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

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

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

Barriers

(A) Durability

(C) Performance

(D) Water Transport within the Stack

Budget

Project funding FY 2012	
DOE:	$ 300 k
NIST:	$ 600 k
Industry:	$ 275 k

Project funding FY 2013	
DOE:	$ 300 k
NIST :	$ 600 k
Industry:	$ 250 k
Total	**$ 1,175 k**

Partners/Users/Collaborators

Project Lead: National Institute of Standards and Technology

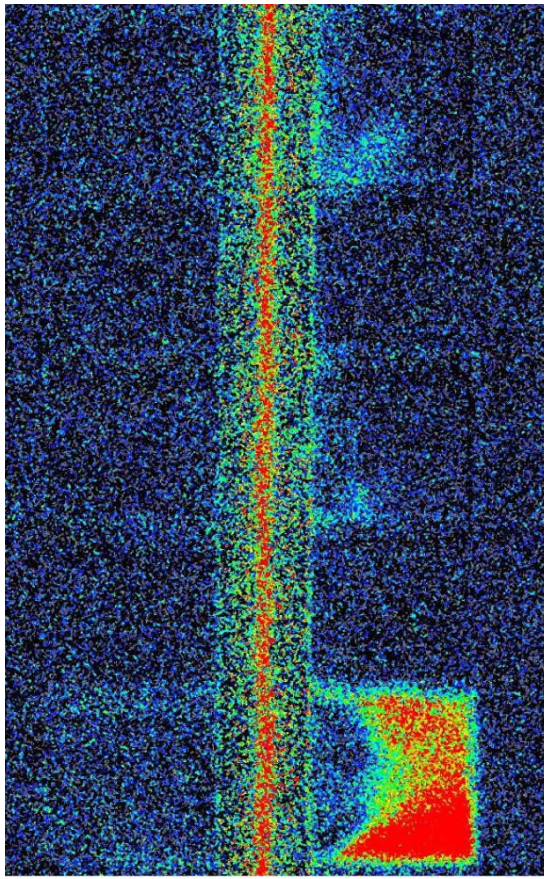
- General Motors
- Ballard
- Ford
- Nissan
- Nuvera
- Proton OnSite
- Automotive Fuel Cell Corporation
- Los Alamos National Laboratory
- Lawrence Berkeley National Laboratory
- Oak Ridge National Laboratory
- Sandia National Laboratories
- CEA (France's Atomic Energy and Alternative Energies Commission)
- Sensor Sciences
- NOVA Scientific
- NASA
- Georgia Tech
- Massachusetts Institute of Technology
- Michigan Technological University
- Rochester Institute of Technology
- University of California, Berkeley
- University of Connecticut
- University of Kansas
- University of Michigan
- University of Tennessee
- Wayne State University

Relevance

- Neutron imaging is the most powerful methods to image water in the fuel cell in situ because neutrons penetrate most fuel cell hardware but are extremely sensitive to liquid water.
- This allows one to study a wide range of fuel cell related issues like:
  - Water transport in the flow fields and manifolds.
  - Steady state liquid water distribution anode versus cathode in diffusion media.
  - Steady state liquid water distribution in the membrane.
  - Catalyst degradation induced by liquid water.
- Objectives
  - 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 related issues
  - To tailor neutron imaging to the needs of the fuel cell community
  - Improving spatial resolution to study relevant length scales like the catalyst layers.

Approach

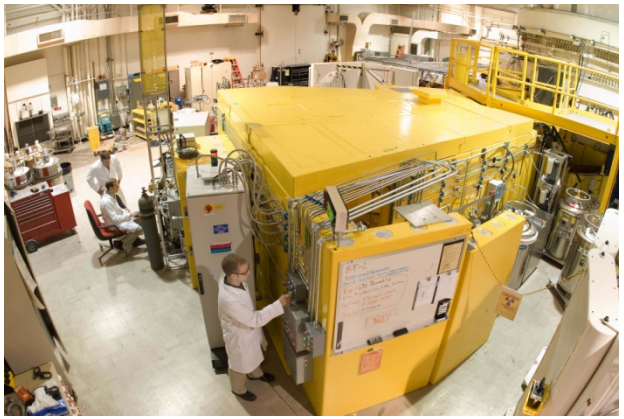
- Apply Quantitative Neutron Radiography to measure the water content in an operating fuel cell
  - Neutrons easily penetrate metal and carbon and are uniquely sensitive to hydrogen bound in liquid water inside the fuel cell.
  - One-sigma sensitivity of ~60 ng of water is possible.
  - High resolution imaging (10 μm) can measure the through-plane water content using one-dimensional test sections to validate models of fuel cell operation using simple edge on radiography
  - Standard imaging (250 μm) can capture transient processes up to 90 frames per second (1/90 s) in the in-plane flow field and manifold water distribution
- Improve fuel cell imaging technology and analysis
  - Current best spatial resolution is 10 μm for resolving anode versus cathode with diffusion media and thick catalyst/membranes
  - New methods show promise for sub-10 μm resolution to resolve catalyst and membrane water distribution
  - Large area CCD and MCP detectors improve coverage of fuel cell to provide better validation data for down-the-channel models
  - Exploring novel neutron optics for a cold imaging facility to improve resolution for studying catalyst/membrane in situ.
  - Develop and distribute analysis methods to improve accuracy of water content measurement including measurement uncertainty

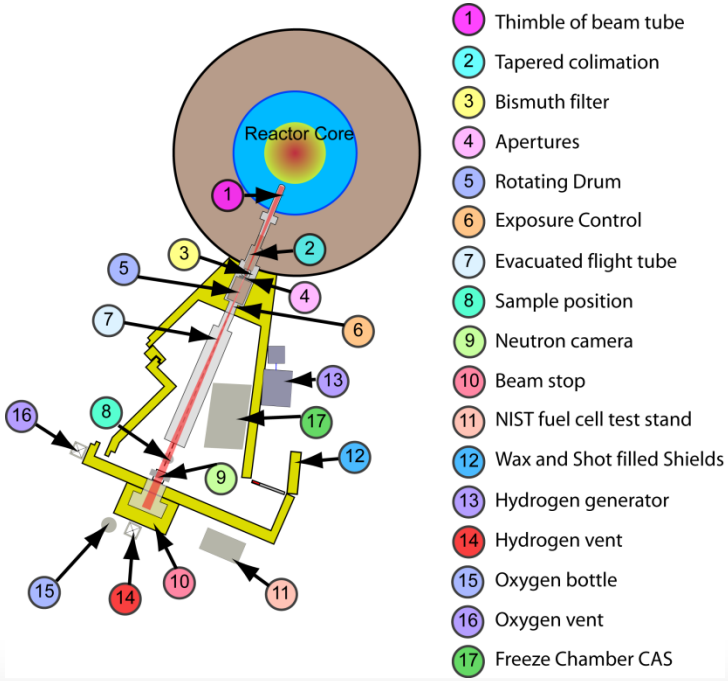


High resolution neutron radiograph of water through edge of operating fuel cell

Approach

- Maintain a national user neutron imaging facility for fuel cell research
  - Develop and maintain state-of-the-art in situ fuel cell testing infrastructure (see Support Slides)
    - Large and small scale fuel cell test stands available.
    - Zahner IM6 Electrochemical workstation (potentiostat with boost load banks up to 100A)
    - In situ freeze testing to -40 °C.
  - Support fuel cell experiments by developing state-of-the-art imaging technology
  - Develop and maintain state-of-the-art data analysis tools
  - 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 with planning, execution, analysis and publication of the data.
- Fee based access for proprietary research
  - Contact NIST for details.
  - Proprietary users trained to use the beam without assistance



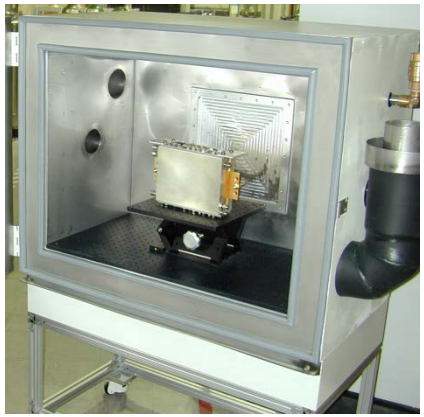


Approach

Fluids:
H_2 (18.8 lpm),
D_2 (1.2 lpm),
N_2, Air, O_2, He,
DI (18 MΩ/cm)

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

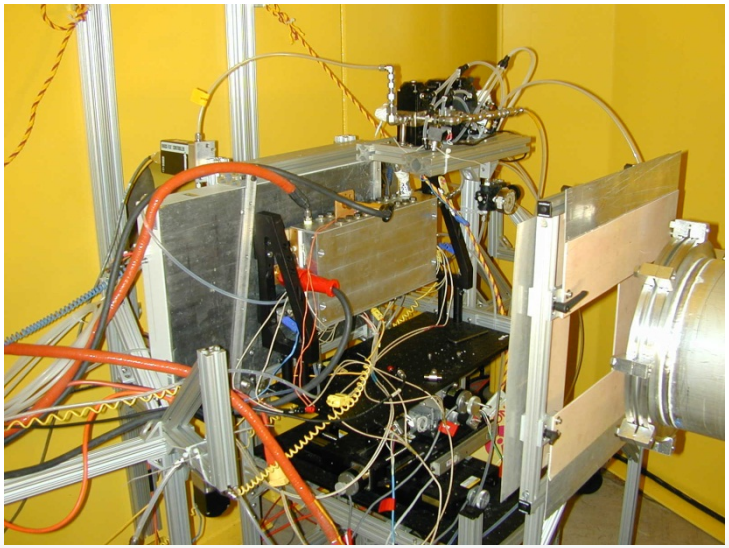
Large scale test stand: 800 W,
6-1000 A @ 0.2 V
0 V – 50 V



Environmental Chamber:
-40 °C – 50 °C
RH 20-90% above 20 °C
1 kW cooling at -40 °C

Approach

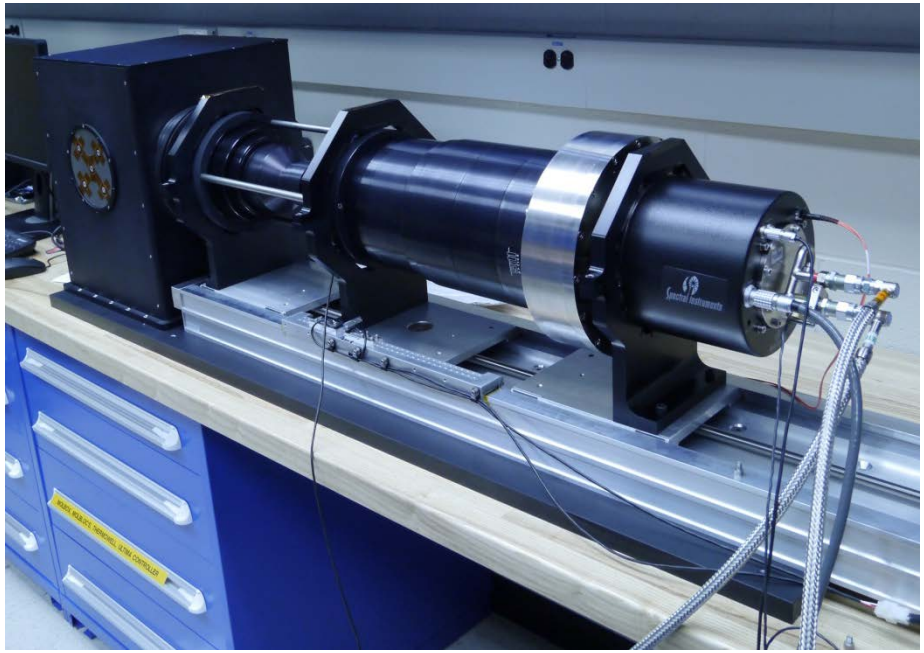
- Setup area for experiments on beamline.
- Beam size at sample 26 cm diameter.
- 6 meters from aperture to sample position.
- Aluminum flight tube evacuated.
- Short sections can be made into a shorter tube for closer positions.
- Closest position is 1 meter.
- Setup shows both 50 cm^2 and full size automotive cell.



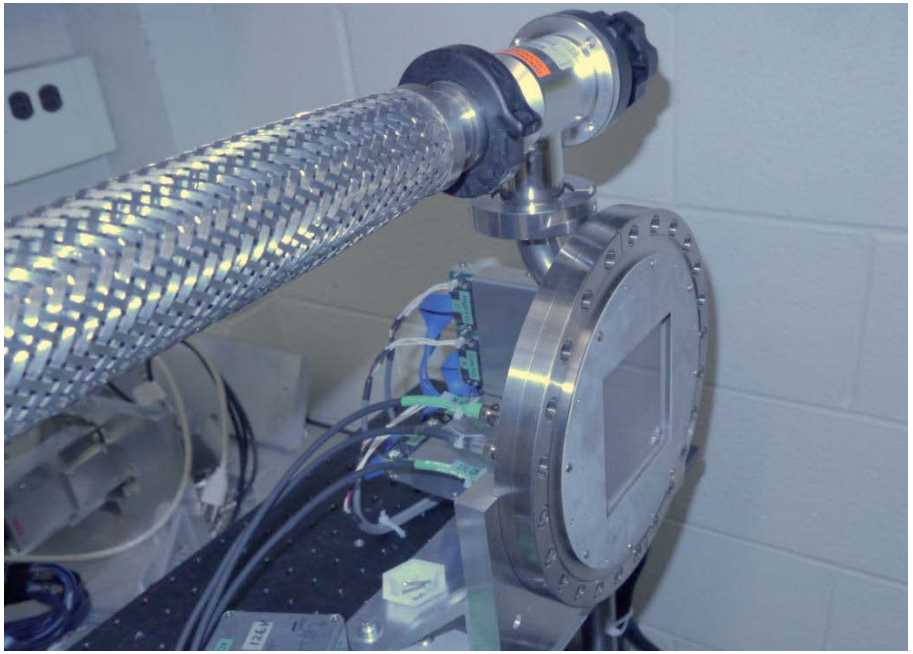
Approach: Milestones

Milestones	Progress	Comments	%
1) Large area, high res. detectors for fuel cells Develop large area detectors (10 cm by 10 cm) with spatial resolution of 15 µm and apply to dry gas purge studies during shutdown.		Details in presentation	100 %
2) High resolution MEA water content Measure the water content in an operating fuel cell membrane electrode assembly with a resolution of at least 5 micrometers.	Image reconstruction algorithms complete, grating fab ongoing, initial tests performed.	Full completion expected Oct. 2013. Details in presentation.	75 %
3) Accuracy of water distribution measurement Correction algorithms for systematic uncertainties in the measurement of the in-plane water content of fuel cells are demonstrated and published.		Details in presentation	100 %
4) Through-plane freeze measurement High resolution measurement neutron imaging of a single PEM fuel cell cold start through-plane water content in the temperature range of -40 °C to 0 °C.	New environmental setup fabrication completed Mar 2013	Full completion expected by Oct 2013.	50 %

Milestone: Large area, high res. detectors for fuel cells



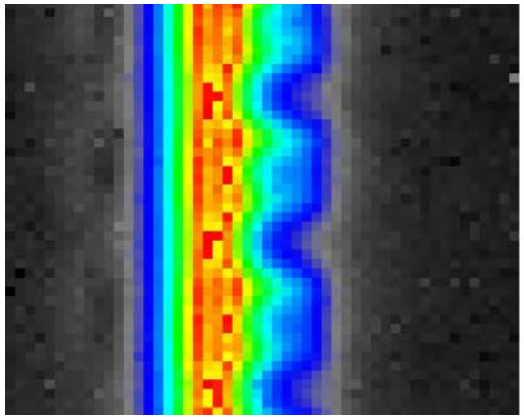
- 10 cm x 10 cm CCD camera
- 9 µm pixel pitch
- 100 Mega Pixel
- resolution ~20 µm
- 10 s read out rate
- low read noise



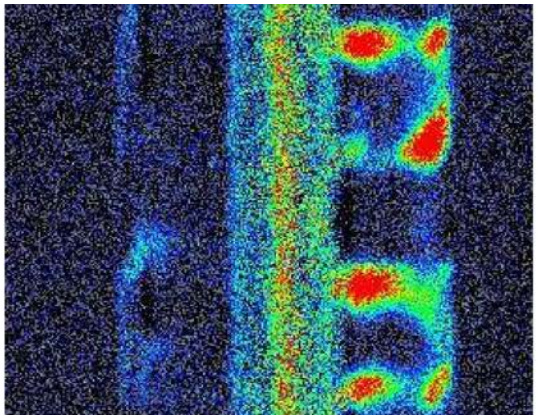
- 9 cm x 9 cm MCP detector
- 6 µm pixel pitch
- 256 MP
- 10% deadtime at 4 MHz
- resolution less than 20 µm (still optimizing)

Milestone: High resolution MEA water content

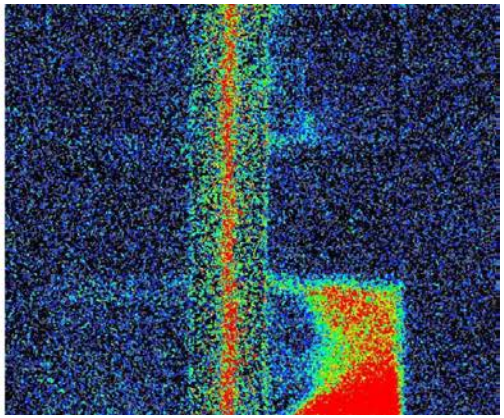
Motivation



250 micron



25 micron



10 micron

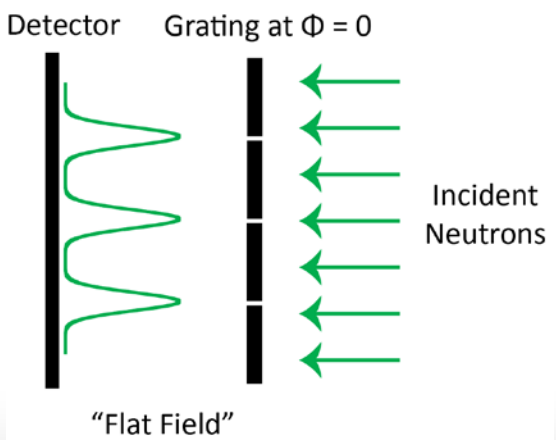
Resolution → 1 micron

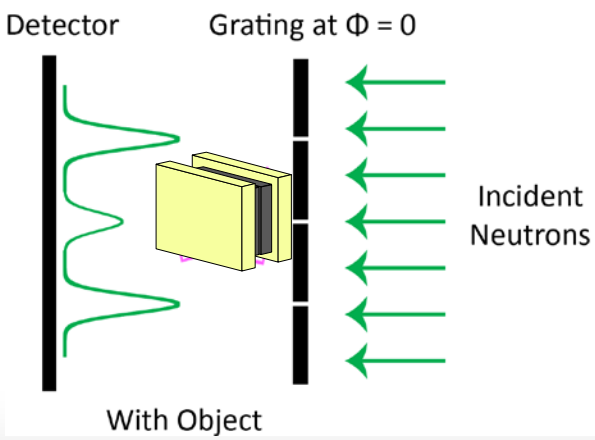
- To study catalysts we are improving the image spatial resolution. To achieve this goal a spatial resolution near 1 μm is critical.
- We have been asked by many in the fuel cell community to achieve this goal.
- Achieving this goal will enable studies of flooding and liquid water related degradation in the catalyst layers of a fuel cell.
- This enables accurate measurement of steady state water content across commercially viable membrane electrode assemblies.

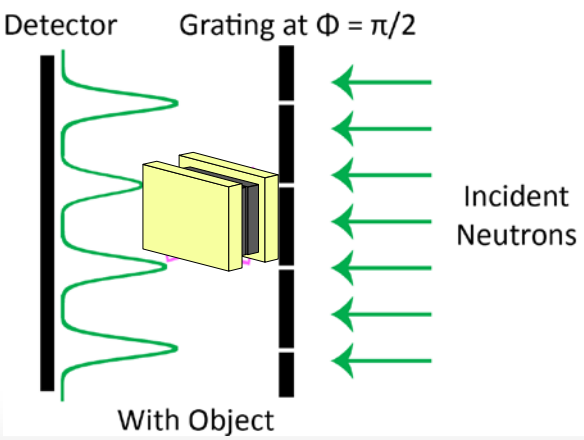
Milestone: High resolution MEA water content

Higher Resolution Inspired by Structured Illumination

- Spatial resolution in any neutron detector is fundamentally limited by the range of the charged particles from the neutron capture
- Using a slit we can further define the spatial resolution by width of the slit
- Technique:
  - Illuminate object with narrow slits on a period that allows detector to resolve the image
  - Translate grating across the object
  - Stitch image together in software

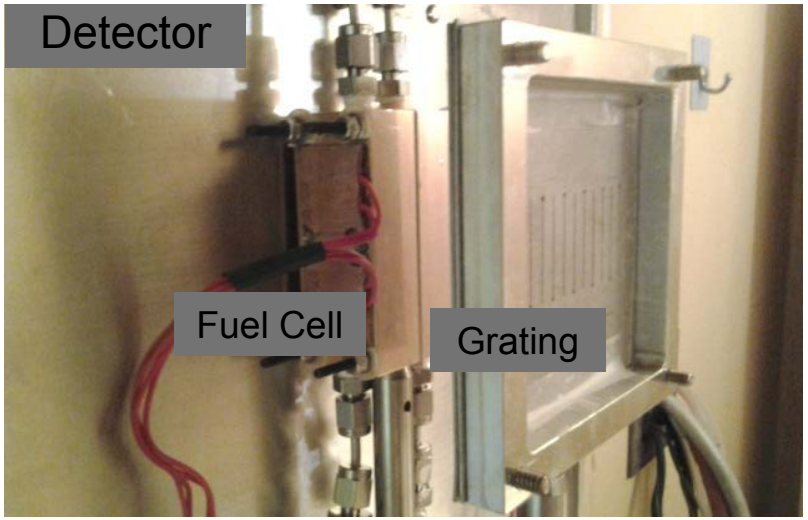


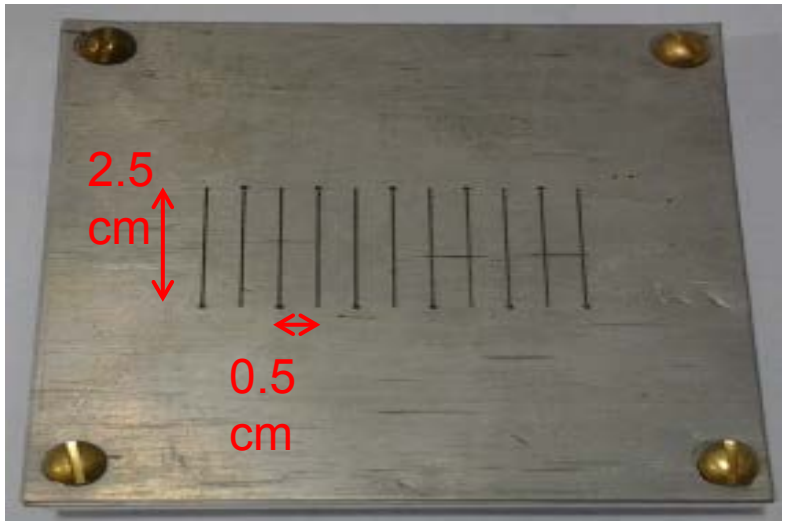




Milestone: High resolution MEA water content

First Test Grating-based Imaging

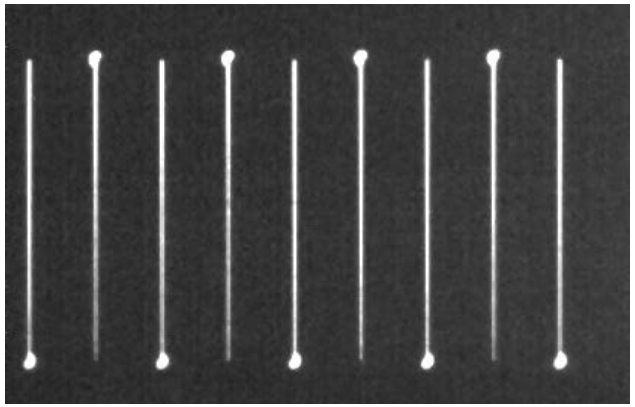




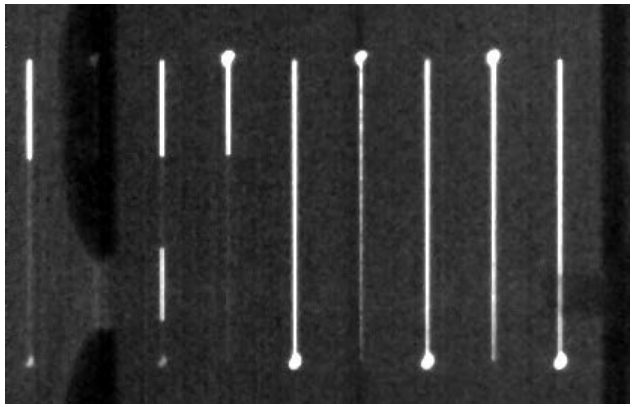
- Test method with a detector with 250 μm resolution
- Use a dry fuel cell to get a test image
- Electrical Discharge Machine ~100 μm in two Cd sheets, align to have 10 μm openings with a 5 mm period
- Spacing and length chosen to keep Cd from sagging

Milestone: High resolution MEA water content

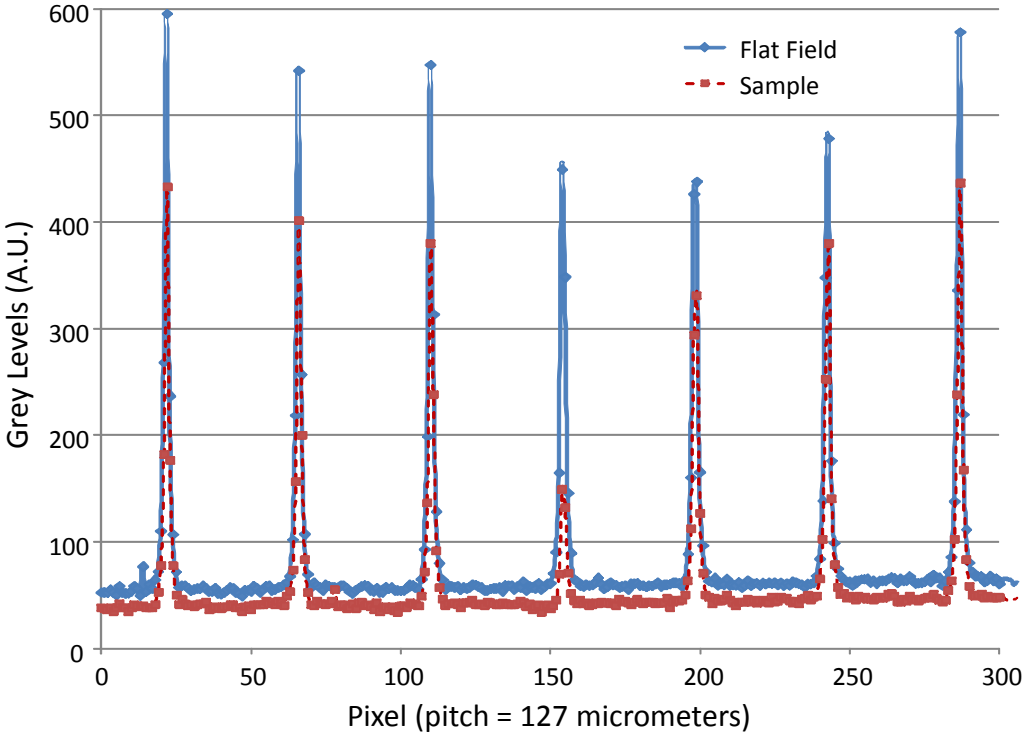
Raw Data



One image of the flat field



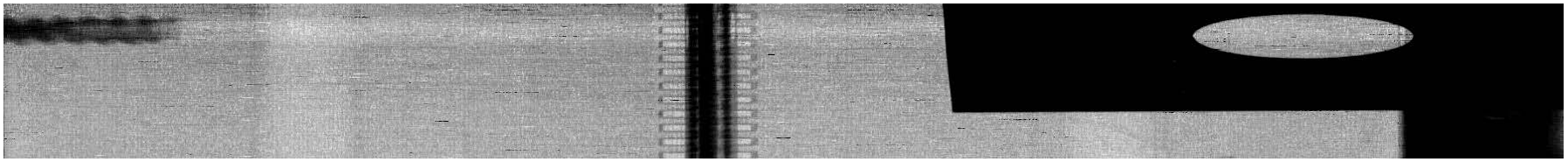
One image of the fuel cell and Gadolinium foil



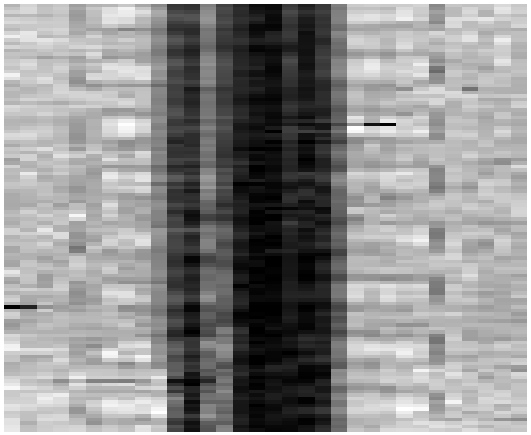
- Fit Gaussian to Flat Field for each slit and each Φ
- Fit object data using Flat Field centroid and σ as fixed parameters

Milestone: High resolution MEA water content

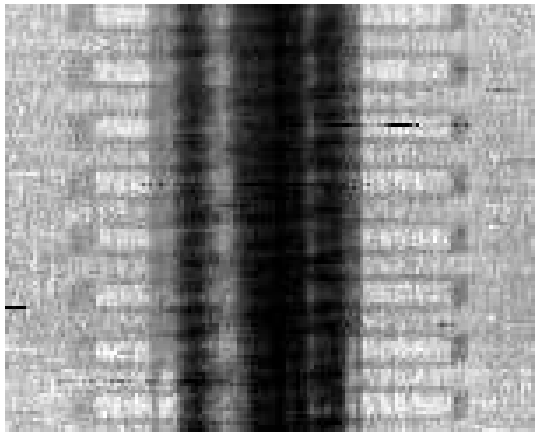
Reconstruction Results



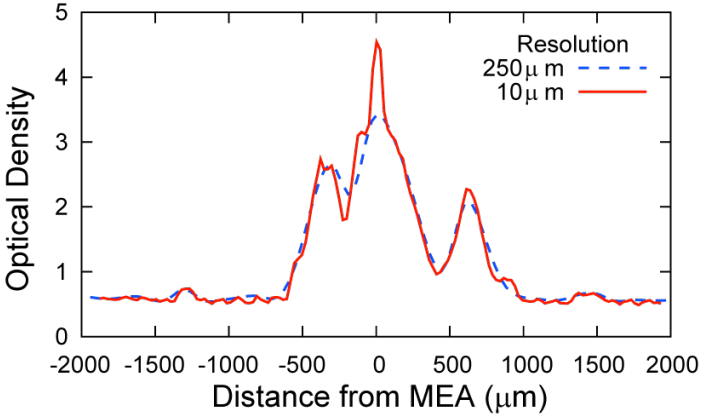
Horizontally Stretched, Stitched Image of
Fuel Cell and Gadolinium Resolution Target



Zoom-in of
original 250 µm
image



Zoom-in of
grating-based
10 µm image

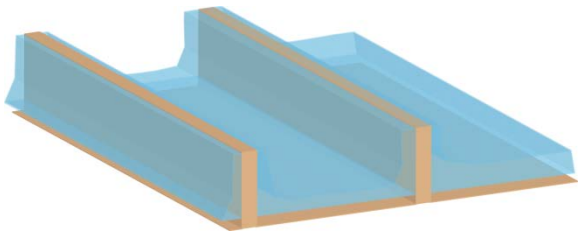


Attenuation from left to right
(averaged top to bottom)
showing improved resolution
of the membrane region

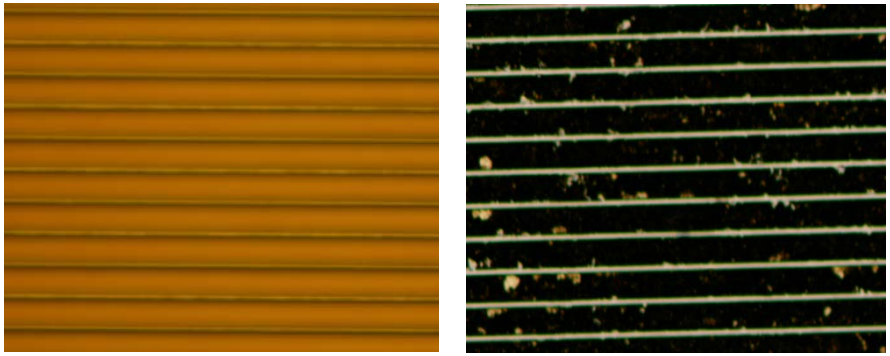
Milestone: High resolution MEA water content

Update: Grating Fabrication Path Towards 1 μm Spatial Resolution

- Technique is established
  - Demonstration performed.
  - Image reconstruction software developed.
- Grating fabrication:
  - Silicon transmits neutrons and Gadolinium is a strong neutron absorber.
  - Fabrication methods have not provided a successful candidate for a grating.
  - Neutron tests with existing gratings October 2012 showed that the ultimate version should have 10 microns of Gadolinium thickness.
  - Current approach is to apply 1 micron at a time and remove Gadolinium on comb top using chemical and mechanical polishing (CMP)
    - Process is slow requiring iterative steps of Deposit ->Polish->Deposit.
    - Gadolinium is highly stressed film requiring slow and careful iterations.
  - Decision point expected October 2013



Use chemical-mechanical polishing to expose silicon resulting in a 1 μm -2 μm wide neutron slit. Challenge: CMP uniformity

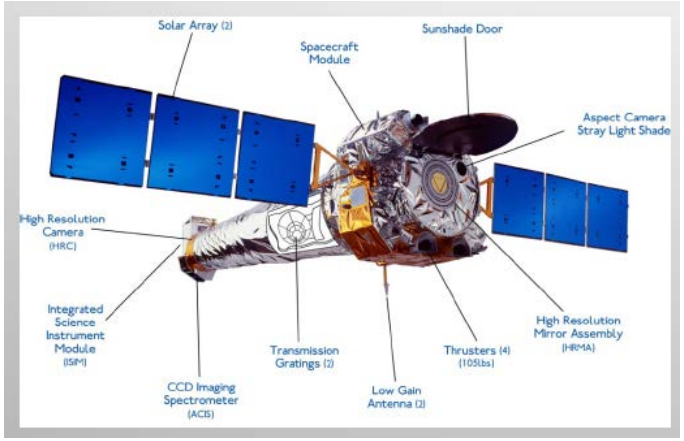


Gadolinium grating: Optical microscope image of Gd-coated (gold color) 2 μm wide combs on 50 μm period before (left) and after (right) CMP. Test grating on right in late March, 2013. Dark areas are Gd and light areas are exposed silicon.

Milestone: High resolution MEA water content

NASA Optical Technology For Fuel Cell Imaging

- NASA's reflective X-ray lens technology was adapted for neutron imaging use
  - A Wolter optic was used for CHANDRA's high resolution mirror assembly (HRMA) shown on the right.
- A breakthrough in optical technology for creating a practical neutron lens.
- This is the first demonstration of a practical neutron imaging lens.
- Resolution of 1 μm can be achieved using 10x magnification with 10 minute exposure time.
- 1000x faster acquisition can be achieved for 10 μm resolution.
- Ongoing collaboration with Boris Khaykovich (MIT), Dahzi Liu (MIT), and Misha Gubarev (NASA) to further develop the technology for fuel cell imaging.



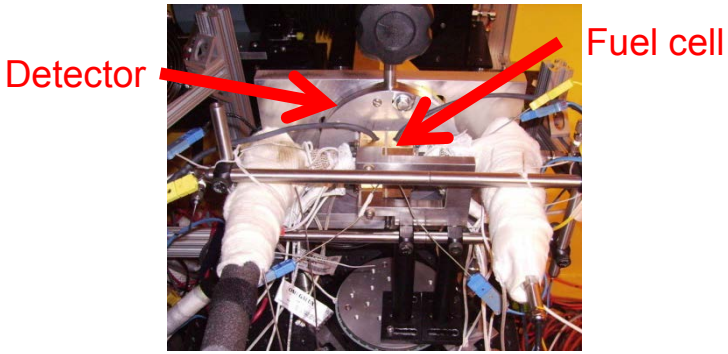
CHANDRA observatory

The hand of god pulsar PSR B1509-58 recently observed by CHANDRA using Wolter optics

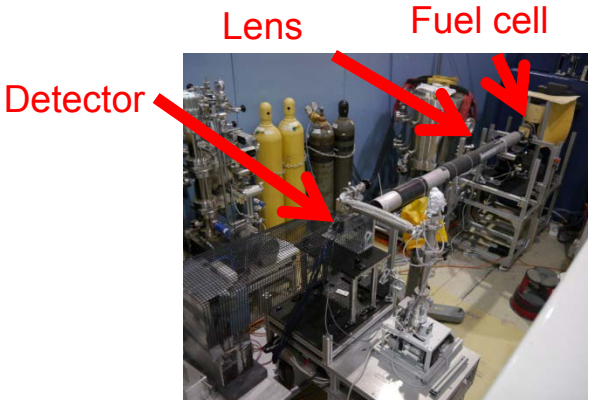
Milestone: High resolution MEA water content

Advantages of Lens to Pinhole Optics

- From NASA technology we get:
- More
  - Space around sample for access
  - Intensity
    - Pinhole collimation is not required to form image
- Better resolution
  - Magnification overcomes physics limit of 10 µm resolution
- Faster acquisition
  - More intensity means less time to take images
- Not cheaper
  - Requires upfront mandrel fabrication costs to make the mirrors



Less space for Pinhole Imaging Setup with 1 cm between sample and detector

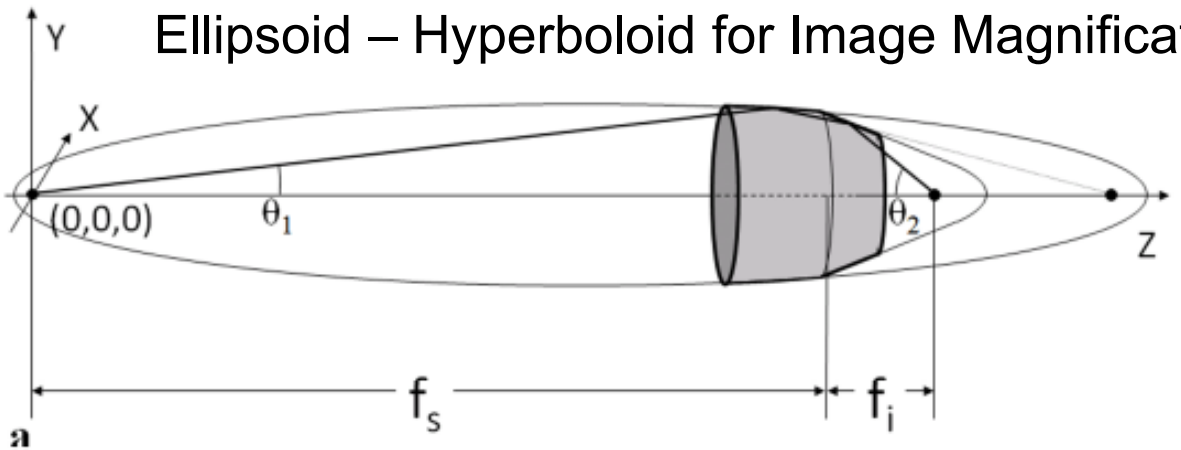


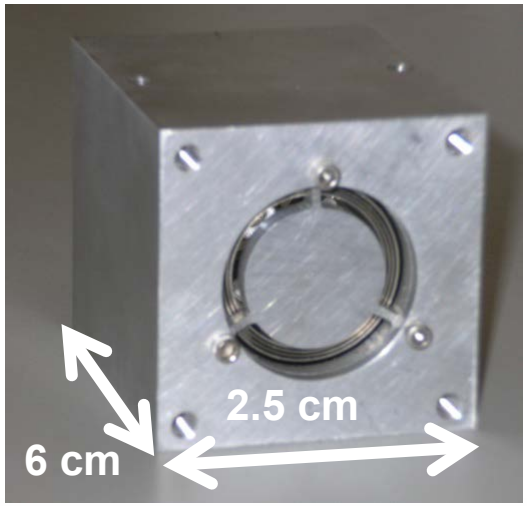
More space for Lens Setup with 60 cm between sample and lens, 2.5 m between lens and detector

Milestone: High resolution MEA water content

First Imaging Test at NIST

Ellipsoid – Hyperboloid for Image Magnification

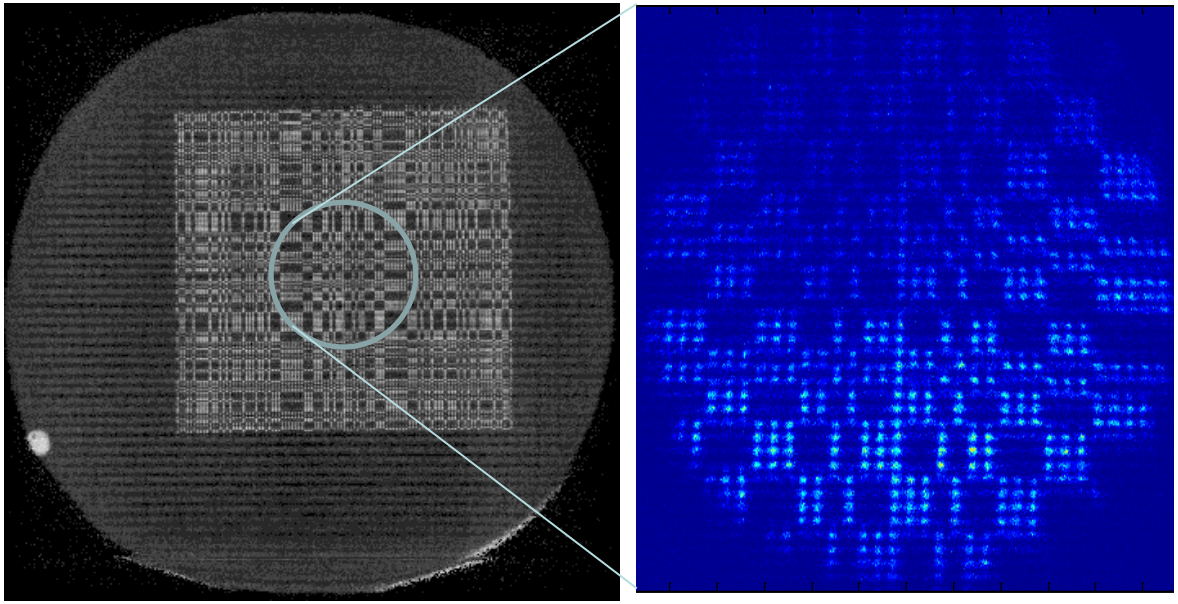


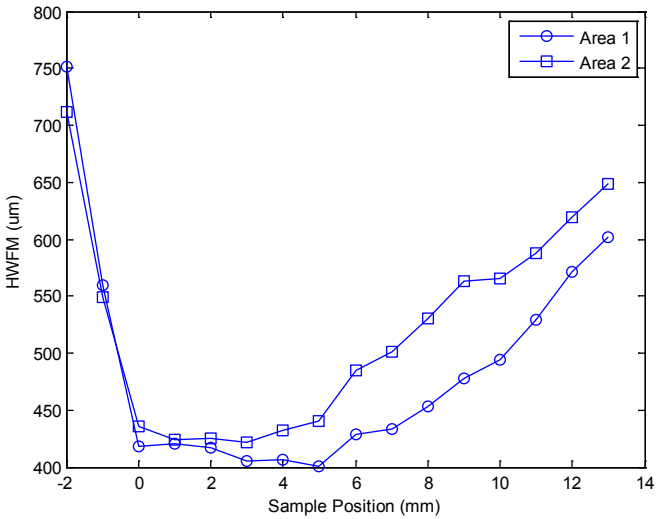


- Prototype lens
- 4 nested Ni mirrors
  - nesting increases flux collection
- Observed Performance:
  - 75 µm spatial resolution
  - 1 cm FOV & 4x magnification
  - 5 mm depth of focus
  - 5x gain in intensity to pinhole

Milestone: High resolution MEA water content

First test results of prototype lens for catalyst/membrane imaging



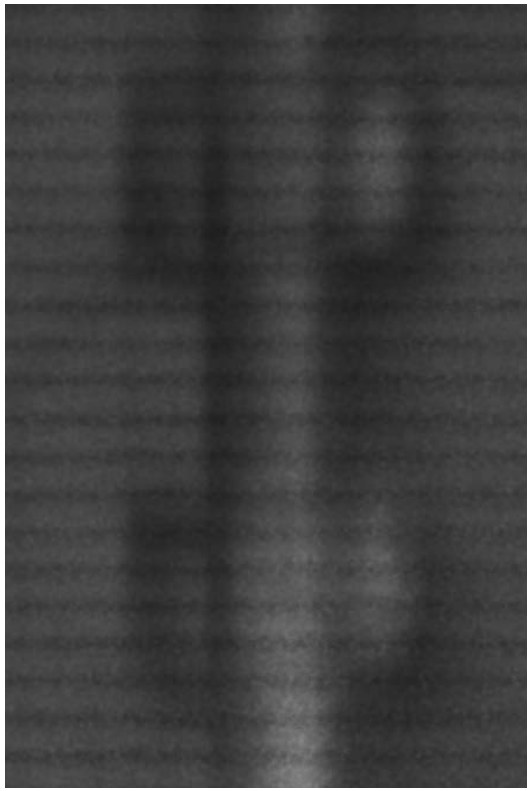


- 2 cm x 2 cm Pinhole mask, with 0.1 mm diameters on 0.2 mm centers
- Left: Contact Image, Right: Lens Image, 4x magnification and 5x more intensity.
- Prototype lens collects only 0.1% of available neutrons. This can be increased to 50 %, thereby increasing intensity from 5x to 2500x.

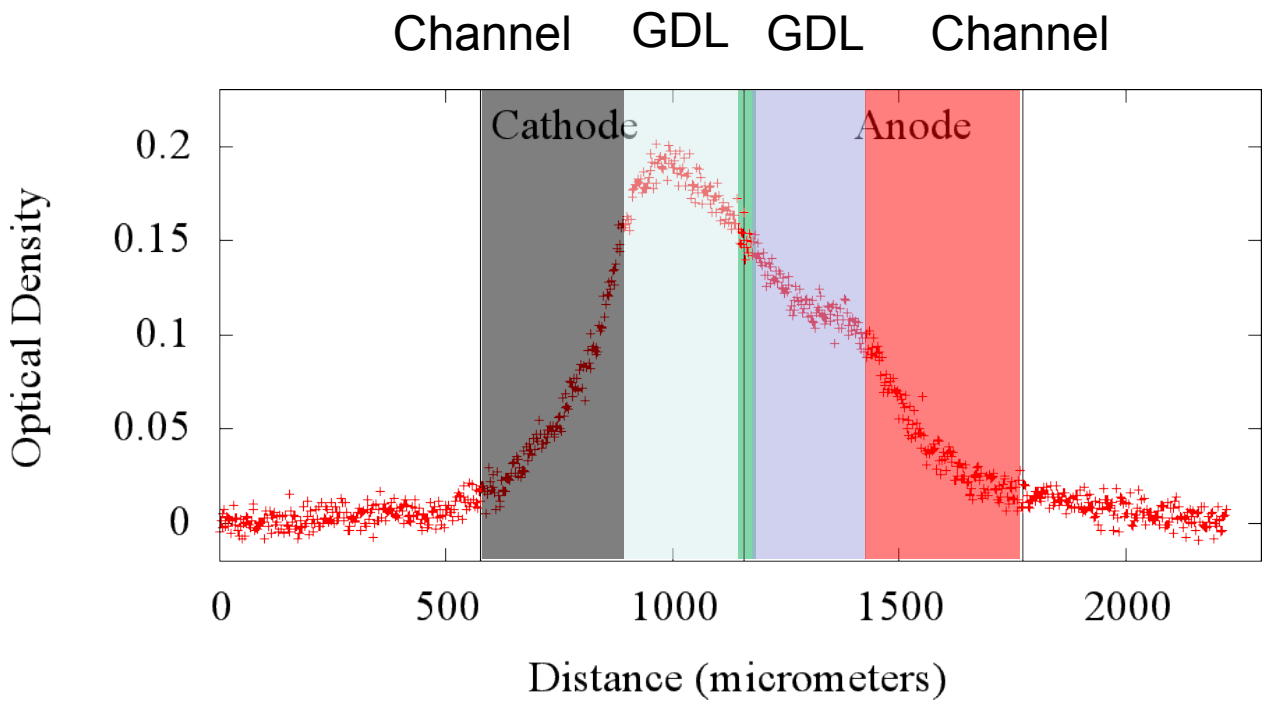
Like an SLR portrait lens, the prototype optic has a finite depth of field of about 5 mm; the fuel cell in total is ~25 mm wide resulting in excessive image blur.

Milestone: High resolution MEA water content

Fuel cell water content at 0.4 V measured with prototype lens



Lens 4x magnified image of a dry fuel cell



Optical density is plotted as calibration experiment was not conducted due to limited time for demonstration experiment

Milestone: Accuracy of water distribution measurement

Accurate measurement of the through-plane water content

- D.S. Hussey, D.L. Jacobson
  - Physical Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
- A.Z. Weber
  - Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
- D. Spernjak, R. Mukundan, J. Fairweather, E.L. Brosha, J. Davey, J.S. Spendelow, R.L. Borup
  - Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

- Journal of Applied Physics, **112**, 104906(2012)
  - http://dx.doi.org/10.1063/1.4767118

Milestone: Accuracy of water distribution measurement

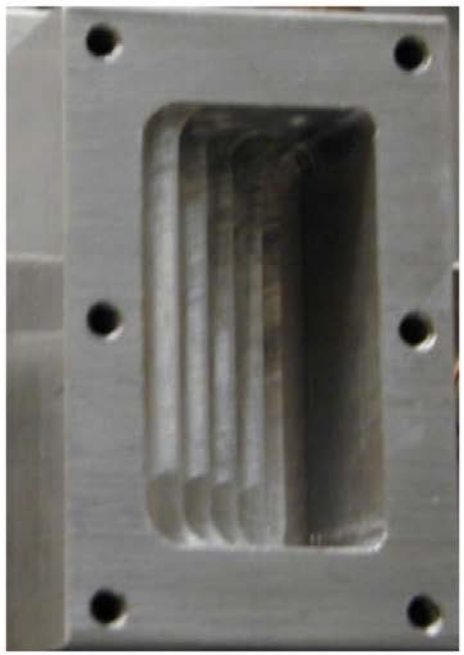
Uncertainties and Accuracy in Membrane Water Content

- Questions about accuracy and uncertainties in water measurements arose motivating a detailed look at measuring water in membranes with neutrons
- Sources of uncertainties and error arising from neutron imaging
  - Reactor neutron distribution center of mass shifting
  - Point spread of detected neutron signal
  - Beam hardening (strongly affected by residual water in membrane)
  - Poisson counting statistics
  - Scattering and refraction of neutrons
- Sources of uncertainty arising from fuel cell membrane
  - Residual water content
    - TGA and Mass Spec employed to measure the residual water in a membrane after a typical dry-out on the neutron beam
  - Membrane swelling
    - Incorporated into the analysis
    - Without correction, overall water content would be reduced
  - In-plane water diffusion under the gaskets
    - Corrected for based on measurement (also estimated based on Fickian diffusion)
  - Spatial resolution effects avoided using thick membranes (10 and 30 mil).
  - Compared sorption data to ex situ DVS water sorption measurements of similar (thick) membranes
  - Compare model and measurement of hydrogen pump operation (thick membranes not suited for fuel cell mode)

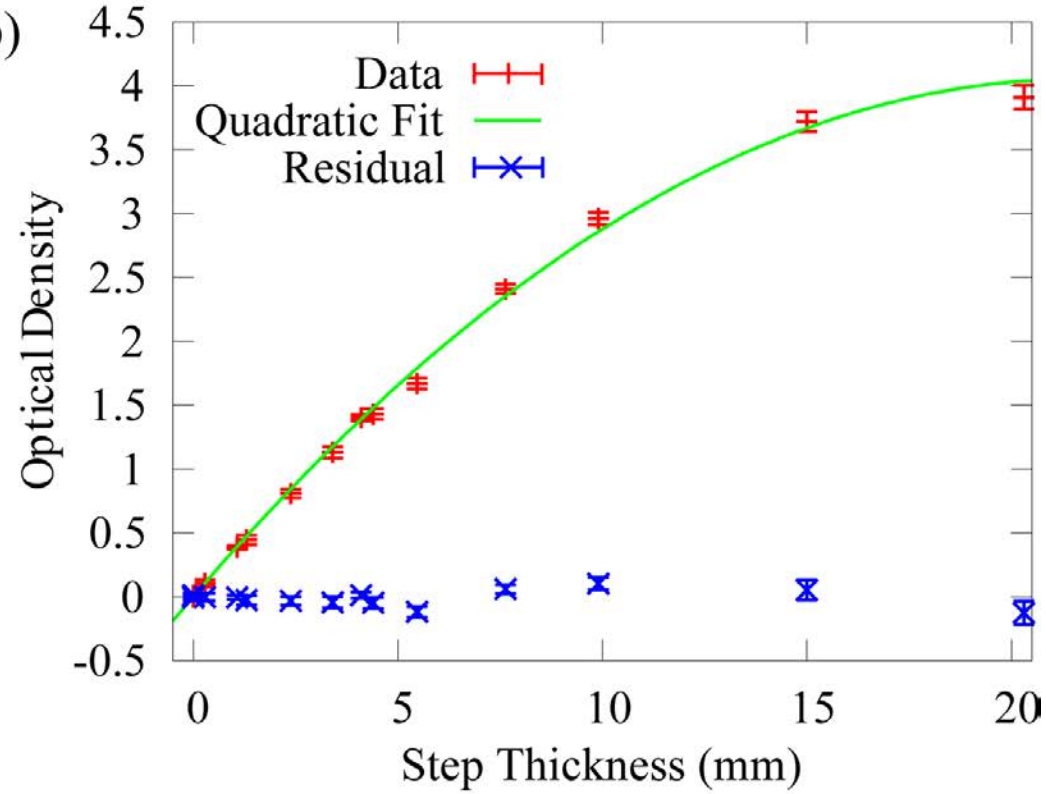
Milestone: Accuracy of water distribution measurement

Calibration and Beam Hardening

(a)



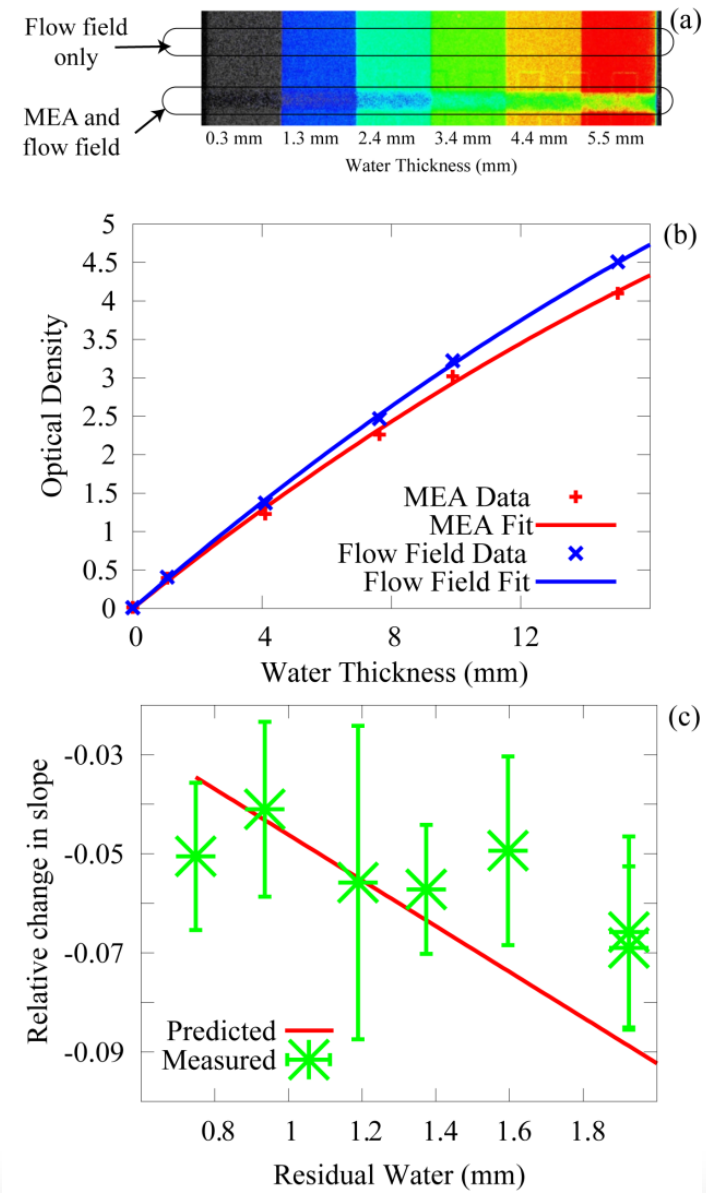
(b)



Milestone: Accuracy of water distribution measurement

Fuel Cell Water Calibration

- Changes to the neutron spectrum result in a change to the water calibration
- Calibration image of wedge with a “dry” membrane shows that the cell has a residual water content that changes the neutron spectrum and therefore the calibration.
- Determining the residual water content is important to correctly calculate the actual water content and distribution.
- Bottom (c) humidity of gas flowing through cell is changed resulting in the residual water content shown and predicted change to the calibration is shown as well.
- **Using this new model, an accurate fuel cell water calibration can be determined.**

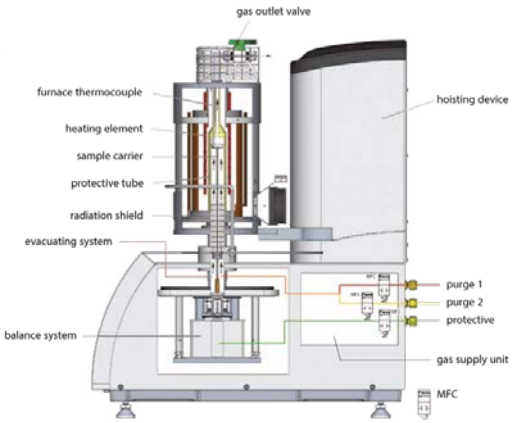


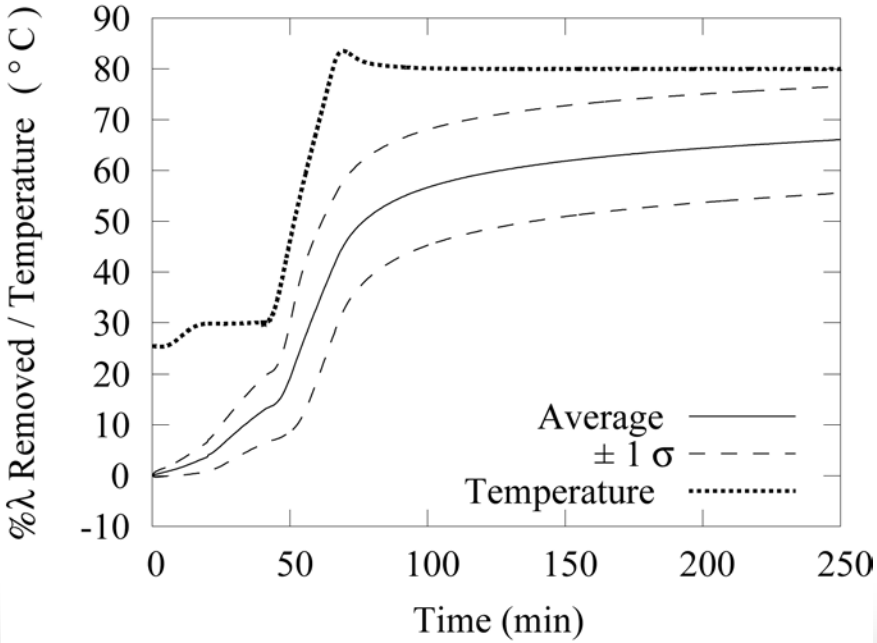
Milestone: Accuracy of water distribution measurement

Residual Water Content Using TGA

- The average water content removed in 8 repeat measurements from Nafion® membranes during a thermogravimetric analysis (TGA) simulating the dry conditions with a dry nitrogen purge used in typical neutron imaging experiments.
- The 1 σ uncertainty is calculated from the standard deviation of the 8 measurements.
- To determine the dry weight of the Nafion, the chamber was subsequently evacuated (70 kPa vacuum pressure) and the temperature raised to 105 °C for 40 h.
- The initial water content varied with environmental temperature and humidity, but was on average:

$$\lambda = (3.64 \pm 0.27)\ mol\,H_2O/mol\,SO_3^-$$





Milestone: Accuracy of water distribution measurement

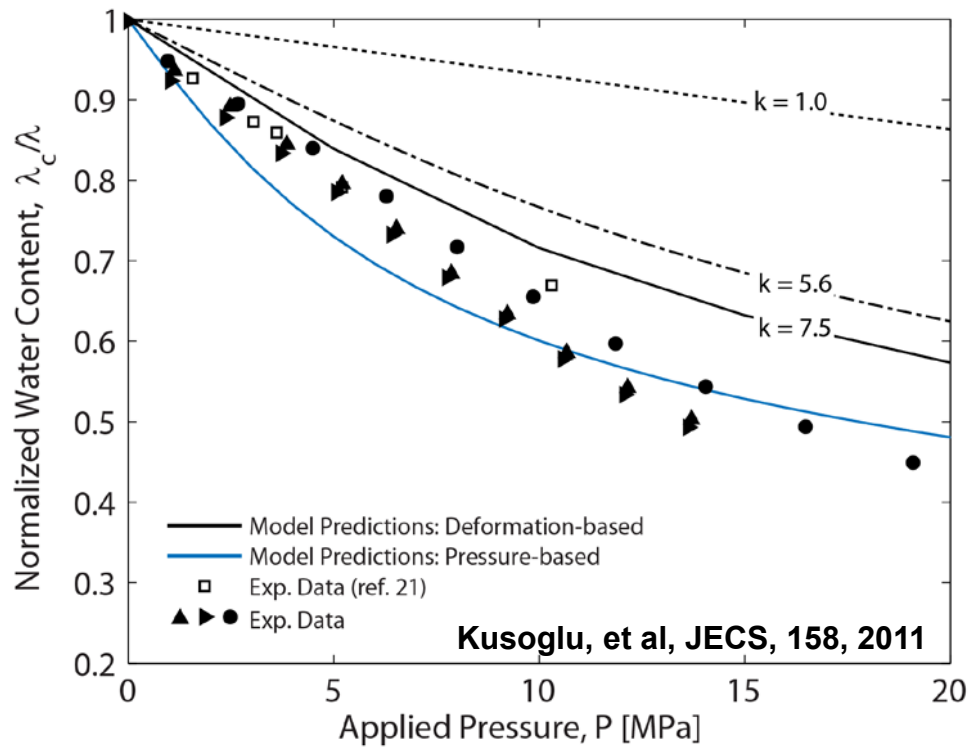
Water in Active Section

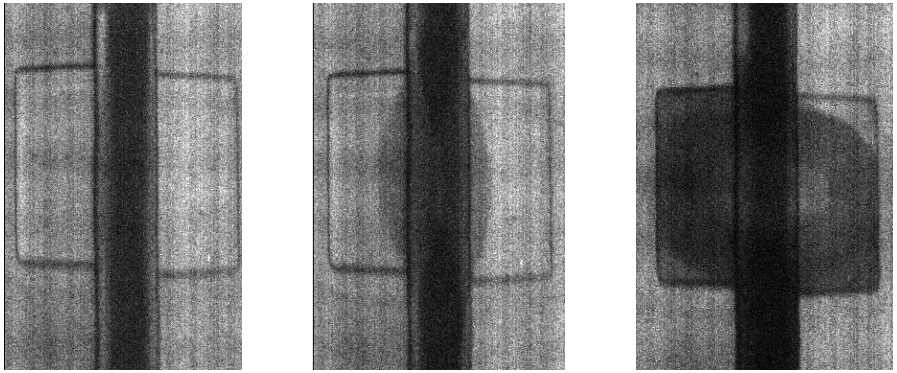
- Based upon TGA, it was determined that the residual water content after drying a Nafion® membrane is reduced by 60 % - 66 % under normal conditions.
- This results in a residual water content of λ = 1.4 mol H_2O/mol SO_3H.
- This was further confirmed using a Netzsch STA-449 TGA with a QMS-403C quadrupole mass spectrometer (QMS) to sample evolved gases.
- Steps:
  - Samples heated to 150 °C in steps of 10 °C min^{-1}.
  - Held isothermal for 7.5 h (sample weight remained constant).
  - Sample ramped to 300 °C at 10 °C min^{-1}.
  - Membrane began decomposing at 220 °C.
  - Water current under decomposition indicated chemically bound water corresponds to $\lambda \approx 1.0$ mol H_2O/mol SO_3H.

Milestone: Accuracy of water distribution measurement

Membrane Swelling

- Nafion® swells as it absorbs water
- Under typical compression in a test sections used at NIST (3 MPa), the membrane state is approximately free-swelling
- If one ignores the swelling in the image analysis, the water content is underestimated as there is less attenuation from the polymer
- One can derive an approximate analytical expression that is quadratic in water thickness (same order as beam hardening) to correct for the swelling



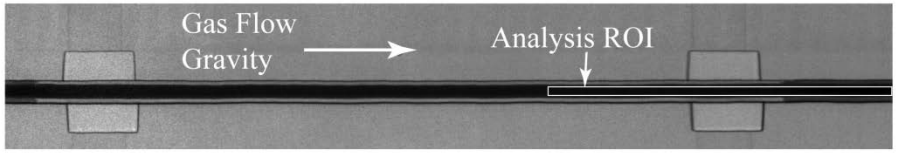


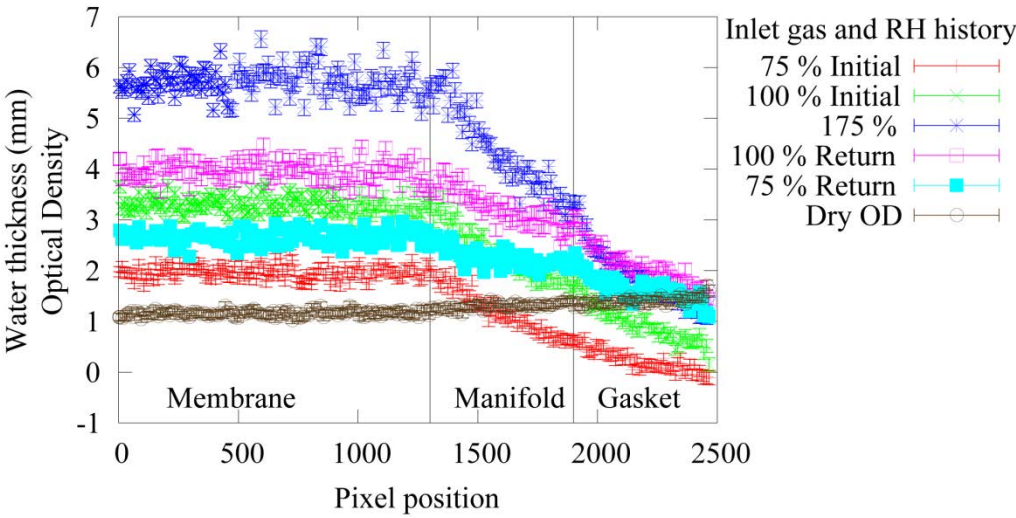
Increasing RH

Milestone: Accuracy of water distribution measurement

Water Under the Gaskets

- Water under gaskets driven by Fickian diffusion
  - Assuming diff. coeff. D_w=1.2x10^{-6} cm^{2}s^{-1}
  - For a saturation λ = 22 mol H_2O/mol SO_3 in the channels to λ = 2 mol H_2O/mol SO_3 in the gaskets results in $\Delta\lambda/\Delta t$ = 1 mol H_2O/mol SO_3 per hour.
- Water content was measured for various starting initial RH values showing water diffusion under gasket region
- Hysteresis was observed when reducing RH from liquid saturation conditions
- Under dry conditions, a reverse gradient is observed from wetter gaskets to dry active section.
- Gasket water content was inferred directly by measurement.

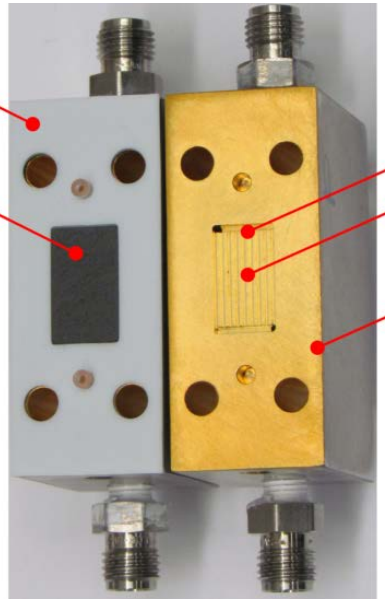




Milestone: Accuracy of water distribution measurement

Sections Tested

- To overcome systematic errors due to spatial resolution, thick Nafion® membranes (Ion Power) were fabricated:
  - Water sorption measurements 178 μm (N117), 203 μm (N1110)
  - Fuel cell and hydrogen pump 1000 μm (N1140)
- In both test sections, a central flat dry region was found where the spatial resolution did not affect the measurement
- Fuel cell flow fields parallel channels 0.635 mm x 0.635 mm with 0.635 mm wide lands machined into aluminum that was then gold plated.
- For sorption measurements, the channels were replaced by metal foam flow fields and compressed to 1.4 MPa to provide uniform support for the membrane.



Milestone: Accuracy of water distribution measurement

Data Processing Steps

1) Background subtract flatfield, dry, and wet images.
2) Average data along the in-plane direction to yield neutron intensity along the through-plane direction, this reduces the bias due to low count data and produces line profiles.
3) Form dry optical density with the flatfield as the reference image (I_0).
4) Use the dry optical density to estimate the dry polymer attenuation in the gasket region, $\Sigma_{PEM}\, t_{PEM}$.
5) Form wet OD with the flatfield as the reference image (I_0).
6) Estimate the residual water content in the gasket away from the active area assuming a λ_{res} corresponding to ambient temperature and humidity.
7) Estimate total water content in the gasket region across the entire cell width via:

$$t_w = -\sqrt{\frac{OD}{B_w} + \frac{A_w^2}{4{B_w}^2}} - \frac{A_w}{2B_w}.$$

$$A_w = \Sigma_w + 2\beta_w t_r - \eta \frac{\bar{V}_m}{\bar{V}_w} \Sigma_{PEM}\, t_{PEM} (1-\chi) L^{-1}$$

$$B_w = \beta_w - \eta \frac{\bar{V}_m}{\bar{V}_w} \Sigma_{PEM}\, t_{PEM} C\, (1-\chi)^2\, L^{-2}$$

Residual Water

Swelling

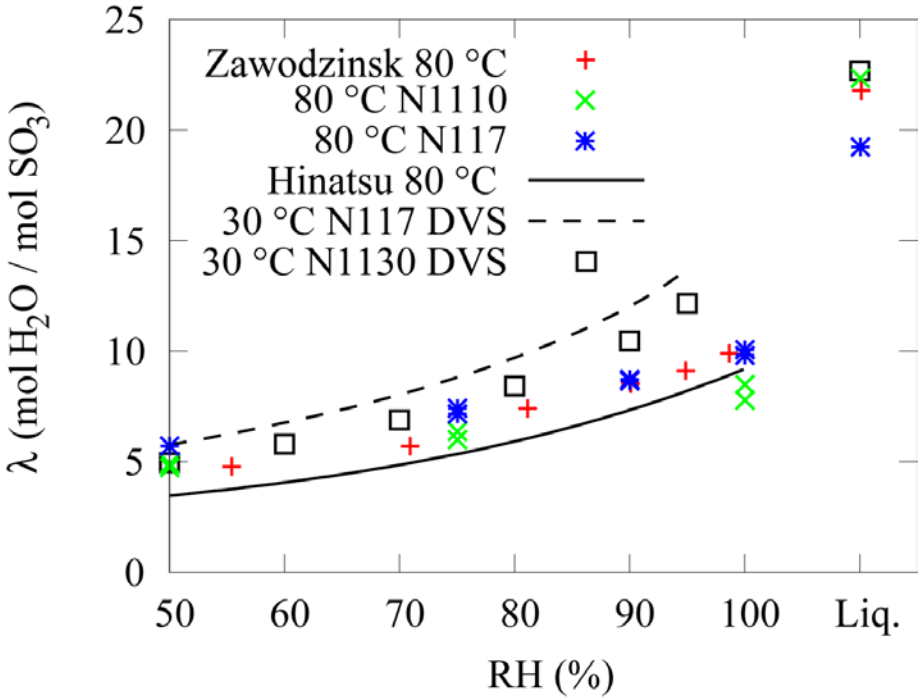
Beam Hardening

8) Estimate the residual water content in the active area assuming a λ_{res} corresponding to ambient temperature and humidity and reduce by the time dried at 80 °C.
9) Estimate total water content in the active area including the surrounding gaskets
10) Calculate the absolute water content in the active area only by subtracting the gasket water (step 7, scaled to the width of gaskets adjacent to the active area) from the water content calculated in step 9.

Milestone: Accuracy of water distribution measurement

Water Sorption Measurement: applying all corrections

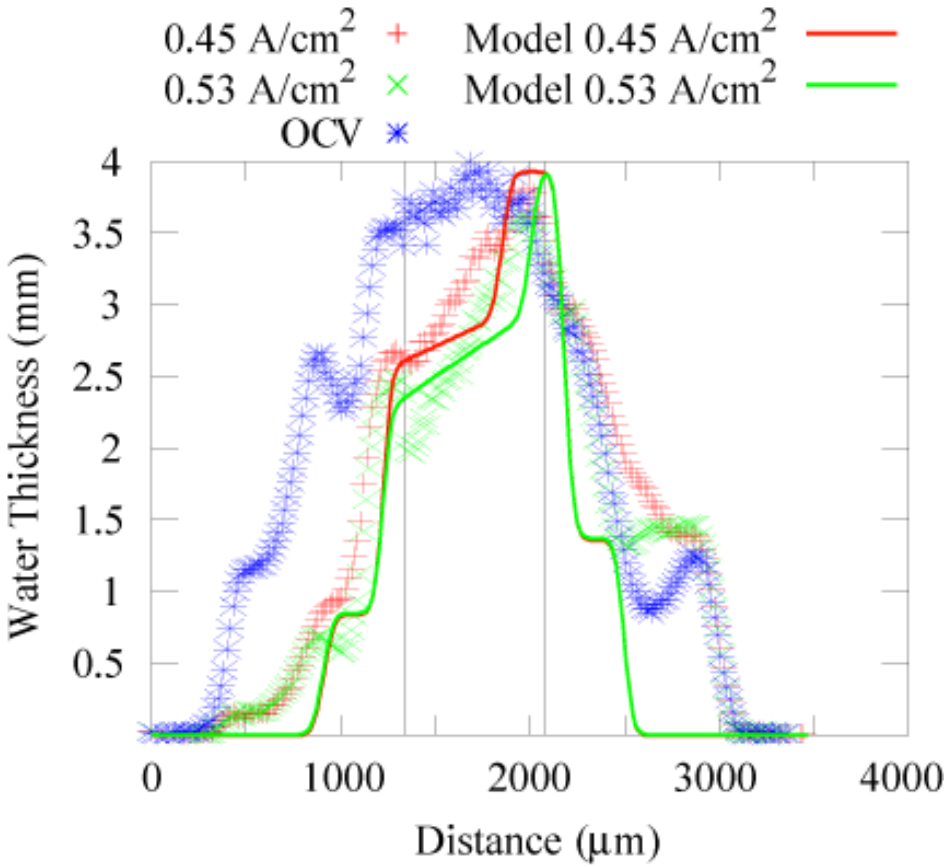
- Neutron measurements were compared with ex situ measurements in a dynamic-vapor-sorption (DVS) apparatus measured near room temperature.
  - DVS RH adjusted between dry to wet in 10 % steps with hold time of 2 h.
  - Dry weights were obtained from drying the membrane at 80 °C.
- Results show good agreement with historic gravimetric measurements.
- Conditions during neutron imaging:
  - Flow 200 sccm (800 sccm) N_2 flows on either side of the test cell for N117 (N1100) case.
  - Humidity was controlled through bubbler-type humidifiers and independently measured with Vaisala HMT338 RH sensors placed at cell outlets.



Milestone: Accuracy of water distribution measurement

Hydrogen Pump Profiles

- Simpler system avoids complications of water production and sluggish oxidation-reduction reaction.
- Model is incomplete due to improper accounting for the mixed liquid vapor content throughout the membrane.
- Current agreement between model and data is 10%, which improves over previous report by Hickner and Weber of a factor of 4 difference between model and data.
- N1140 membrane, 6 mg/cm^2 Pt-black catalysts anode and cathode with Nafion® binder.
- Operating conditions:
  - 300 sccm H_2 was fed to both sides and over-humidified to 175 % RH with 71 kPa outlet pressure.



Conclusions

- **Large area, high resolution detectors for fuel cells**
  - Large field of view 10 cm x 10 cm
  - Spatial resolution 20 microns
  - Image flow fields and manifolds with high spatial resolution
- **High resolution MEA water content**
  - Steady progress made towards grating method
  - Demonstrated prototype neutron microscope to image catalyst/membrane layers
- **Accuracy of water distribution measurement**
  - Earlier measurements did not correct for the systematic uncertainties examined here, which likely resulted in the observed severe underestimation of experimentally observed water content.
  - Current modeling results show that the modeling and experiment are converging when proper accounting is made of all sources of systematic error.
  - Overall uncertainty in λ is ±1.0 mol H_2O/mol SO_3H and is dominated by the systematic effects in the membrane.
- **Through-plane freeze measurement**
  - New environmental enclosure fabricated and ready for fuel cell testing.

Future Fuel Cell Imaging Research Directions

- Develop measurement technique to image catalyst degradation mechanisms due to carbon corrosion and freeze thaw with neutrons.
- Incorporate systematic corrections to MEA water content measurements into the NIST analysis software in a user friendly way.
- Provide a NIST set of high resolution testing hardware to ensure user testing compatibility with beam line setup.
- To study catalysts, we will continue to improve the image spatial resolution with a goal of 1 μm.
  - Deploy grating based structured illumination method to user program.
  - Develop neutron lens to achieve higher spatial and time resolution.
- Provide support for automotive-sized fuel cell hardware testing.
- Support imaging larger cells using large area detectors that maintain high spatial resolution.

Acknowledgements

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