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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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 FY16 :	$ 300 k
DOE FY17 Planned :	$ 300 k
Total Received:	**$ 600 k**

Other Project funding FY16

NIST :	$1,200 k
Industry:	$ 50 k

Barriers

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

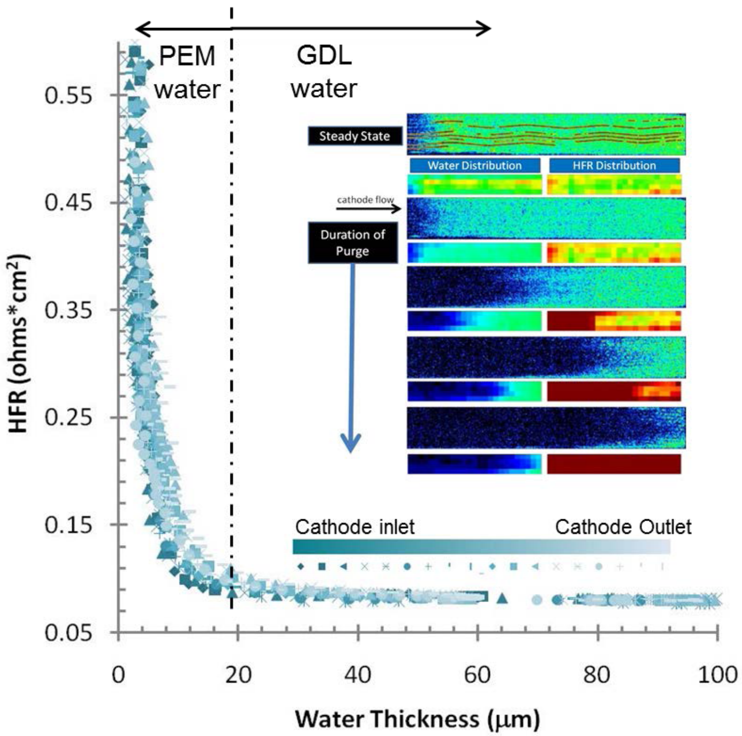
Partners/Users/Collaborators

Project Lead: National Institute of Standards and Technology

- General Motors
- Honda
- HySA Infrastructure
- NASA, MSFC
- Lawrence Berkeley National Laboratory
- Los Alamos National Laboratory
- NECSA
- Oak Ridge National Laboratory
- Sensor Sciences
- Toyota
- Colorado School of Mines
- Massachusetts Institute of Technology
- Pusan National University
- Rochester Institute of Technology
- University of California, Merced
- University of Connecticut
- University of Hawaii
- University of Michigan
- University of Tennessee
- University of Toronto

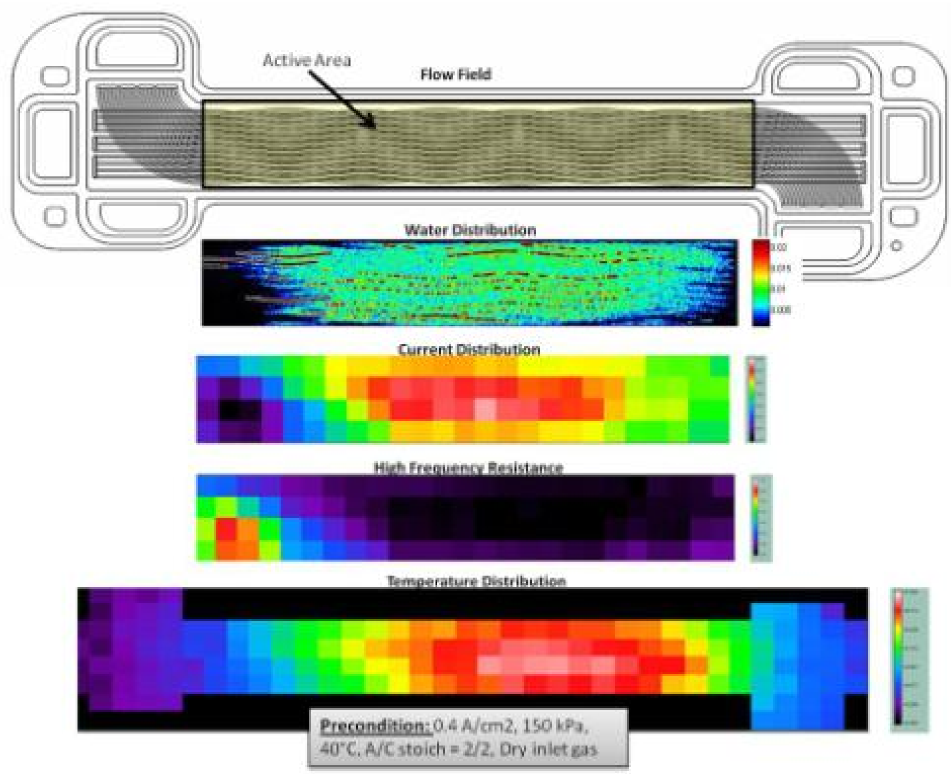
Relevance

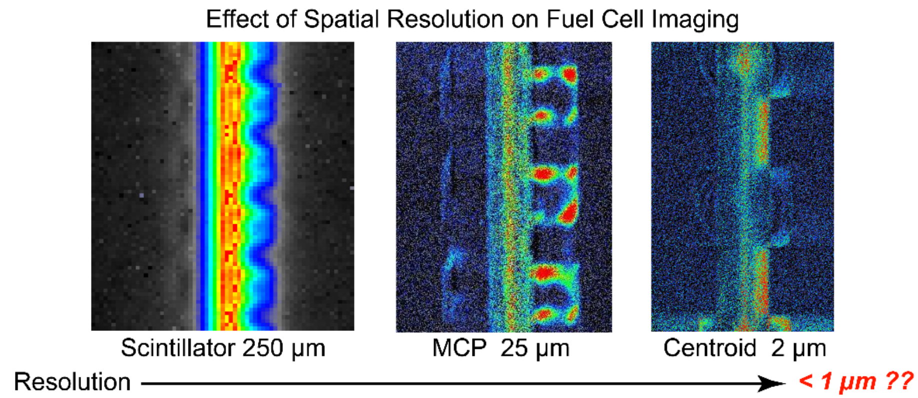
- Neutron imaging is the most powerful and sensitive method to *non-destructively* image water in the fuel cell *in operando* as neutrons readily penetrate common fuel cell hardware yet accurately measure small volumes of liquid water
- This enables one to develop a complete picture of the heat and mass 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

As an example of the method, the data shown below include water content, current and temperature distribution, and HFR measured simultaneously by General Motors at NIST.

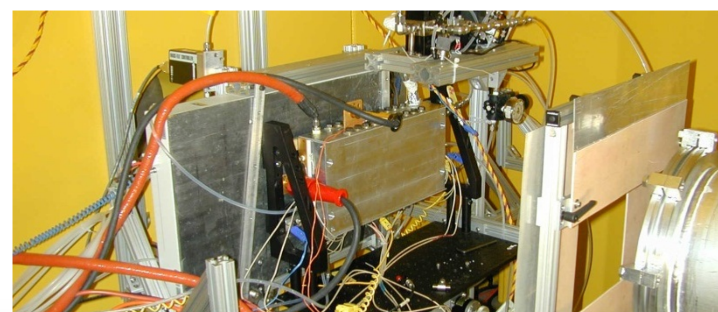




- Extend this capability to the catalyst layer by engaging in a continuous effort to enhance the image spatial resolution
- Improve image analysis to correct systematic effects and ensure accurate water content measurements
- Make state-of-the-art detectors, methods, and analysis available to the fuel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

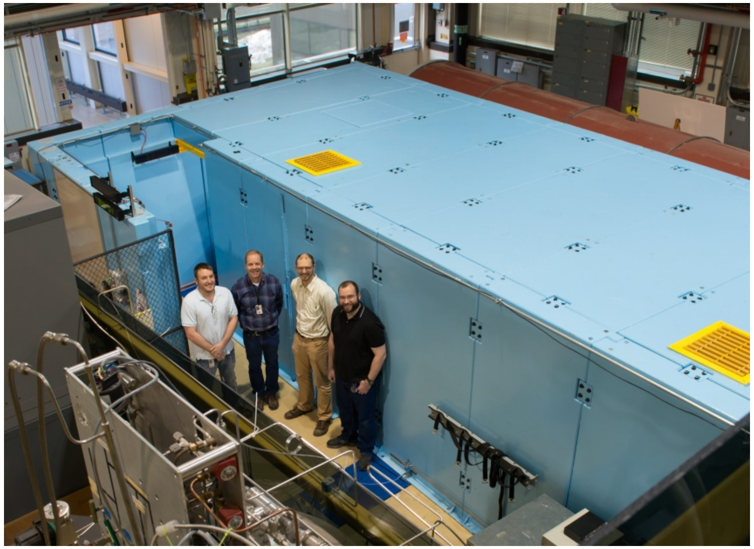
Approach

- 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

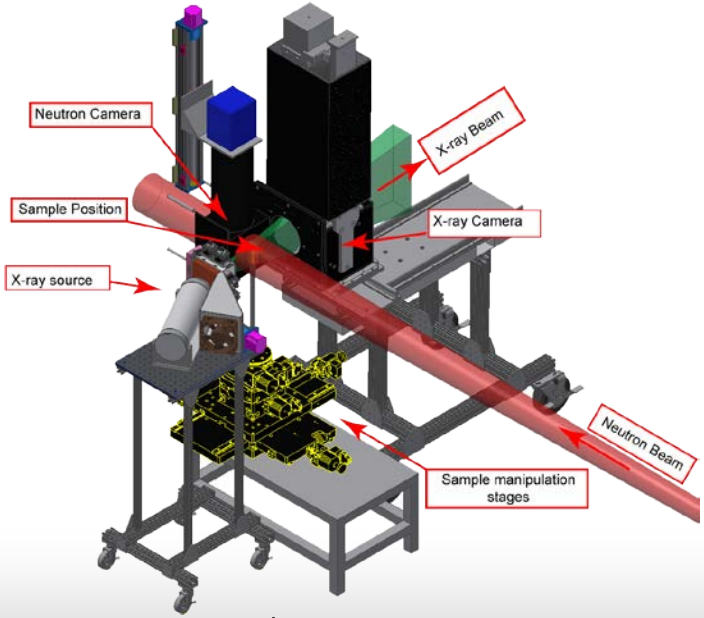


Milestones

- Cold Imaging Facility Developments – 100%
  - Tested Engineering unit for 1:1 Neutron Microscope Lens (JUL 2016)
  - Installed Hydrogen Gas supply (JUL 2016)
  - Ice / water contrast (APR 2017)
- Methods to improve image spatial resolution – Ongoing
  - Slit Imaging with 2 μm resolution, 18 h image acquisition time (SEP 2016)
  - Scintillation light centroiding with 2 μm resolution, 2 h image exposure time (DEC 2016)
  - Neutron microscope project is receiving development support from NIST; delayed due to unexpected production delays at NASA, expect:
    - 20 μm spatial resolution, 10 s time resolution available 2020
    - 1 μm spatial resolution, 10 min time resolution available 2021
- Complementary x-ray imaging system – 100%
  - Acquired first simultaneous dual x-ray / neutron tomogram of operating fuel cell
- User program – Ongoing – 100% complete in 2016
  - 6 new fuel cell proposals from last call for proposals
  - 20 % of open beamtime allocated to Fuel Cell and hydrogen storage experiments
  - Centroid imaging investigating Ionomer/Carbon ratios with LANL (FEB 2017)
  - Comparison of slit and centroid imaging (RIT and GM MAY 2017)
  - Planned experiments investigating electrolysis, SOFC, AEFC, and PEM contaminants to be conducted in summer 2017

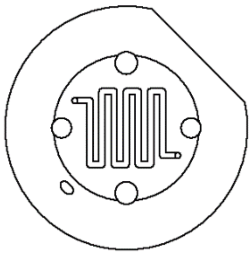


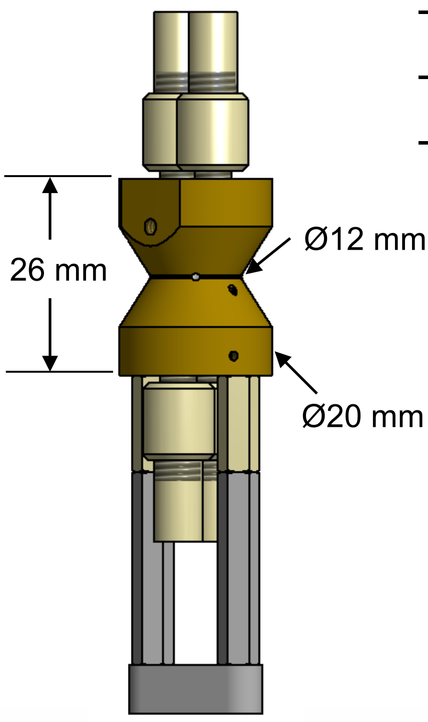
NIST Cold Neutron Imaging Instrument.



Dual x-ray/neutron tomography

Accomplishment: Simultaneous x-ray neutron tomography



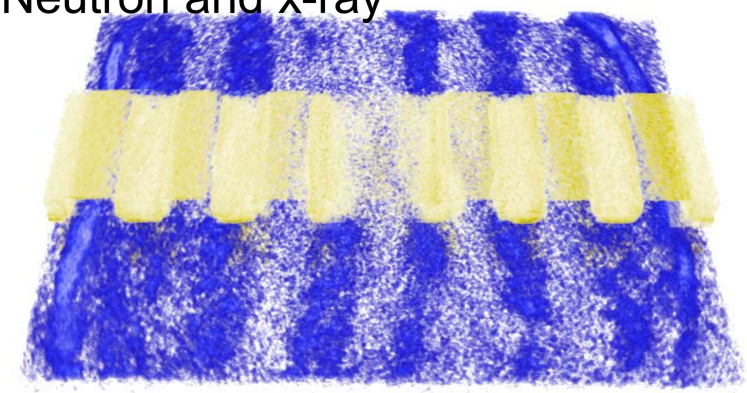


Test Conditions:

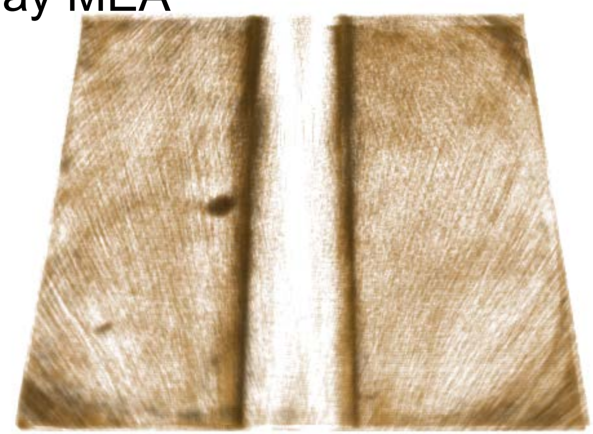
- 0.36 cm^2 active area
- Ambient temperature
- 200 sccm both sides
- 150 kPa$_a$ exhaust pressure
- Dew point set to 25°C
- 18 h scan time
- 200 mV shown (1.9 A cm^{-2})

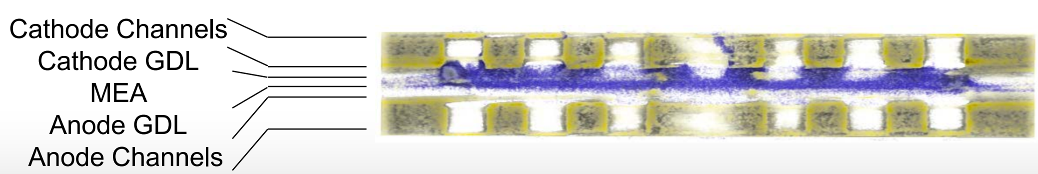
Technique shows promise in identifying interfaces in water transport issues.

Neutron and x-ray



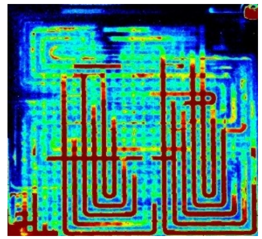
X-ray MEA



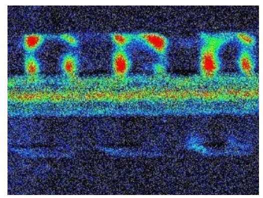


Spatial Resolution Development Timeline

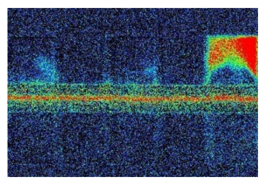
2001: 250 µm



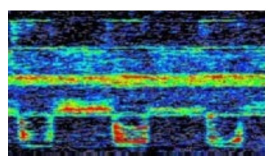
2006: 25 µm



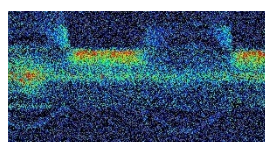
2009: 10 µm



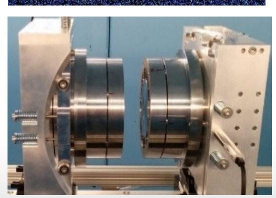
2016: 4 µm w/ slits



2017: 2 µm w/ slits and centroiding

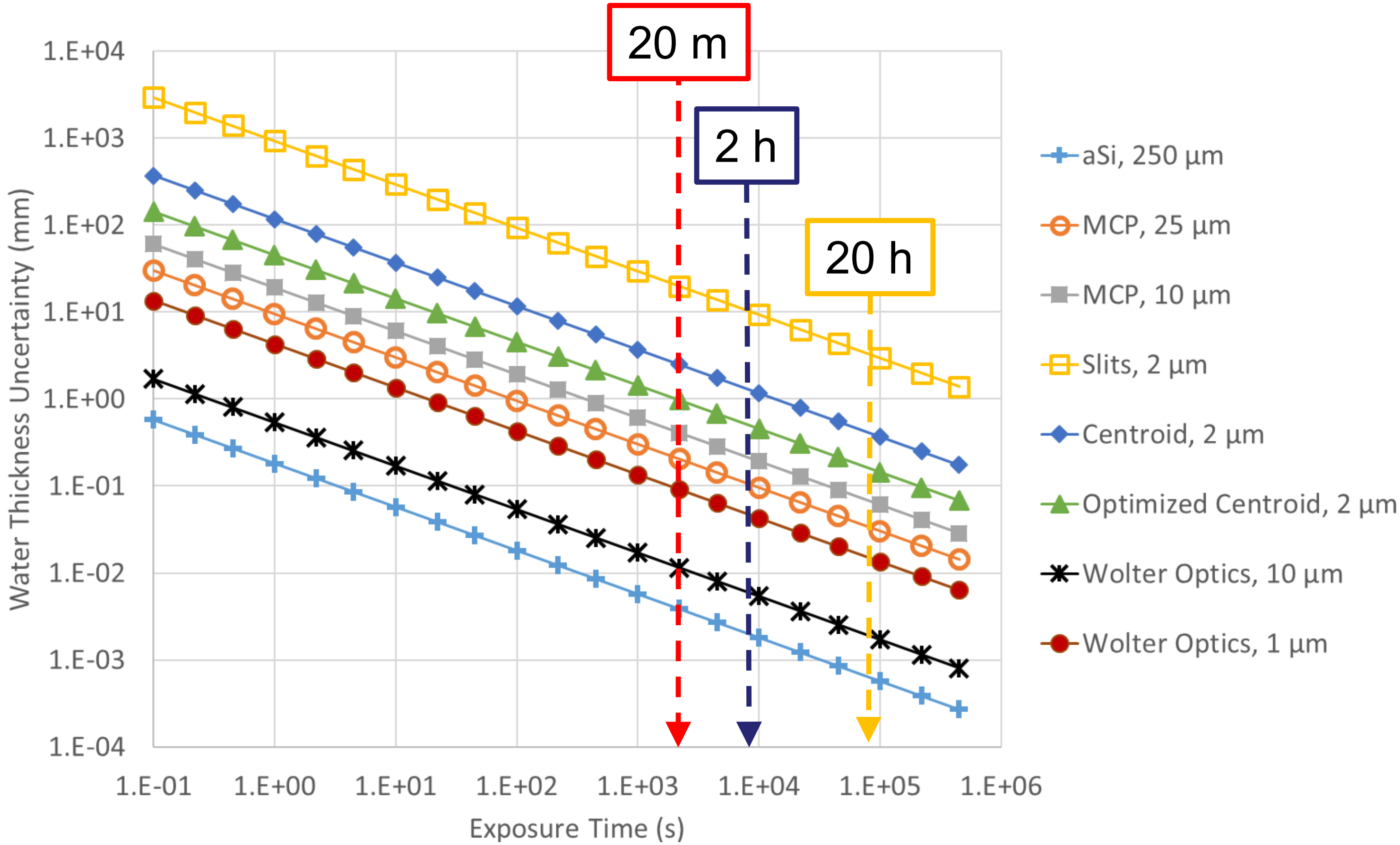


2021: 1 µm w/ Wolter Optics



- 250 µm **(1-30 Hz frame rate)**: In-plane studies of total water content and manifold.
- 25 µm (**20 minute**): Through plane water distribution to begin GDL transport studies.
- 10 µm (**20 minute**): More accurate measurement of diffusion media as well as temperature driven phase change flow and thermal osmosis, studies of PGM-free catalyst layers.
- ***To resolve water in state of the art MEAs, need resolution of 1 µm ... at the very least***
- 2 µm (**2 – 20 hours respectively**): Recent work on centroiding & slits improves resolution but these require long exposure times.
- **Goal 1 µm (20 min):** A neutron lens (Wolter optics) is under development which will improve ***both*** spatial and time resolution.

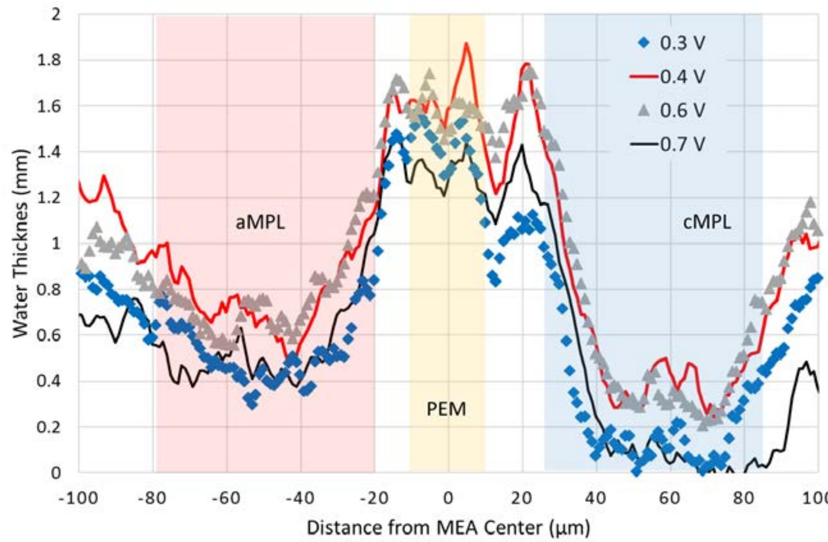
Liquid water uncertainty for various methods/detectors

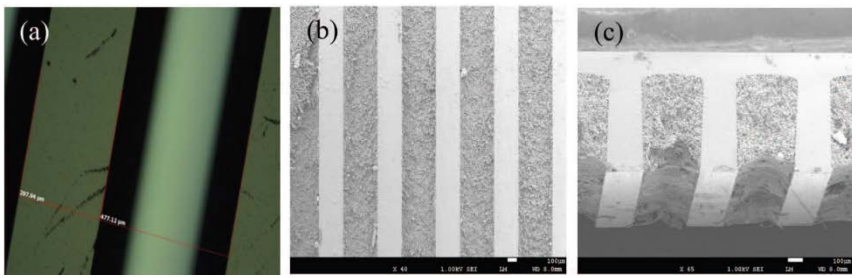


- The exposure time includes dead time, for instance the time to scan a slit
- To reduce exposure time, one can also average over many pixels in the in-plane direction to reduce the water thickness uncertainty in the through-plane direction

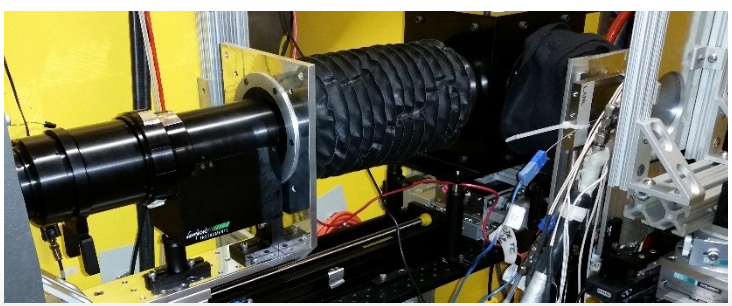
Accomplishment: Slit Imaging, 2 μm Spatial Resolution

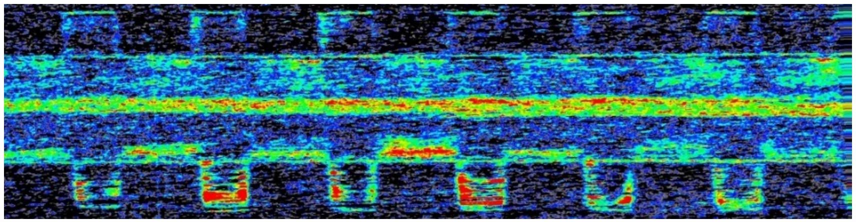
- Align two absorbing gratings with period 350 μm and 40% duty cycle to create a 1 μm wide opening
- Scan assembly across active area of fuel cell
- Stitch image intensity together to create high resolution image in one direction
- 3 min/slit position, 350 positions, 20 h acquisition
- Operate a differential cell in constant voltage mode to avoid possibly reversing the cell



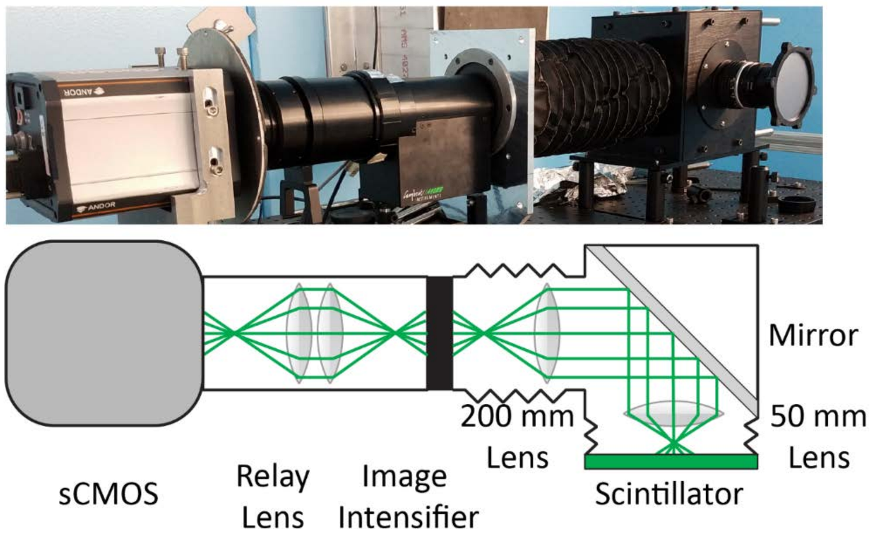


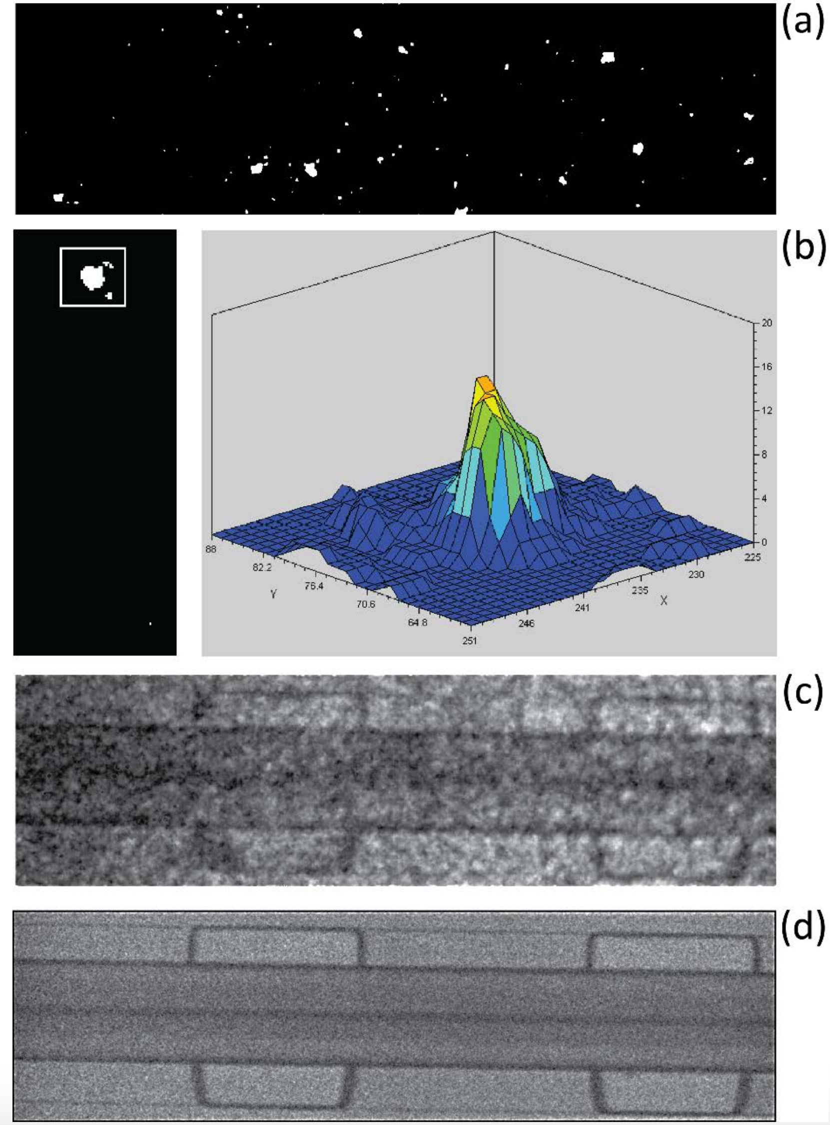
- MEA: Gore 5730, 0.14/0.4 mg Pt/ cm^2 a/c, SGL 25BC with MPL a/c
- Operating Conditions: 60ºC, 80% RH, 0.1/0.2 slpm a/c, 175 kPa outlet





Accomplishment: Centroid Imaging, 2 μm Spatial Resolution



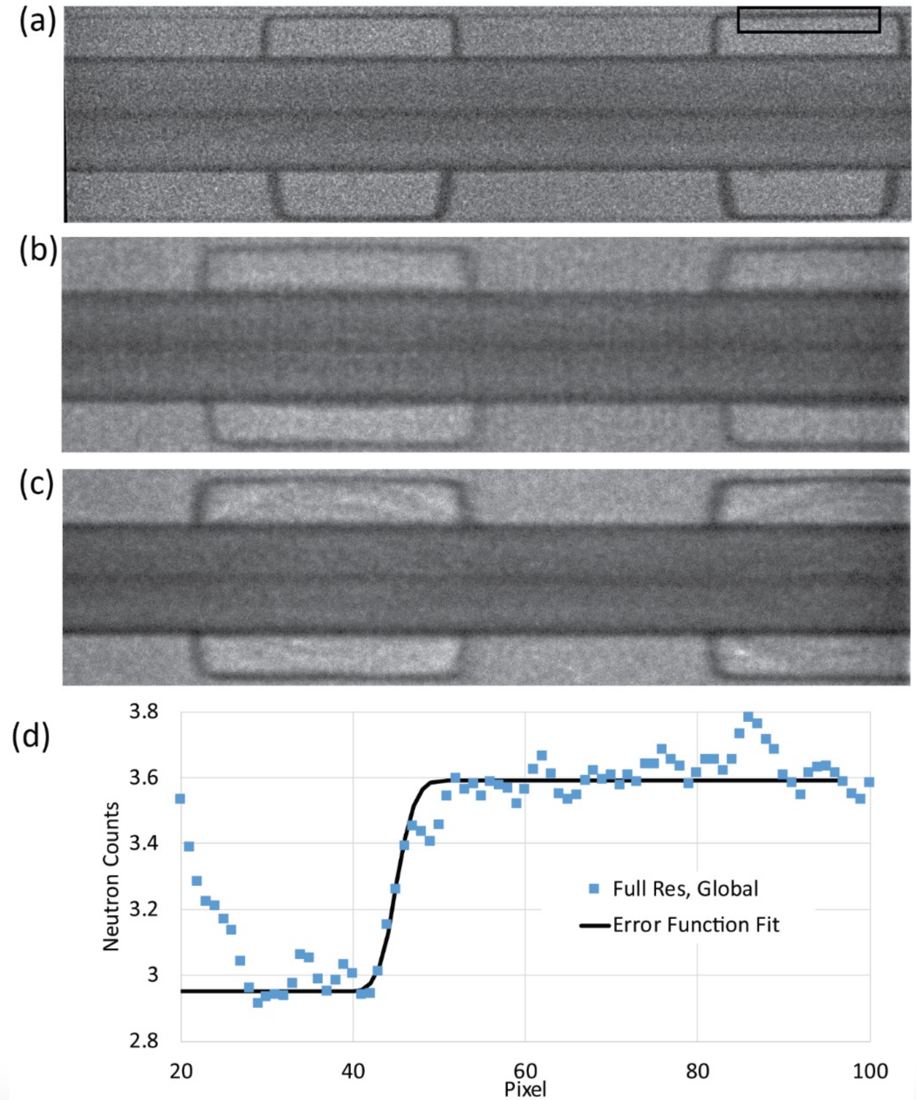


a) Capture Frames with short exposure times (3 ms) to see individual neutron capture events
b) Close up of a typical scintillation light bloom
c) Sum of 3000 frames after thresholding only
d) Sum of 80k frames and centroiding

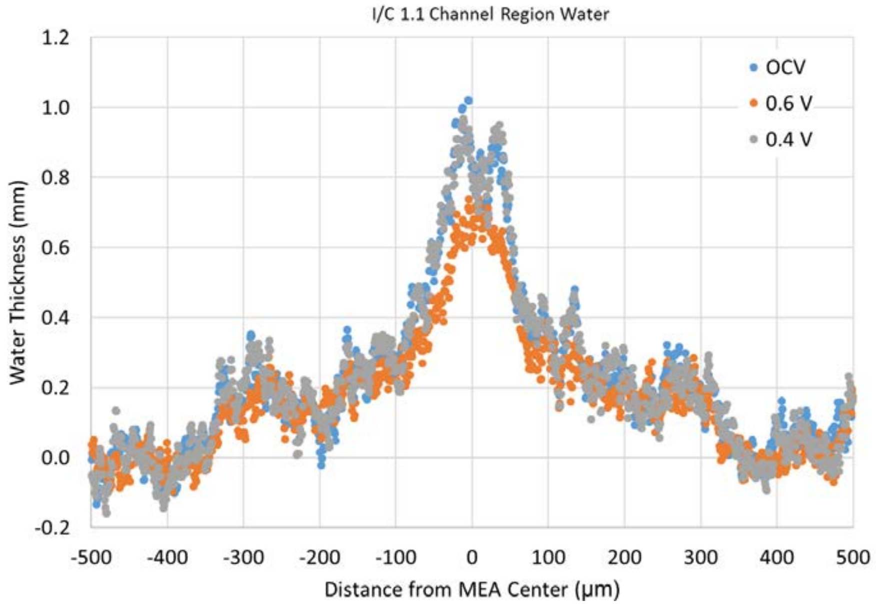
Accomplishment: Centroid Acquisition Time Improvements

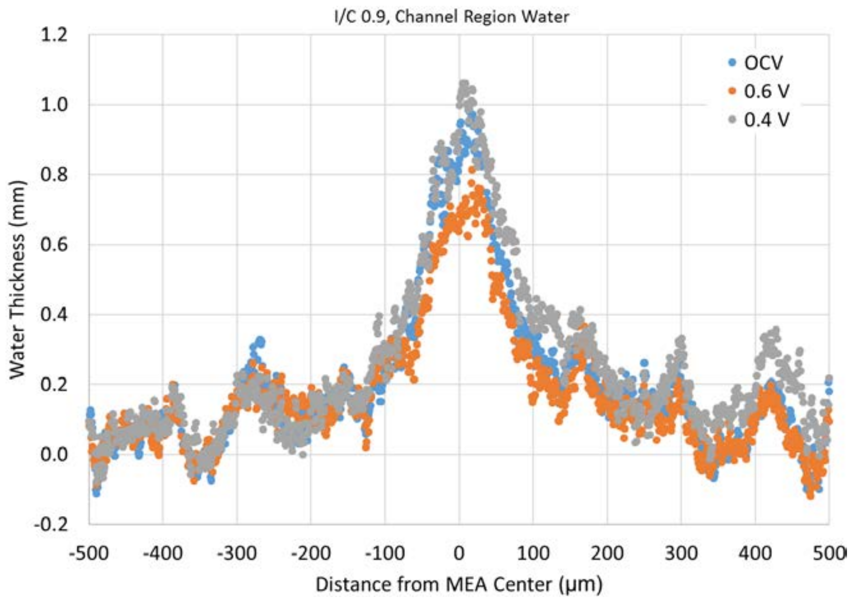
a) No binning, Global Shutter, 80k frames, 10 FPS, MAR 2016
b) 2x2 Binning, Global Shutter, 400k frames, 30 FPS, FEB 2017
c) 2x2 Binning, Rolling Shutter, 400k frames, 70 FPS, FEB 2017
d) Vertical line profile in ROI indicated in (a) with a fit yielding a spatial resolution (10% MTF) of 2 μm

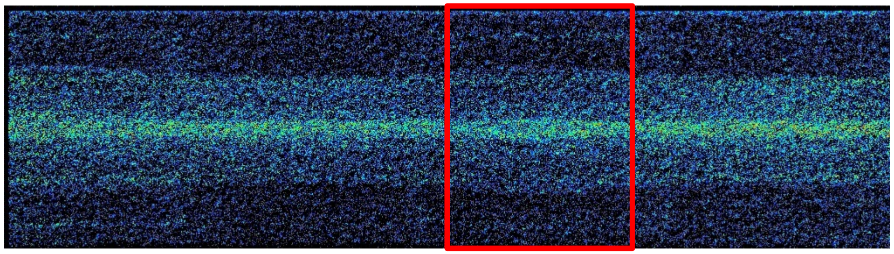
- Each frame exposure time is 3 ms
- At 70 fps, 400k is ~2 h acquisition
- 400k frames is effectively a 20 min exposure time vs. 3 min for slits
  - ***For same total exposure time, centroid imaging has 10x high measurement precision of water content compared to slit method***

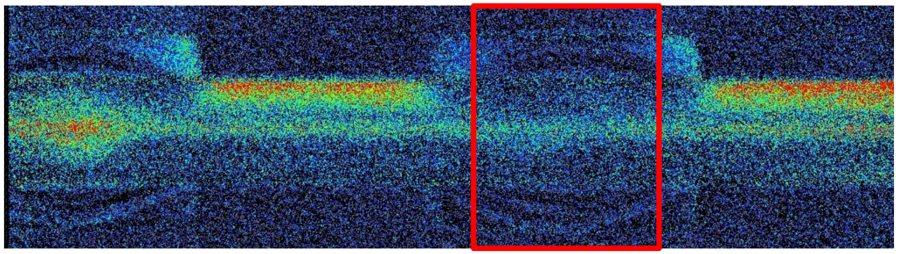


Accomplishment: MEA Water Imaging, 2 µm Spatial Resolution





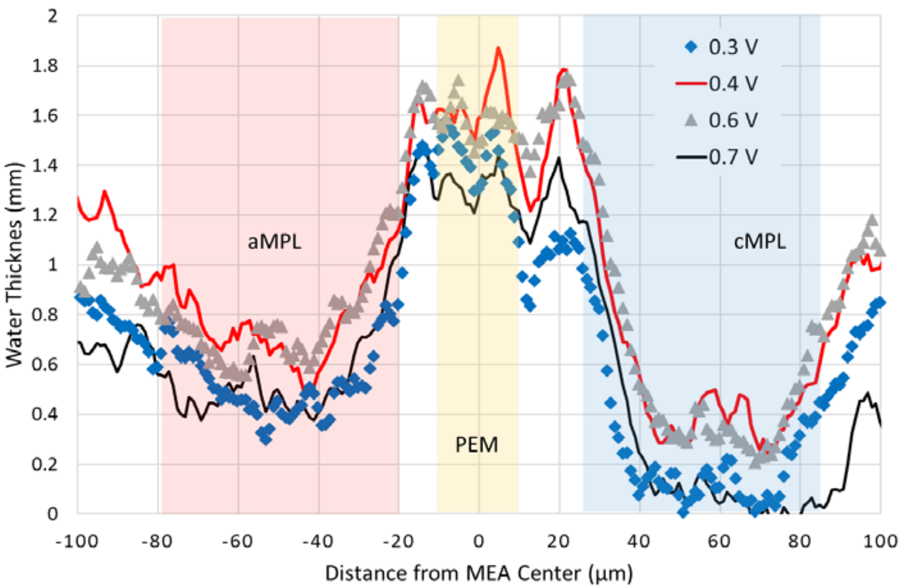




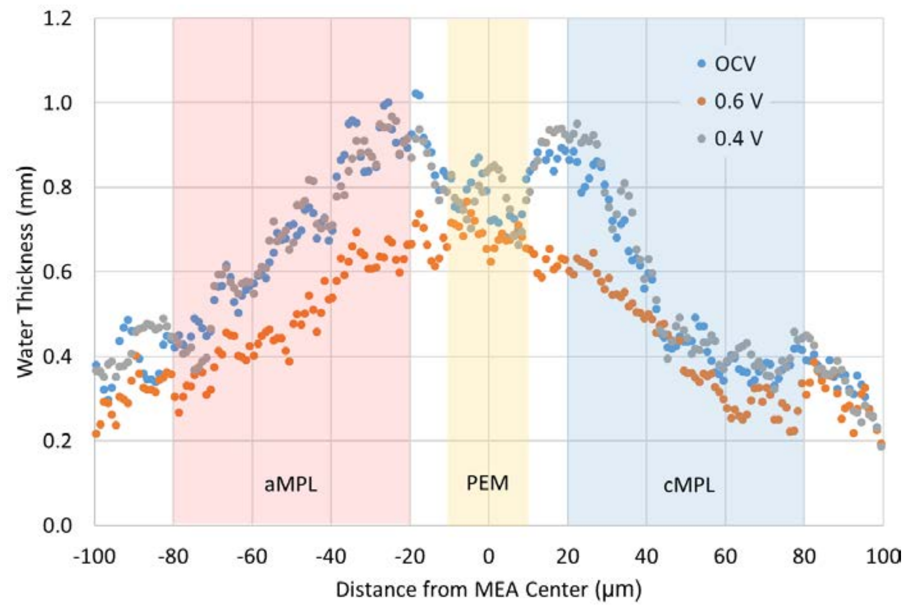
Water content comparison for two different Ionomer/Carbon ratio catalysts, 80ºC
Constant Voltage operation, OCV, 0.4 V 100% RH, 0.6 V 75% RH
Images at 0.4 V with Cathode on Top; Plots cathode positive distance from MEA center

Collaboration: Slit vs. Centroiding Water Content

Slit Imaging, 2 µm, 60ºC



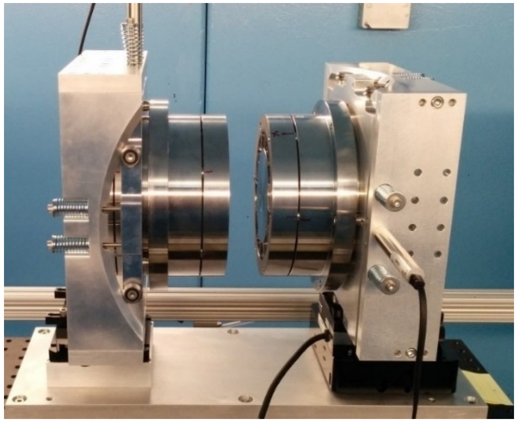
Centroid Imaging, 80ºC, I/C 1.1

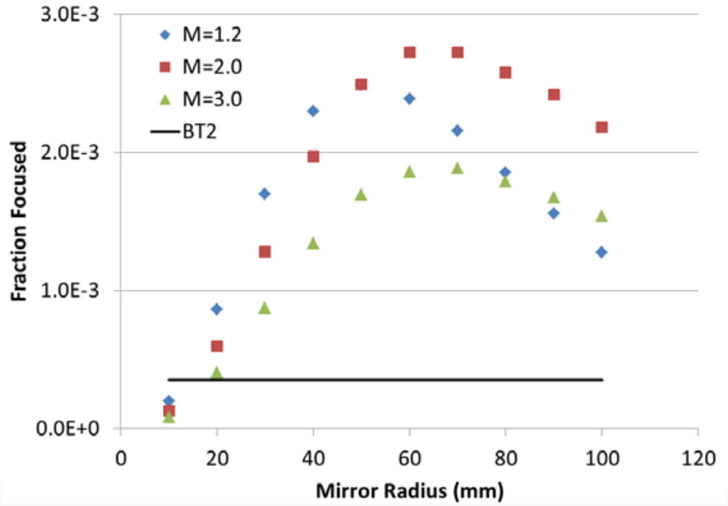


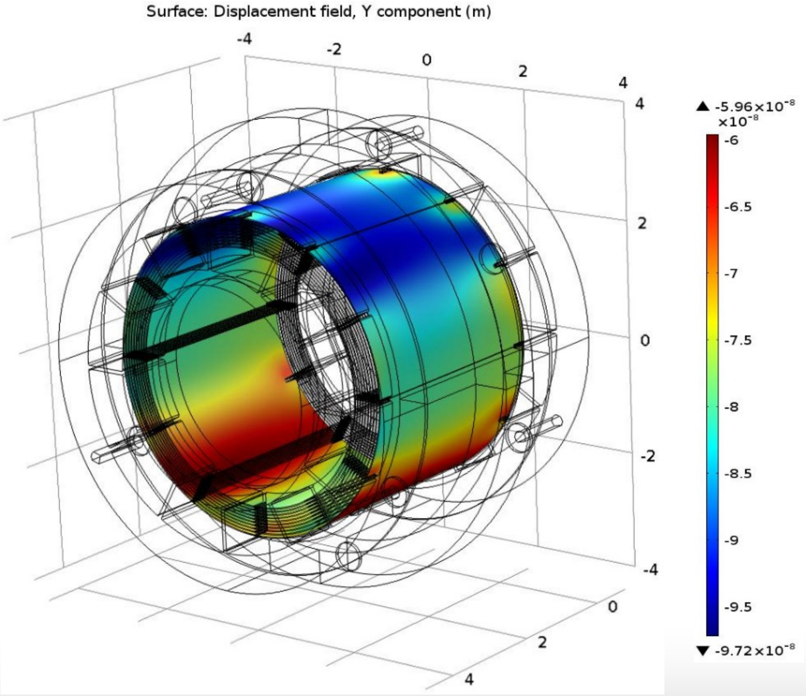
- Not exactly a fair comparison due to different operating temperatures and conditions
- Plan to conduct a direct comparison with LANL, GM, RIT in May 2017

Accomplishment: 1:1 Optic Test and Design

- Test engineering optic JUL 16, verifying good figure, surface roughness to be improved with differential deposition
- 10 mirrors, 70x faster than BT2 (1 s vs. 120 s)
- More shells, higher M-guides increase intensity
- Gravity causes ~80 nm sag of mirrors, contributes 0.1 arcsec to resolution (10%)
- Mandrel fabrication for 9 remaining shells to begin SEP 17







Future Work

- Centroiding
  - Pursue detector package optimization that reduces light losses and incorporates hardware based centroiding to:
    - Reduce deadtime to near zero
    - Provide images in real time
  - Fabricate planar test section
- Fuel cell testing infrastructure at cold neutron imaging
  - Model hydrogen release for facility safety analysis
  - Install hydrogen infrastructure at cold imaging facility to support fuel cell experiments
  - Identify test stand for use at the new facility
- Neutron microscope
  - Work with NASA and collaborators to fabricate 1:1 optic
  - Develop prescription for 1 μm resolution lens
- Last Call For Proposals: 6 new fuel cell related proposals

- Any proposed future work is subject to change based on funding levels

Response to 2016 Reviewers' Comments

- The experiments that researchers wanted at the existing resolution have slowed down before higher resolution can be developed … There will still be a wait until 1 μm resolution can be obtained. In the meantime, fuel cell technology has advanced to a place where 1 μm resolution is necessary to extract information about catalyst layer performance and durability.
  - *Response: We have demonstrated the ability to obtain images with 2 μm spatial resolution of the water content in an operating fuel cell and this capability is available to facility users*

- User work seems to be down this year. While the focus on future work is important, the current capabilities of the facility seem to be underutilized.
  - *Response: With the recently improved spatial resolution, there is renewed interest.*

- The project is dependent on others for experiments and guidance
  - *Response: We believe this is important in order to provide the most relevant research capabilities to the fuel cell community.*

Summary

- We have made excellent progress towards measuring liquid saturation values in the catalyst and membrane
  - Slit scanning
    - 2 μm resolution demonstrated slit (1 μm slit size), Acquisition time is 20 h
  - Centroiding 2 micron resolution demonstrated
    - Method has been improved using available resources
    - Available through the user program
    - Future: develop hardware based centroiding to
      - Improve throughput by reducing acquisition time from 2 h current to 20 m
      - Allow real time image reconstruction versus current 1.5 day post acquisition reconstruction time per image.
  - Wolter optics
    - NIST will design and fabricate mechanical lens fixtures for beam line
- 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
  - User proposals has increased due to interest in new spatial resolution
  - 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

Acknowledgements

Special Thanks to

Nancy L. Garland

DOE Technology Manager

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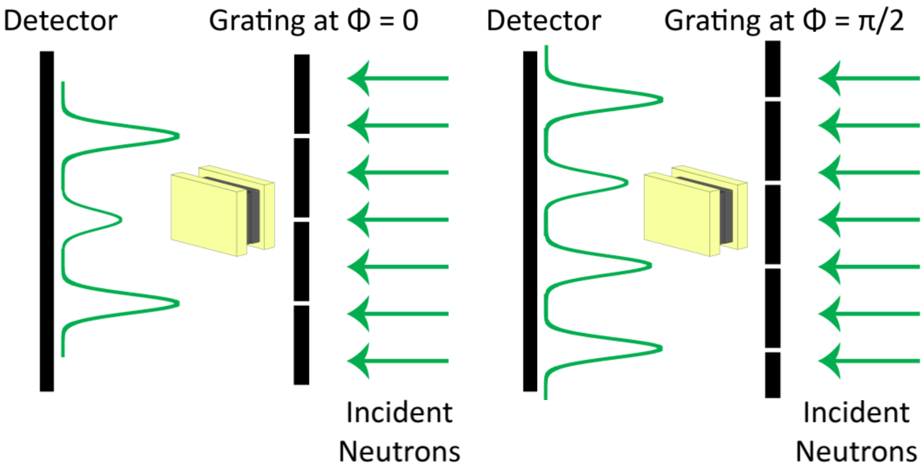
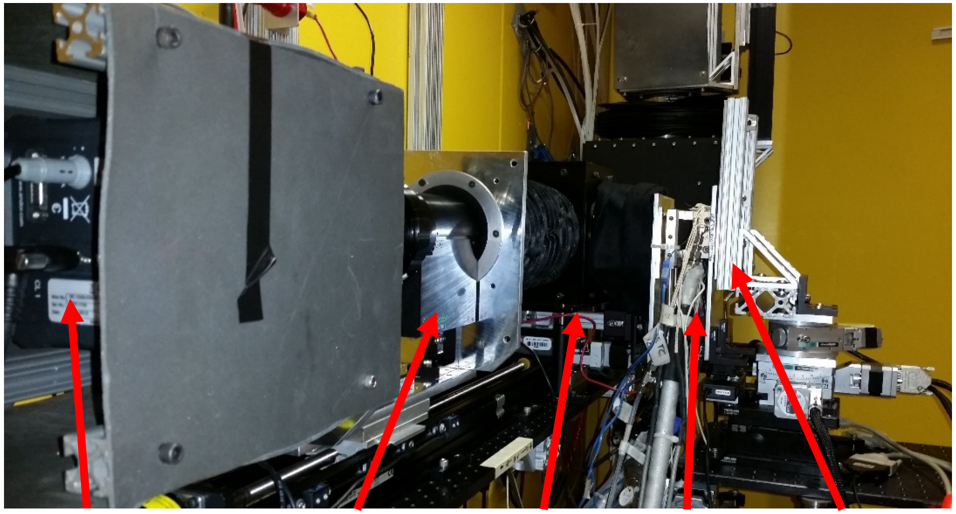
Technical Back-Up Slides

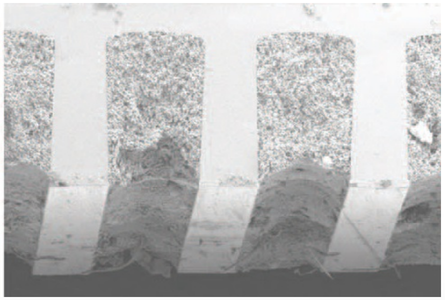
Slits: Brute force method to improve spatial resolution in 1D

- Using two identical gratings composed of GadOx, create 1 μm wide opening
- Translate grating across the object, observing a bright line at each position
- Stitch lines into an image in software
- Image intensifier amplifies weak light signal well above camera read noise
- Binning camera pixels further increases signal to noise, useable data in 180 s per slit position
- Acquisition time is unpleasantly long: period of grating * T one image ~ 10-20 hours
- In 1μm ×1mm region, there are ~10 neutron s^{-1}
  – 30 μm water uncertainty in 180 s exposure



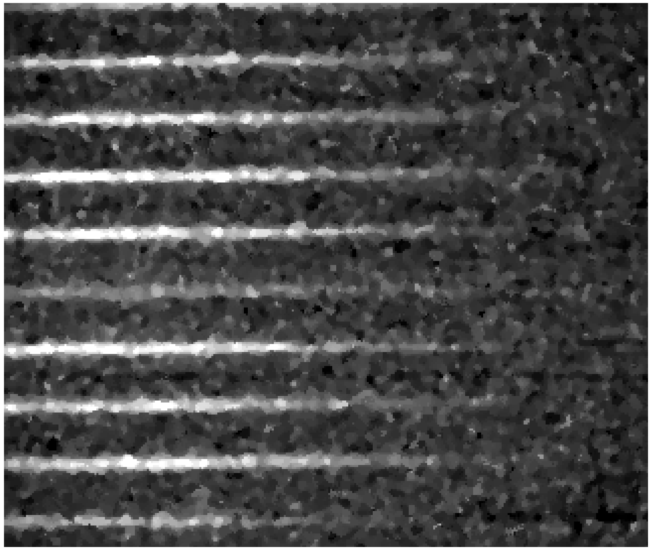


Camera | Image Intensifier | "Macro-scope" | Fuel Cell | Slit Assembly

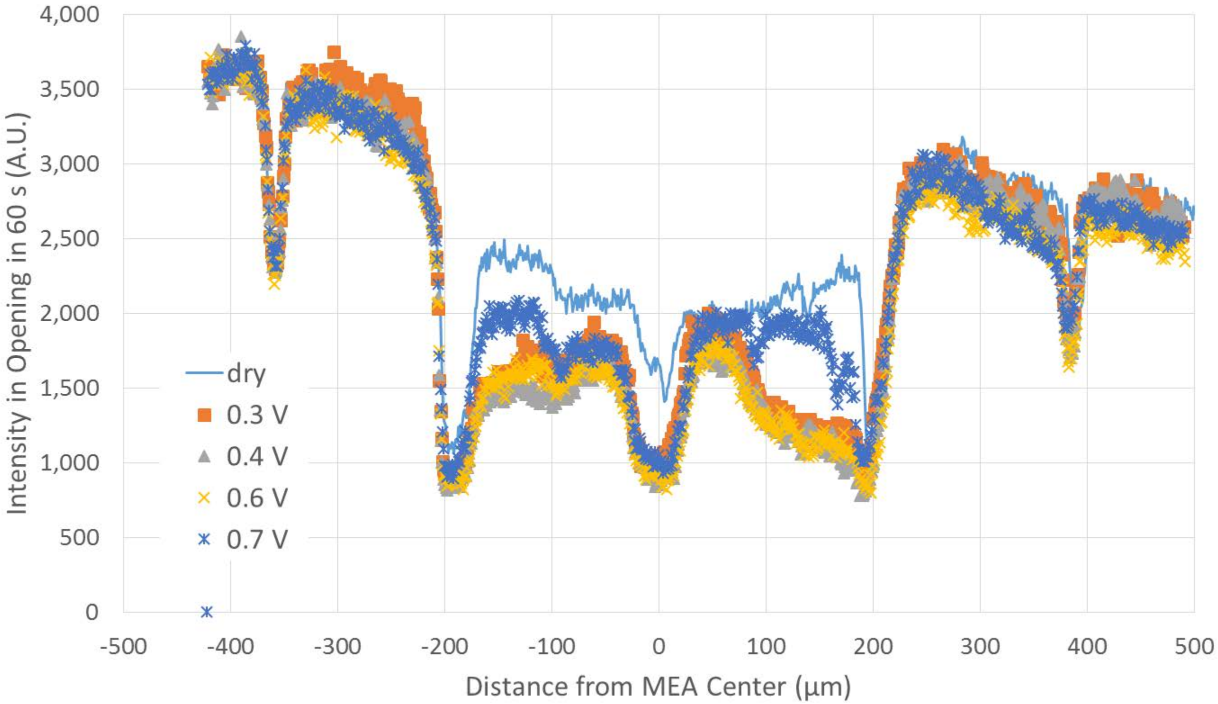


GadOx Fills 0.5 mm trenches in Silicon

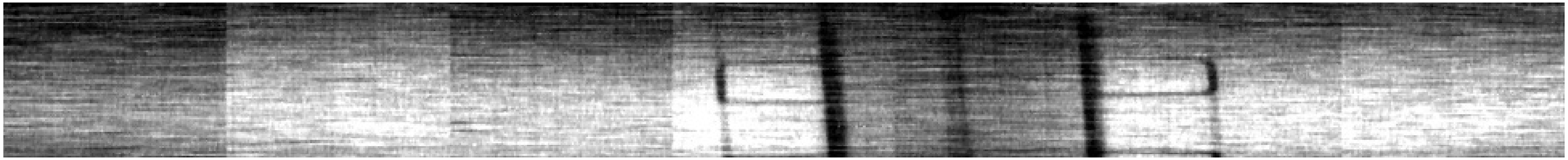
Slit imaging process



1. Collect images thru one grating period

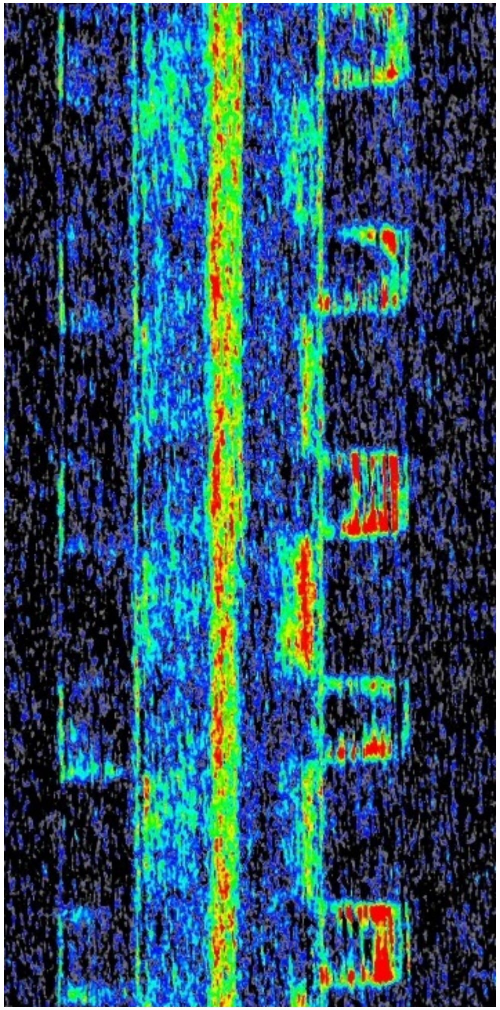


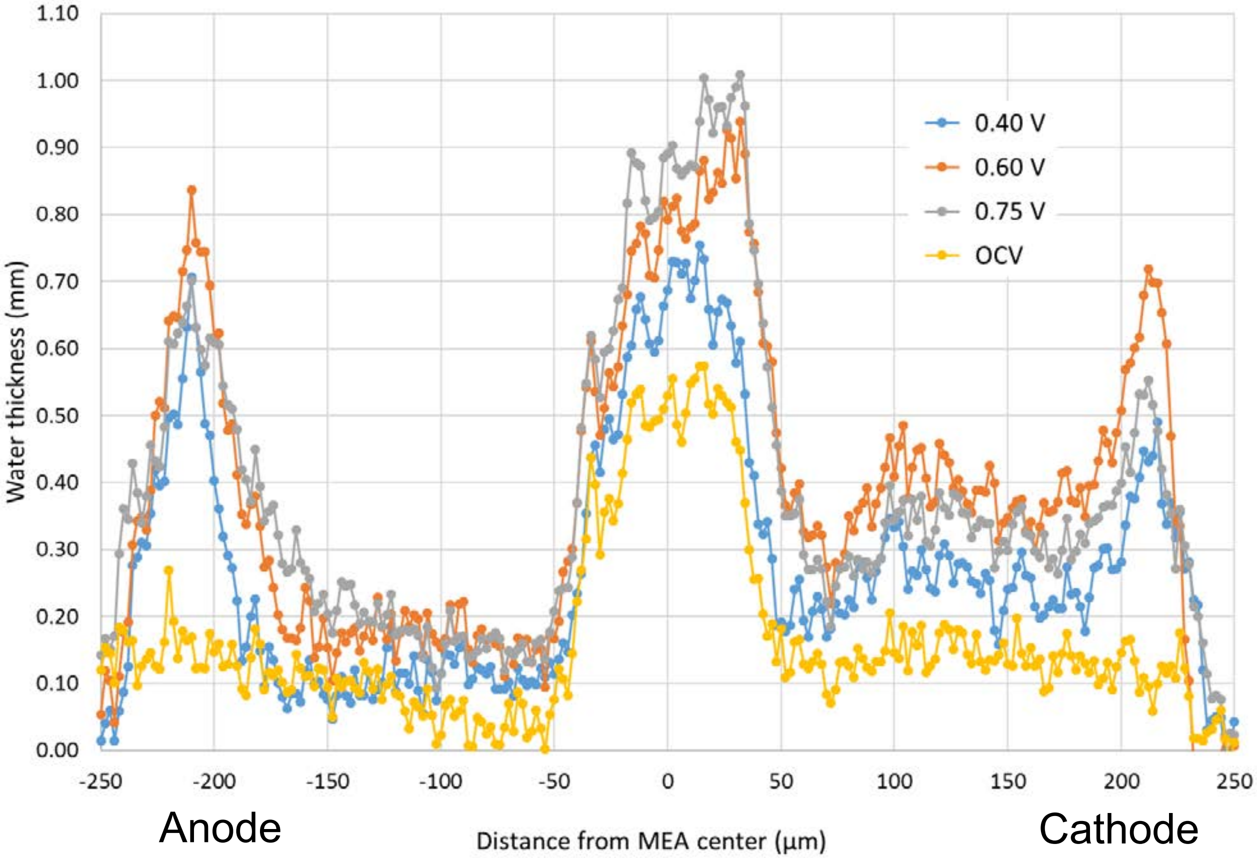
3. Plot average intensity along the through-plane direction



2. Stitch images together to create stretched image along scan direction

Slit Imaging, FEB 2016 measured water content, 4 µm resolution, Cell Temp. 35ºC





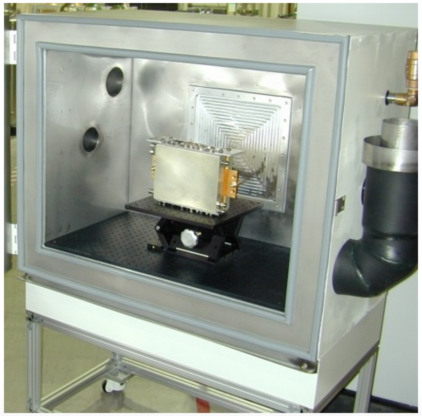
See influence of MPL strongly suppressing water content at cCL/MPL interface, possibly see evidence of aCL & cCL being more hydrated than membrane

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