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

Neutron Imaging Study of the Water Transport in Operating Fuel Cells

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FC021

Wednesday June 8, 2016

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

DOE Project funding	
DOE FY15 :	$ 300 k
DOE FY16 Planned :	$ 300 k
Total Received:	**$ 450 k**

Other Project funding FY16	
NIST :	$1,200 k
Industry:	$ 250 k

Barriers

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

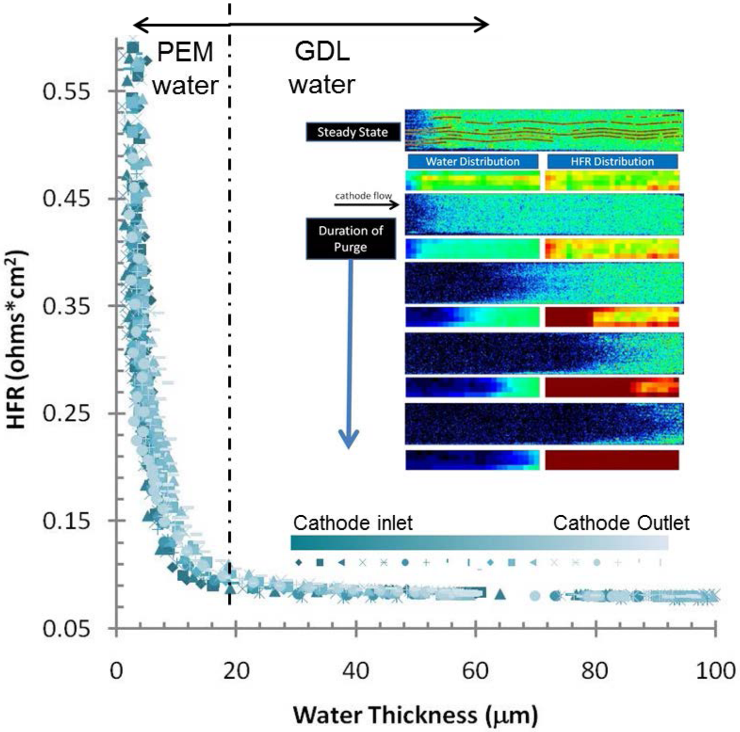
Partners/Users/Collaborators

Project Lead: National Institute of Standards and Technology

- 3M
- Army Research Laboratory
- Automotive Fuel Cell Corp.
- Ballard
- CEA (Commissariat à l’énergie atomique)
- Ford
- General Motors
- Honda
- HYSA Infrastructure
- Nissan
- NASA, MSFC
- Lawrence Berkeley National Laboratory
- Los Alamos National Lab
- Massachusetts Institute of Technology
- Michigan Technological University
- NECSA
- Oak Ridge National Laboratory
- Pusan National University
- Rochester Institute of Technology
- Sensor Sciences
- University of California, Merced
- University of Connecticut
- University of Michigan
- University of Tennessee
- Wayne State University

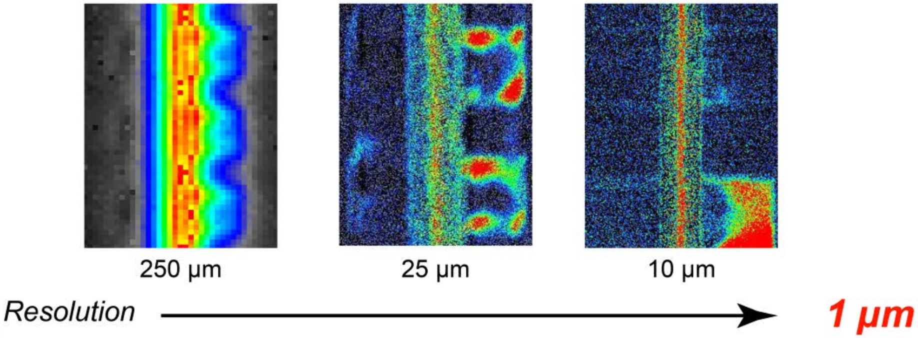
Relevance

- Neutron imaging is the most powerful and sensitive method to *non-destructively* image water in the fuel cell *in operando* as neutrons readily penetrate common fuel cell hardware yet accurately measure small volumes of liquid water
- This enables one to develop a complete picture of the heat and mass transport in a fuel cell namely:
  - Dynamic water transport in the flow fields and manifolds
  - Liquid water distribution anode versus cathode
  - Cold start and freeze-thaw effects
  - Catalyst degradation induced by liquid water
  - Catalyst layer liquid saturation level
- Objectives of the project include:
  - Study water transport in single cells and stacks
  - Enable fuel cell community to utilize state of the art neutron imaging capabilities to study water transport phenomena
  - Tailor neutron imaging to needs of the fuel cell community
  - Improve the spatial resolution to provide more detail of the water content in commercial MEAs

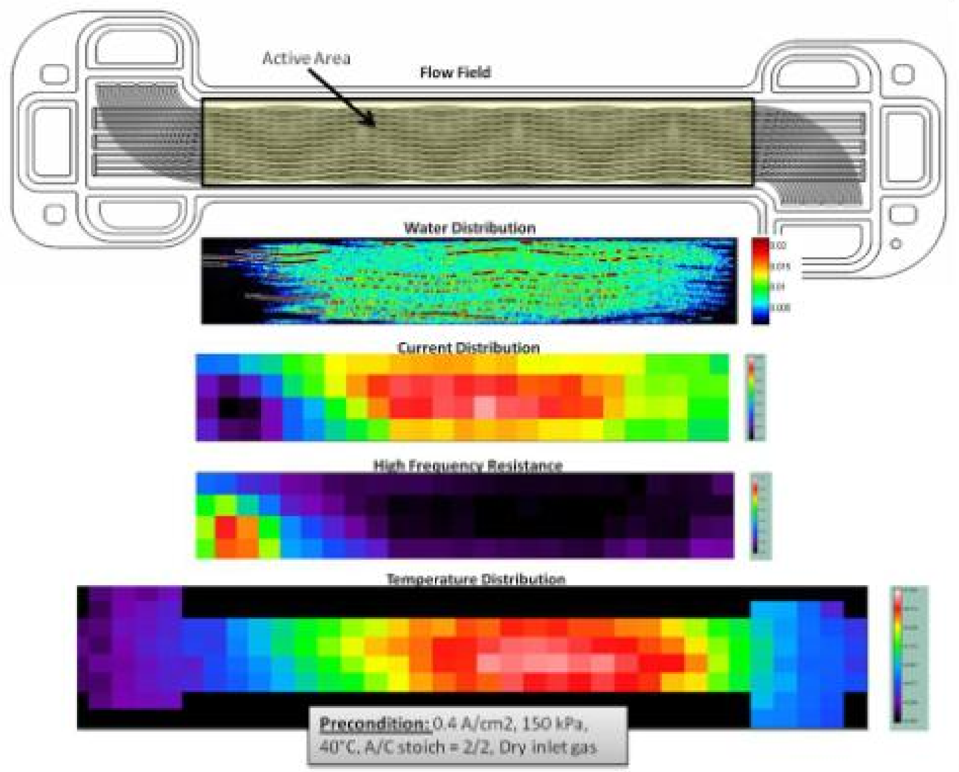


Approach

An example of the method the data shown below includes the water content, current distribution, HFR and temperature distribution measured by General Motors.

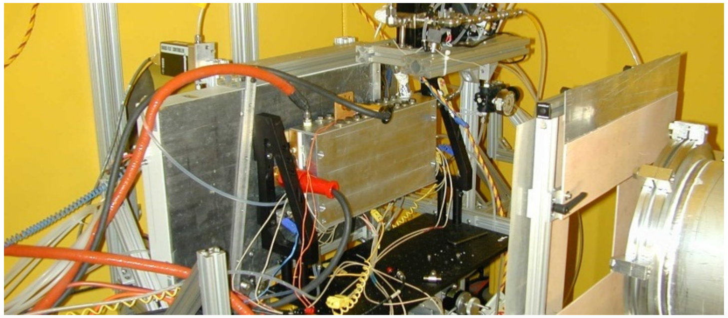


- In order to extend this capability to the catalyst layer we are engaged in a continuous effort to enhance the image spatial resolution
- Improve image analysis to correct systematic effects and ensure accurate water content measurements
- Make state-of-the-art detectors, methods, and analysis available to the fuel cell research community



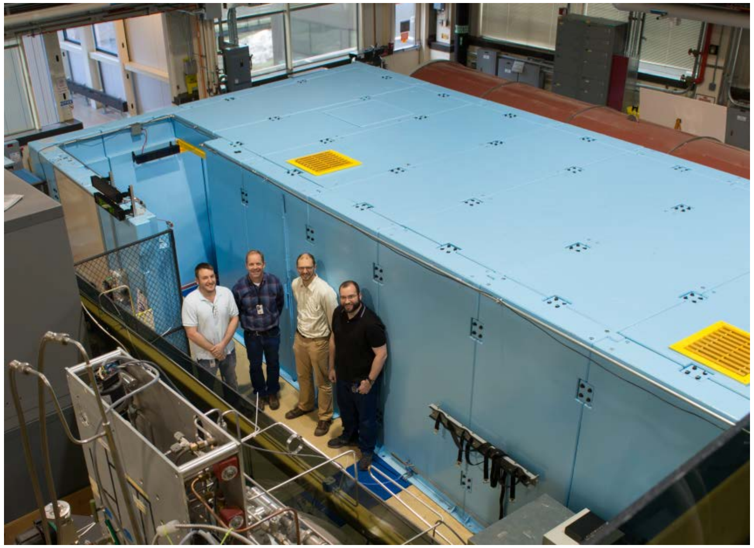
Approach

- Maintain a national user facility for neutron imaging of fuel cells
  - Develop and maintain state-of-the-art fuel cell testing infrastructure
  - Pursue facility improvements through collaboration and feedback with testing partners at General Motors and the fuel cell community
- Free access for open research
  - Experiments are proposed by users and selected through a peer review process managed by NIST
  - We collaborate as needed, data must be published
  - ***"Mail-in" service for high resolution imaging***
- Fee based access for proprietary research
  - Contact NIST for details
  - Stack developer owns data outright
  - Proprietary users trained to take and analyze image data
- User friendly operation
  - Ample area on beamline for complex setups
  - Can image automotive cells with 26 cm dia. beam
  - Photos show both 50 cm^2 and full size automotive cell
  - Test stands fully integrated with GUI and scripting
  - Image analysis software is tailored to fuel cell user needs

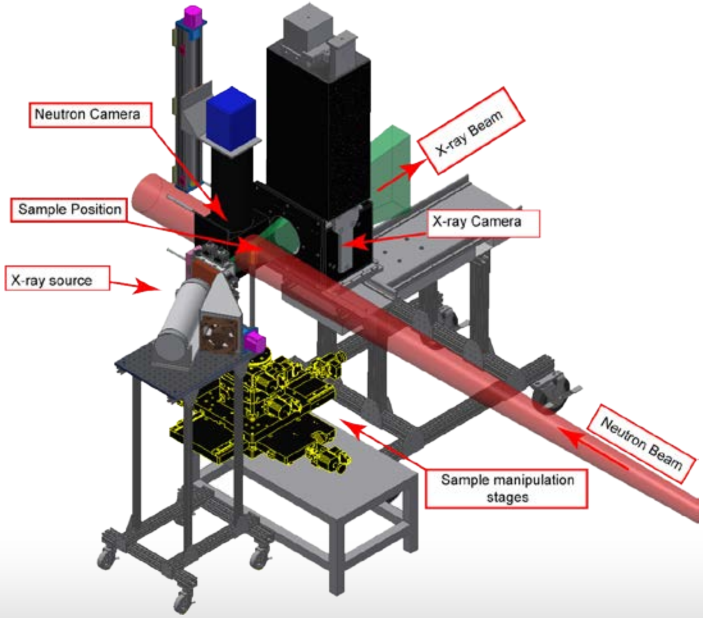


Milestones

- New Cold Imaging Facility – 100% in FY2015
  - Commissioned in September 2015
- Methods to improve image spatial resolution - Ongoing
  - Image intensifier available January 2016
  - Centroiding with detector macroscope resolution <9 µm
  - Grating resolution 4 µm.
  - Neutron microscope project is receiving support for development by NIST
    - 20 µm spatial resolution, 10 s time resolution available 2017 (planned)
    - 1 µm spatial resolution, 10 min time resolution available 2018 (planned)
- Complementary x-ray imaging system – 100 % in FY15
  - Commissioned June 2015, available to all users.
  - Enables simultaneous in operando neutron/x-ray analysis
- User program – Ongoing – 100% complete in 2015
  - 20 % of open beamtime allocated to Fuel Cell and hydrogen storage experiments
  - Univ. of California-Merced: Water content of non-precious group metal catalysts (mail-in experiment)

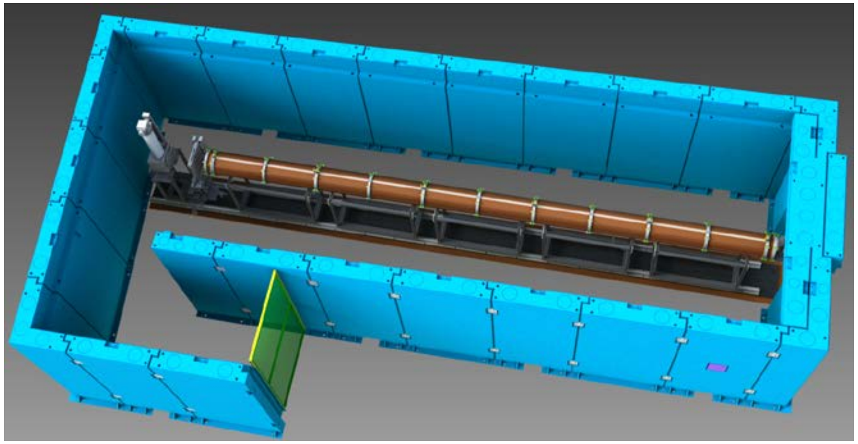


NIST Cold Neutron Imaging Instrument.



Accomplishment: NEW cold neutron imaging instrument

- Installed AUG 2015
- Test bed for high resolution imaging development
  - Higher sensitivity to small amounts of water
- Potential to resolve ice and water
  - Will perform calibration measurements in 2016
- Neutron lens
  - Demonstrate fabrication is feasible June 2016
  - Magnification 1x with ~10 s image time increase with 20 μm resolution by end 2017
  - Neutron image magnification with ~20 min image time with 1 μm resolution by end 2018
- Install test stand in early 2017
  - Working with General Motors to install second “Micro” stand; interim there is a FCT stand
  - Hydrogen generator installed at instrument
  - Freeze chamber installed by early summer 2016
  - Hydrogen safety analysis completed this fall



Accomplishment: Spatial Resolution Development Timeline

2001: 250 µm

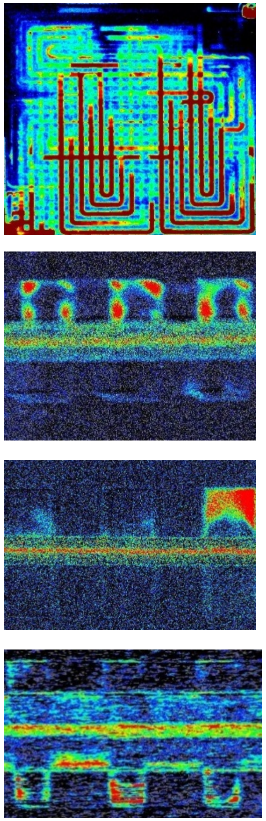
2006: 25 µm

2009: 10 µm

2016: 4 µm w/ slits

2017: 5 µm w/ centroiding

2018: 1 µm w/ Wolter Optics

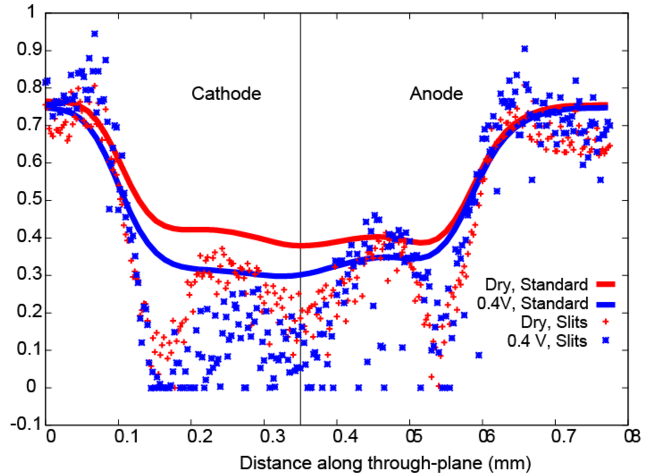


- With 250 µm in plane studies of total water content and manifold was enabled
- Improving to 25 µm resolution enabled accurate measurement of through plane distribution with many user experiments
- Further improvements to 10 µm resolution allowed more accurate measurement of diffusion media as well as temperature driven phase change flow and thermal osmosis.
- ***User community wants to resolve liquid water in catalyst layer and membrane***, which means the resolution needs to improve to 1 µm.
- We report here on detector developments (slits & centroiding) to improve resolution but these require long exposure times
- A neutron lens (Wolter optic) is under development which will improve resolution and time resolution

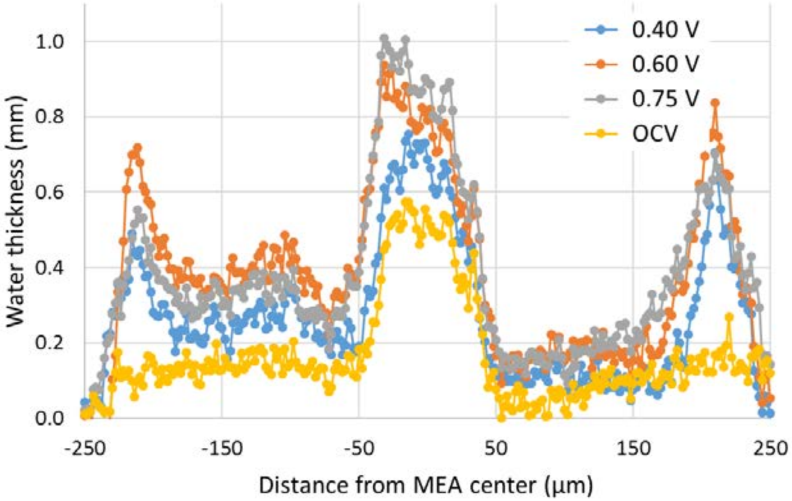
Accomplishment: Slit Imaging

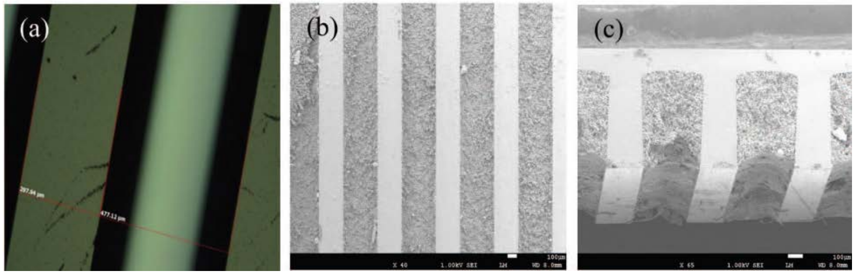
- DEC 2015: Received image intensifier to amplify weak scintillation light signal which reduces noise
- JAN 2016: Received opaque gratings using GadOx powder filling method which improve reconstruction
  - Slits currently have 350 μm period, requiring about 17 hours to acquire one image
  - Smaller period possible to reduce acquisition time, but may result in small field of view

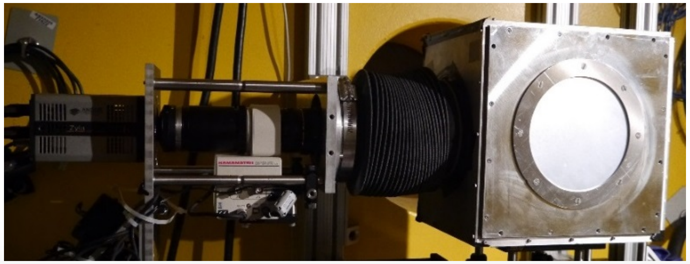
Status in 2015

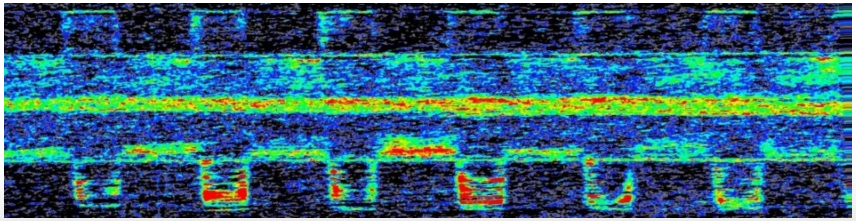


Status in 2016



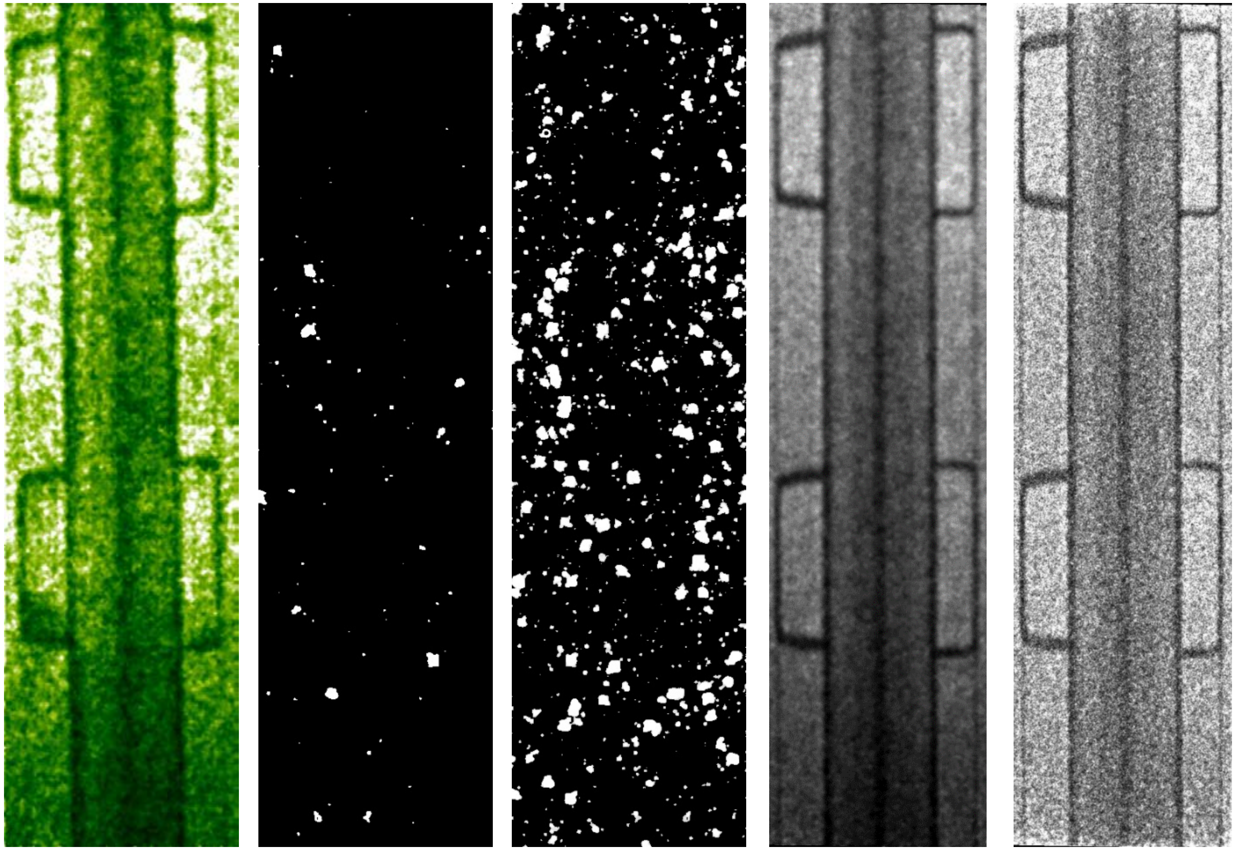






Future Work: Centroid Imaging

- Image intensifier and magnifying the scintillation light enables measuring each neutron capture event
- Scintillation light from GadOx does not have a uniform shape
- Initial reconstruction algorithm shows spatial resolution better than 9 μm
- 5 ms exposure time with 30 Hz frame acquisition gives 85% dead time and 4 h total exposure time
- Continue to refine method:
  - High frame rate camera to reduce dead time and acquisition time to about 1 h
  - Refine reconstruction algorithm to improve spatial resolution and
  - Use hardware rather than post acquisition analysis in software for fast image reconstruction
  - Expect better than 5 μm resolution



Accumulation of scintillation light

1 frame

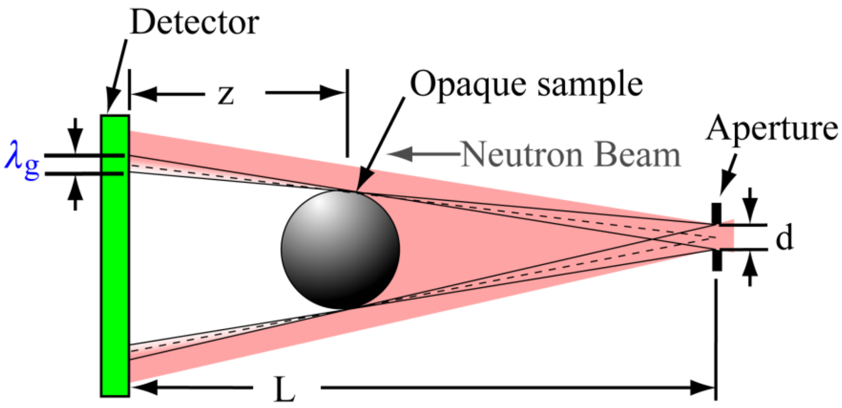
20 frames

80k frames

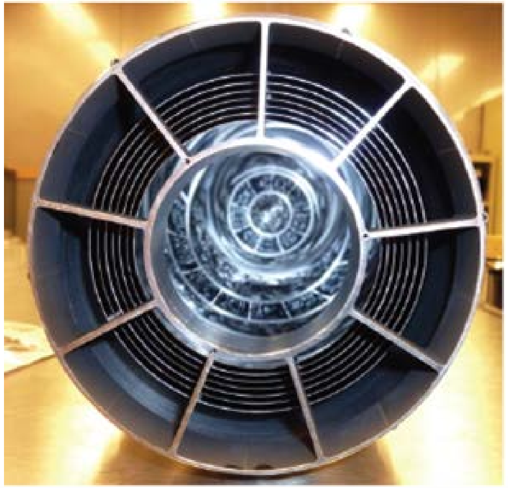
Centroid Image

Future Work: Neutron Microscope

- Pinhole optics describes conventional neutron image formation
- Fundamental resolution from collimation, where “geometric blur” is given by: $\lambda_g \approx z\, d / L$
- Neutron sources are weak compared to synchrotrons, need d~1 cm
- No magnification, so intrinsic detector resolution only path to higher resolution
- Since Flux goes as $(d/L)^2$, Small *d* & large *L* → small Flux for high resolution of real objects
- But in a 1 µm pixel with a typical flux 10^6 cm^{-2} s^{-1}, there’s only 1 neutron every 100 s.
- Neutron refraction is small and strongly chromatic ($n \sim 1 - 10^{-6} * \lambda^2$)
- Neutron *reflection* deviates beams more strongly, can create reflection-based lenses
- NASA x-ray telescope technology can be adopted to create a neutron microscope and dramatically increase both spatial and temporal resolution



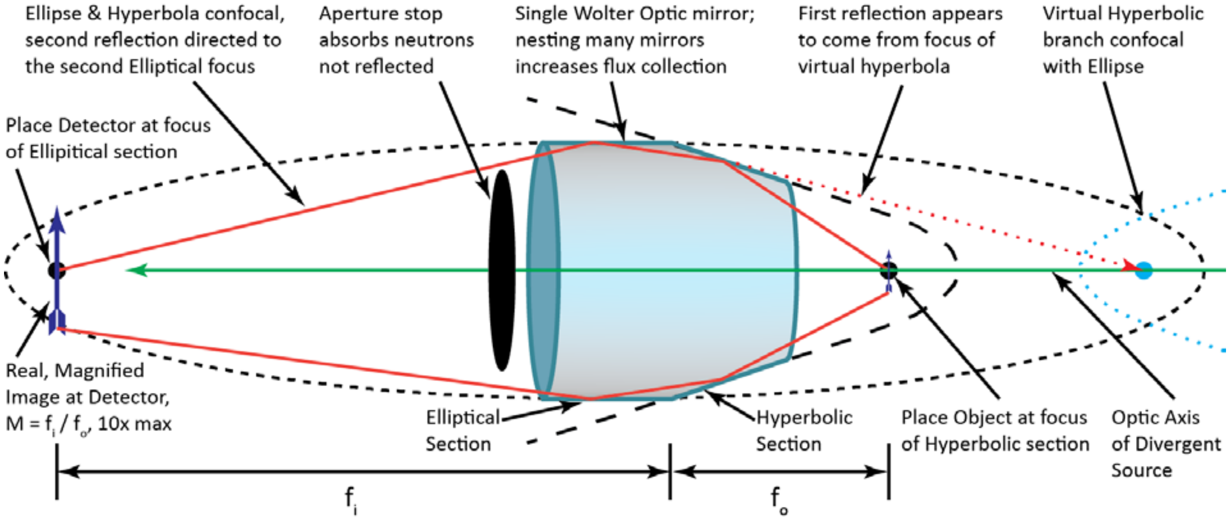
Pinhole optics geometry



The Wolter optic used in the Focusing Optics X-ray Solar Imager (FOXSI) is composed of thin Nickel foil mirrors

Future Work: Neutron Microscope

- With a lens, the image spatial resolution by the lens NOT the collimation
- Can realize a x100 increase in flux so that time resolution for 20 μm images will be less than 10 s
- Ratio of focal lengths gives magnification of the neutron distribution
  - Magnification of 10 is feasible
  - Anticipate spatial resolution of about 1 μm with 20 min acquisition time
- In year 3 of NIST-funded project
  - 2016: Test NASA's improved fabrication methods
  - 2017: 1:1 optic for 20 μm resolution in 10 s
  - 2018: Magnifying optic for 1 μm in 20 min



Ellipse & Hyperbola confocal, second reflection directed to the second Elliptical focus

Aperture stop absorbs neutrons not reflected

Single Wolter Optic mirror; nesting many mirrors increases flux collection

First reflection appears to come from focus of virtual hyperbola

Virtual Hyperbolic branch confocal with Ellipse

Place Detector at focus of Ellipitical section

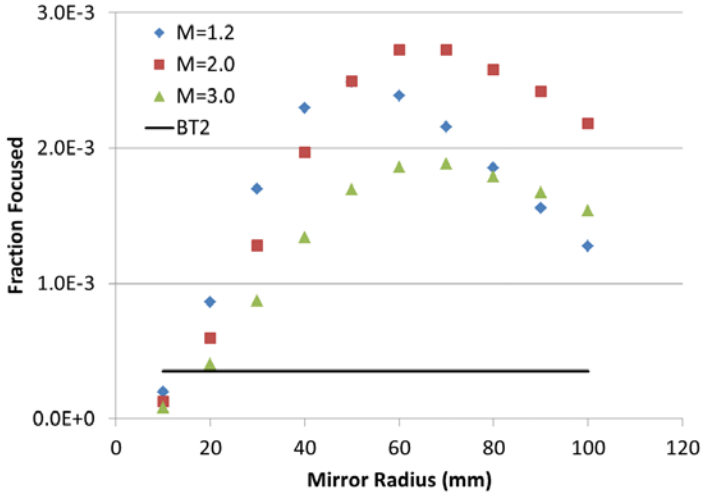
Real, Magnified Image at Detector, $M = f_i / f_o$, 10x max

Elliptical Section

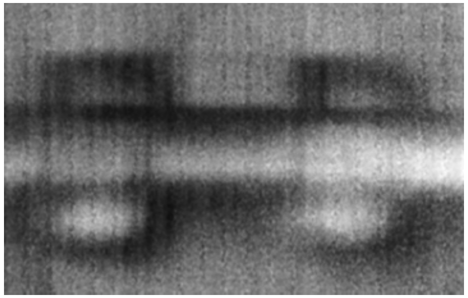
Hyperbolic Section

Place Object at focus of Hyperbolic section

Optic Axis of Divergent Source



Fraction of flux focused for one shell with 7.5 m focal length for 3 neutron guide coatings

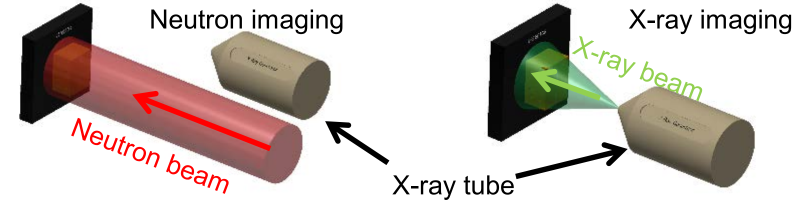


Prototype neutron lens with Magnification=4 image of a fuel cell with 120 μm resolution

Combining X-rays with Neutron Imaging

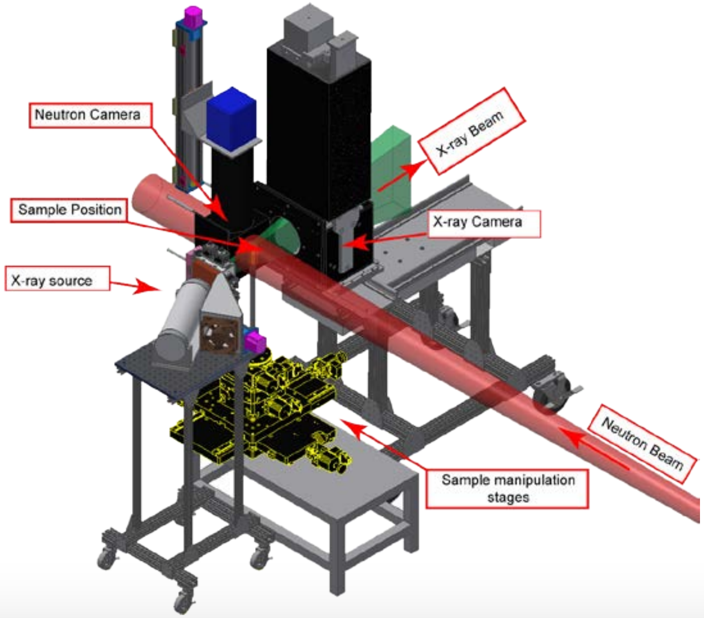
- X-ray system available to users since June 2015
- Currently 90 keV microfocus x-ray source
- Image the same sample region with x- & n-ray to improve composition determination
- Future: PEMFC Hardware for multimodal imaging will be fabricated and ready for testing in June 2016
- Future: Methods will be developed through the summer and made available to all interested users

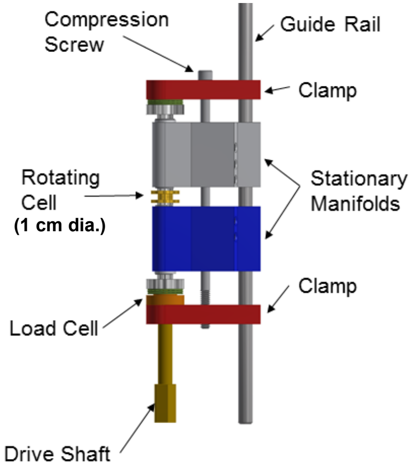
Serial Imaging for X-ray snapshots of cell state



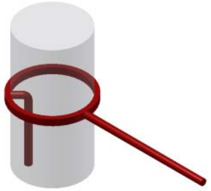
Scheme: Mount X-ray tube collinear with neutron beam on a stage to toggle probes. Take X-ray snapshots at each test point to gain additional information on location of Catalyst interfaces to improve the quantification of the neutron radiographs.

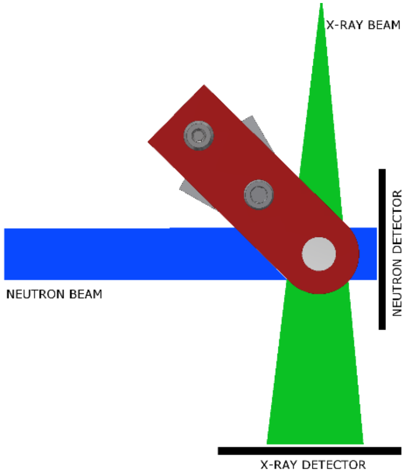
Designing a PEMFC test section for simultaneous tomography. Design minimizes material in the beams and uses a stationary manifold so that cabling does not rotate with the active area. Active area is 0.6 cm^2 with exchangeable flow fields.





A stationary inlet or outlet manifold keeps hoses/wires away from field-of-view by coupling to the cell shaft as shown

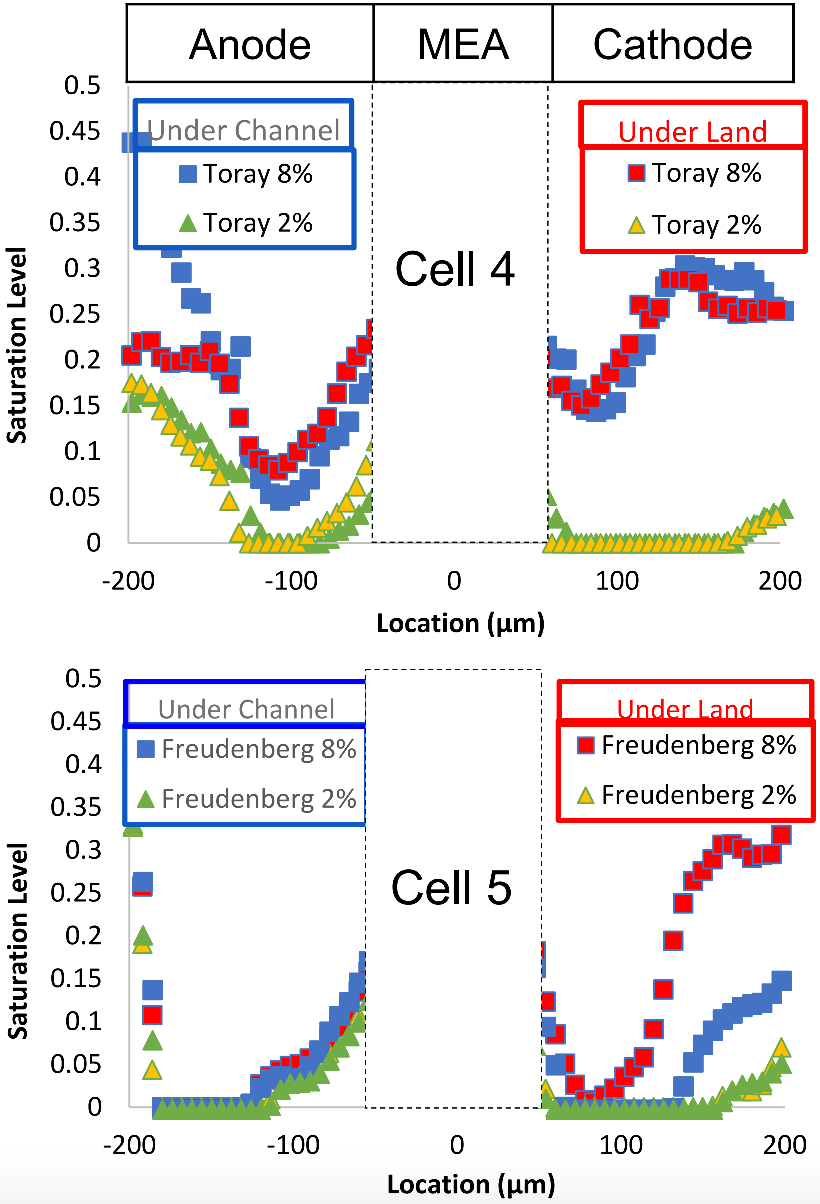




Highlights/Milestones User Program

Po-Ya Abel Chuang, Thermal and Electrochemical Energy Laboratory (TEEL), University of California-Merced

- Study of Onset Liquid Water Condensation
- Cell design based on LANL high resolution cell
- Cell 4, Membrane-Nafion XL(~30 μm), DM-Toray(~178 μm)
- Cell 5, Membrane-Nafion XL(~30 μm), DM-Freudenberg(~203 μm)
- Test conditions:
  - 50°C, 77% RH; 0.3V; 300 kpa abs, high flow conditions (> 30/30)
  - 100% hydrogen concentration
  - 2%, 8%, and 16% oxygen concentration
- Under dry condition (2% O_2), the water saturation in the DM is similar.
- Under wet condition (8% O_2), liquid water is saturated throughout the diffusion media thickness for Toray DM. In contrast, liquid water is only saturated away from the MEA near the land for Freudenberg DM.
- The same trend is observed for DM under the channel area.
- It can be clearly observed that Freudenberg DM provides much more open path for oxygen diffusion compared to Toray DM.



Response to 2015 Reviewers' Comments

- In actual fuel cell operation, water management issues are specific to a given flow field, which is typically proprietary. Although general water management can be understood, specifics for a real stack and a real cell cannot be extrapolated based on these data in subscale cells.
  - *We agree. Stack developers can and DO use the facility to study proprietary designs by paying a full cost recovery fee. Under this mode, the developer owns all the data they generate outright.*

- The project should include a strategic plan on what the use of a higher resolution detector will allow from a fuel cell design activity and what type of processes could be quantified with the higher resolution capability.
  - *According to the Water Transport Working Group's review article: A.Z. Weber et al "A Critical Review of Modeling Transport Phenomena in Polymer-Electrolyte Fuel Cells" doi: 10.1149/2.0751412jes, JECS (2014)* ***161*** *(12) p.F1254-F1299, the saturation values in the catalyst layer aren't known from experiment. Measurements of such quantities would provide badly needed model validation data.*

- The project should include a translation from water thickness into a value of local saturation within the MEA; this would make the data more translatable for use in analyses and provide better correlation to performance.
  - *This process was detailed in: Hussey, D. S., D. Spernjak, J. Fairweather, J. Spendelow, R. Mukundan, A. Z. Weber, D. L. Jacobson & R. Borup, Accurate measurement of the through-plane water content of proton-exchange membranes using neutron radiography. Journal of Applied Physics, v. 112, 104906 (2012).*

Summary

- New cold imaging facility will allow more rapid development of high resolution methods to measure MEA water content
- We have made good progress towards measuring liquid saturation values in the catalyst and membrane
  - Slit scanning
    - 4 mm demonstrated
    - Acquisition time is 17 h, but could be improved to less than 8 hours
  - Centroiding sub 10 micron resolution appears to be possible
    - Method needs further refinement
    - Future: develop hardware based centroiding to allow high throughput
  - Wolter optics
    - Validation of NASA fabrication techniques during summer 2016
    - 2017 high speed 20 micron optics, 2018-1 micron optics
- New in operando x-ray imaging capability will allow higher resolution studies of porous materials with in operando neutron measurement of water transport
- User program
  - New cold imaging facility is currently being upgraded to include full support
  - Including EIS into the scripting of the test stand would be a great benefit to the users
  - It was observed from fuel cell testing that Freudenberg DM shows improved performance under wet and cold operating condition due to improved oxygen diffusion over Toray DM.

Acknowledgements

Special Thanks to

Nancy L. Garland

DOE Technology Development Manager

This work was supported under the Department of Energy interagency agreement No. DEAI01-01EE50660, the U.S. Department of Commerce, the NIST Radiation Physics Division, the Director's office of NIST, and the NIST Center for Neutron Research.

End of Presentation
Additional support material follows

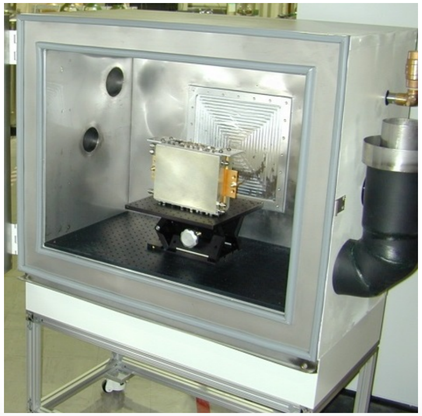
Approach

Fluids:
H_2 (18.8 slpm), D_2 (1.2 slpm), N_2, Air, O_2, He,
DI (18 MΩ/cm)
New H_2 Generator FY14

Large scale test stand: 800 W,
6-1000 A @ 0.2 V
0 V – 50 V,
Liquid coolant
H_2/Air: 11/27 slpm
Contact humidifier (dew pt. 35-85 °C)
First User Data 03/15

Small scale test stand: Cell area ≤50 cm^2, dual & liquid temperature control, absolute outlet pressure transducers

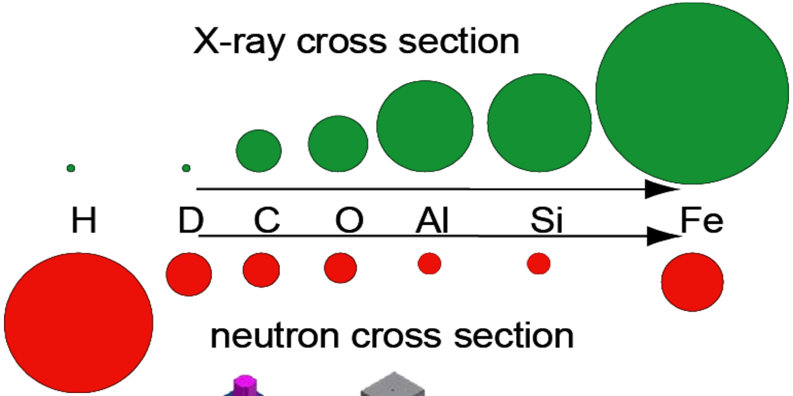
2016 coming upgrade:
Full integration of EIS acquisition into scripting

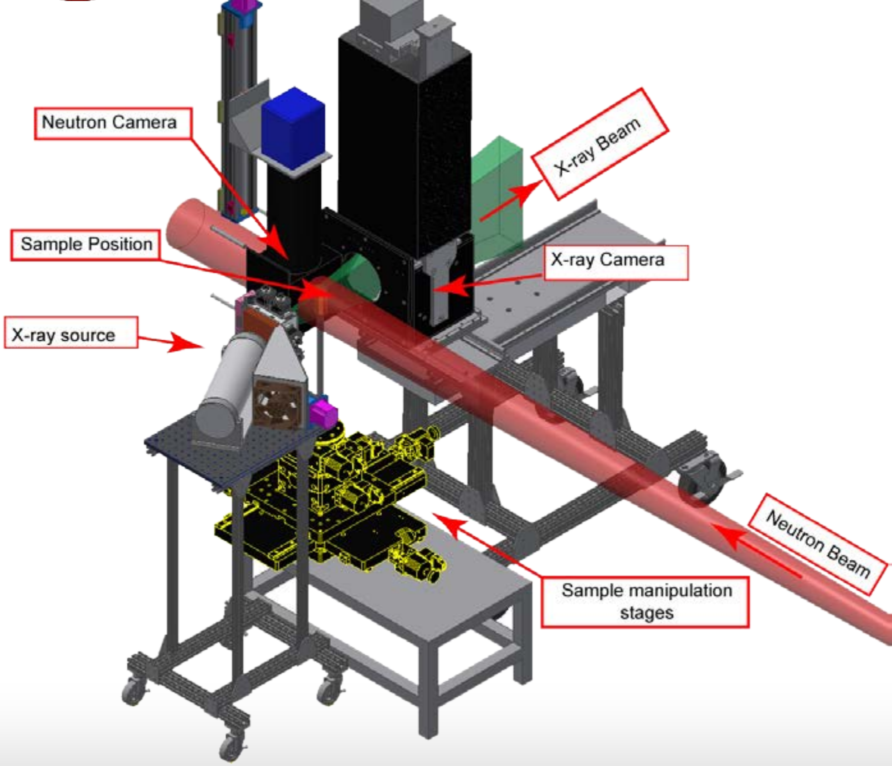


Environmental Chamber:
-40 °C – 50 °C
RH 20-90% above 20 °C
1 kW air cooling at -40 °C
Also available, liquid cooling to -45 °C

Future Work: Simultaneous Neutron and X-ray Imaging

- Installed June 2015
- Image the same sample region with x- & n-ray to improve composition determination
- Can match image spatial resolutions or have superior x-ray resolution
- X-ray microfocus source
  - 20 keV – 90 keV
  - 80 W max power
  - 13-20 μm spot size





Rich, complementary data set from combined x-ray and neutron tomography

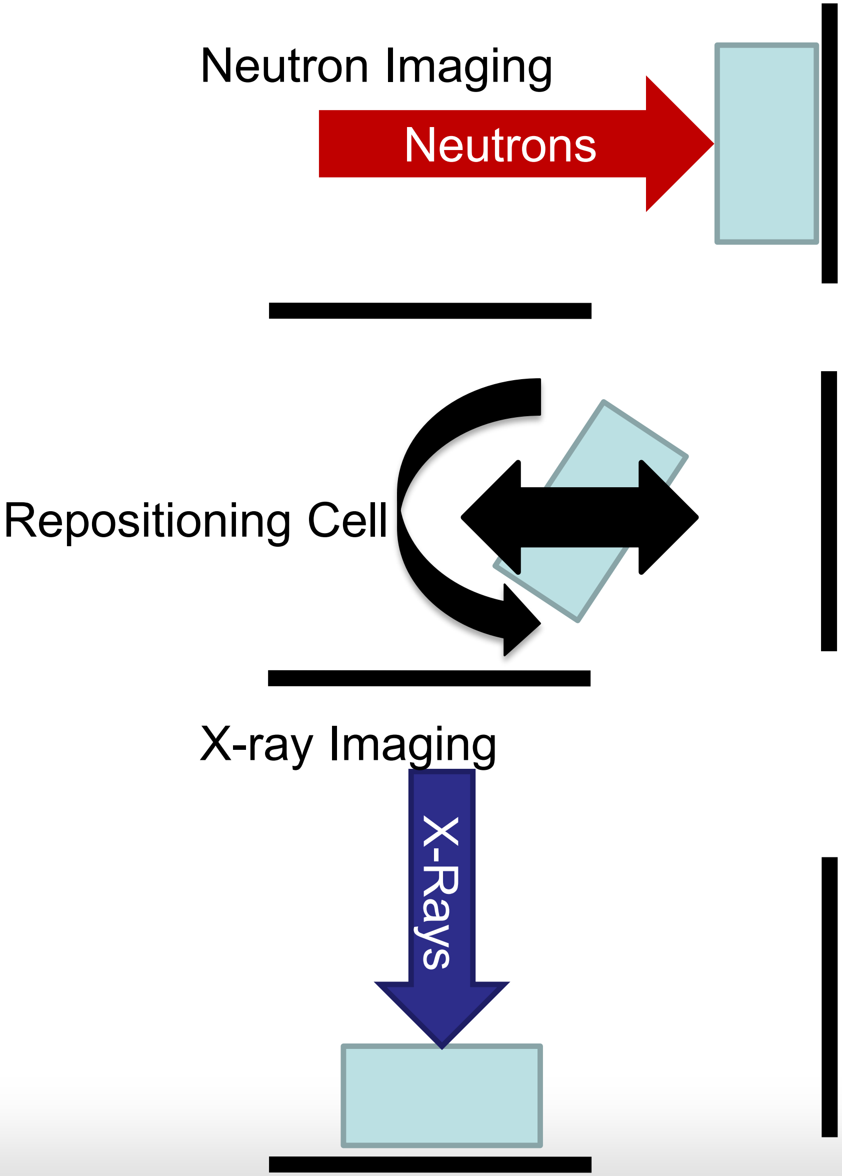
A Hot Wheels car (right) was imaged with neutrons (bottom left) and x-rays (bottom right)

Neutron image

X-ray image

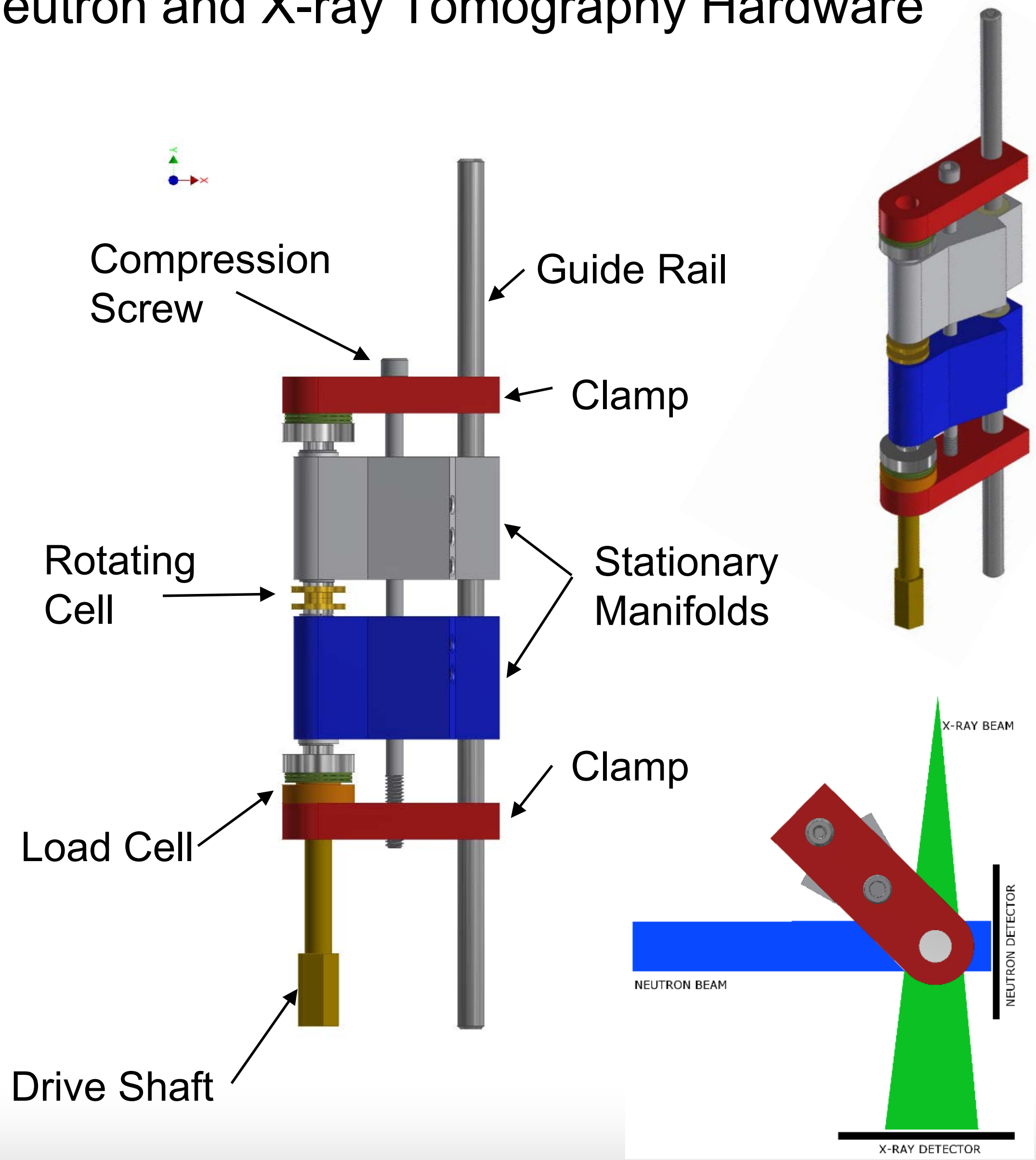
X-ray Radiography for Improved Interface Identification in Neutron Radiography

- X-rays will be used to identify the material interfaces within the cell to enhance neutron imaging results
  - Improved boundary identification allows improved porosity prescription for conversion of water thickness to saturation
- Technique development for serial imaging
  - Cell is imaged at constant conditions with neutrons as done currently
  - At end of image set for that condition, cell is moved to X-ray beam
  - X-ray image(s) taken
  - Cell moves back to neutron imaging position and continues to next test point



Development of Simultaneous Neutron and X-ray Tomography Hardware

- Hardware in development to support simultaneous neutron/X-ray imaging and tomography
- Cell rotates will gas inlets remain stationary
  - Reduces leaks
  - Better angular repeatability
- Minimal material in view area
  - Clamp fixture moves screws away from cell (reduced x-ray artifacts)
- Small 0.6 cm^2 active area
- Flow field can be changed to suit experimental needs



Future Work for Combined Neutron and X-ray Imaging

- Hardware for serial imaging and simultaneous tomography will be fabricated and ready for testing in June 2016
- Methods will be developed through the summer and made available to all interested users
- A search for a new X-ray source is ongoing with the goal of purchasing a tube with a focal spot size of ≤ 1 μm to gain improved resolution
- As X-ray resolution improves it will be possible to image and reconstruct the porous network through the GDL fibers and allow for 3D overlays of water distributions and fiber matrix