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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Overview

Timeline

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

Budget

Project funding FY 2015	
DOE:	$ 300 k
NIST :	$ 1,200 k
Industry:	$ 250 k
Total	**$ 1,875 k**

Barriers

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

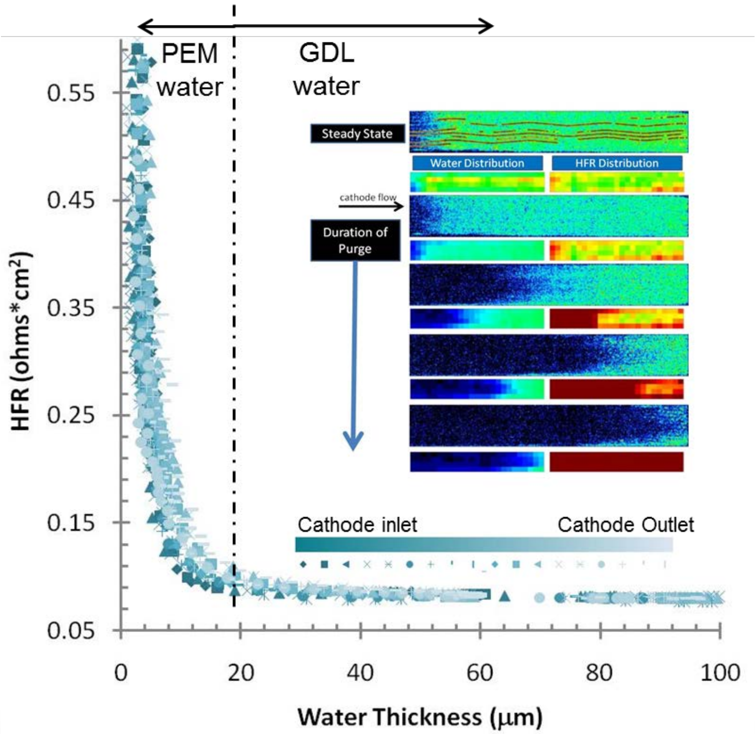
Partners/Users/Collaborators

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
- Nissan
- NASA, MSFC
- Lawrence Berkeley National Laboratory
- Los Alamos National Lab
- Massachusetts Institute of Technology
- Michigan Technological University
- 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

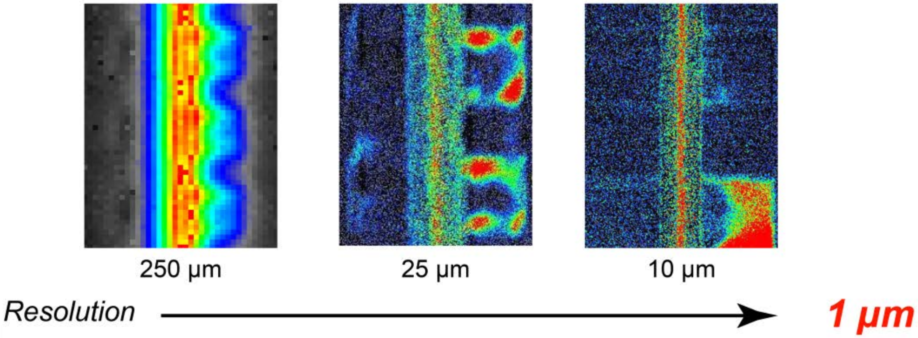
Relevance

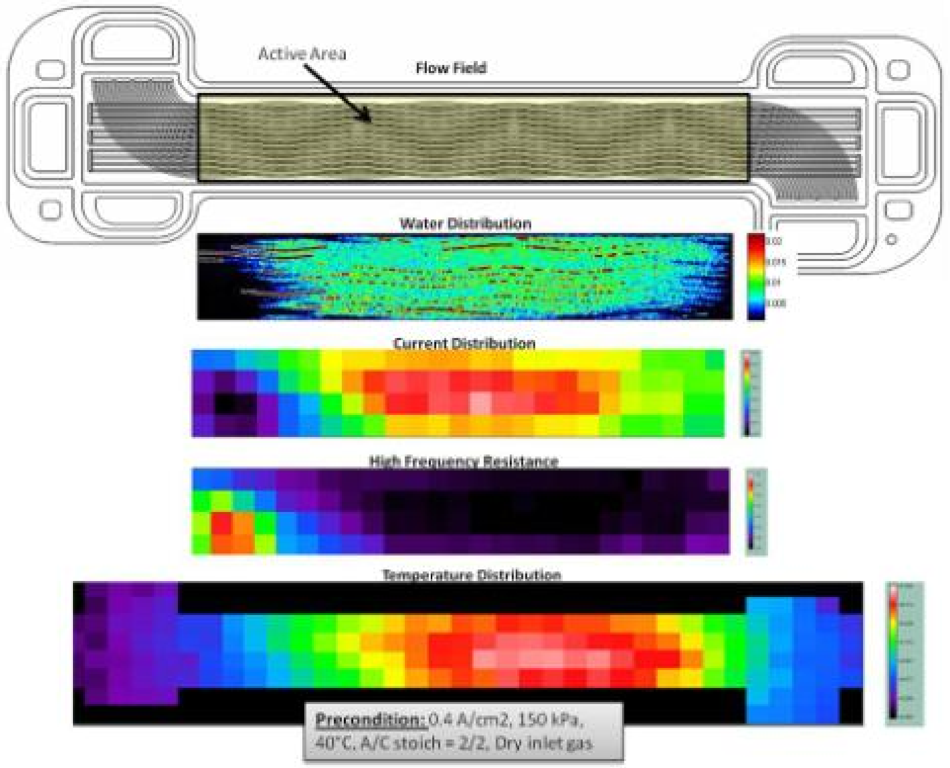
- Neutron imaging is the most powerful and sensitive method to image water in the fuel cell *in situ* as neutrons readily penetrate common fuel cell hardware yet provide accurate measurement of extremely small volumes of liquid water
- This allows one to study a wide range of fuel cell water management questions:
  - 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
- 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 the needs of the fuel cell community
  - Improve the spatial resolution to provide more detail of the water content in commercial MEAs



Approach

Apply quantitative neutron radiography to measure the water content in an operating fuel cell to provide a complete picture of heat and mass transfer and cell performance





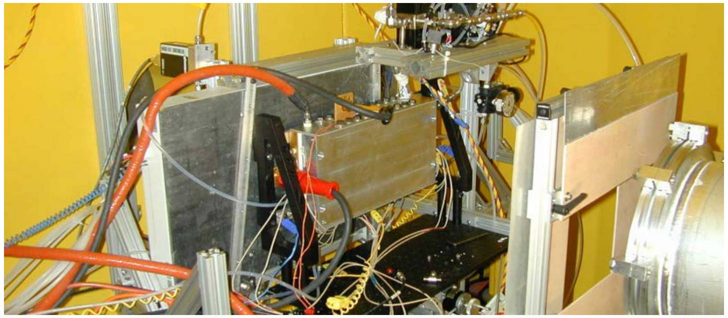
Precondition: 0.4 A/cm2, 150 kPa, 40°C, A/C stoich = 2/2, Dry inlet gas

Continuous effort to:

- Enhance image spatial resolution to provide detailed measurement of water content in MEAs
- 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
  - ***NEW: "mail-in" service for high resolution imaging***
- Fee based access for proprietary research
  - Contact NIST for details
  - 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

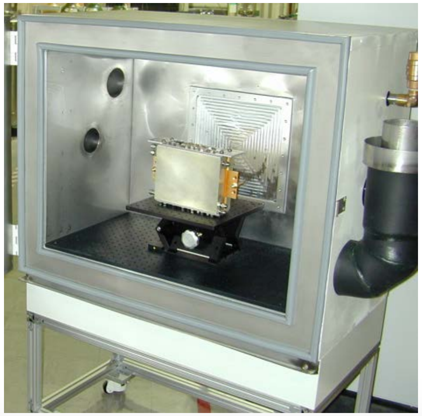


Approach

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
2015 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

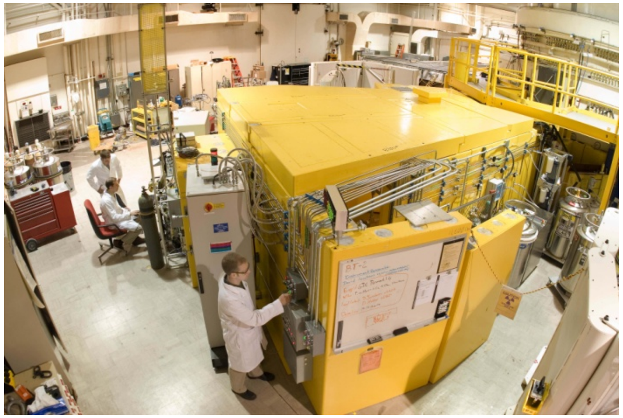
Milestones

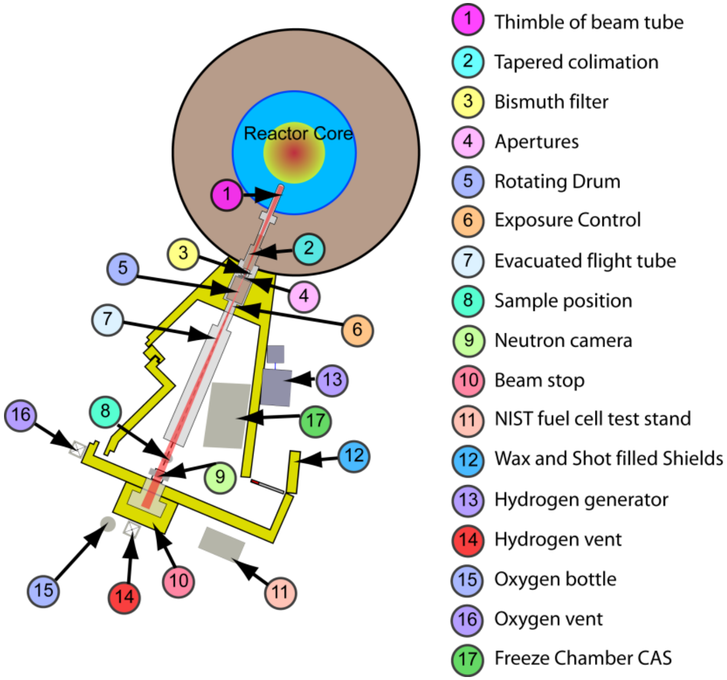
- User program – Ongoing – 100% complete in 2014
  - 43 % of open beamtime allocated to Fuel Cell and hydrogen storage experiments
  - LANL: Water content of non-precious group metal catalysts (mail-in experiment)
  - CEA: First testing non-proprietary 5 cell stack test with full scale hardware fuel cell test stand
  - Univ. of Tenn./General Motors: saturation effects on GDL thermal properties

- New Cold Imaging Facility – 100% in FY2015
  - Commissioning July 2015

- Refine method to achieve 1 μm resolution - Ongoing
  - Neutron microscope project is receiving support for development by NIST
    - 10 μm resolution available 2016 (planned)
    - 1 μm resolution available 2018 (planned)
  - Grating testing and deployment planned for new cold imaging facility
  - Detector macroscope for higher resolution scintillators
  - Image intensifier purchased and available fall 2015

- Future work: Complementary x-ray imaging system
  - Commissioning May 2015, available to all users summer 2015.
  - Enables simultaneous in situ neutron/x-ray analysis

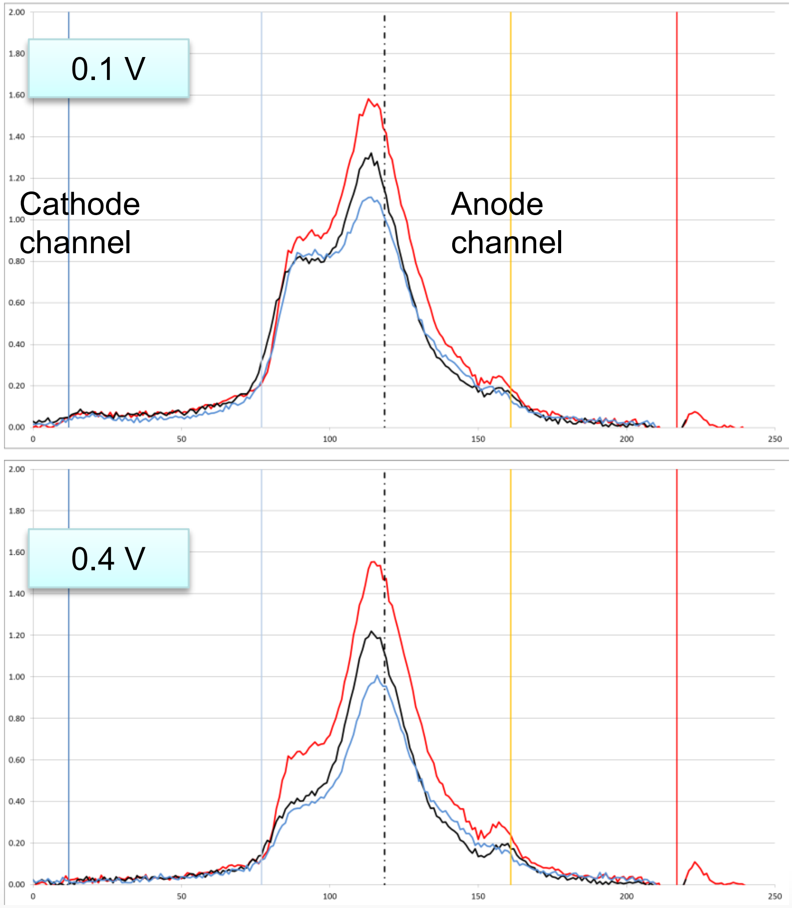




NIST Neutron Imaging Facility.

Accomplishment: NPGM Cathode Thickness Effect

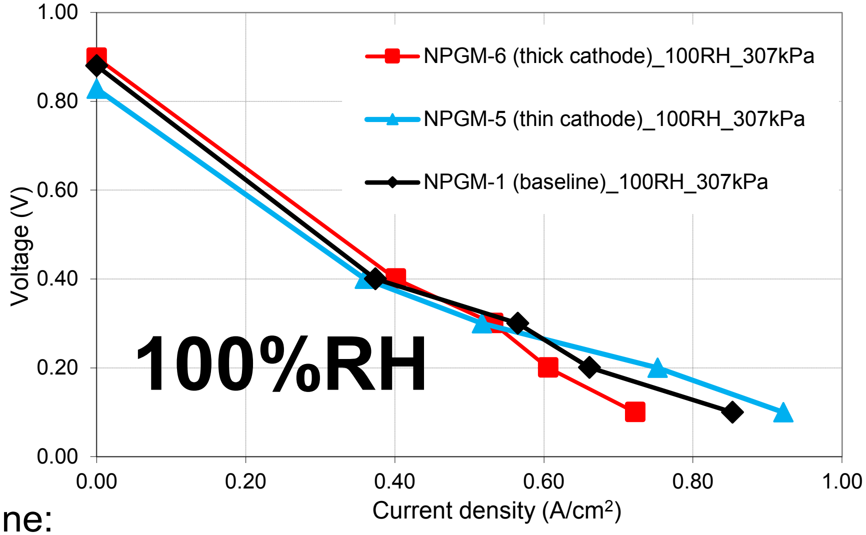
Performance of LANL's Fe-based catalysts can be improved with water management strategies

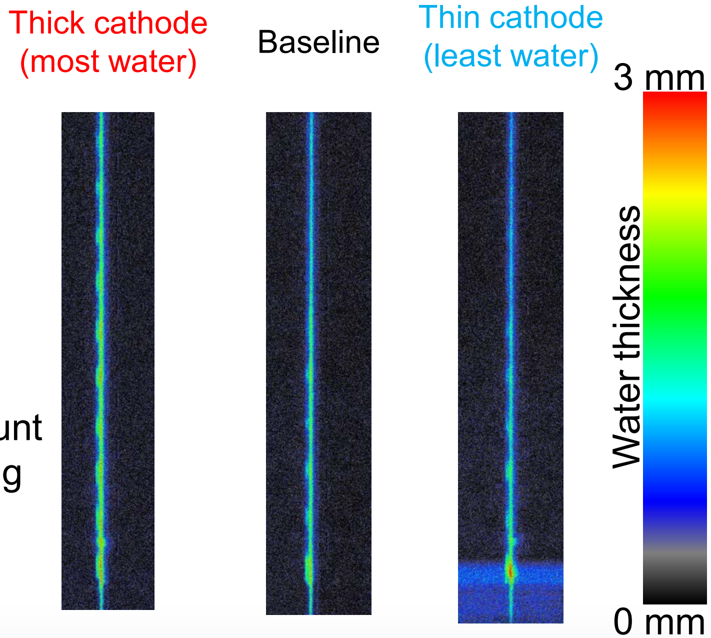


NPGM-1 Baseline: 4 mg/cm^2

NPGM-5 Thin cathode: 2 mg/cm^2

NPGM-6 Thick cathode: 6 mg/cm^2

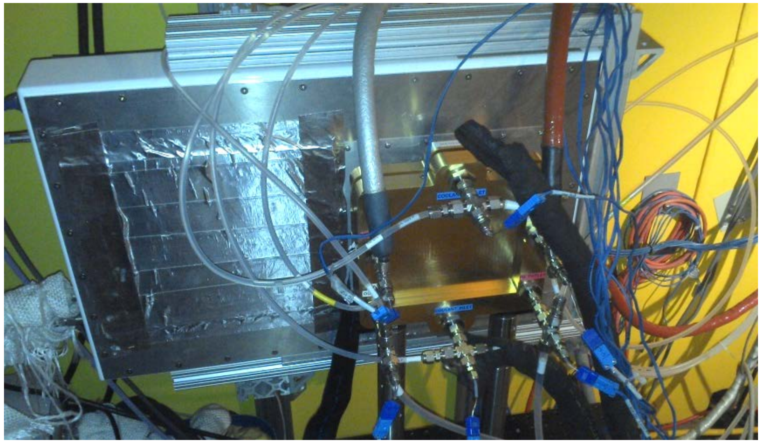




Thin cathode retains least amount of water, benefiting performance at higher current.

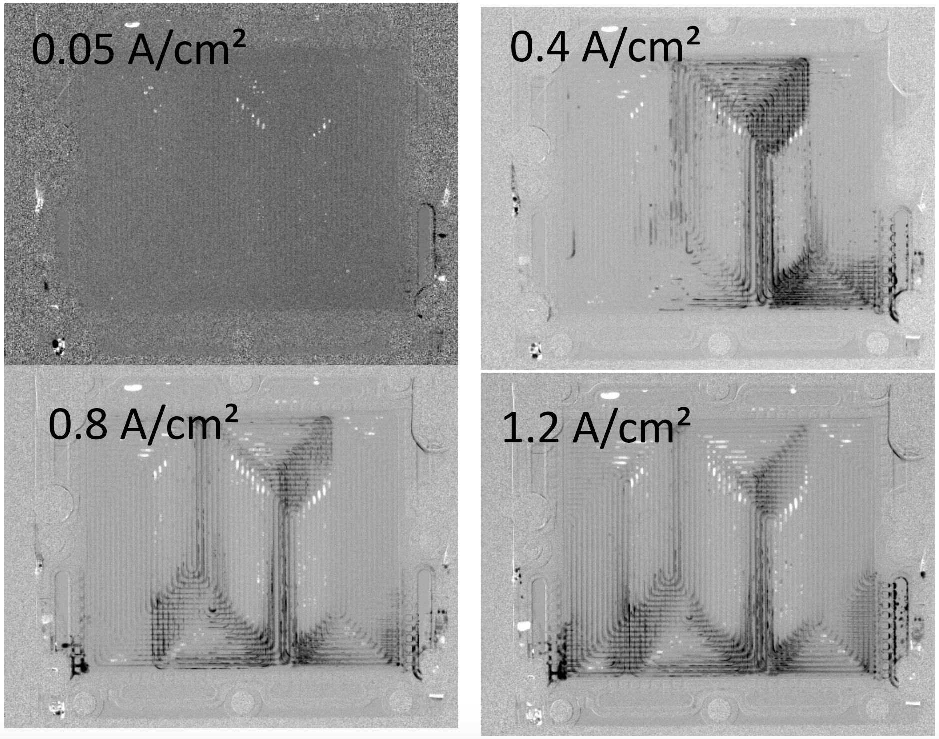
LANL

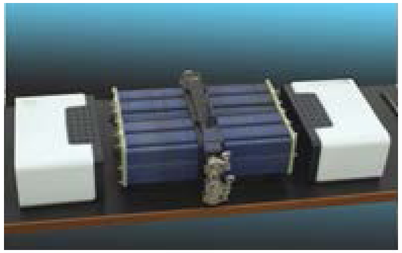
Accomplishment: First Open User Stack Imaging Experiment with CEA



5 CELLS STACK based on metallic bipolar plate for automotive applications
DESIGN 2003: CEA/PSA
Surface active area : 220 cm^2
SPECIFIC POWER: 1.6 kW/l and 1.1 kW/kg

80°C 1.5 Bar H_2/Air 50/50 %RH st. 1.5/2
Decreasing current
Coolant flow: 1.8 l/min

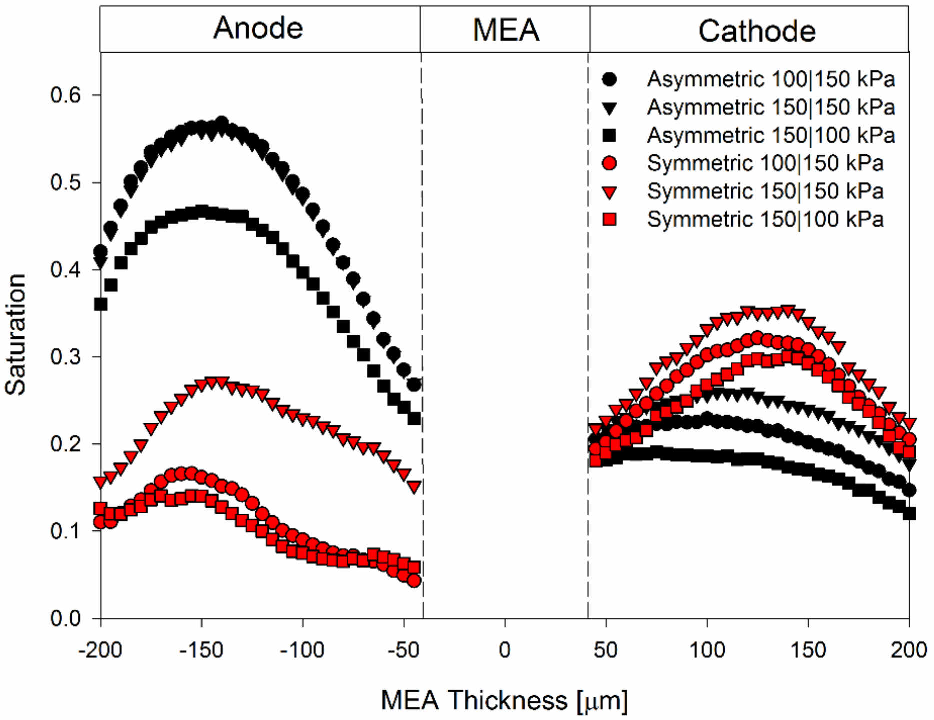




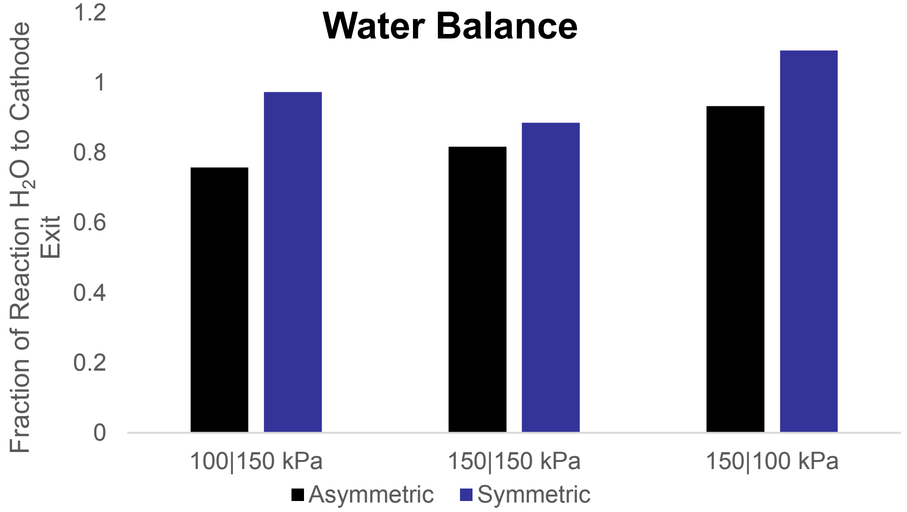
GENEPAC Stack
80 kW

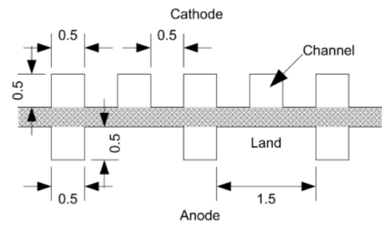
Accomplishment : Asymmetric channel geometry alters thermal transport from cathode to anode

60°C, 1.2 A/cm², 95|95%RH, 2|2 stoich

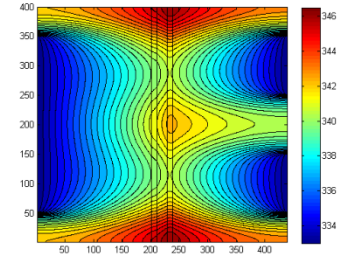


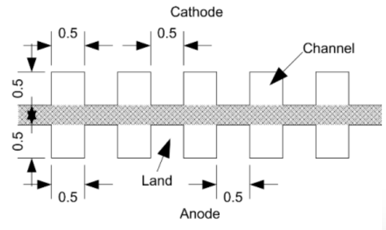
1) Asymmetric architecture can be used to reverse thermal trend from net cathode to net anode
2) Low conductivity DM allows for ΔT > 10°C at higher current densities which facilitates thermal transport



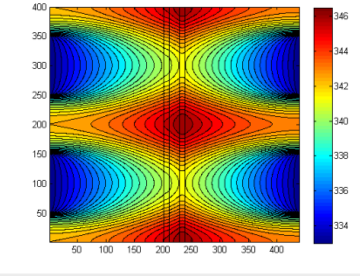


(A)



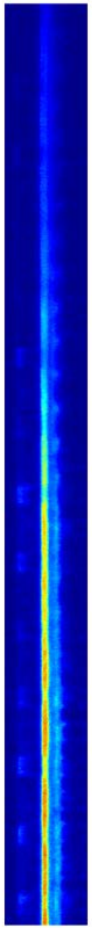


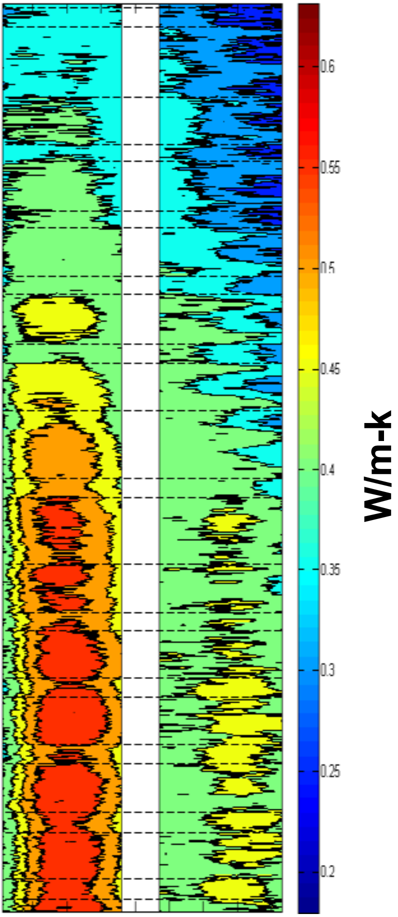
(B)



University of Tennessee and GM

Accomplishment: Localized thermal conductivity as a function of saturation measured with neutrons



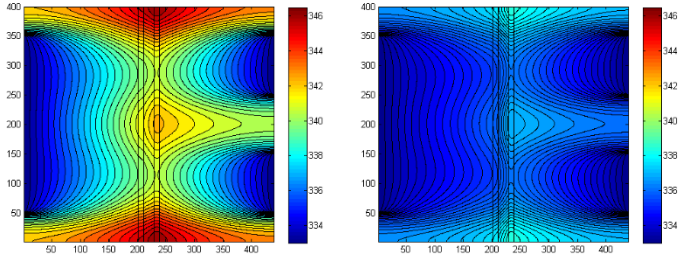


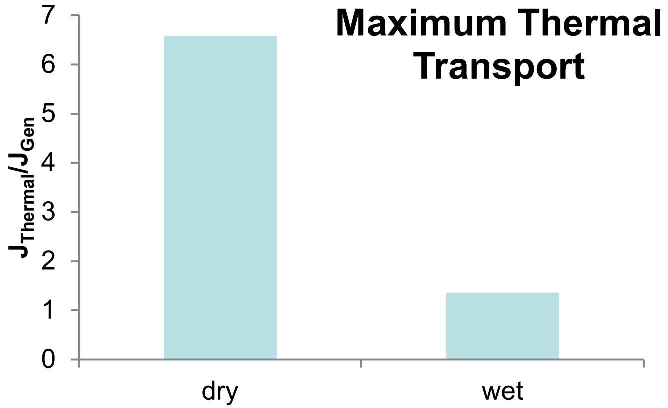
Saturation data converted to thermal conductivity based on experimentally measured thermal conductivity values

Testing methodology:

- **TPS 2500S transient plane source method**
- **All tests points at 2 MPa compression**

Simulated Temperatures

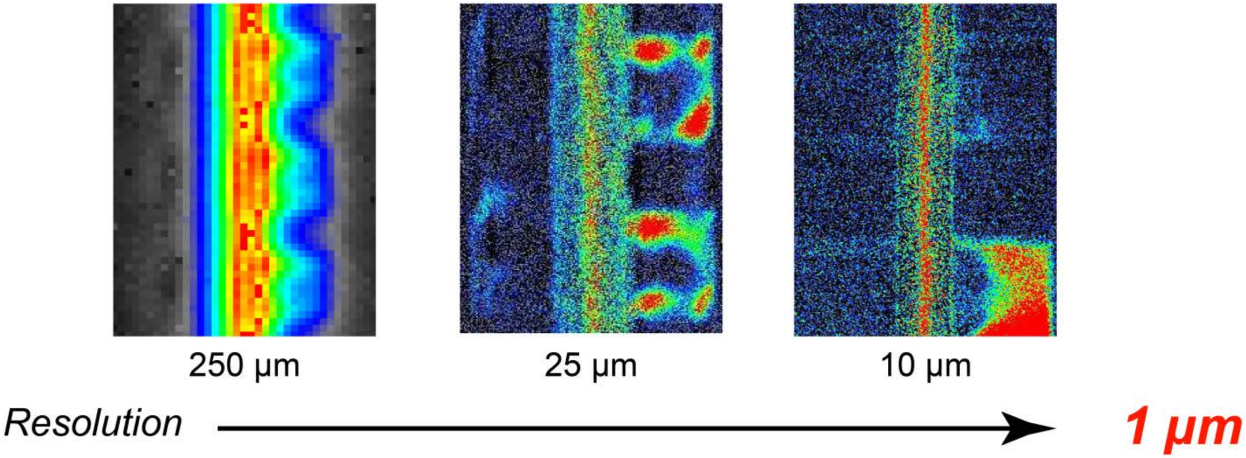




1) Saturation strongly reduces peak cell temperature
2) Reduction in T_{peak} attenuates thermally driven transport
3) Alters water transport direction from net anode to net cathode

University of Tennessee and GM

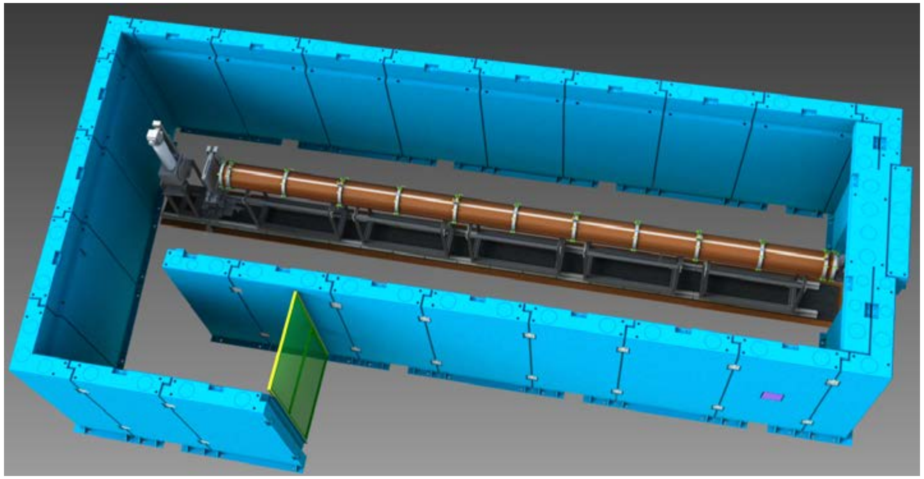
Progress: Paths towards improved spatial resolution



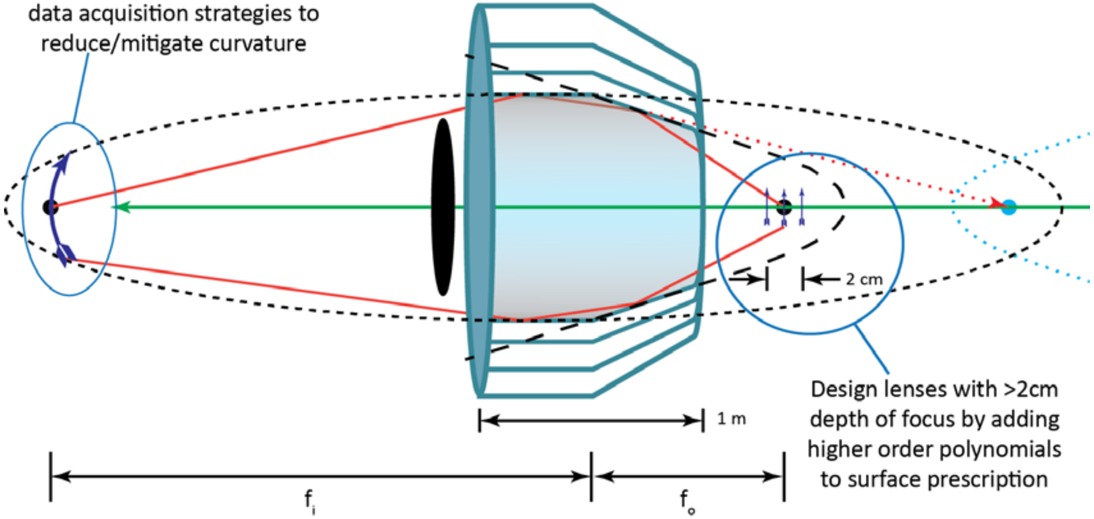
- Wolter optics at the cold neutron imaging instrument
  - Higher time resolution for 10 µm (10 s vs. 20 min); Neutron image magnification for 1 µm
- Slit illumination using gratings
  - Gratings with thicker Gd and shorter period; Light amplification with intensifier
- Magnification of scintillation light with a “macroscope”
  - New detector scheme based on infinity-corrected optics; New scintillators with higher resolution and light output; Light amplification
- Centroiding scintillation light from individual neutron capture events
  - Similar to how a neutron MCP detector works; relies on macroscope and intensifier

Progress: NEW high resolution cold neutron imaging instrument

- Expected to be operational by July 2015
- Test bed for high resolution imaging development
  - More time available for dedicated high resolution imaging methods
- Potential to resolve ice and water
  - Will perform calibration measurements in 2015
- Neutron lens based on Wolter Optics
  - Magnification 1x with ~10 s image time increase with 10 μm resolution by end of 2017
  - Neutron image magnification with ~20 min image time with 1 μm resolution by end of 2018



Progress: Wolter Optics Design

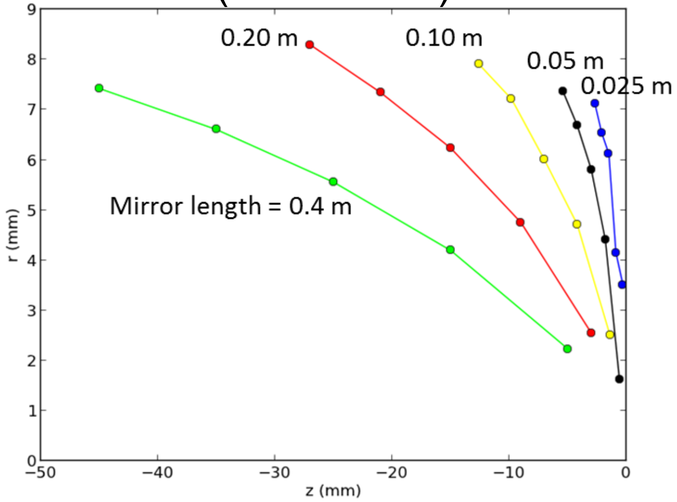


Flat field is parabolic, need to investigate lens designs or data acquisition strategies to reduce/mitigate curvature

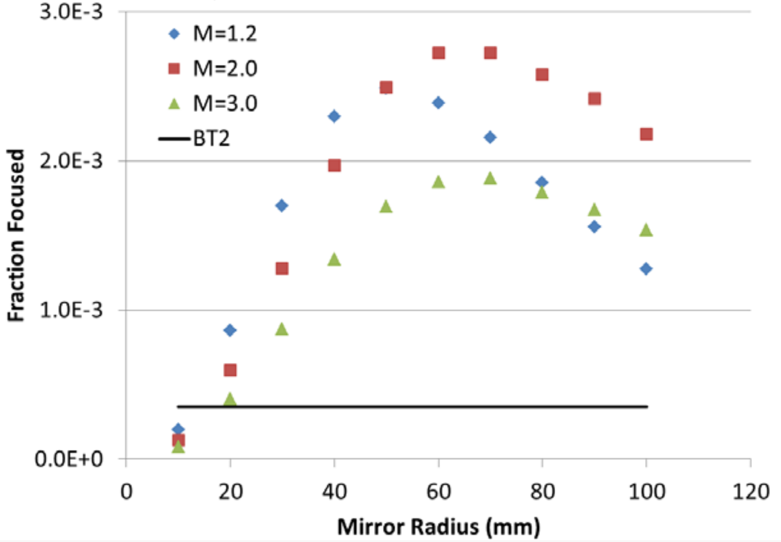
Design lenses with >2cm depth of focus by adding higher order polynomials to surface prescription

- Paraboloid-Paraboloid configuration, M = 1, 7.5 m focal length
- Field curvature is determined by quadratic fit
- Curvature found to vary as L / √R
- ***Prescription: Nest 10 cm long mirrors with radii optimized for flux collection – 100x over BT2 with 14 mirrors***
- NASA to begin R&D on optic resolution in 2015, complete in CY2016.

Field Curvature vs. Mirror Length (R = 3.5 cm)

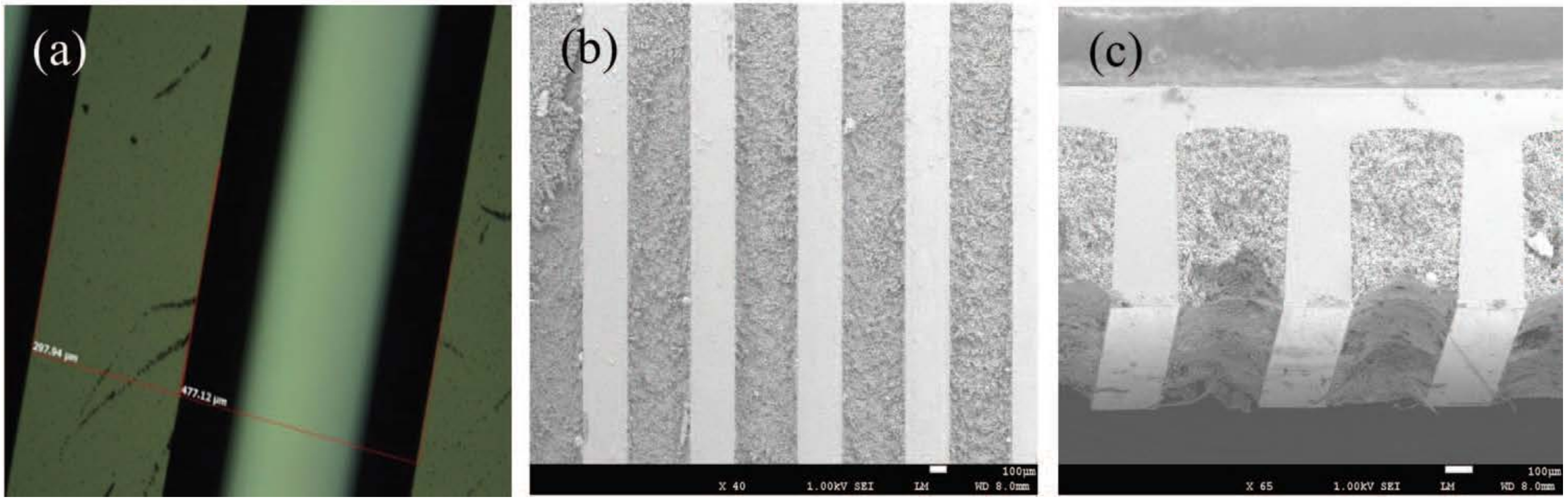


Single Mirror Flux Collection



Progress Update: Slit Imaging for 1 μm – Making better gratings

- Illuminate the test section with a narrow slit; a grating reduces acquisition time
- Deposition and subsequent etching of thick Gd films is challenging
- Colleagues at Pusan National University, South Korea have developed a method to fill trenches in Silicon with GadOx particles
  - Can fill up to 500 μm tall trenches, will test in second half of 2015
- Image Intensifier will also greatly improve measurement quality and acquisition time

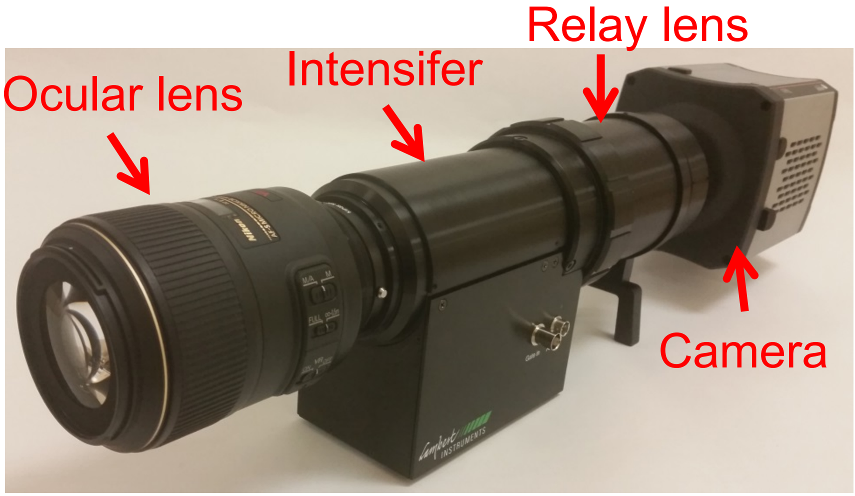


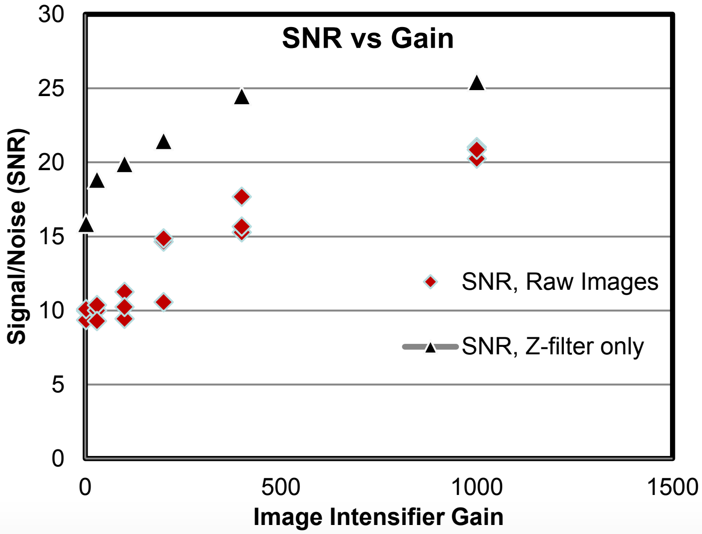
(a) An optical microscopy image of the fabricated silicon grating surface, (b) SEM images of the grating surface, and (c) SEM images of the grating cross section.

J. Kim et al. RSI, **84**, 063705 (2013).

Progress Update: Improve fuel cell high resolution image time

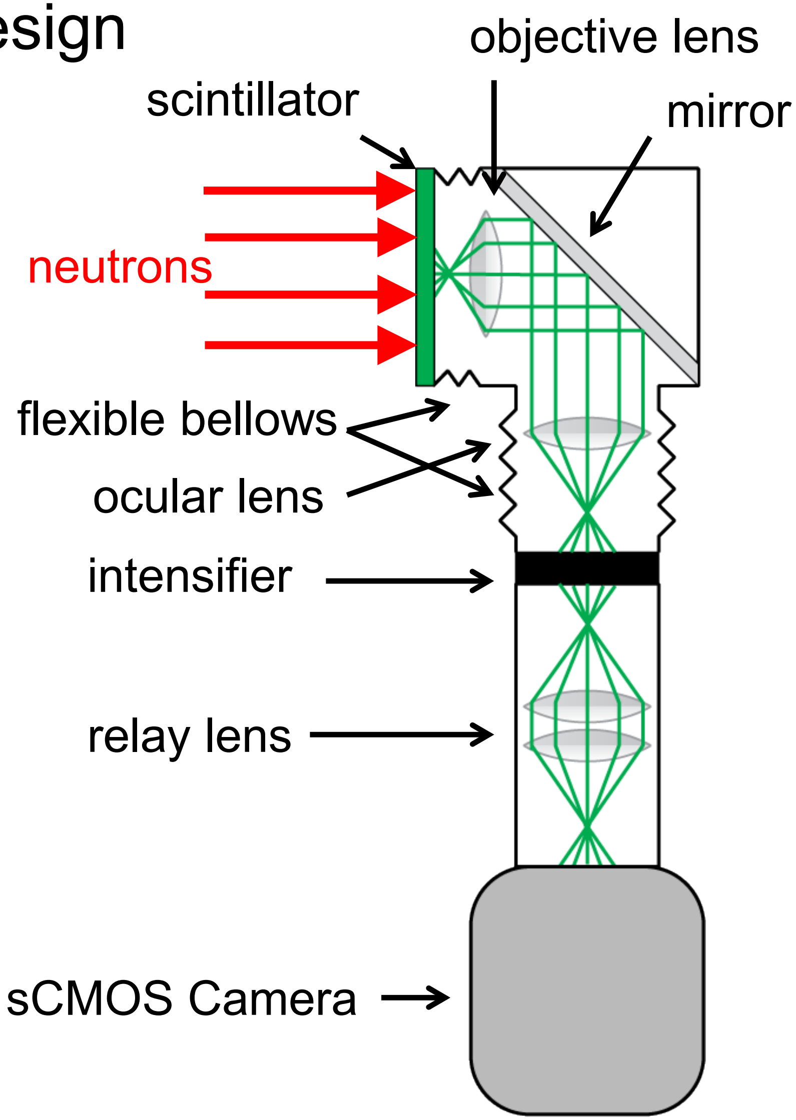
- Improving acquisition time using more efficient detectors for high resolution imaging
- Current MCP efficiency is ~20 %
- Low light, high resolution Gadox screens can be improved
  - 20 μm spatial resolution
  - 80 % neutron detection efficiency
  - 100x less signal
- Using high resolution image intensifier the signal can be amplified by 10,000x
- Concept was tested and reported 2014
- Update:
  - Intensifier was procured September 2014
  - Arrived March 25, 2015
  - Measured resolution was 18 μm not 11 μm as specified
  - Vendor working to correct resolution of system
  - Expect working unit in fall 2015.



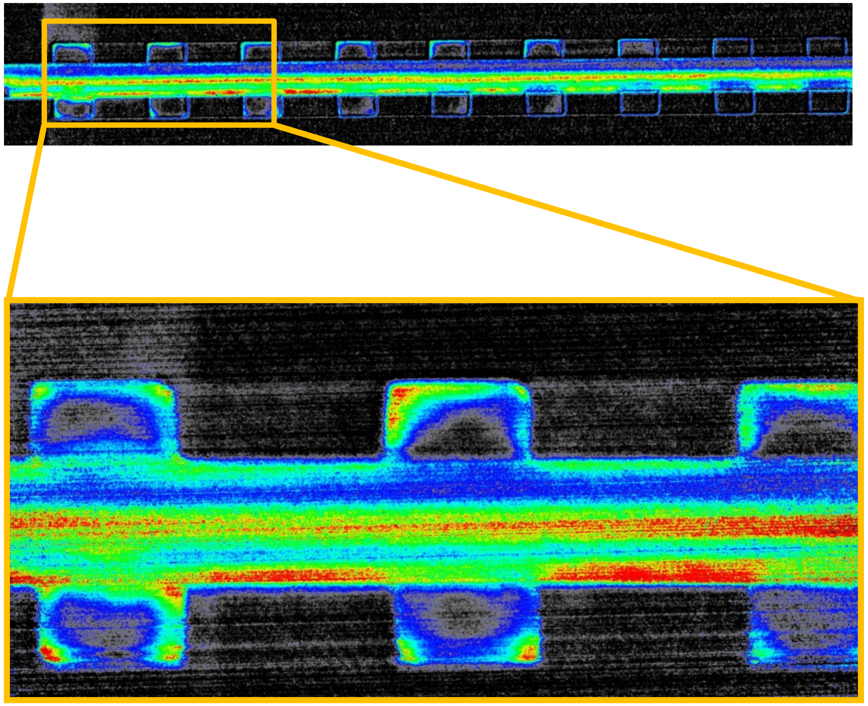


Future Work: NEW Macroscope Design

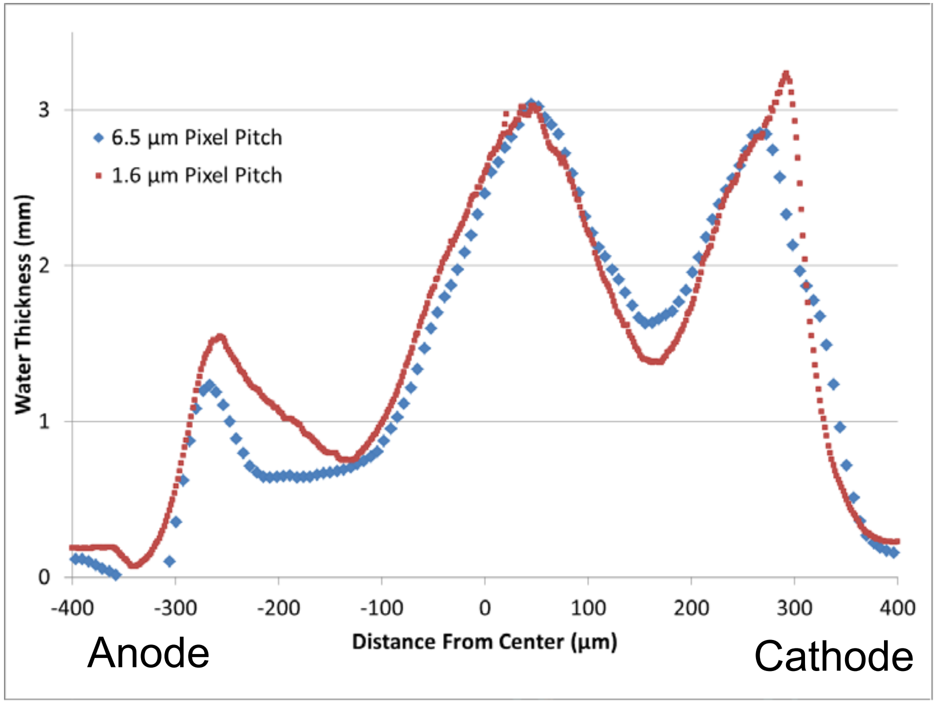
- Objective lens added to work close to screen
  - Like conventional light microscope
  - Improves light collection efficiency
- Ocular lens focuses light on intensifier which amplifies low light signals
  - Magnification is the ratio of the ocular lens focal length to objective lens (for example if ocular lens is 200 mm and objective is 50 mm, magnification = 4x
- Relay lens (Objective + Ocular lens) transfers the image from the intensifier to the sCMOS Camera with a 1x magnification (1:1 reproduction ratio)
- System can make use of scintillators with sub 10 μm resolution
- Not limited by light production of scintillator
- Will be critical in implementing centroiding to further improve resolution, but requires intensifier



Future Work: Higher Spatial Resolution Possible with Macroscope at M=4



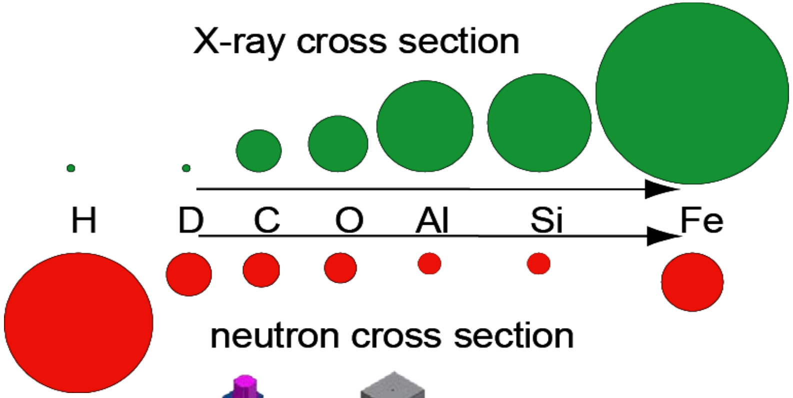
Through-plane water content of LANL baseline 211 MEA with thick 0.3 mg Pt/cm^2 catalysts to image catalyst layer water.

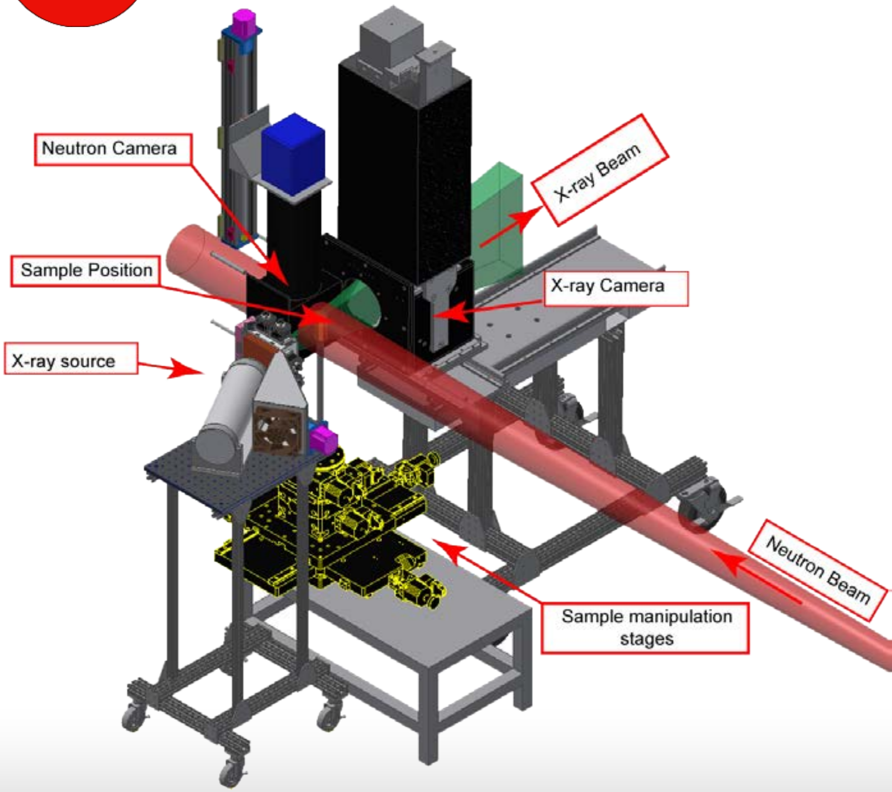


- Sharper features resolved. Similar counting statistics for 5 hours with M=4 vs 20 minutes for standard setup
- Higher resolution scintillators (GGG, GI:Ce) will further improve detail of MEA water content

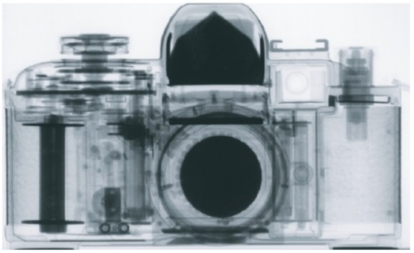
Future Work: Simultaneous Neutron and X-ray Imaging

- Installation May 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
  - 20 keV – 90 keV
  - 80 W max power
  - 20 μm spot size

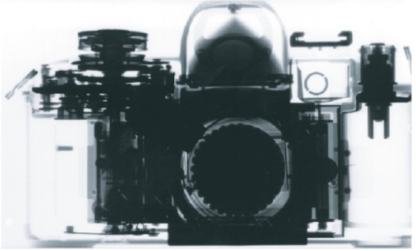




Rich, complementary data set from combined x-ray and neutron tomography



Neutron image of a film SLR camera



X-ray image of a film SLR camera

Response to 2014 Reviewers' Comments

- For issues such as interfaces and ionomer and catalyst layer limitations, it is not clear that neutron imaging will reach resolutions that we need for understanding.
  - Creating thicker or engineering flatter layers would enable the method to provide saturation values for models. The same model should be able to use this date to extrapolate to thinner layers. The work on NPGM catalysts presented here shows the utility of such measurements to improve performance of catalyst layers.
- NIST should think about adding flexibility into the standardized hardware in terms of compression, pressure control, and utilizing next generation material sets.
  - The standardized small-scale hardware set enables users to bring their own, next generation material sets without the need to develop the flow fields. The design is straightforward to use which provides reasonable flexibility and presents a low barrier to use.
- There could be a lack of capacity for everyone to do experiments.
  - NIST strives to accommodate all good proposed research projects with beam time including by releasing internal time to the user program.
- This technique is clearly not mobile or accessible to many partners and it will always remain a fairly expensive tool.
  - Neutron imaging is valuable for process and materials development, not factory floor inspection. Beam time is free and available through a peer-reviewed process. Proprietary rates are set by full cost recovery; industry feedback indicates NIST rates are highly competitive compared to other methods and facilities.
  - ***Mail-in service will eliminate travel expenses for users interested in bench-marking the performance of their materials, making the measurement free.***

Summary

- User program
  - Potential to standardize some measurements, including incorporating EIS into test stand scripting which will be a great benefit to the users
  - First tests of the full scale hardware test stand were performed
  - Still a broad number of water transport phenomena that can be studied
  - Neutrons are the best non-destructive way to measure water transport as the neutrons do not affect the cell performance
- New in situ x-ray imaging capability will allow higher resolution studies of porous materials with in situ neutron measurement of water transport
- New Macroscope
  - Improves the optical resolution and the optical light gathering power
  - Allow testing of scintillators with 7 μm resolution or better
  - Will enable higher resolution through centroiding
- New cold imaging facility will allow more rapid development of high resolution methods to measure MEA water content
  - Second beam line allows for a larger number of users and provides more time for experiments
- Wolter optics promise to **increase flux by 100x** to image at 10 μm in 10 s (rather than 20 min) and to **magnify the neutron image by 10x** to image at 1 μm in about 20 min.

Acknowledgements

Special Thanks to

Nancy L. Garland

DOE Technology Development Manager

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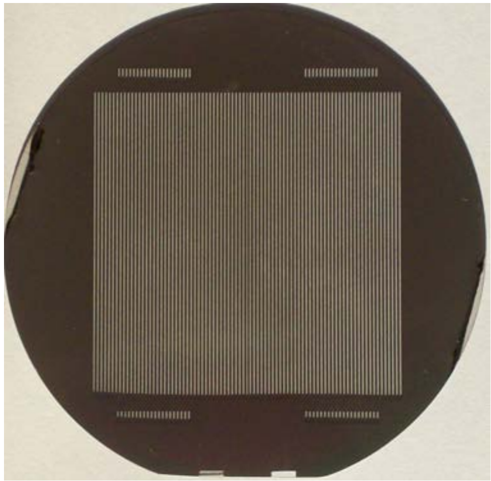
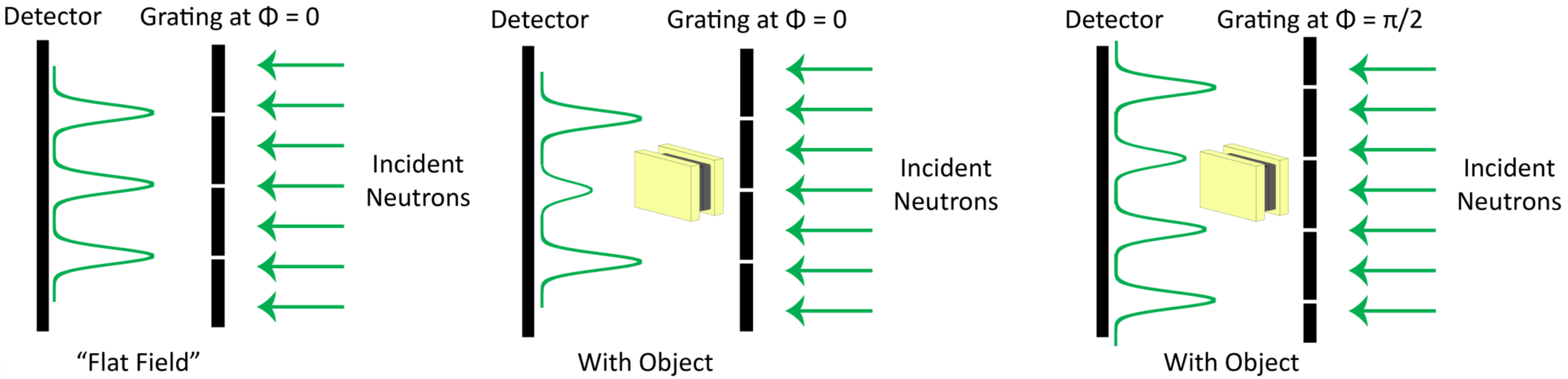
End of Presentation
Additional support material follows

Technical Backup: High resolution MEA water content
Higher Resolution Inspired by Structured Illumination

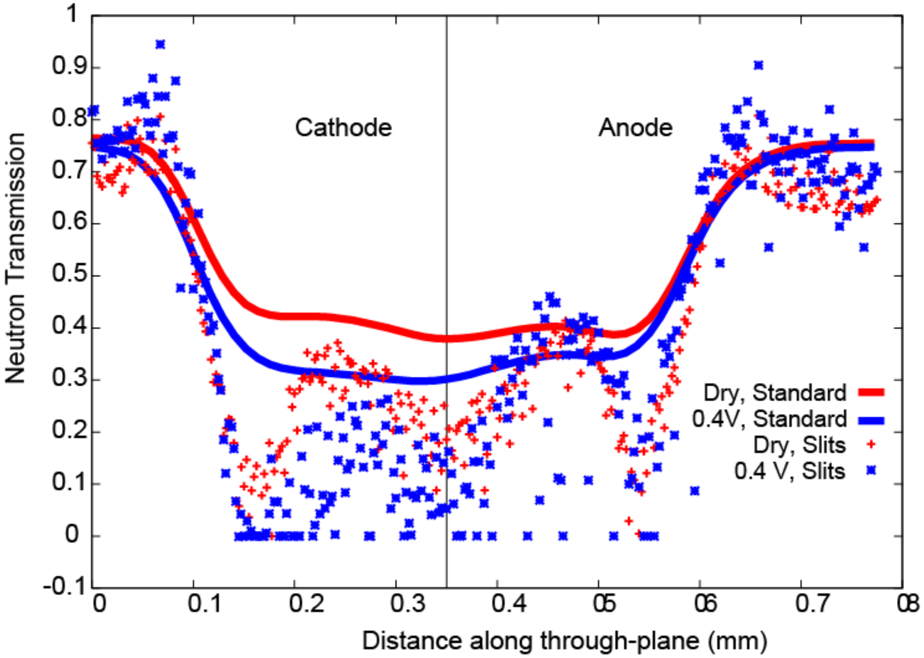
- Spatial resolution in any neutron detector is fundamentally limited by the range of the charged particles from the neutron capture
- Using a slit we can further define the spatial resolution by width of the slit
- Technique:
  - –Illuminate object with narrow slits on a period that allows detector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

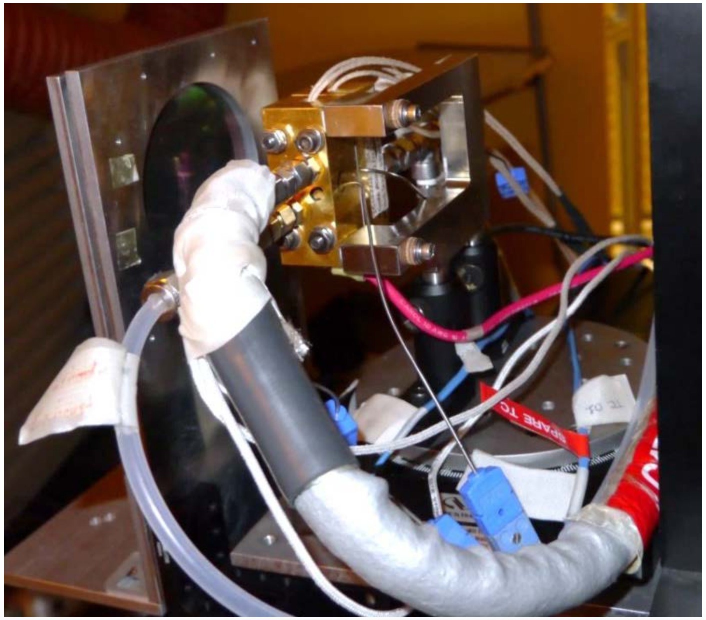




Technical Backup: High resolution MEA water content
First results sub 10 μm

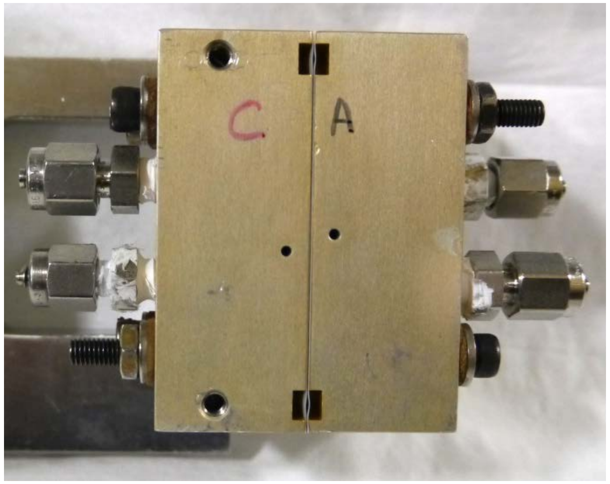
- Used two gratings with ~3 μm of Gd that allowed us to create an small (5 μm) opening
- Line profiles show clearly sharper features and demonstrate need for better signal-to-noise
- Images acquired over period of 15 h

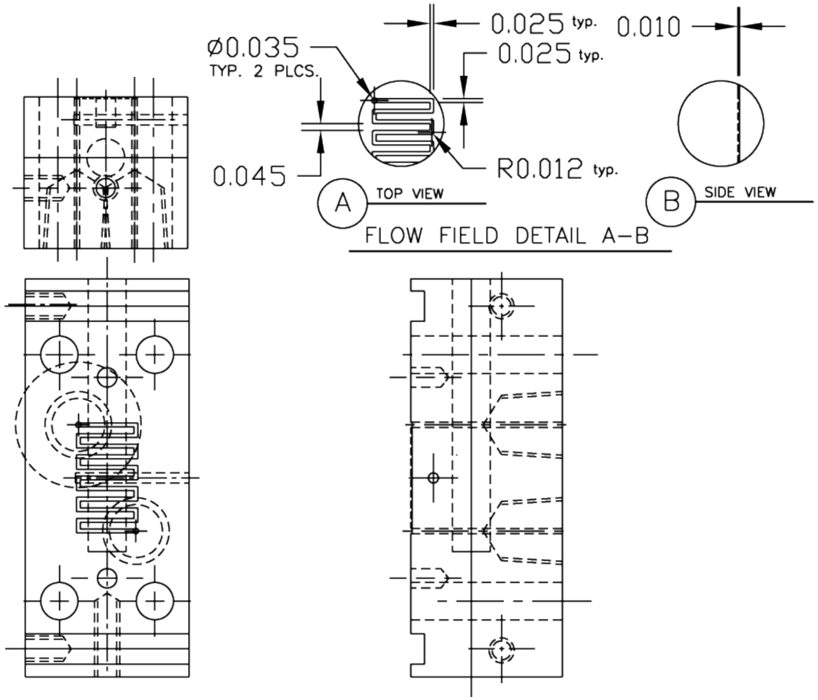




Line profiles from standard imaging with resolution 25 μm compared to slit method for a dry fuel cell and during operation at 0.4 V (about 2 A/cm^2)

Technical Backup: Standard High Resolution Fuel Cell





- Robust design (LANL)
  - Lots of use with neutron imaging
  - Easy to build, good performance
  - MEA can be cut from existing 50 cm^2 soft goods
- High resolution fuel cells
  - porous metal foam flow fields
  - No non-uniformities from rectangular flow fields
- Gauge block spacer
  - Avoids wedge, improves plane parallel