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

Project funding FY 2010

DOE:	$ 584 k
NIST:	$ 550 k
Industry:	$ 266 k
Total	$ 1,400 k

Project funding FY 2011

DOE:	$ 590 k
NIST : (1 year increase)	$ 2100 k
Industry:	$ 275 k
Total	$ 2,965 k

Barriers

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

Partners/Users/Collaborators

Project Lead: National Institute of Standards and Technology

- Ballard
- Ford
- General Motors
- Georgia Tech
- Lawrence Berkeley National Laboratory
- Los Alamos National Laboratory
- Michigan Technological University
- Nissan
- NOVA Scientific
- Nuvera
- Oak Ridge National Laboratory
- Pennsylvania State University
- Rochester Institute of Technology
- Sandia National Laboratories
- Sensor Sciences
- University of California, Berkeley
- University of Connecticut
- University of Kansas
- University of Michigan
- University of Tennessee
- Wayne State University

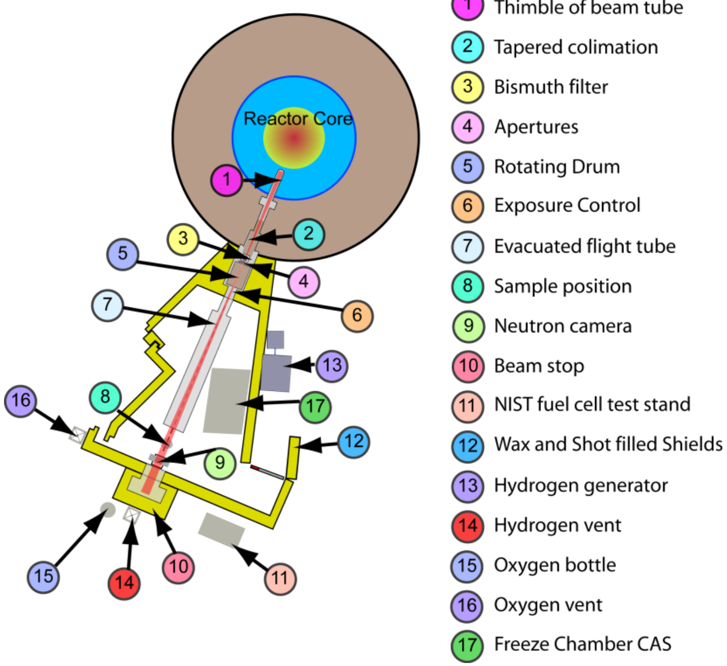
Relevance/Objectives

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

- **F**orm collaborations with industry, national lab, and academic researchers
- **P**rovide research and testing infrastructure to enable the fuel cell / hydrogen storage industry to design, test and optimize prototype-to-commercial grade fuel cells and hydrogen storage devices.
- **M**ake research data available for beneficial use by the fuel cell community
- **P**rovide secure facility for proprietary research by Industry
- **T**ransfer data interpretation and analysis algorithms techniques to industry to enable them to use research information more effectively and independently.
- **C**ontinually develop methods and technology to accommodate rapidly changing industry/academia need

Approach/Milestones

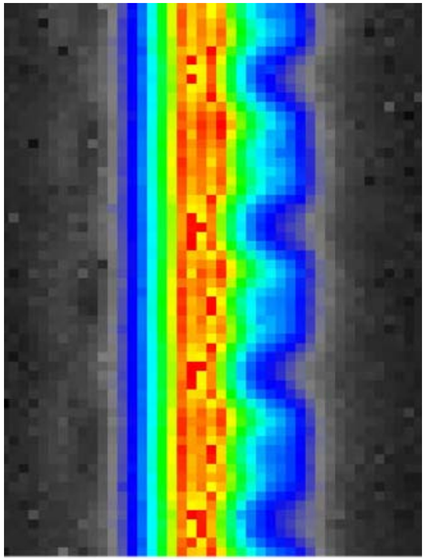
- **NIST Neutron Imaging Facility**
  - National user facility access to beam time through peer reviewed proposal system
  - Experiments published in open peer-reviewed literature
  - State-of-the-art imaging technology
  - High flux neutron source
  - Proprietary access provided to fuel cell industry
- **Fuel cell testing infrastructure**
  - State-of-the-art small scale fuel cell test stand and EIS fully supported (details in supplementary slides) .
  - **Environmental Chamber for freeze testing** -40°C to +50°C
- **Radiography**
  - Only way to measure transient processes
  - One-dimensional cells can be made to validate simple edge on radiography
- **Improving imaging technology**
  - **New methods developed show promise for sub 10 μm resolution**
  - **High resolution neutron imaging 13 μm resolution**
    - *Resolve Water distribution in GDL and thick MEAs*
    - *Unambiguous discrimination of anode from cathode*
  - **High resolution CCD/Gadox scintillator < 20 μm**
- **Milestones 2011**
  - Performed in situ corrosion studies on the beamline
  - Large area detectors for fuel cell imaging currently being fabricated
  - Studies of flooding phenomena in non-precious metal catalyst layers using high resolution neutron imaging recently performed and data currently being analyzed

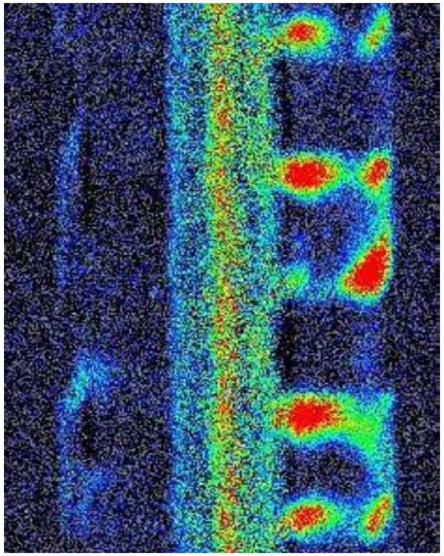


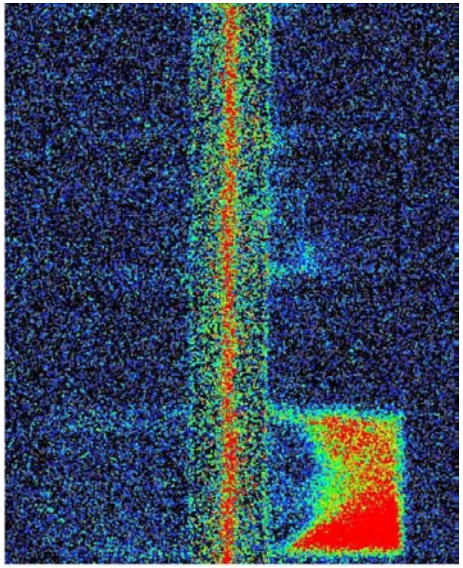
NIST Neutron Imaging Facility. Full facility capabilities provided in supplemental slides.

Technical Accomplishments/Results

Current Neutron Imaging Capabilities



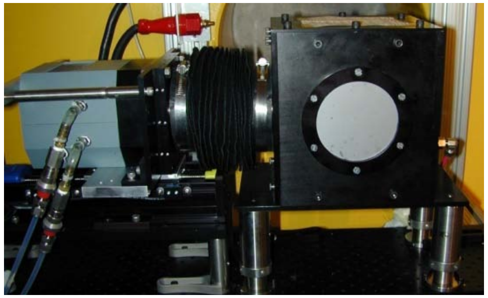


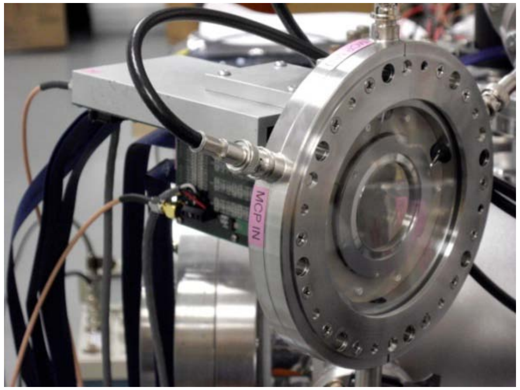


Amorphous silicon
Spatial Resolution: 250 µm
Field of View: 25 cm x 20 cm
Frame Rate: 30 frame/s

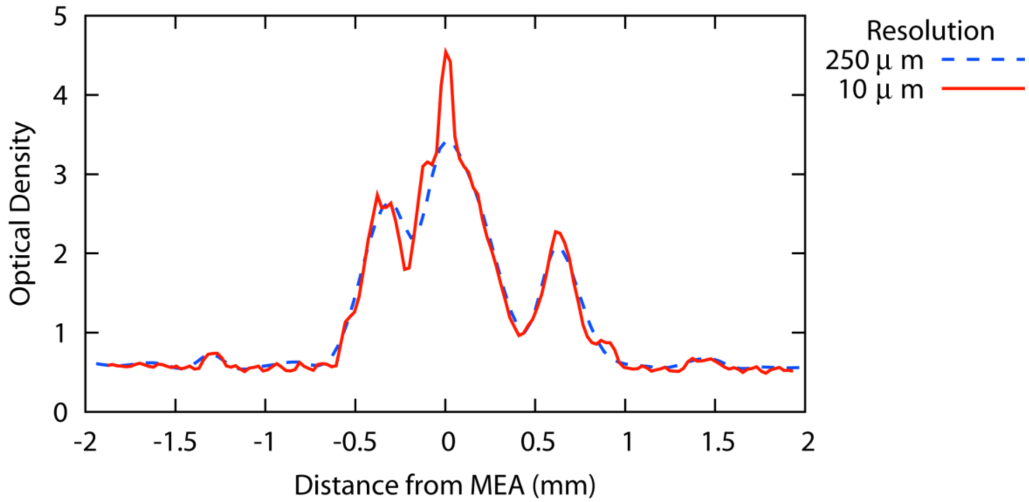
CCD
Spatial Resolution: 18 µm
Field of View: 1 cm x 1 cm
Frame Rate: 0.5 frame/s

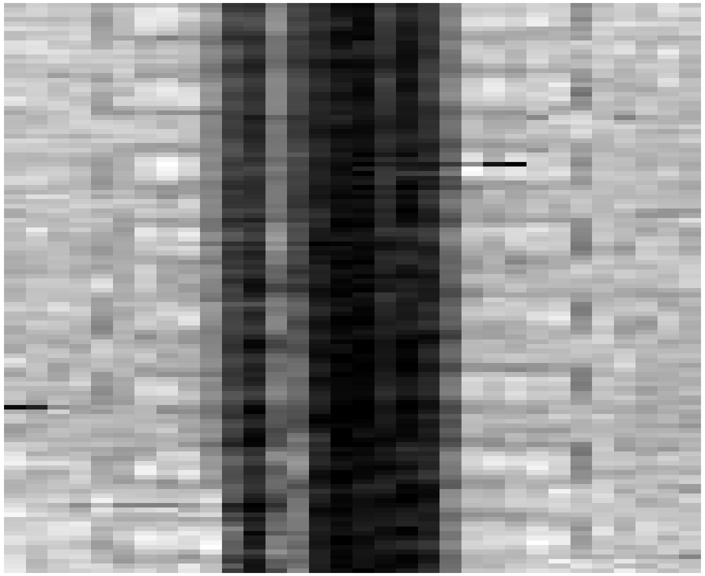
MCP
Spatial Resolution : 13 µm
Field of View: 3.5 cm x 3.5 cm
Frame Rate: 10 s – 20 min



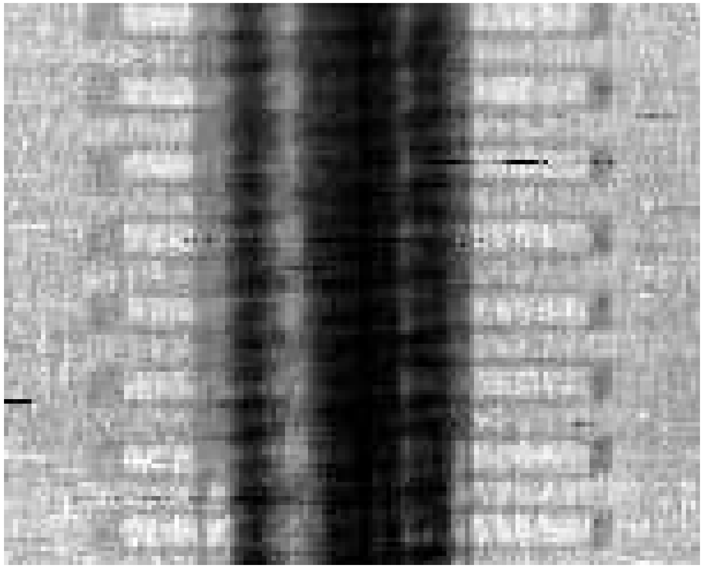


New methods to improve spatial resolution





Original 250 μm image with a-Si detector



10 μm image taken with a-Si detector

- Neutron detectors based on MCPs and scintillators have reached the theoretical limit of the spatial resolution
- Further improvements to the spatial resolution require new approaches
- One method has shown a factor of 25 improvement in spatial resolution
- Improvements to the design of this method will be pursued to achieve **~1 μm** resolution to enable measurement of water distribution within commercial MEAs

Collaborator work presented here

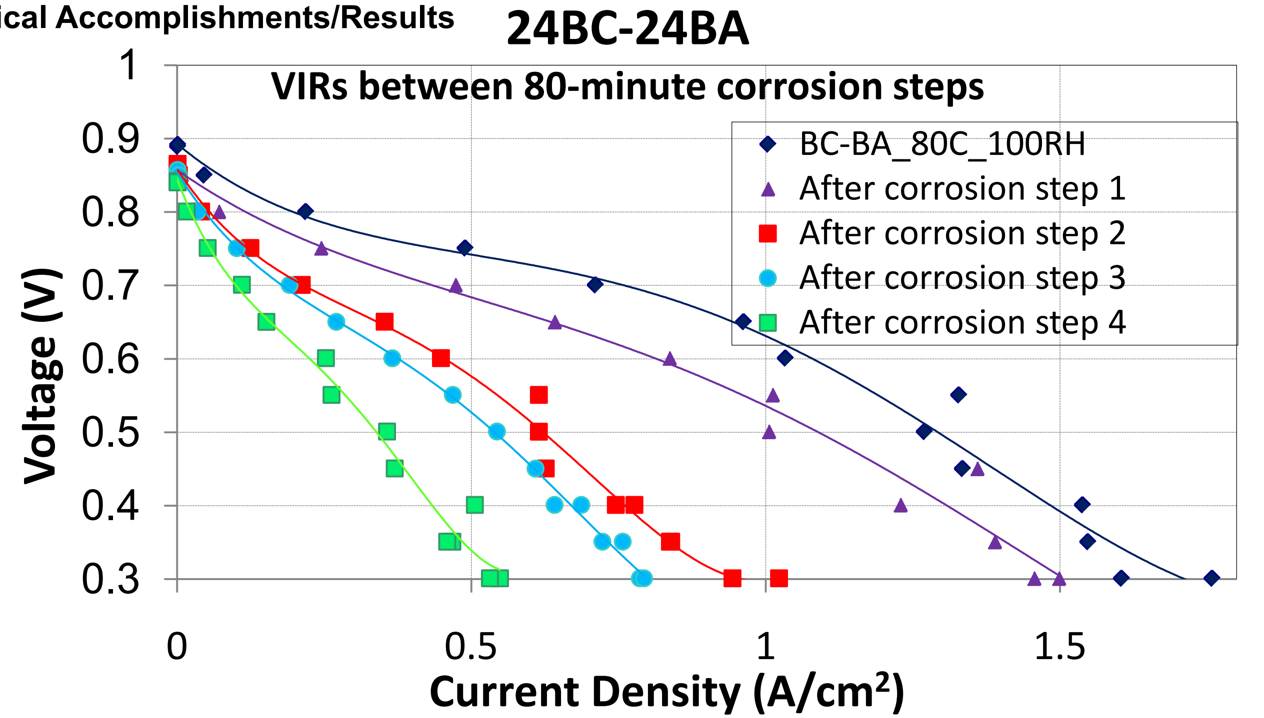
- J.J. Gagliardo, J.P. Owejan, General Motors
- R. Borup, R. Mukundan, J. Davey, J. Spendelow, T. Rockward, D. Spernjak, J. Fairweather, G. Wu, B. Li, P. Zelanay, Los Alamos National Laboratory
- S. Wessel, D. Harvey, V. Colbow, Ballard Power Systems Inc.

Los Alamos LANL In Situ Neutron Imaging Corrosion

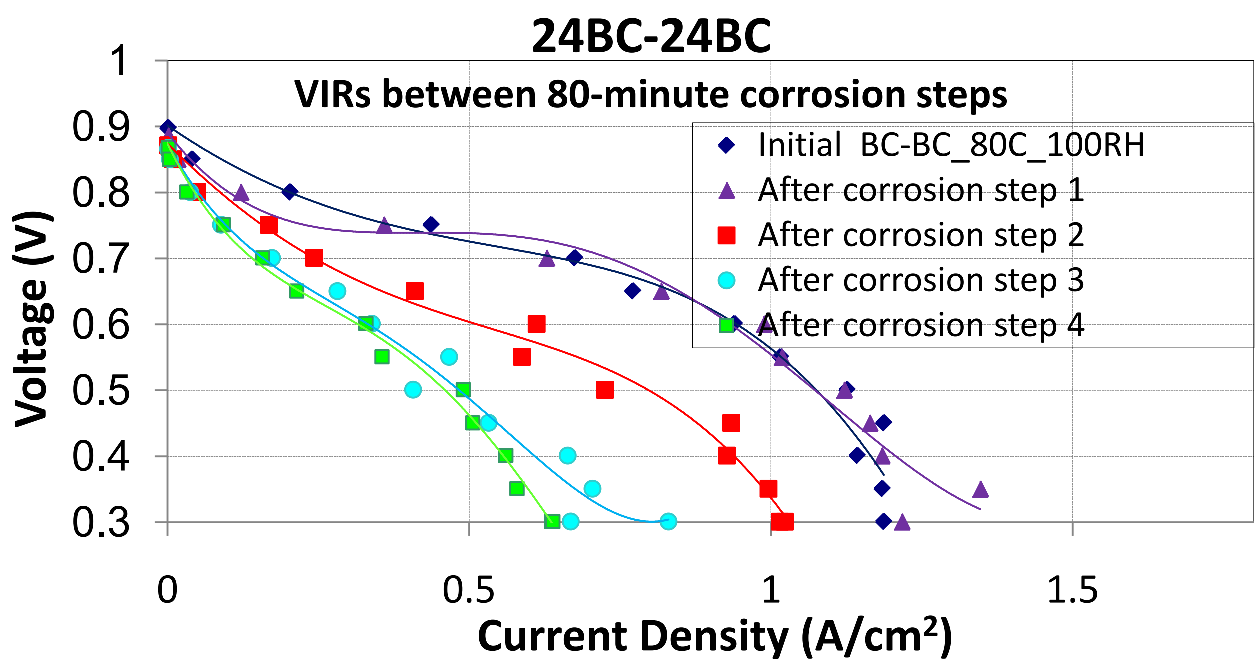
- Study Water Profile Changes due to changes in Catalyst Layer/GDL Hydrophobicity due to corrosion at 1.3 V steady-state hold
- All cells: 24BC on the anode; vary cathode GDL
  - 24BC-24BA (BA = no MPL)
  - 24BC-24BC
- **Corrosion steps** = 80 minutes at 100/200 sccm of H_2/N_2, zero backpressure, 100%RH, fixed 1.3 V
- **Characterization** steps:
  - 1 hour of imaging at 0.8 A/cm^2
  - 5 minutes at 0.8 V (no imaging)
  - Impedance at 0.8 A/cm^2 and 0.8 V and VIR

Cell Performance for Different GDLs

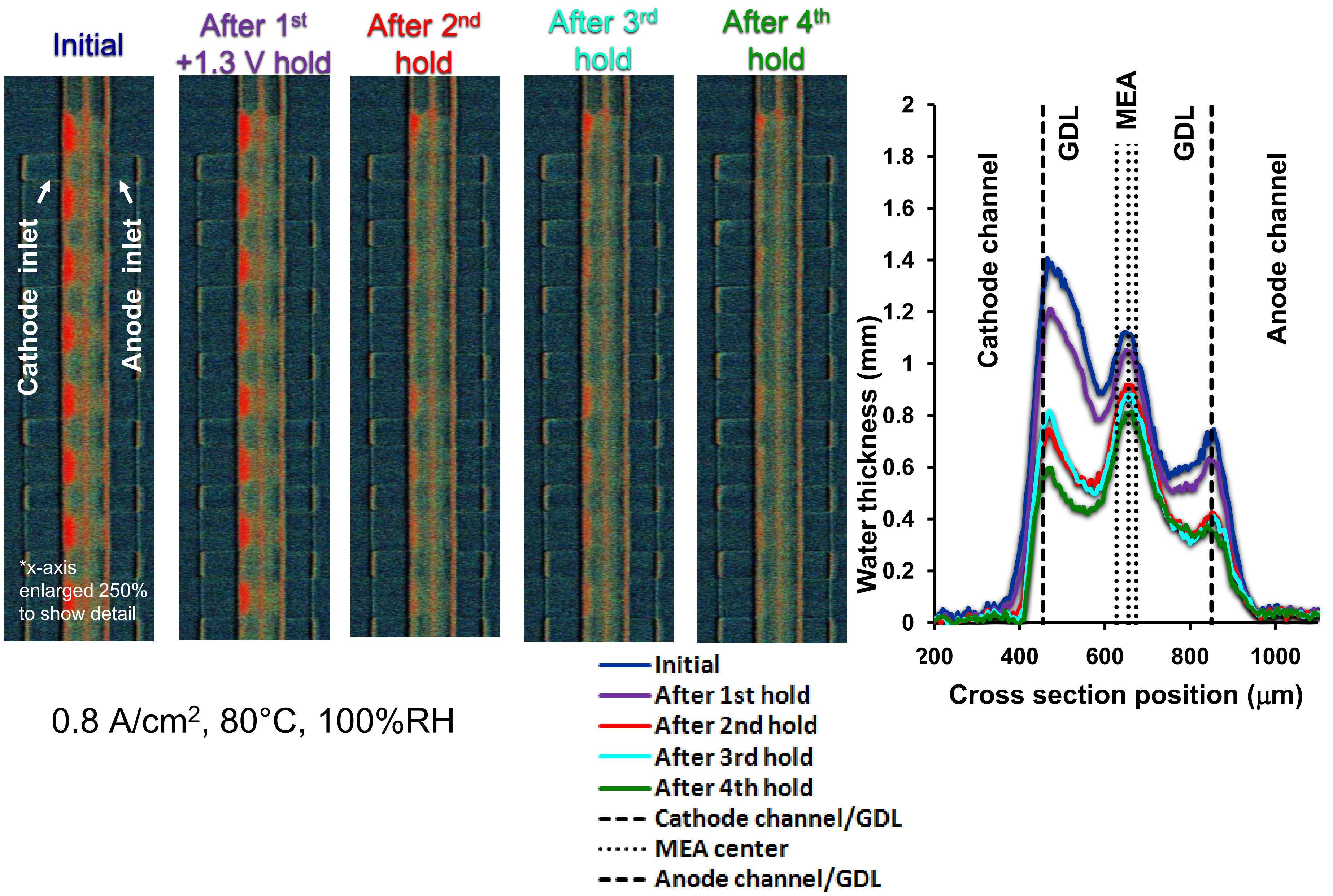
Performance During Carbon Corrosion
80-minute corrosion steps



- Small performance loss after one corrosion cycle
- Large performance loss after 2nd corrosion cycle
- Quicker performance loss for 24BC-24BA (no MPL)

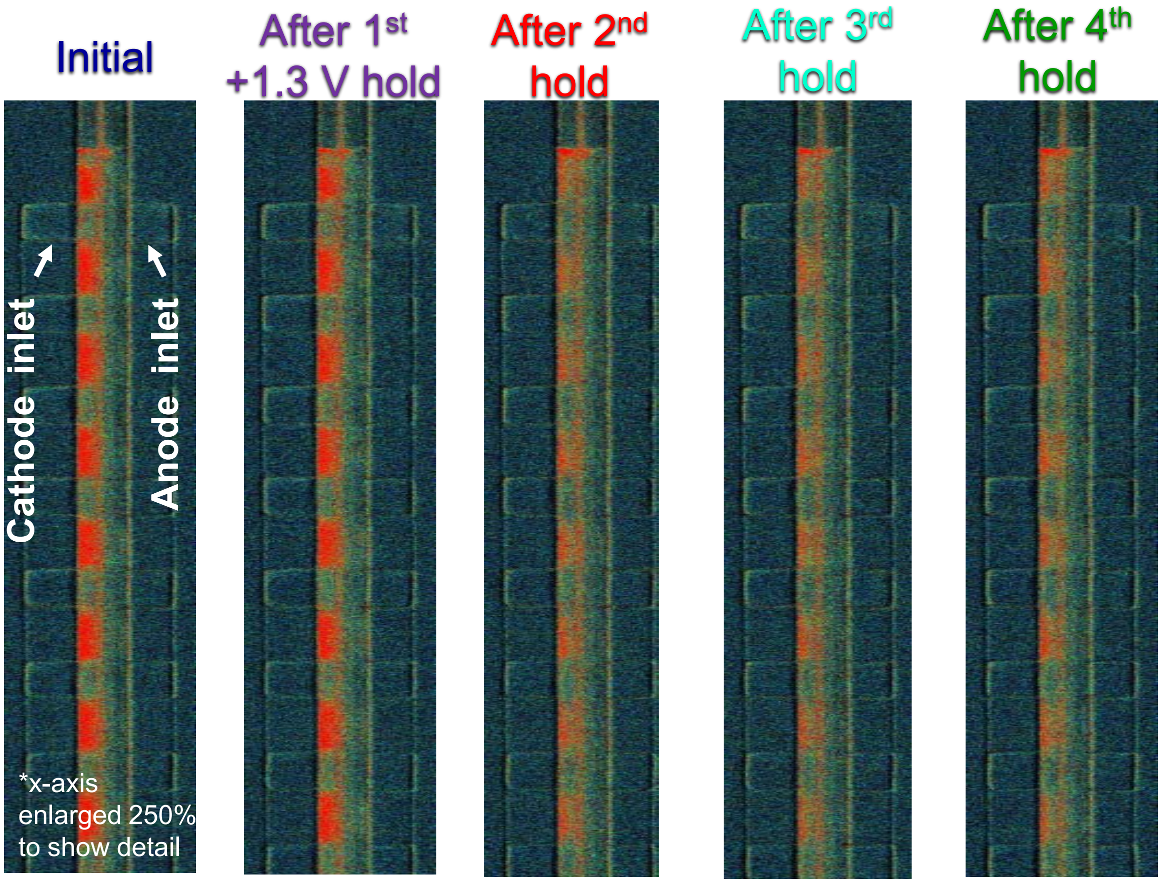


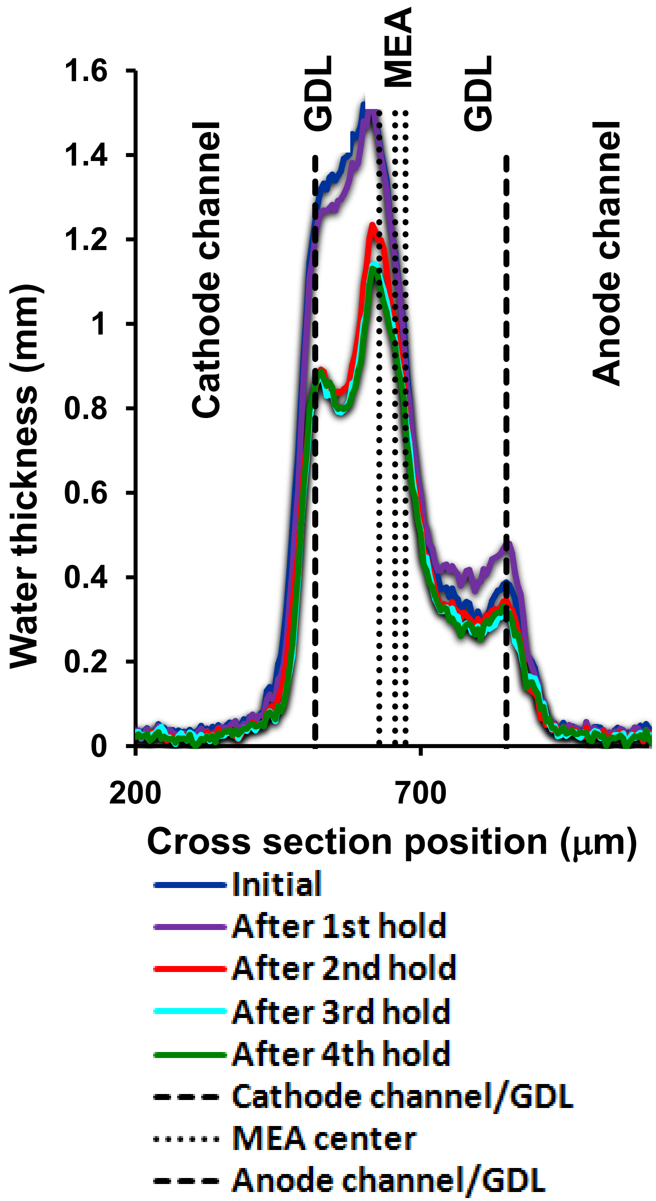
Neutron Images of 24BC/24BC (Cell 12) corrosion series



0.8 A/cm², 80°C, 100%RH

Neutron Images of 24BC/24BA (Cell 13) corrosion series





0.8 A/cm², 80°C, 100%RH

LANL Corrosion Study Summary

- BA (no MPL) has significantly more water next to catalyst layer (in GDL)
- Water in both MEAs is initially similar
  - Induces more carbon corrosion
  - Induces more mass transfer limitations – these mass transfer limitations are not due to water build-up in catalyst layer

- Water content in the electrode layer goes down during carbon corrosion
  - Nearly all change in water content above land
  - Nearly no change in water content above channels

- **Water profiles do not indicate changes due to increased hydrophilicity**
- **Water profiles match heat generation.**

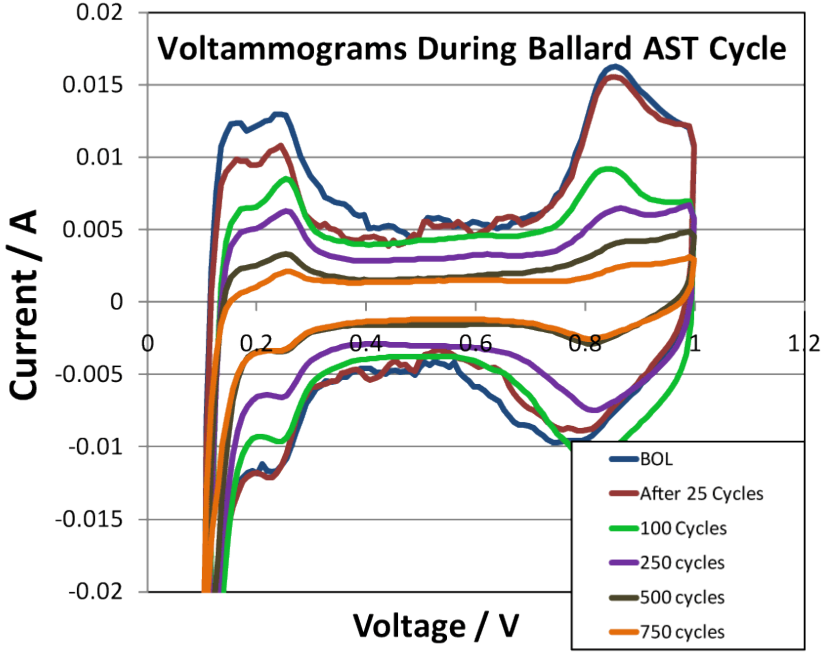
- Changes due to electrode structure collapse?
  - Measure by SEM & TEM

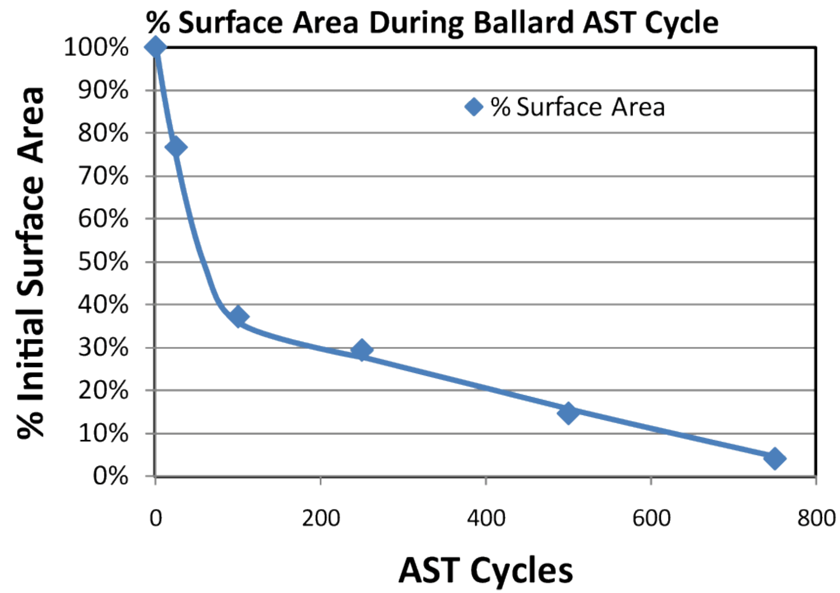
Los Alamos
BALLARD

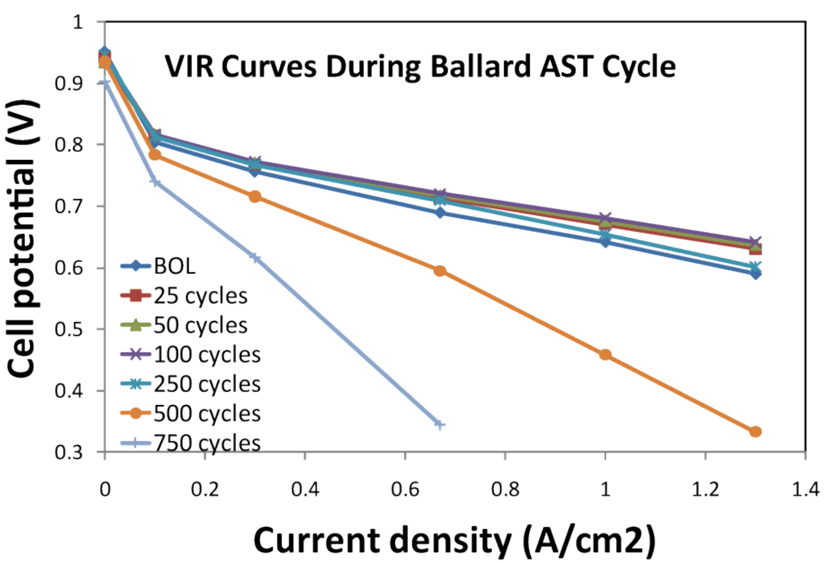
In Situ Neutron Imaging During Corrosion of Commercial MEA

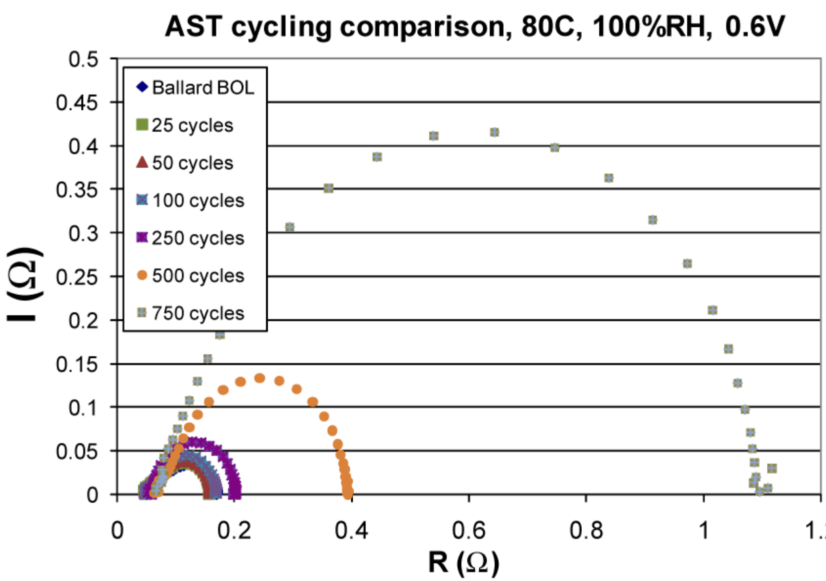
- Improve the understanding of commercial grade MEA durability through high resolution imaging of water in PEM fuel cells
- Neutron imaging allows to evaluate:
  - The effect of MEA degradation on Water Content between Beginning of Life (BOL) and End of Life (EOL) samples subjected to high potential ASTs
  - The change of the MEA water content over the course of a high potential AST protocol
- AST profile: 30 s @ 0.6V, 60 s @ 1.4V, 100% RH, 80°C, 5psi, 1.5 lpm H2 and 2.5 lpm Air
- Measure water content at each current in a polarization curve at BOL, at intermediate cycles and at EOL, in addition measure CV and EIS at intermediate stages.

Electrochemical Performance Data During AST

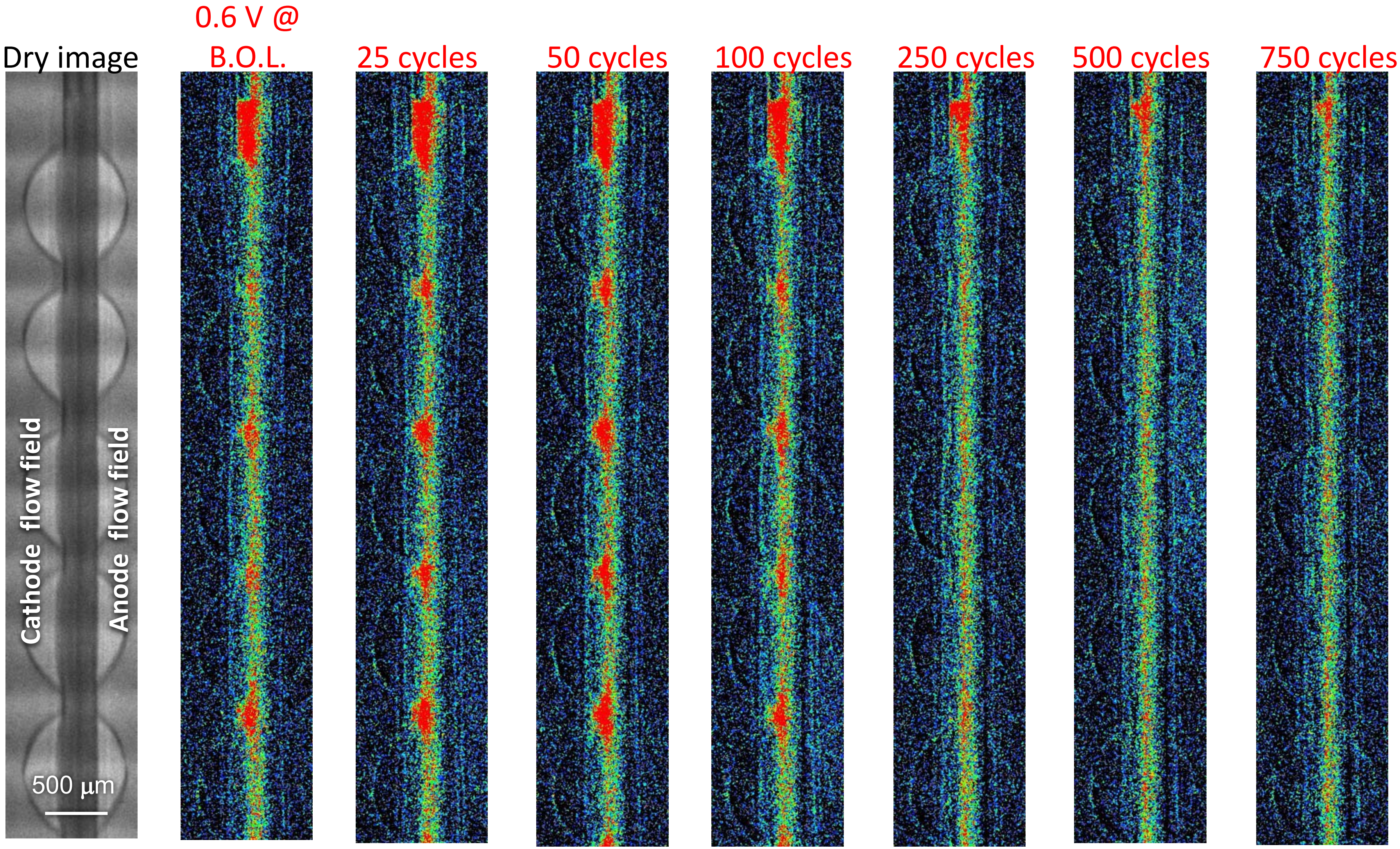






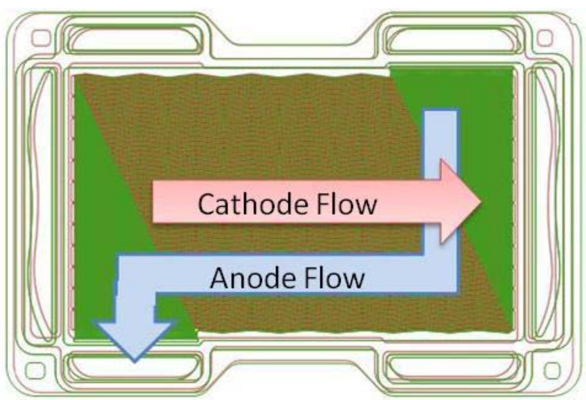


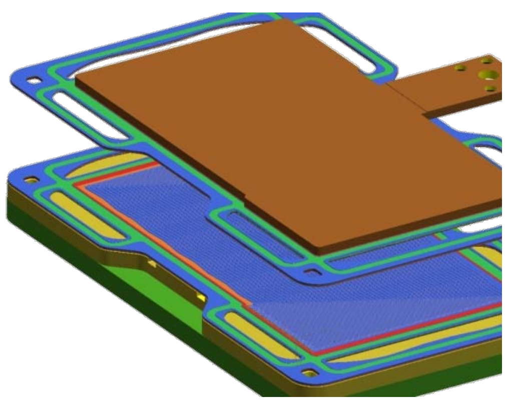
Ballard AST test: 0.6 V images, 80°C, 100%RH; after cycles of 0.6 – 1.4 V in H_2/air

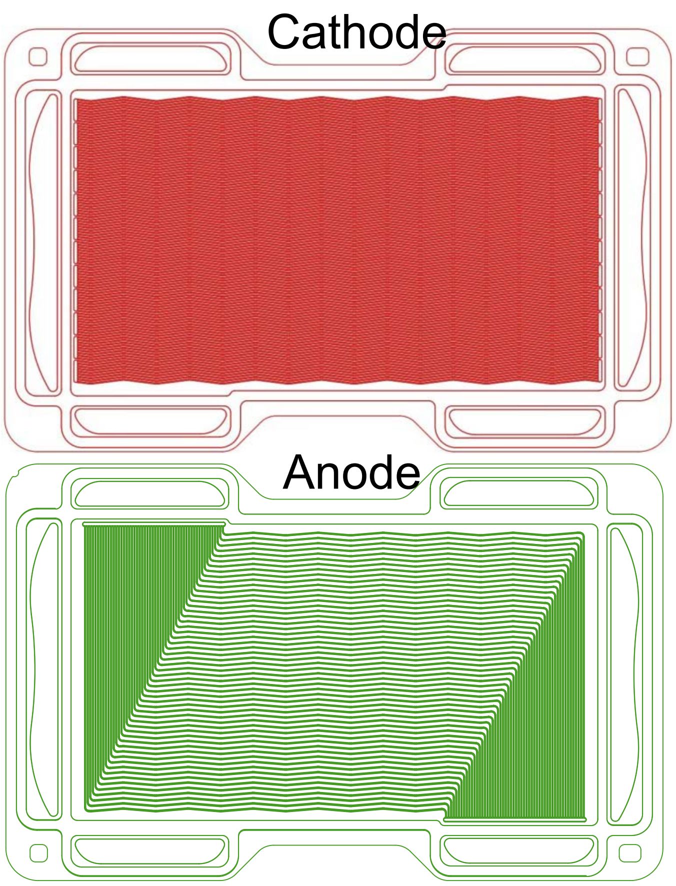


Full-Scale Neutron Imaging of Water in Fuel Cells

- GM has conducted a wide range of neutron imaging studies to optimize full-scale test sections
- The following is an example of some of the investigations carried out at the NIST imaging facility

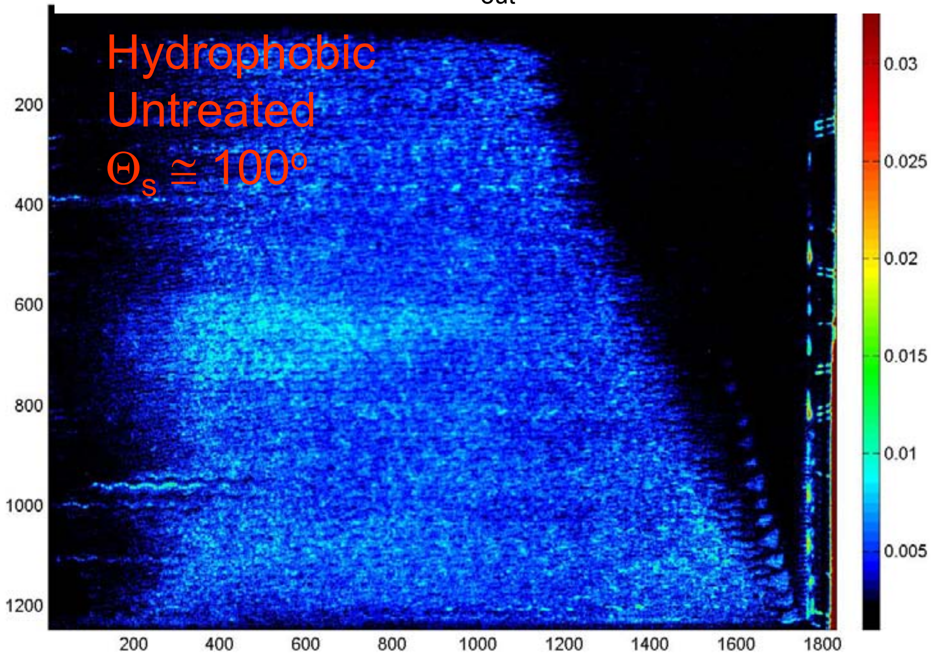


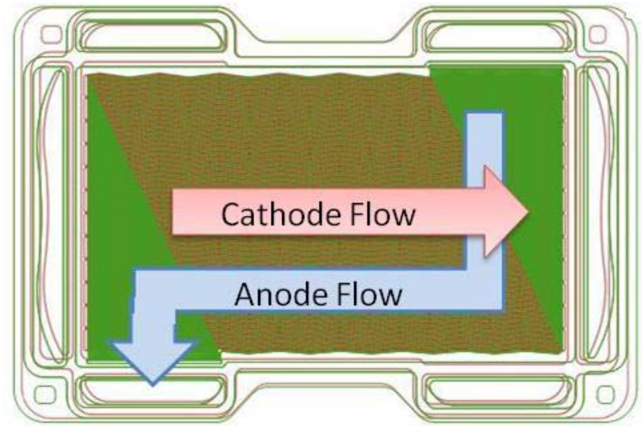




Flow Field Surface Treatments for Improved Water Removal

0.1 A/cm^2, 75^{o}C, A/C RH_{out} = 121/108%





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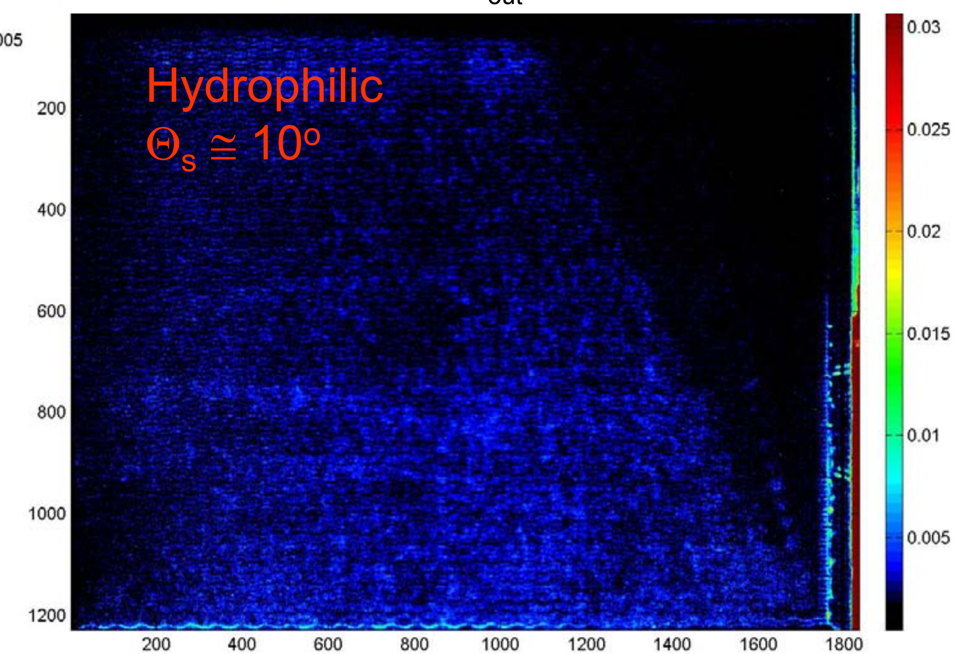
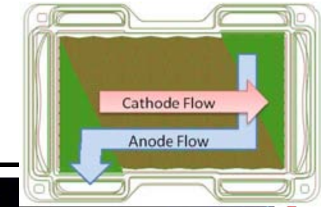
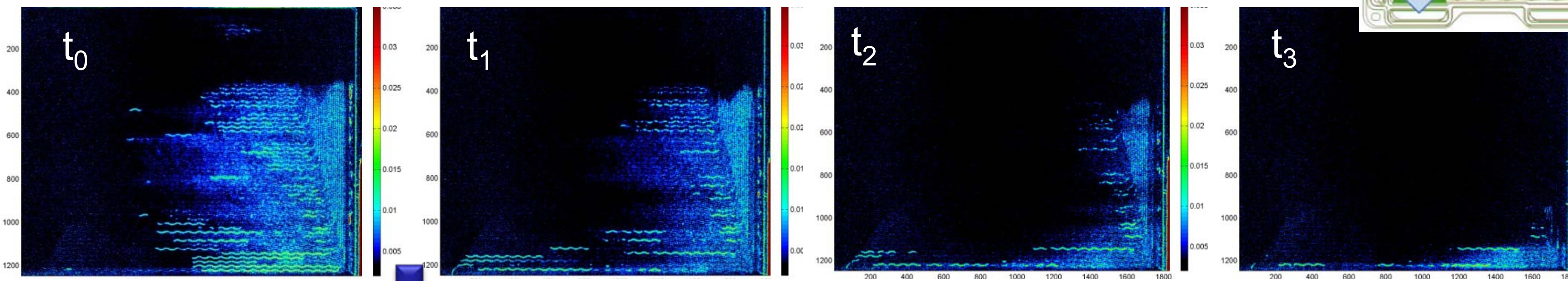


Water profile in active area is very similar, but hydrophilic plates yield a 40% reduction in total water volume.

Optimization of Shutdown Purge for Robust Freeze Start



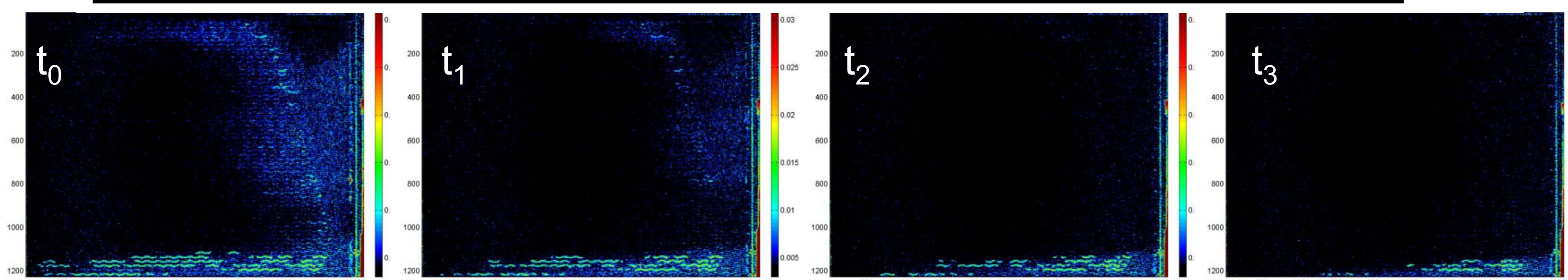
Uncoated Bipolar Plate



Idle operating point (low current density)

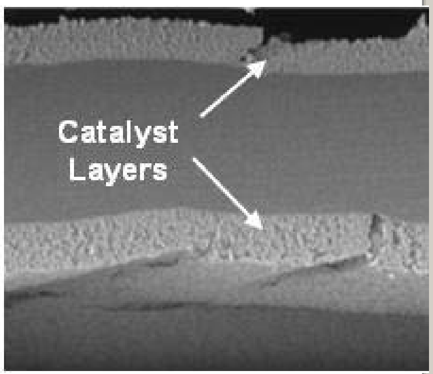
Cathode Purge

Hydrophilic Bipolar Plate

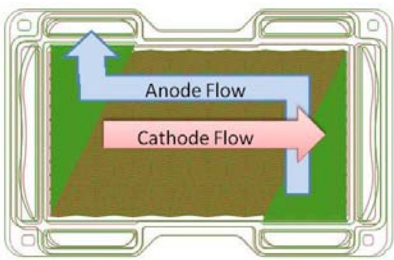


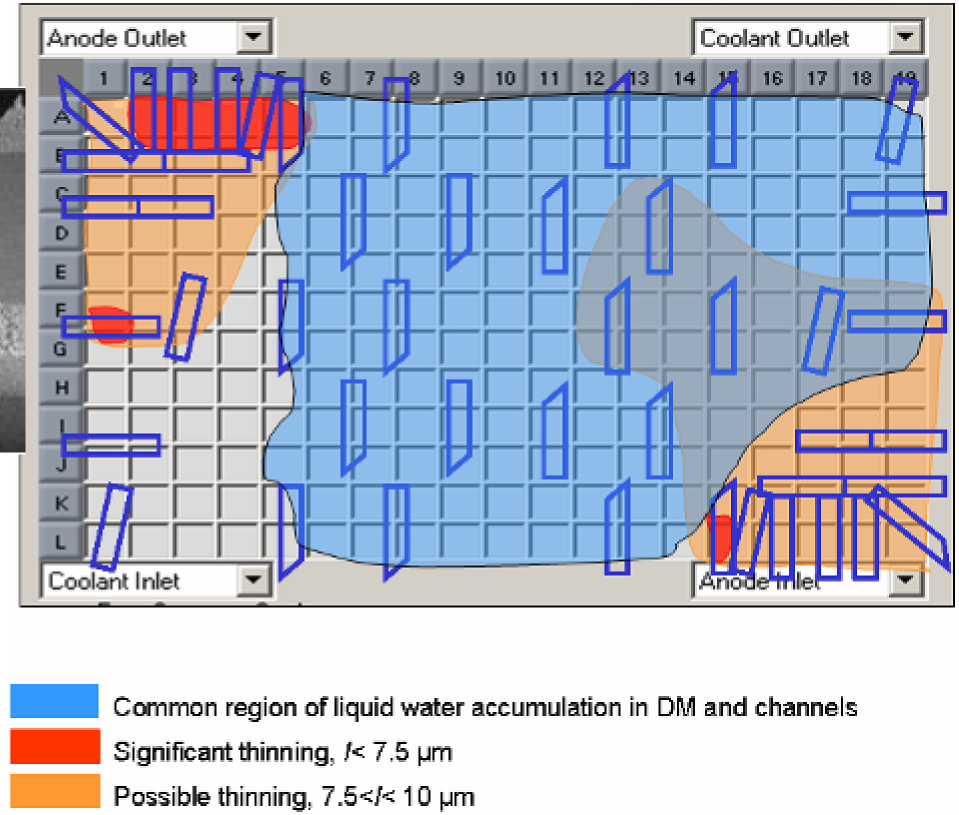
Hydrophilic plates reduce energy required for freeze preparation

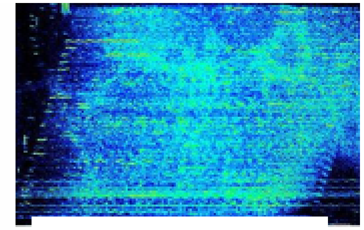
Combining Diagnostics to Investigate Failure Mechanisms



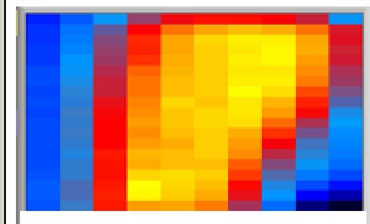
MEA Cross-Sectioning



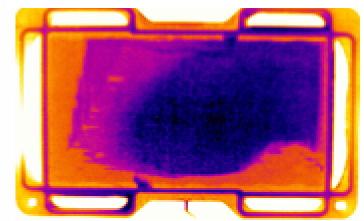




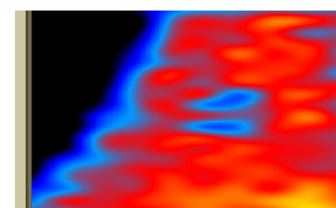
Neutron Imaging



Current Distribution



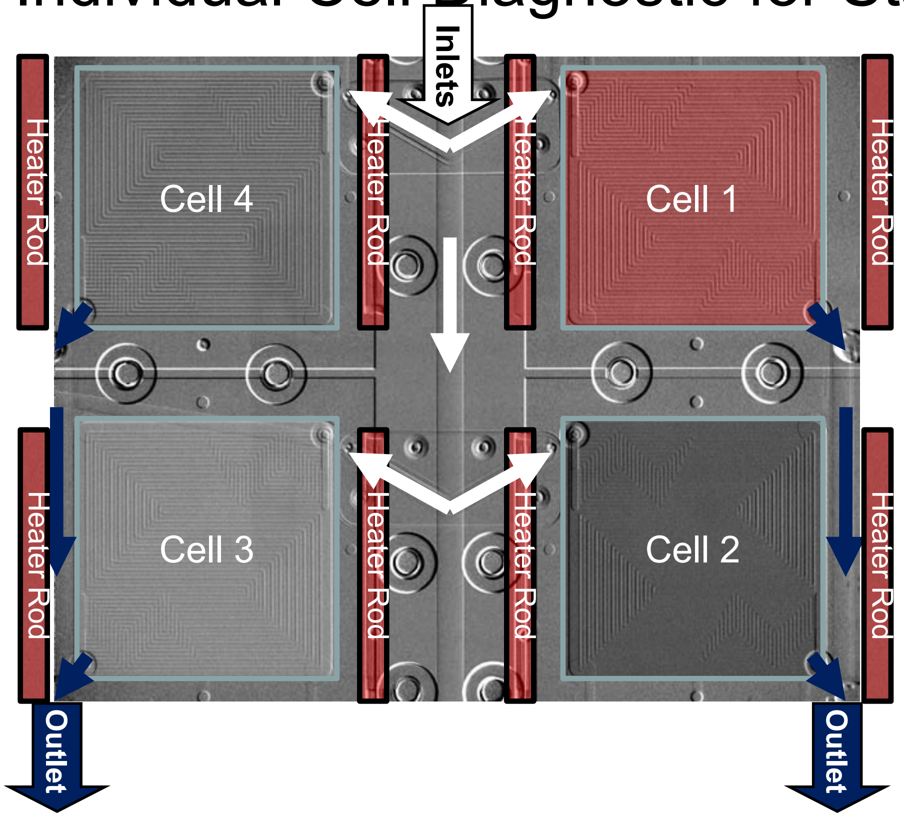
IR Imaging

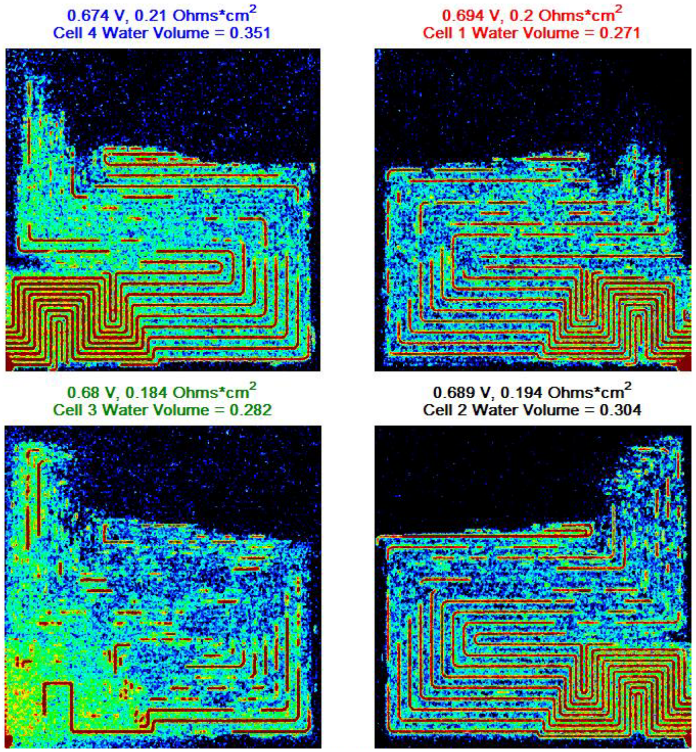


Distributed HAD

Neutron imaging was used to monitor areas of water accumulation during a 2000+ hour durability experiment. Common areas of liquid water accumulation (anode and cathode DM) during operation does not correlate to cathode electrode thinning. Areas of degradation correlate to the areas of the cell that are most frequently dry.

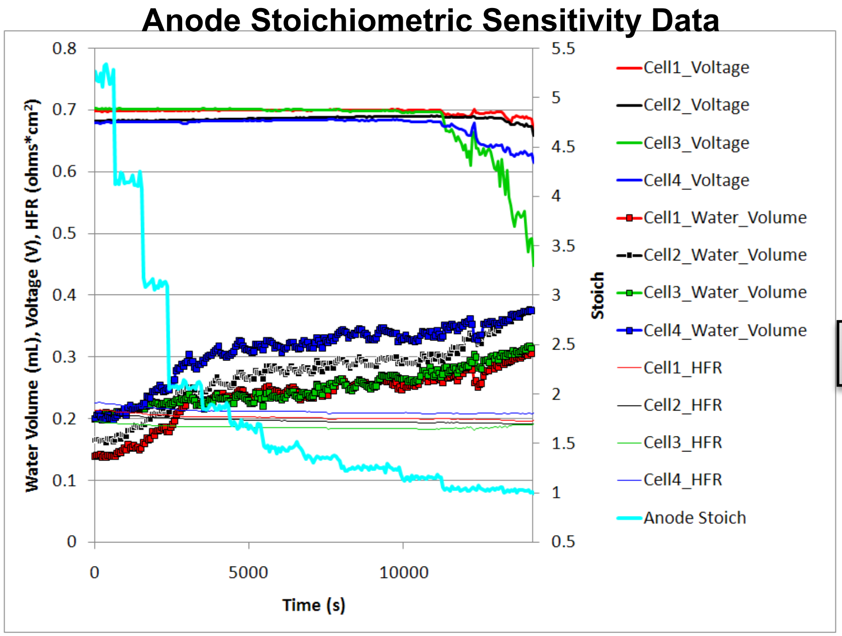
Individual Cell Diagnostic for Stack Transport Dynamics

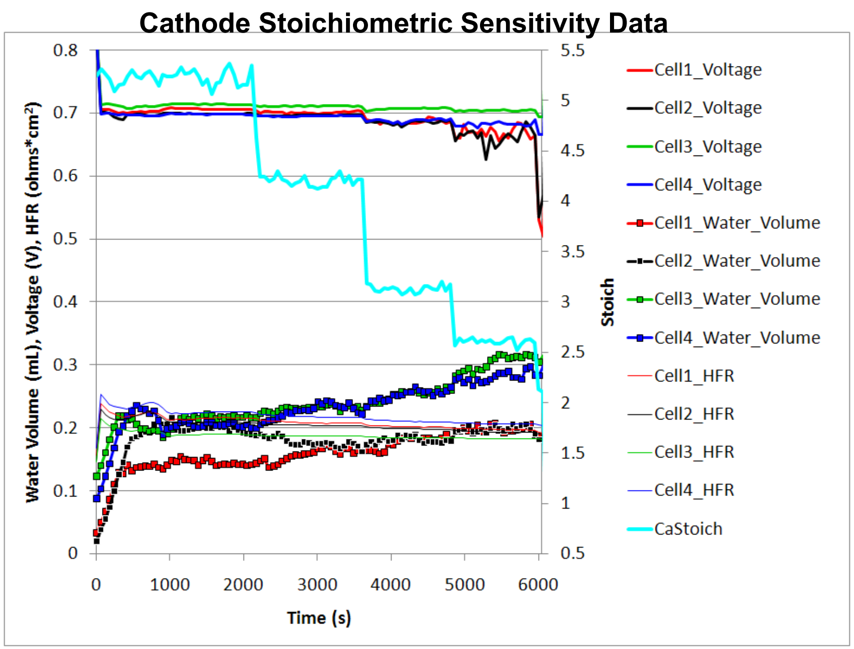


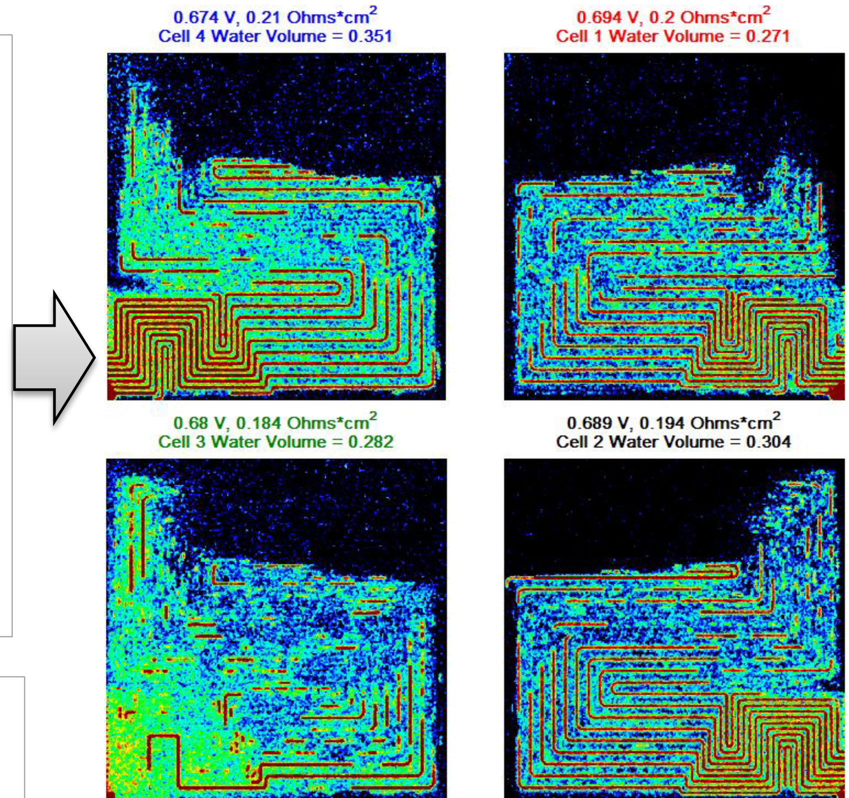


- Planar 4 cell stack to observe liquid stack-level water transport in individual cells during polarization, stoichiometric ratio sensitivity, purge and start-up experiments.
- Enables one to directly observe relationship between liquid water accumulation and performance with precise control of flow and temperature.
- Cells are 50 cm^2 active area with co-flow reactant gas flows. All four cells in stack share the same active area plane electrically connected in series by external bus bars.

Individual Cell Diagnostic for Stack Transport Dynamics







Liquid water distribution at the time of voltage drop during anode stoichiometric sensitivity experiment.

- Repeated experiments demonstrate that the cell with the highest GDL water content fails first.
- In repeated experiments, the first cell to become unstable varies.
- No correlation with channel-level water slugs.
- Blocked channels increase convection through GDL which lowers GDL saturation and enables cell to remain stable at low stoichiometric ratio.

Future Work

- Continue to develop advanced imaging methods for fuel cell research
  - Apply encouraging new high resolution techniques to improve the spatial resolution to sub 10 micrometers with a **goal of 1 micrometer**
  - Can be applied to large scale fuel cell stacks.
- Continued advancement of imaging technology and capabilities at the facility
  - Improve field of view while maintaining spatial resolution to look at larger fuel cells
  - New large format detectors will be incorporated into the facility to improve acquisition capabilities for looking at full scale hardware.
  - Provide higher frame rate capabilities up to 100 frames per second in response to user needs.
- Add new cold imaging capabilities using new facility to be built for expansion of the NCNR

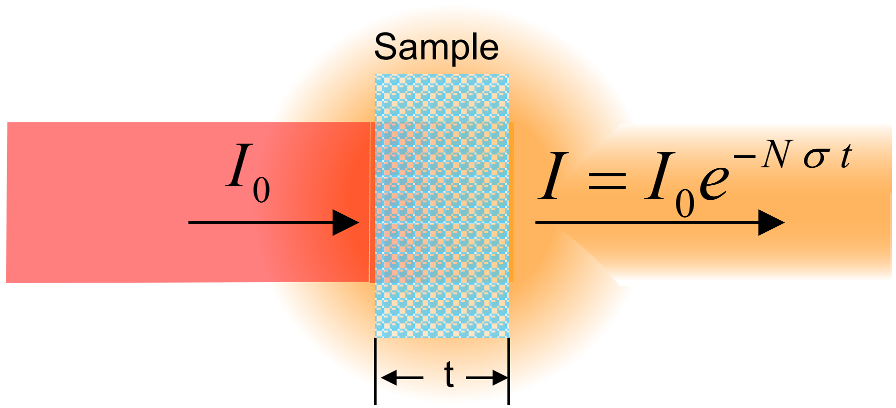
Summary of Technical Accomplishments/Results Presented

- Ultra-High Resolution Experiments
  - Devised new method that is a path to overcome conventionally accepted 10 micrometer resolution limit for MEA imaging.
  - Demonstrated method by improving a detector with 250 micrometer resolution to a spatial resolution of 10 μm; **a 25 fold improvement**.
- LANL Study of Water Distribution due to Carbon Corrosion
  - Although corrosion creates a hydrophilic electrode the increase in overpotential creates more heat, which dominates the water transport.
- LANL/Ballard Accelerated stress testing of Ballard MEA
  - The effect of MEA degradation on Water Content between Beginning of Life (BOL) and End of Life (EOL) samples subjected to high potential ASTs
  - In situ CV/EIS/VIR/Neutron Imaging shows loss of catalyst surface area correlates to less water after many cycles (small increase in water content after a few cycles)
  - MEA tested is commercial grade demonstrating the relevancy of the methods used here
- GM Imaging of Full Scale Fuel Cell Hardware
  - A wide range of studies using full scale hardware tested at NIST beamline
  - One example of 2000+ hours of durability testing shown
  - Electrode degradation observed to be more prevalent in dry areas of cell
  - Purge studies show hydrophilic plate treatment improves purge performance

Technical Back-Up Slides

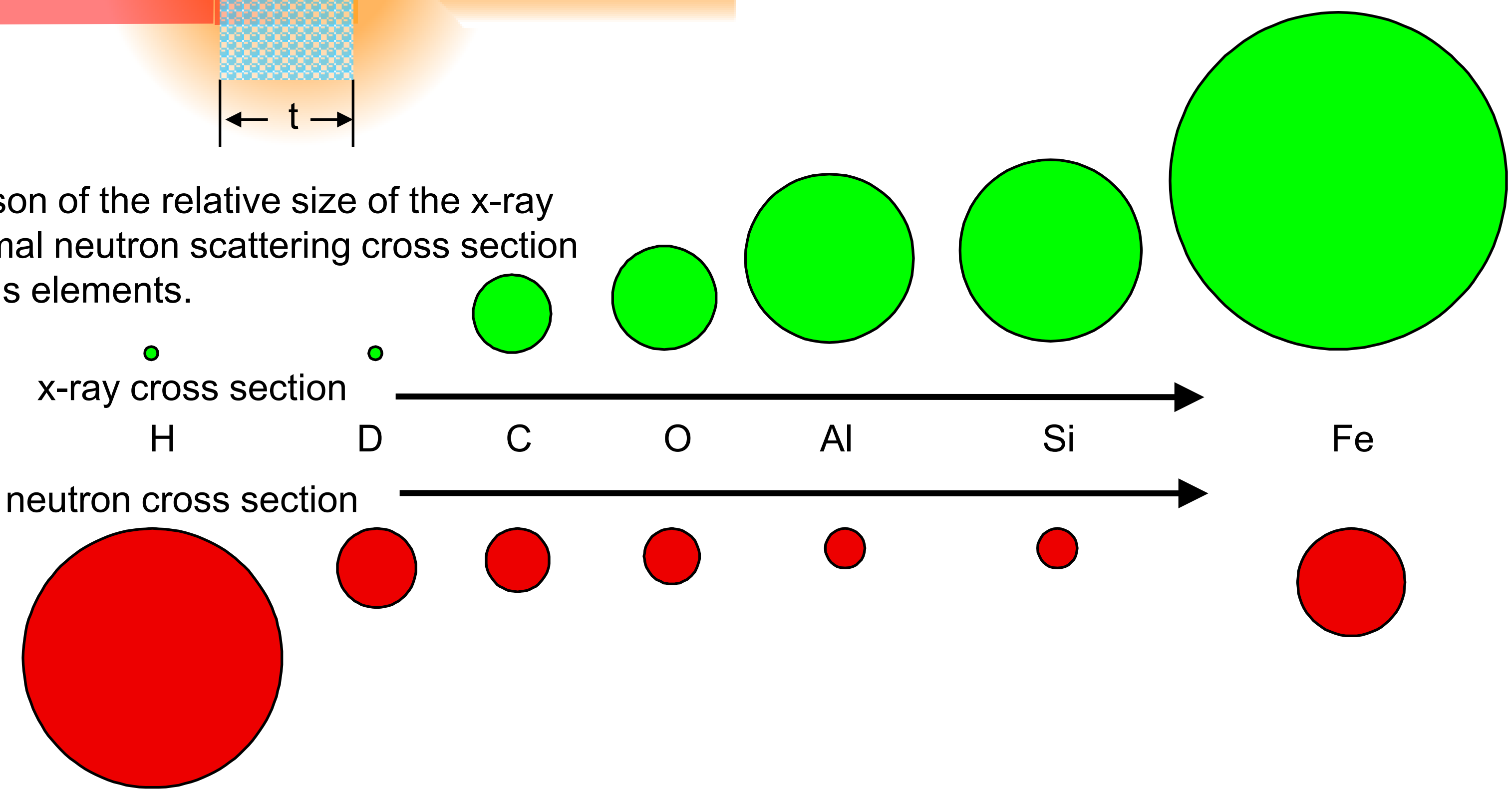
Why Neutrons

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

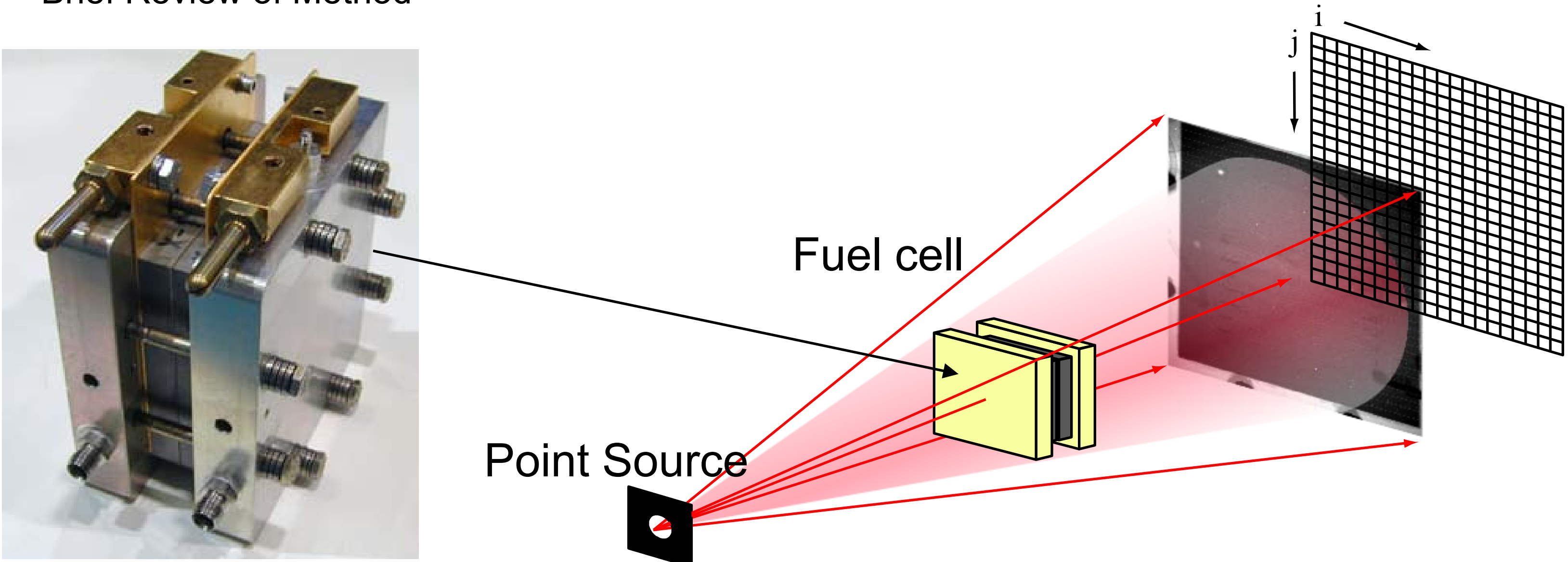


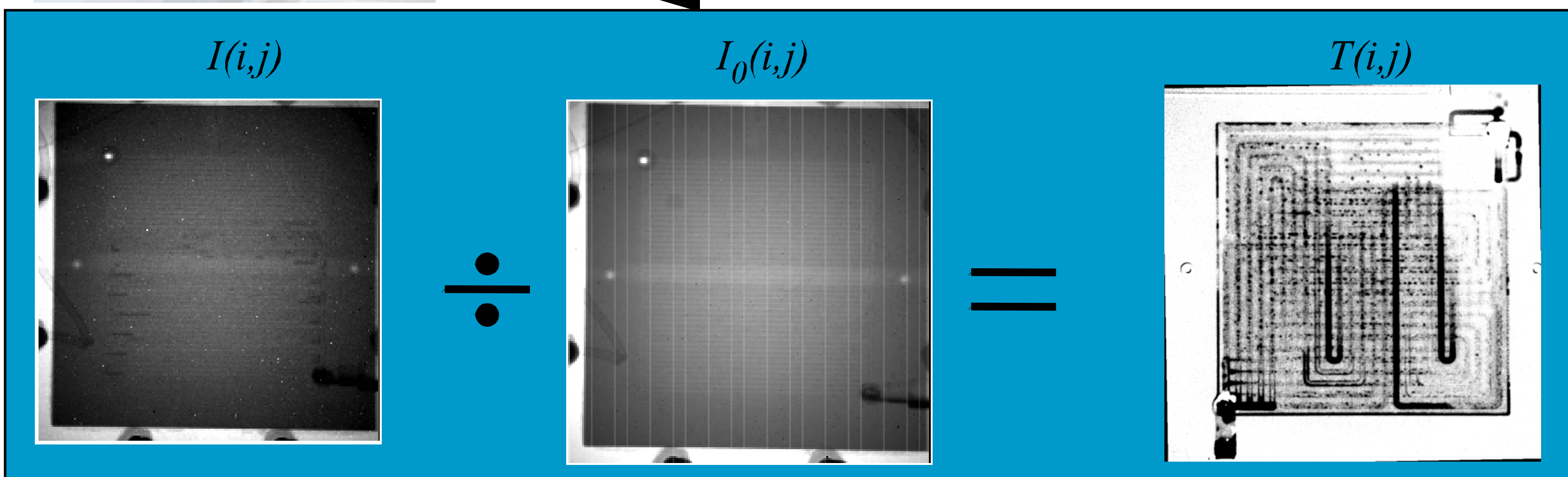
- N – numerical density of sample atoms per cm^3
- I_0 - incident neutrons per second per cm^2
- σ - neutron cross section in ~ 10^{-24} cm^2
- t - sample thickness

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



Brief Review of Method





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

NIST Fuel Cell Infrastructure

- Hydrogen Generator, max flow 18.8 slpm
- State of the art Fuel Cell test stand, with graphical User Interface
- Flow control over H_2, Air, N_2, He, O_2:
  - H_2: 0-50, 0-500 and 0-3000 sccm
  - N_2: 0-2000 sccm
  - Air: 0-50, 0-100, 0-500, 0-2000, 0-8000 sccm
  - O_2: 0-500, 0-5000 sccm
  - He: 0-600, 0-6000 sccm
- 1.5 kW boost power supply allowing Voltage control of the cell to a minimum of 0.01V
- Heated Inlet gas lines, Built-in humidification
- 8 T-type thermocouple inputs
- 2 Viasala dew point sensors available
- Interfaced with facility hydrogen safety system
- Freeze Chamber Available to All Users
  - **-40°C to +50°C, 1000 kW cooling at -40°C**
  - **32" W, 24" H, 18" D sample volume**
  - Explosion-proof, and Hydrogen safe
- **Zahner IM6eX Electrochemical Workstation available**
- ***All users of the NIST NIF have full access to all fuel cell infrastructure***

Fuel Cell Stand

Freeze Chamber Installed inside the Imaging Facility