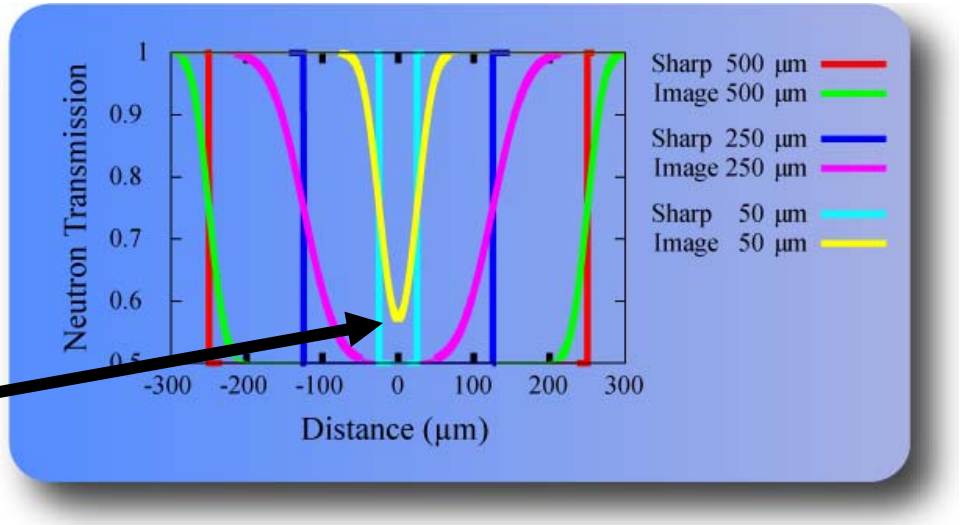


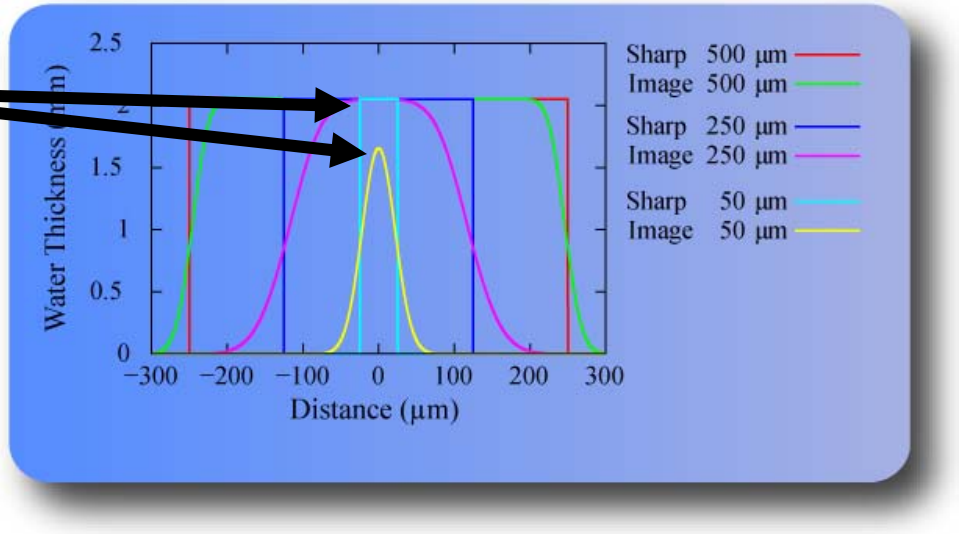
MCP w/ XDL – 25 µm

- Direct measurement of the GDL water content with 25 µm MCP
- Easily resolve anode from cathode and channel slugs
- 25 µm insufficient to resolve water in auto-competitive membrane
- New 10 µm MCP and slit aperture system will improve situation
- But … there is a systematic uncertainty from the finite resolution

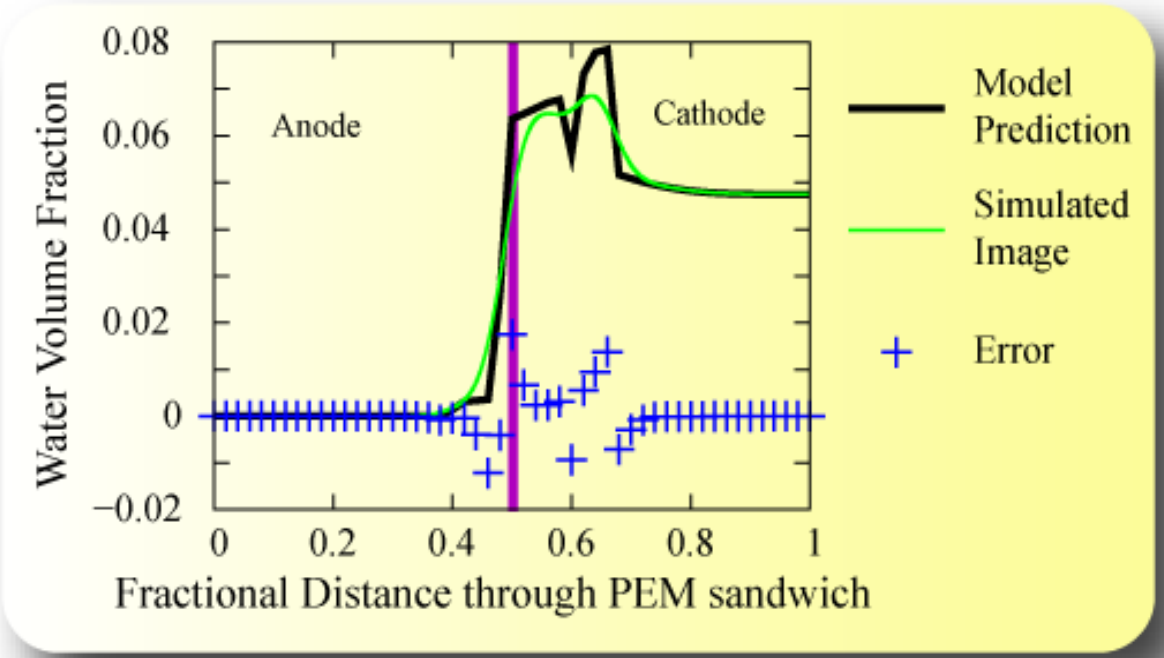
Systematic Error from Finite Spatial Resolution

- The resolution quantifies the blur in the image of an object
- When imaging a slab with sharp edges, the edges are blurred
- If the slab is too thin, the attenuation of the slab is not resolved
- **Large error** (25 % here) in the water measurement as the slab width approaches the resolution
- These profiles assume 25 μm image resolution



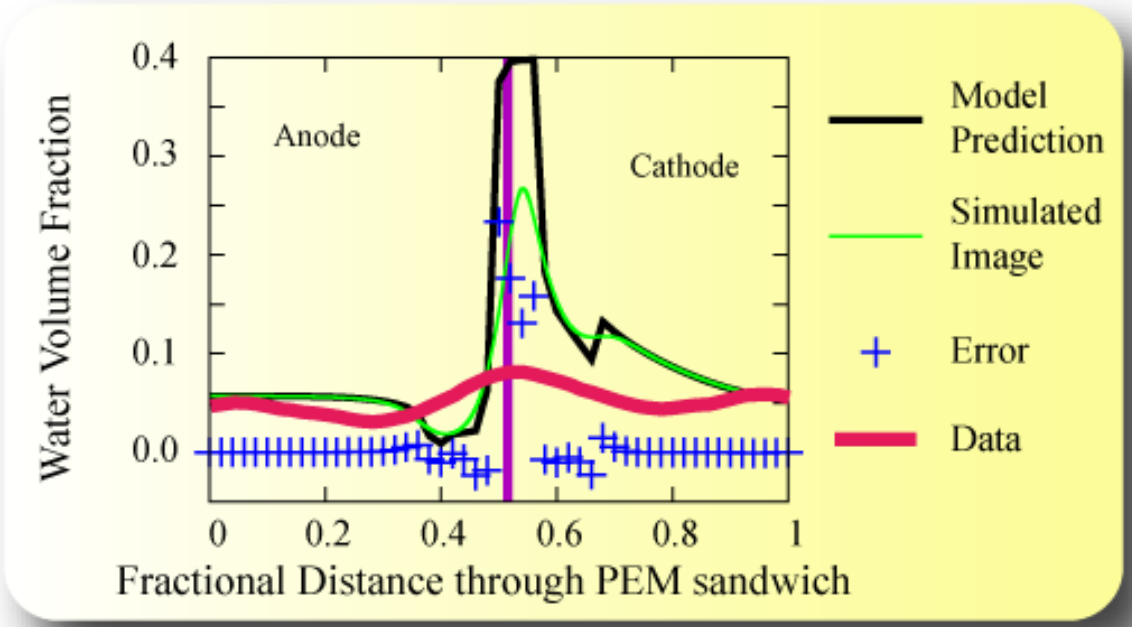


Simulated Profile: 80 °C



- Assume detector + geometry gives overall resolution of 50 μm
- Simulate image from 80 °C model prediction (courtesy A.Z. Weber)
- Simulation predicts small error in measured water content
  - *Low overall water content at higher temperature*

60 °C Case: Model, Simulation, Data



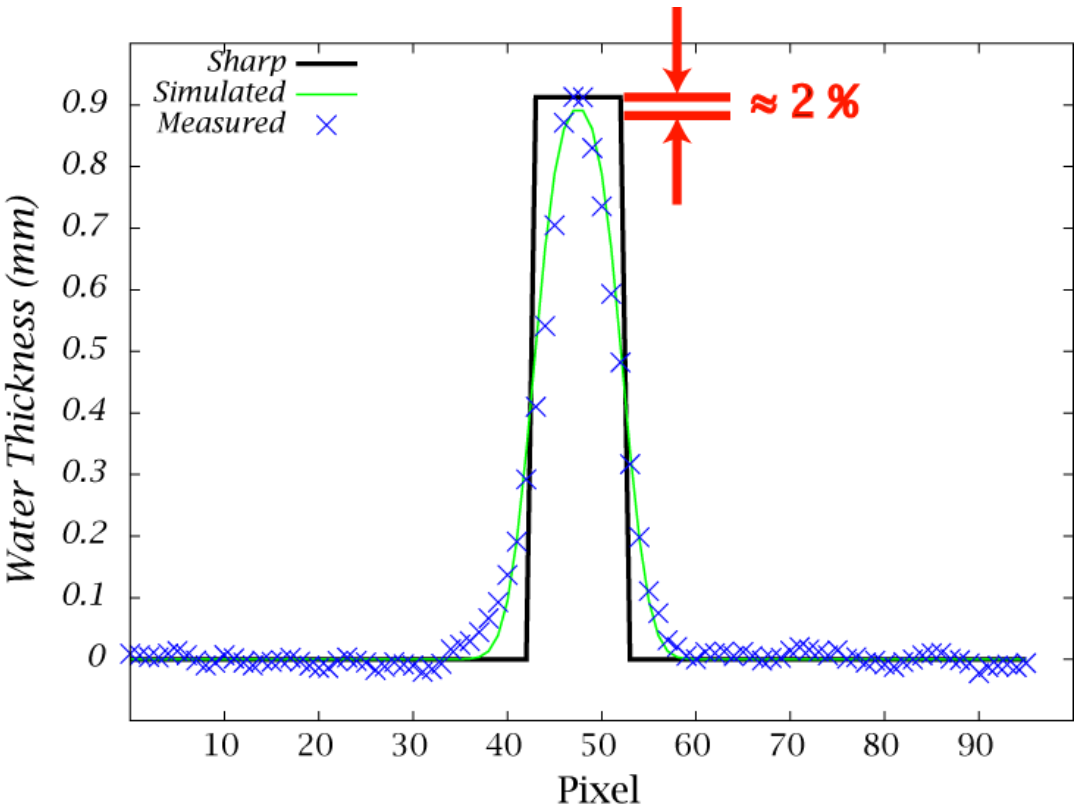
- Assume overall resolution of 50 μm, Simulate image from 60 °C model prediction
- Simulation predicts larger error in measured water content
  - *High MEA water content (λ=22) with dry GDLs*
- The measured water content is still significantly less than the simulation
- ***One more question:***
  - How does a radiography measurement of λ(RH) compare?

Measurement of λ(RH)

- With LANL, use a bare Nafion® 117 membrane, 11 mm wide, 20 mm long between flow fields (unknown amount of compression)
- Flow humidified N_2 for 1 hour – use last 30 minutes for analysis
- Perform measurement at 40 °C and 80 °C
- Dry out at 80 °C with dry N_2 purge for 1 hour
- Recently repeated measurement with a 40 mil Nafion® membrane

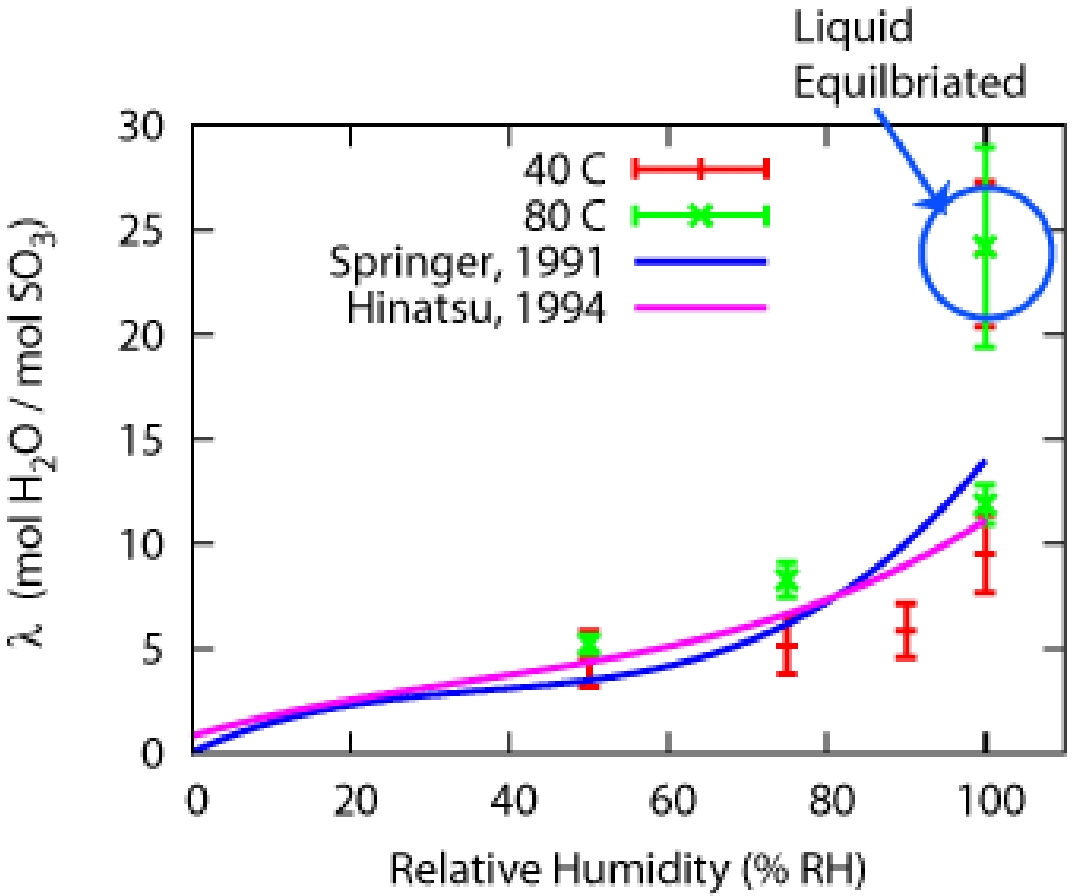
Estimate error due to Finite Resolution

Membrane water profile for 40 C, 75 % RH



- Estimate the possible size of water measurement error due to resolution
- Assume membrane is uniformly hydrated with water content taken from the peak
- Empirically, the overall image resolution was determined to be about 50 μm
- ***For all cases the discrepancy was about 2 % or less***

Nafion® 117 Water Sorption



- Measured water uptake of bare N117
- Flow 200 sccm of humidified N_2 for 1 h
- Membrane water content may not reach equilibrium, especially at high RH
- Dry measurement after 1 h purge in N_2
  - ***Uncertainty in λ dominated by incomplete drying***
- Neutron counting statistics uncertainty about x10 less than other systematic uncertainties

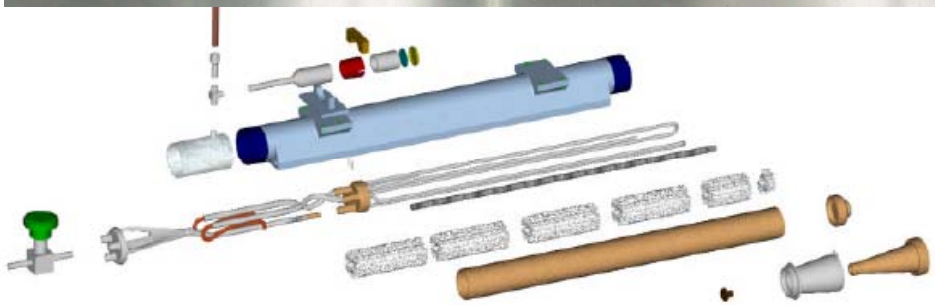
Systematic Uncertainties Conclusions

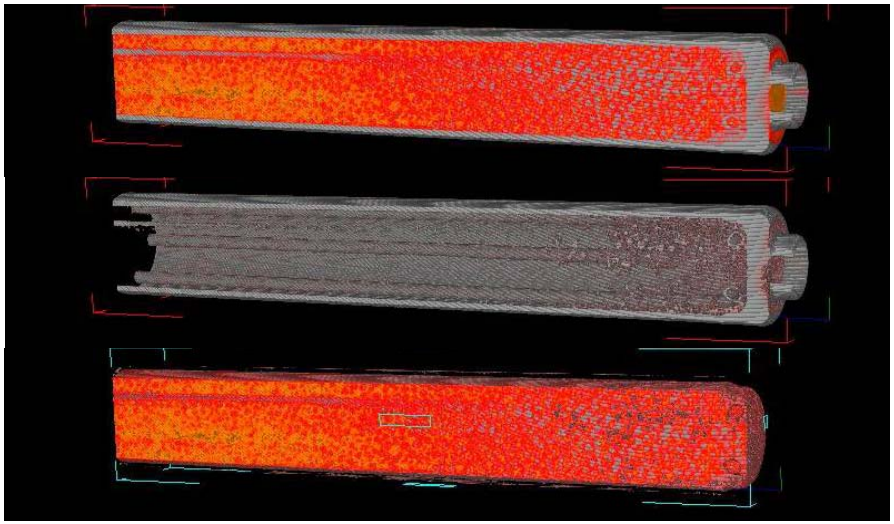
- Neutron radiography accurately measures the liquid water content typically of operating fuel cells – no evidence for deviation from Lambert-Beer Law
- A systematic error in the water thickness measurement due to finite image spatial resolution has been identified and the effect can be simulated and included in image analysis
- Membrane hydration measurement by neutron radiography in agreement with gravimetric methods
  - Measurement uncertainties are dominated by fuel cell component and operation unknowns such as dry state
- Discrepancy between measured data of Hickner, *et al*, with model predictions can't be completely explained by radiography systematics

- This work was supported by the U.S. Department of Commerce, the NIST Ionizing Radiation Division, the Director's office of NIST, the NIST Center for Neutron Research, and the Department of Energy through interagency agreement no. DE-AI01-01EE50660

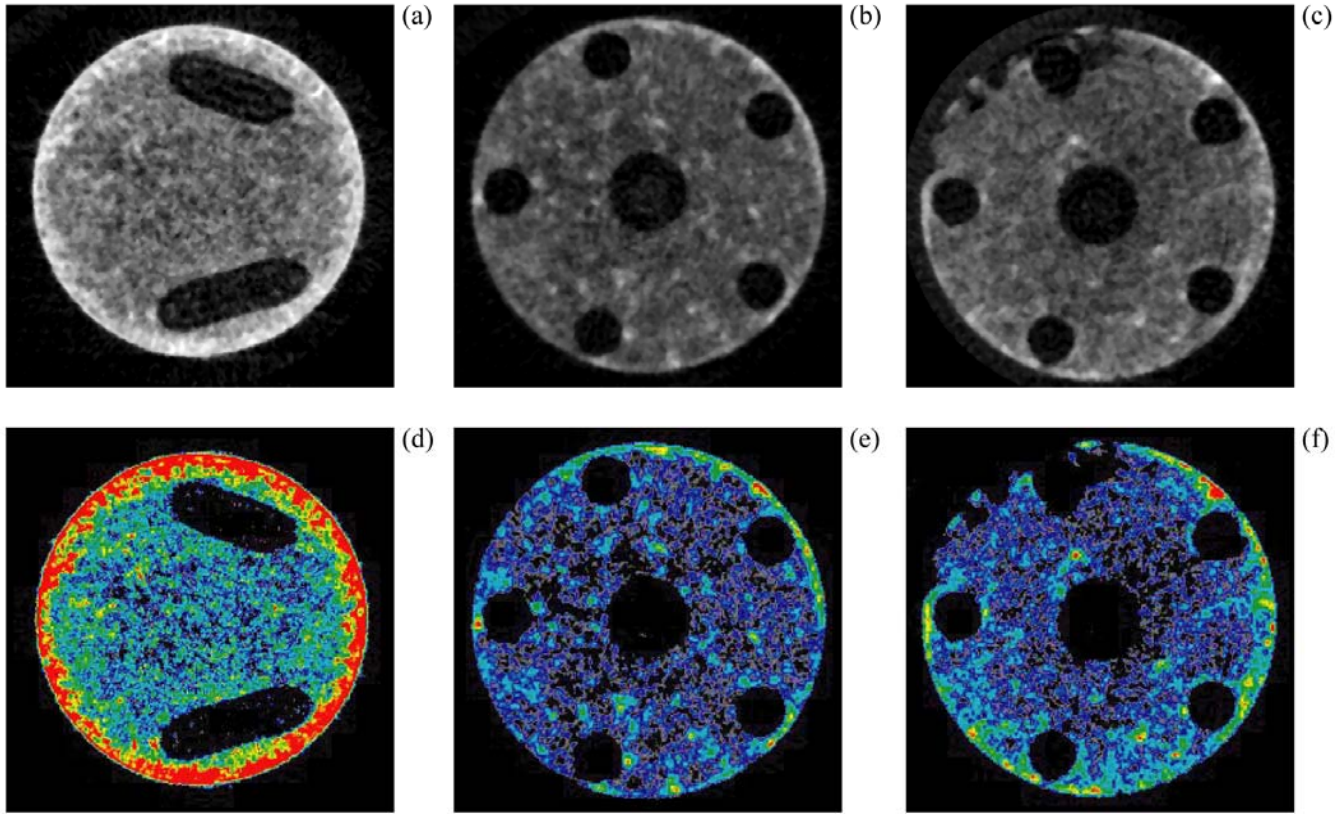
Future Directions: Hydrogen Storage Beds

- Exploratory experiment
- Engineered hydrogen storage device used in space missions.
- Storage medium $LaNi_{4.78}Sn_{0.22}H_6$
- Although thick section of hydrogen, deuterium can be used to ensure transmission of thermal neutrons.
- Can measure uptake in real-time (1 Hz) with radiography to measure distribution along the bed length





3-D Hydrogen Reconstruction: Axial Slices

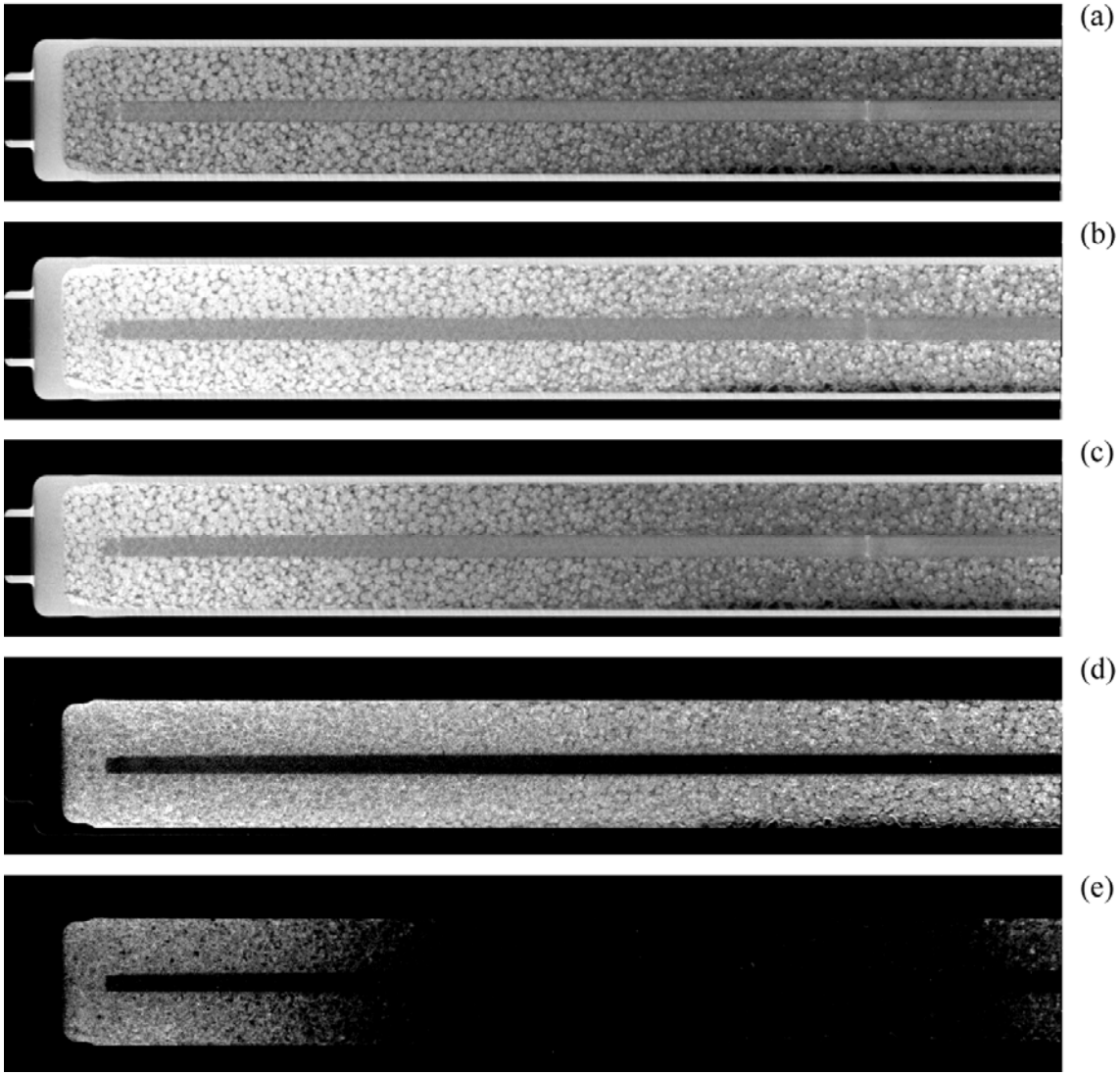


- Radial hydrogen distribution at different points along the bed (a) near the end of the bed at the bends in the internal heaters (b) near the center of the imaged area (c) at the opposite end of the imaged area, (d-f) are colorized images at the same locations..
- Hydrogen is seen to be absorbed preferentially at the outer radius, which is presumably cooler than the interior of the bed. (d-f) are colorized images at the same locations.

3-D Deuterium Reconstruction: Sagittal Slices

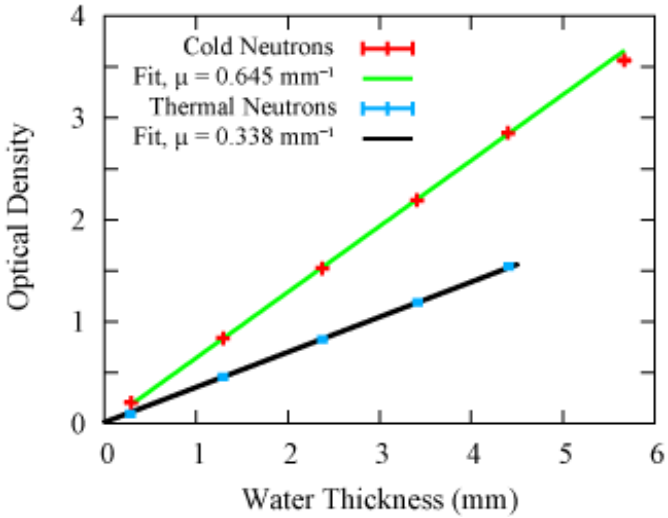
- Bed was filled with about 100L of Deuterium
- Incrementally drained the bed
- Subtract empty bed to obtain deuterium distribution
- Tomograph the bed between each drain sequence

a) Slice of the empty bed
b) Slice of the filled bed
c) Slice after removal of 60 L
d) Deuterium distribution of filled bed
e) Deuterium distribution after removal of 60 L



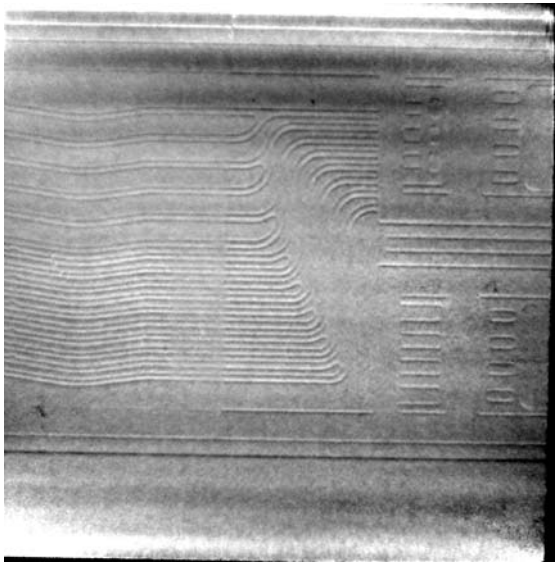
Future Directions: Cold Neutron Imaging Facility

- We are building a cold neutron imaging facility as part of the NCNR expansion
- New Facility will focus on high resolution and neutron phase imaging
- Cold neutrons have higher sensitivity to water, and have a higher detection efficiency which will reduce the time to acquire a high resolution image
- Cold neutrons are more sensitive to phase effects, and may enable scanning for part defects



Water uncertainty proportional to 1/μ.

Cold neutrons have ~2x better sensitivity



Phase imaging could potentially rapidly scan stamped flow fields for measuring residual stress and part defects

Future Work

- Continue to develop advanced imaging methods for fuel cell research
  - Image Distortion Correction tools
  - Uncertainty analysis
  - Real image modeling capabilities
- Develop complimentary hydrogen storage test and control infrastructure
  - Hydrogen/Deuterium gas delivery manifold
  - Mass flow measurement control
  - Publication of method development and use
- Continued advancement of imaging technology and capabilities at the facility

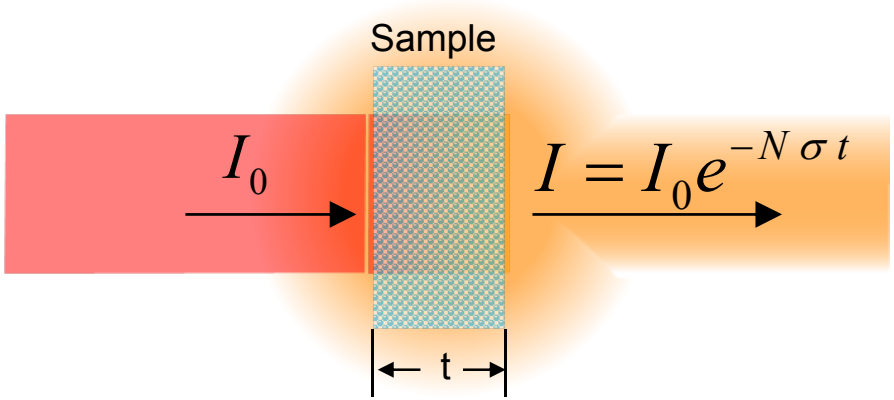
Summary of Technical Accomplishments

- Search for systematic errors in neutron radiography
  - Currently none explain discrepancies seen between experiment and modeling
- Study of water hydration of membranes
  - Neutron Radiography is consistent with existing measurements
- High Resolution Neutron Imaging
  - Dramatic improvement in spatial resolution with new slit apertures without sacrificing overall intensity
  - New system has been tested for operation and is undergoing deployment
  - Additional backup high resolution detector systems coming online to ensure reliable operation of the imaging facility
- Imaging of hydrogen storage beds
  - Developing methods to image storage beds, a critical future development for fuel cell vehicles
- Cold neutron imaging
  - Demonstrated potential advantages of cold neutron imaging
  - NCNR expansion project will result in new cold neutron imaging facility expected in 2011

Supplemental Slides

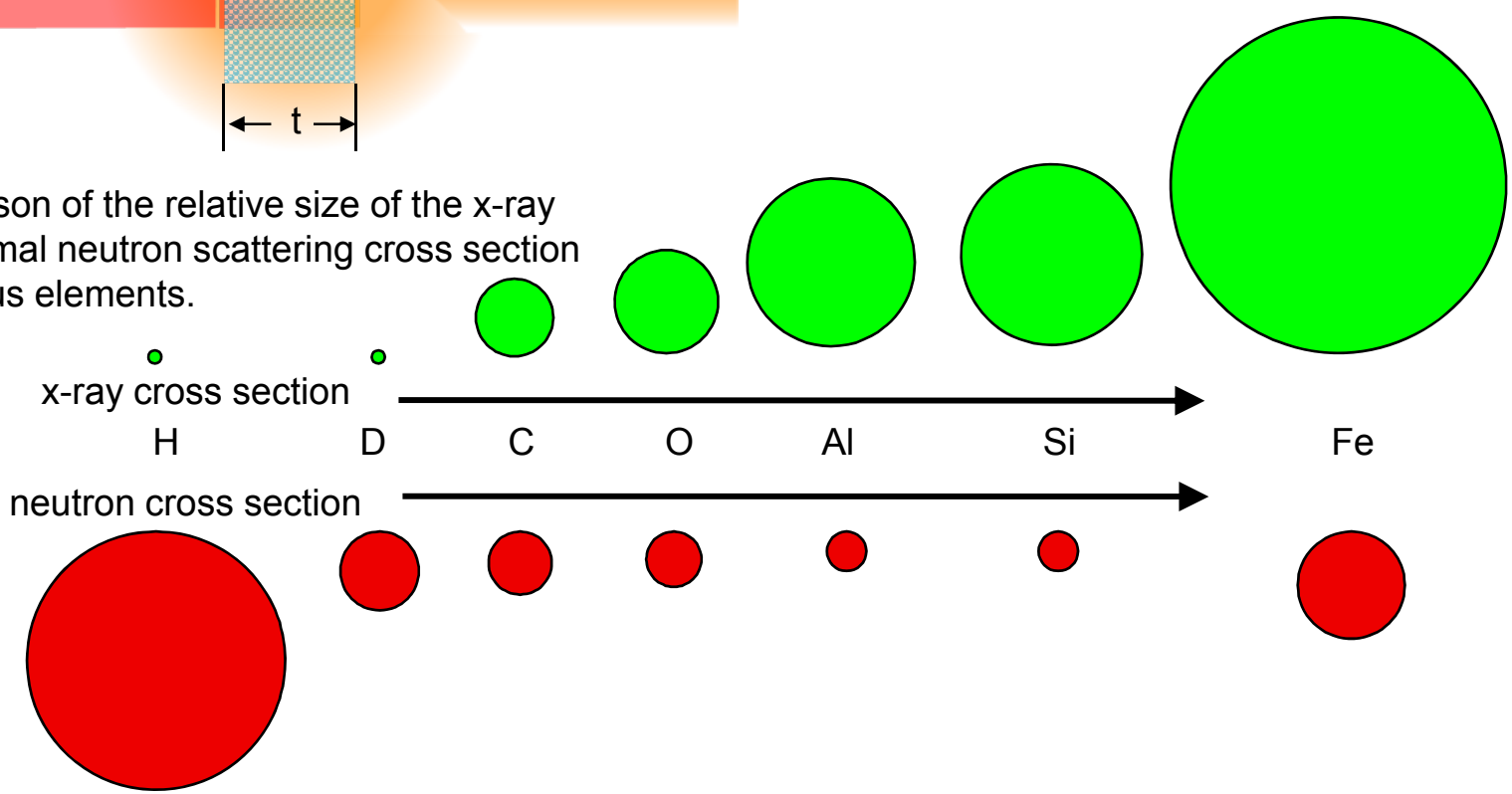
Why Neutrons

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

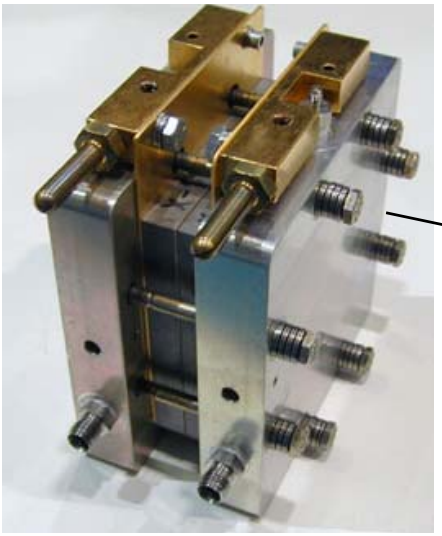


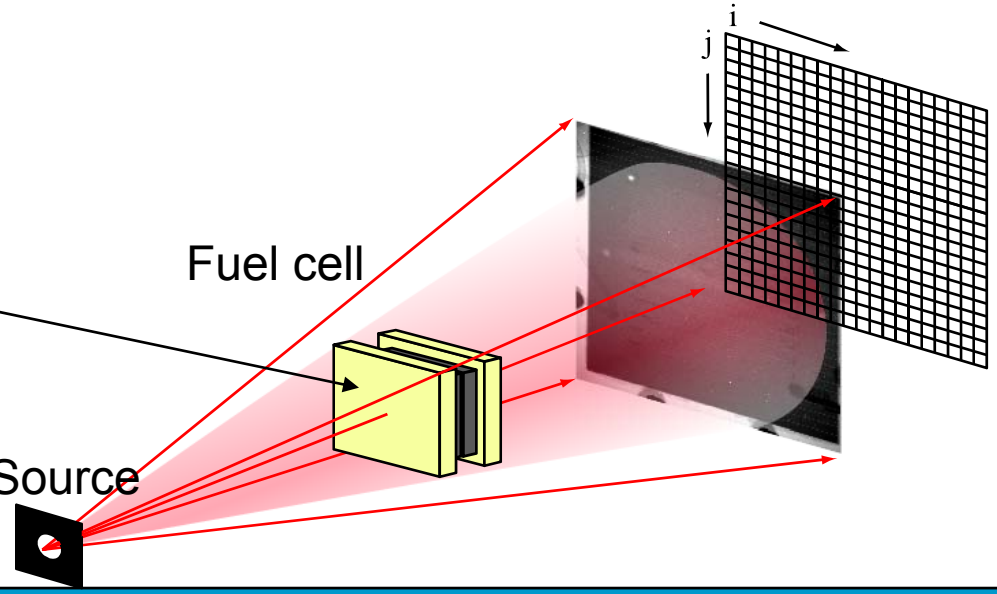
- N – numerical density of sample atoms per cm^3
- I_0 - incident neutrons per second per cm^2
- σ - neutron cross section in ~ 10^{-24} cm^2
- t - sample thickness

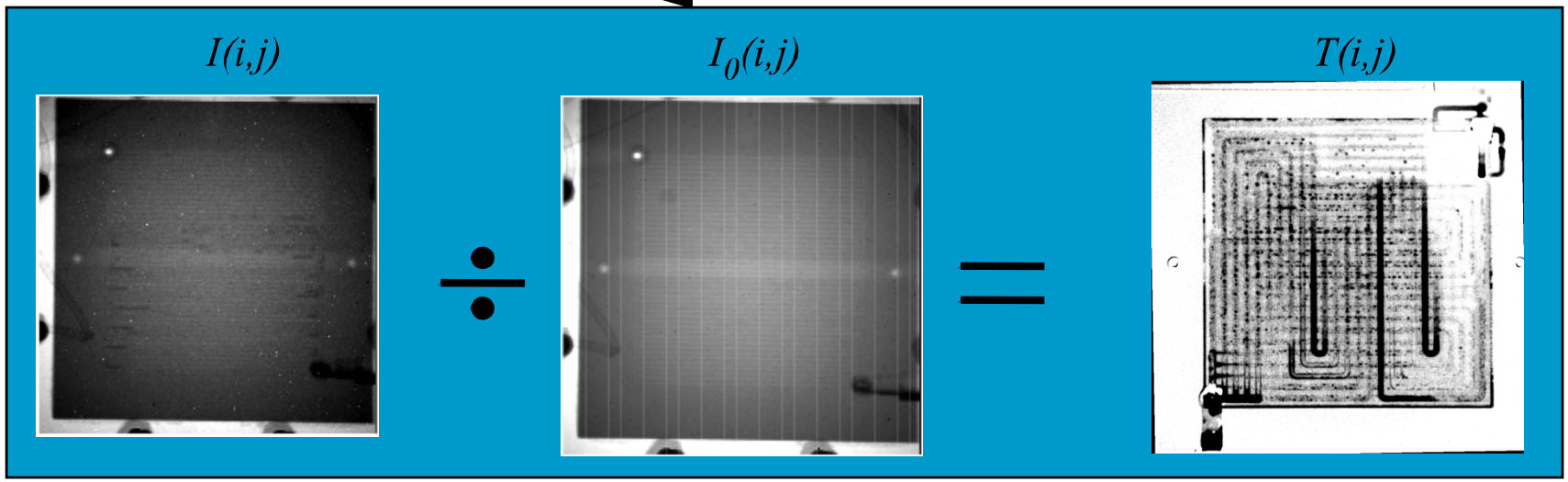
Comparison of the relative size of the x-ray and thermal neutron scattering cross section for various elements.



Brief Review of Method







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

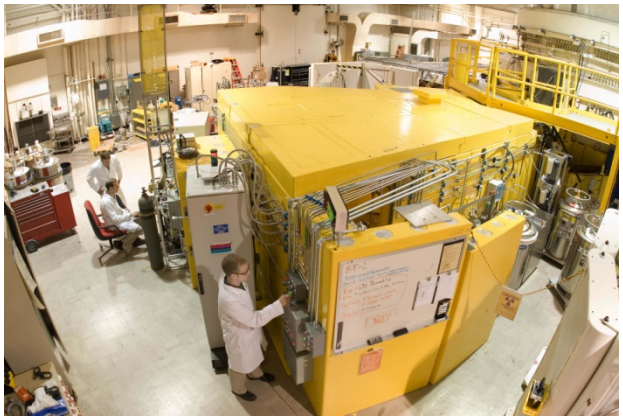
NIST

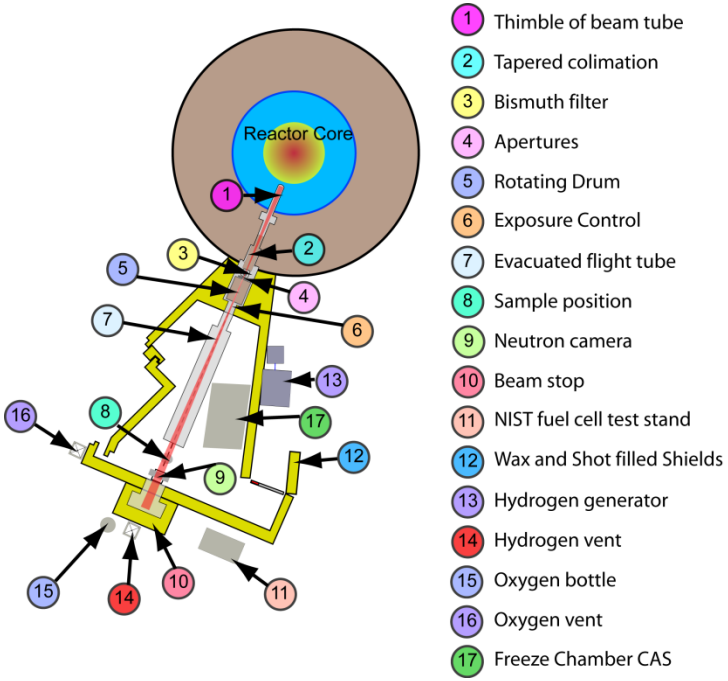
The NIST Neutron Imaging Facility at BT2

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

New Aperture System installed October with horizontal and vertical slits to boost L/D in one direction, but maintain intensity





NIST

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

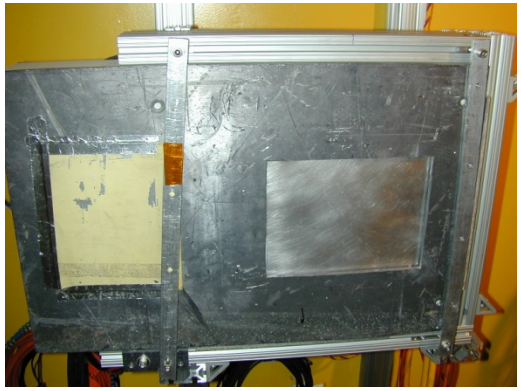
Current Neutron detectors: a-Si and MCP

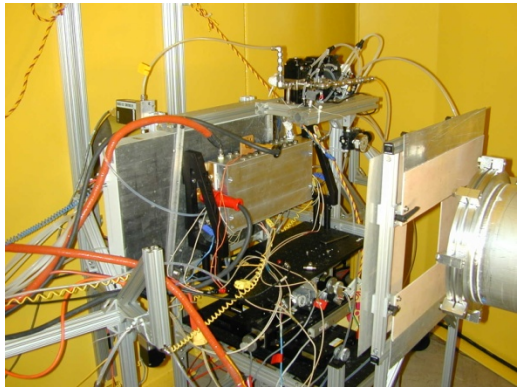
a-Si Panel with ZnS

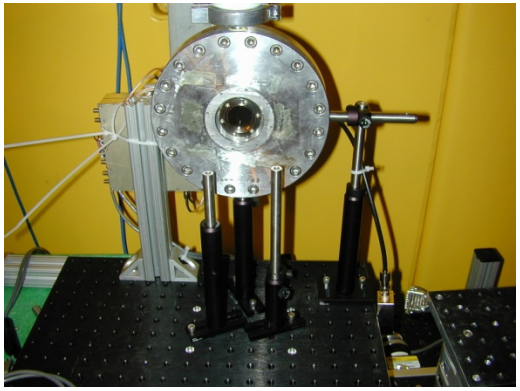
- **250-300 µm** Spatial Resolution
- 127 µm Pixel Pitch
- 25 cm x 20 cm Field of View
- 30 Hz max frame rate
- 1 Hz min frame rate
- 10 µm water thickness resolution in about 10 seconds
- Automatic dark image removal simplifies processing

MCP Detector with XDL

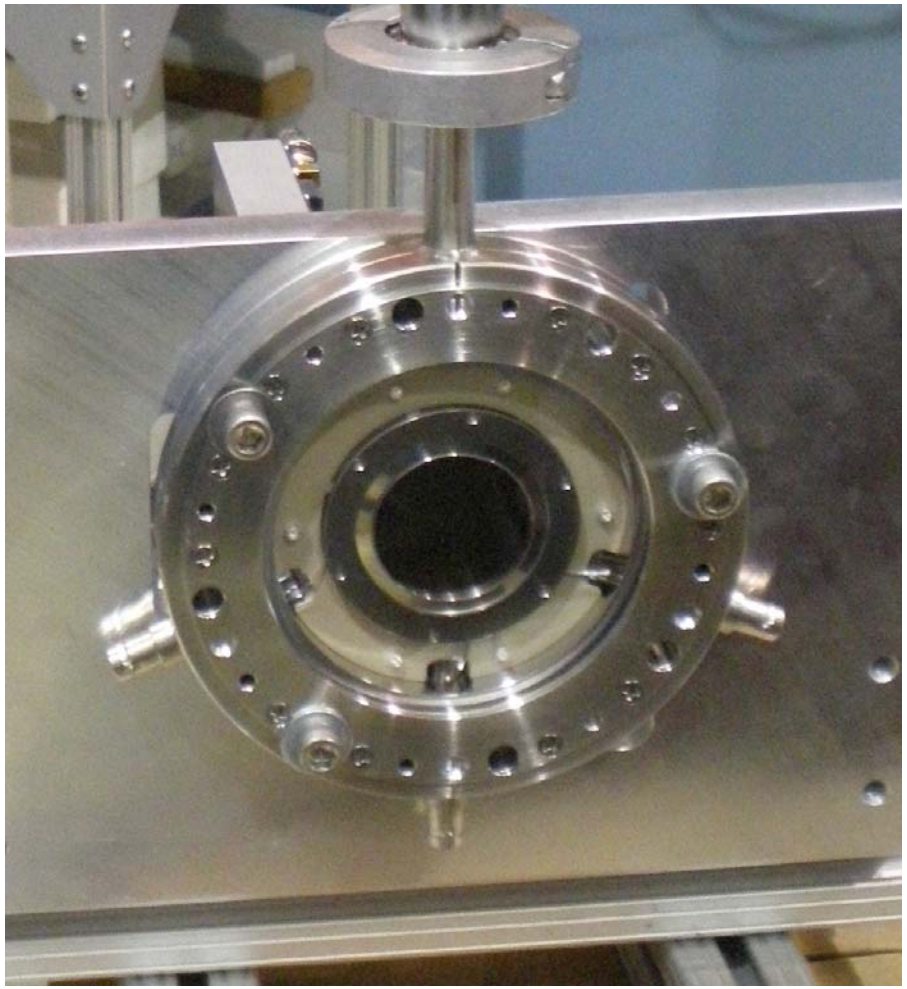
- **25 µm** Spatial Resolution
- 15 µm Pixel Pitch
- 2.5 cm diameter Field of View
- ≈ 0.1 Hz max frame rate - Noisy
- 30 µm water thickness resolution per pixel in about 1 h
- Gamma sensitive glass, requires taking dark image



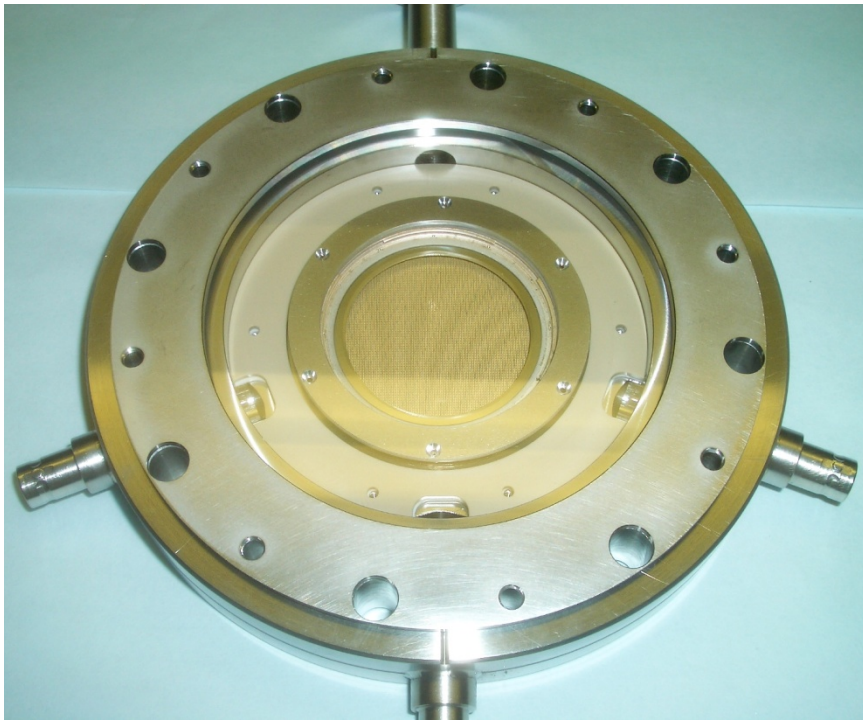




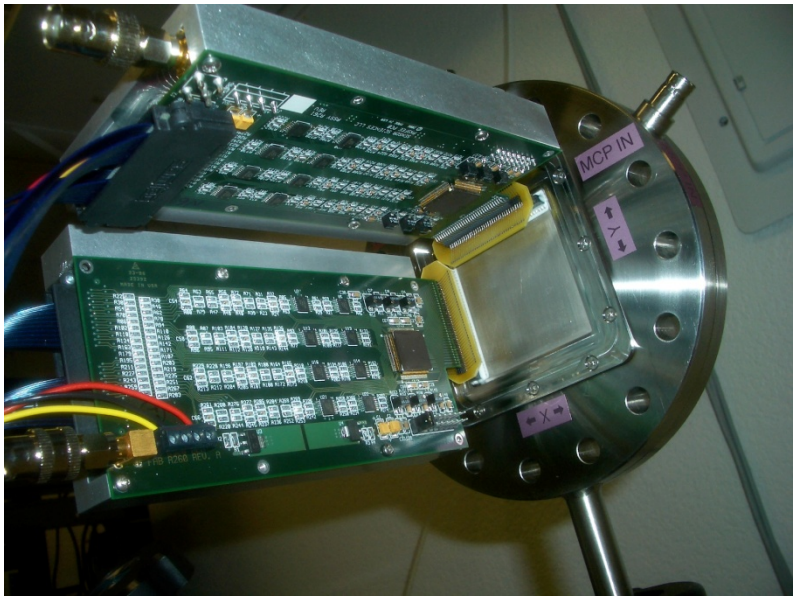
40mm Cross Strip (XS) neutron detector



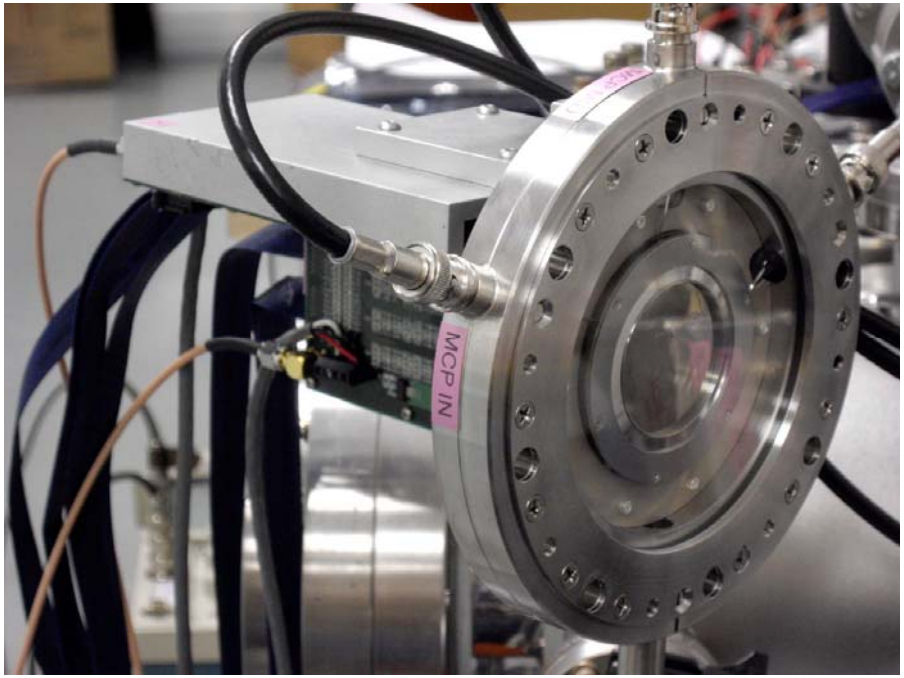
Front of NIST 40mm XS neutron detector, showing the neutron sensitive MCP, and the large sapphire entrance window - Left. Microchannel plates removed to show the Cross Strip anode - below.



40mm Cross Strip (XS) neutron detector

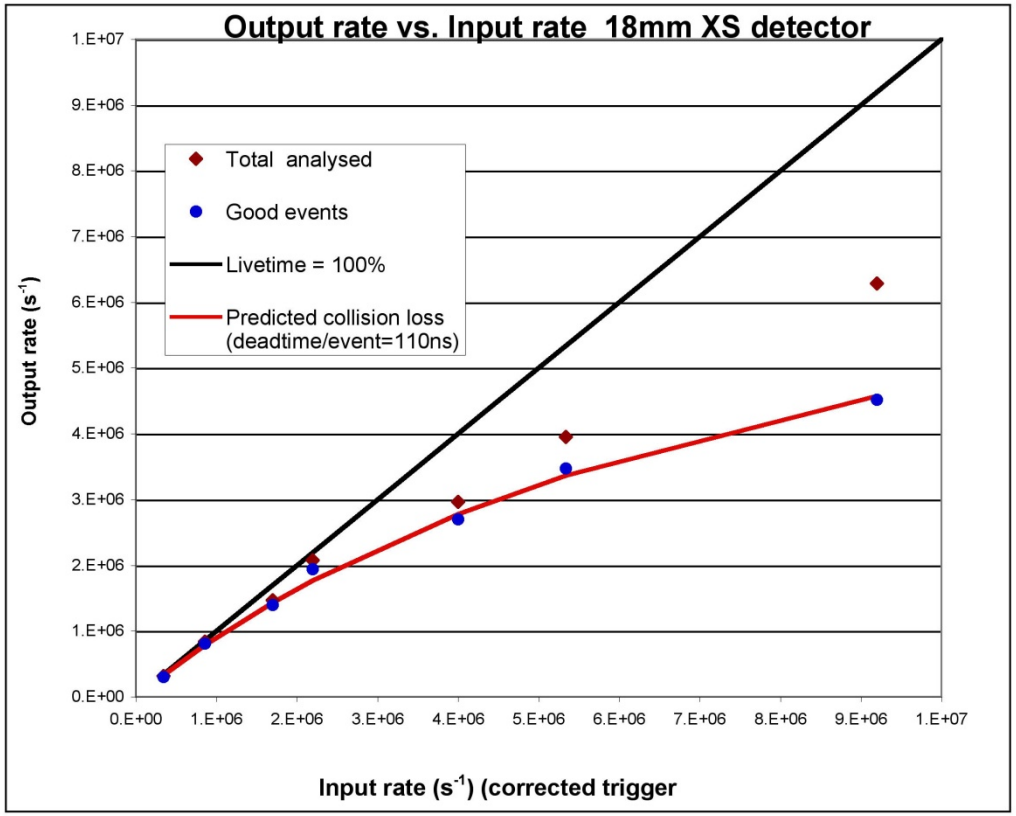


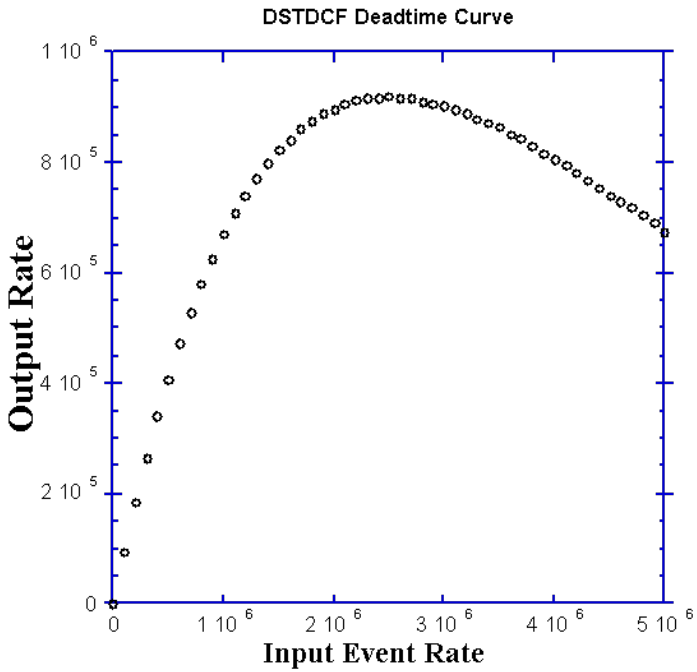
40mm XS anode neutron detector showing the back of the detector with the amplifier boards for X and Y axis event position encoding.



40mm XS anode neutron detector showing the front of the detector on the 6” conflat flange, and the HV connections.

Rate Tests with XS Detector

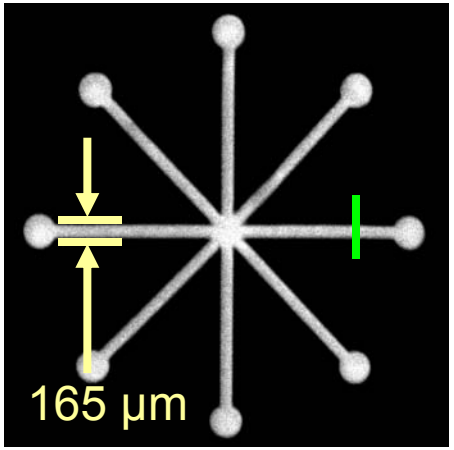




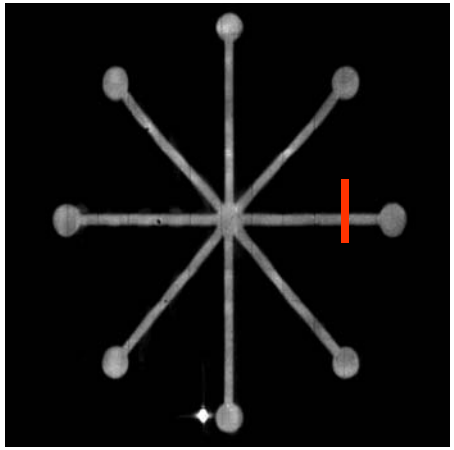
Existing XDL electronics rate performance.

Rate tests up to 9MHz. Rate limit is determined by the amplifier and F/W algorithm

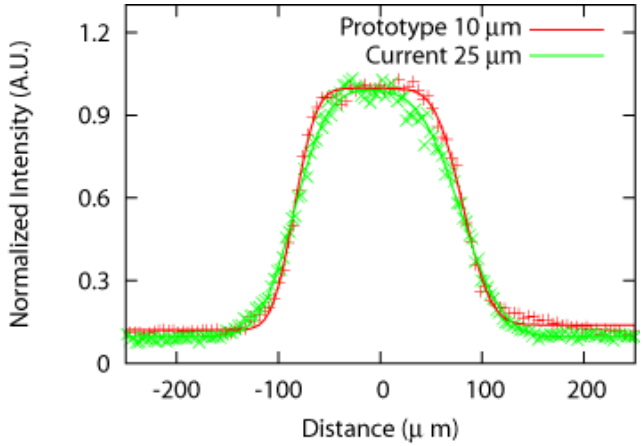
Spatial Resolution of Current and Future MCPs



Current 25 µm detector



Prototype 10 µm detector

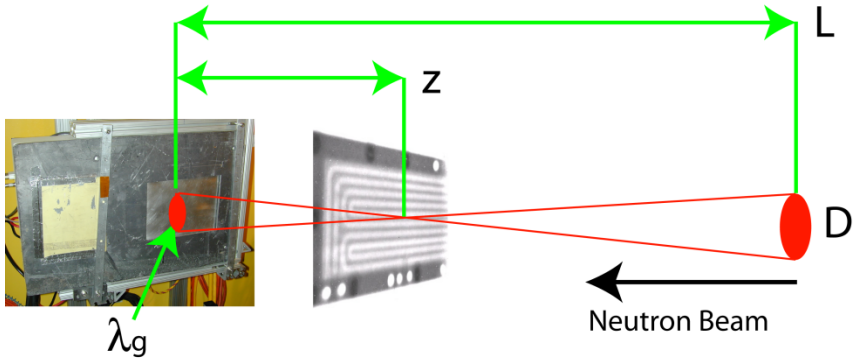


Prototype 10 µm detector shows 30 % improvement in spatial resolution compared to current 25 µm detector

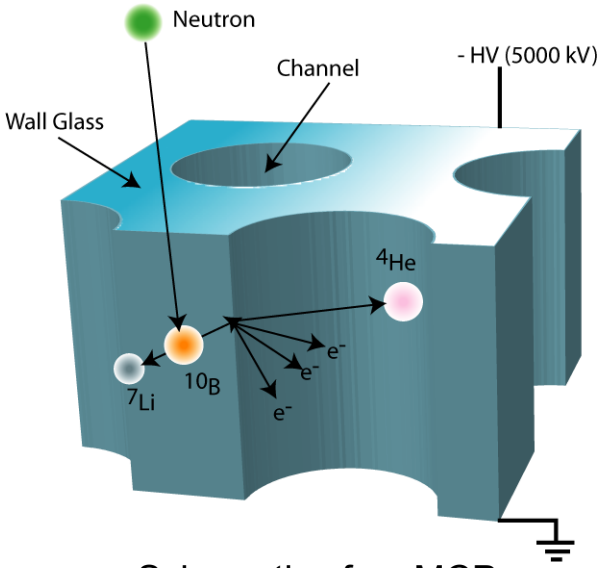
- Detector LSF measured with lines in a 1 mm thick Cd foil in direct contact with detector
- Model the LSF as an error function
  - $LSF(x) \sim erf(x / \sqrt{2}\, \sigma)$
  - $PSF(x) \sim exp(- x^2 / 2\, \sigma^2)$
- Rayleigh Criterion:
  - $PSF(x = \delta_d) \sim 0.34$
  - $\delta_d = \sigma * \pi / \sqrt{\{ 2 \ln(10) \}}$
  - $\delta_d = \sigma * 1.464$
- Prototype 10 µm detector shows promise of the new technology with 30 % improvement in resolution

Contributions to Image Spatial Resolution

- Image spatial resolution composed of Geometric Blur (λ_g) and Detector Resolution (δ)
- $\lambda_g \approx (z D) / L$
  - Decrease D or Increase L reduces neutron intensity,
  - Reduce thickness of object to place next to detector
  - ***INSTALLED SLITS TO NEARLY ELIMINATE GEOMETRIC BLUR FOR IMAGING OF THROUGH-PLANE WATER CONTENT***
- MCP Resolution limited by:
  - Pore Separation: 12 - 5 µm
  - Charged particle range: 5 µm
- Image Resolution = $\sqrt{(\delta^2 + \lambda_g^2)}$
- Image Resolution is modeled as Gaussian blurring



Layout of a neutron imaging beam



Schematic of an MCP

Deviation from Beer's Law

- Neutron scattering cross-section from water is neutron energy dependent, increasing with decreasing energy
- Passing through a thick section of water could result in a transmitted neutron beam with a more energetic spectrum, which is more penetrating
- This more penetrating beam could result in a non-linear relationship between the water thickness and the neutron attenuation
- Using a water wedge with a thickness of 5 mm calibrates the instrument for water thickness typical of high resolution fuel cell imaging.