Technical-Assistance to Developers

Testing and Analytical Assistance

May 18, 2009

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(Assistance provided by entire LANL FC team)

FCP_02_Rockward

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

Overview

- Timeline
  - Start: 10/03
  - End: ongoing
  - % complete: N/A
- Budget
  - "Technical Assistance to Developers" funded at \$570K/y
    - DOE share: 100%
    - Contractor share: N/A
  - Most DOE-directed effort under the parent task generates proprietary data
  - **FY09 funding: $**570K/y

- Barriers
  - A. Durability
  - B. Cost
  - C. Electrode performance

- **Partners/Collaborators**
  - Full list Available

Technical Assistance to Developers

This task supports Los Alamos technical assistance to fuel-cell component and system developers as directed by the DOE. This task is expected to include testing of materials and participation in the further development and validation of a single cell test protocols. This task also covers technical assistance to the U.S. Council for Automotive Research (USCAR) and the USCAR/DOE Freedom Cooperative Automotive Research (FreedomCAR) Fuel Cell Technology Team. This assistance includes making technical experts available to the Tech Team as questions arise, focused single cell testing to support the development of targets and test protocols, and regular participation in working and review meetings.

In addition, LANL scientists interacted with several of the 'solicitation winners' outside and/or beyond any proposed collaborations.

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Technically-Assisted Collaborators/Partners

- USFCC
  - Single Cell Task Force
  - Durability Task Force
- Working Group 12 Doc: ISO 14687 Hydrogen Quality Standard
- Cabot Fuel Cells
- W.L. Gore
- SGL Carbon
- BASF
- CIDETEC - Centro de Tecnologías Electroquímicas
- Palmetto FC Technologies
- Ca Fuel Cell Partnership
- DANA Corp.
- Smart Chemistry Corp.
- FreedomCAR (GM, Ford, and Daimler-Chrysler)
- Nuvera
- Brookhaven National Laboratory
- University of New Mexico
- Oak Ridge National Laboratory
- Argonne National Laboratory
- Sandia National Lab
- University of Illinois Urbana-Champaign
- University of California – Riverside
- University of California – Santa Barbara
- Fuel Cell Technologies
- General Motors
- NREL (National Renewable Energy Lab)
- Virginia Polytech and State University
- NIST (National Institute of Science and Technology)

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Case Western Reserve University

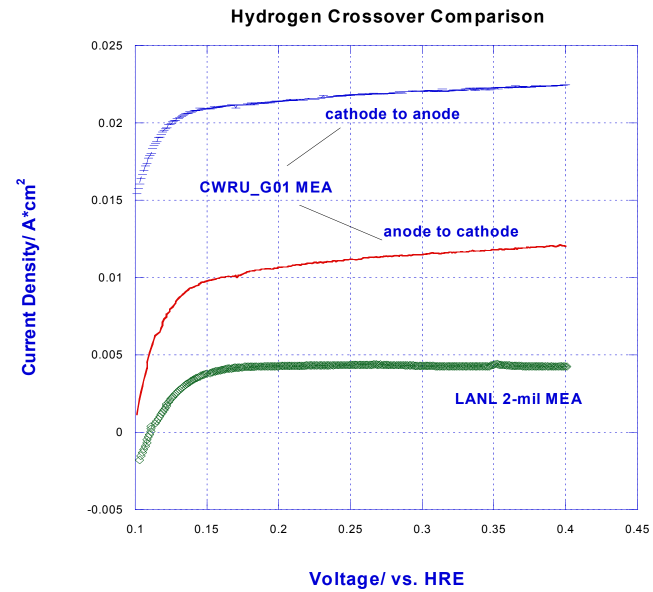
Task:

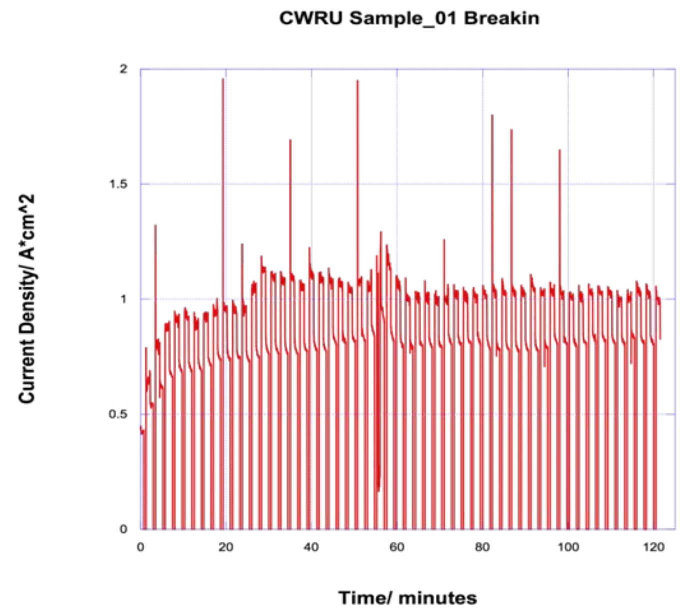
Investigate performance concerns with commercially available CCMs

Approach:

1.CWRU provided an MEA for testing at LANL's facility for comparison with their results)

2.Summary and email-exchange of findings





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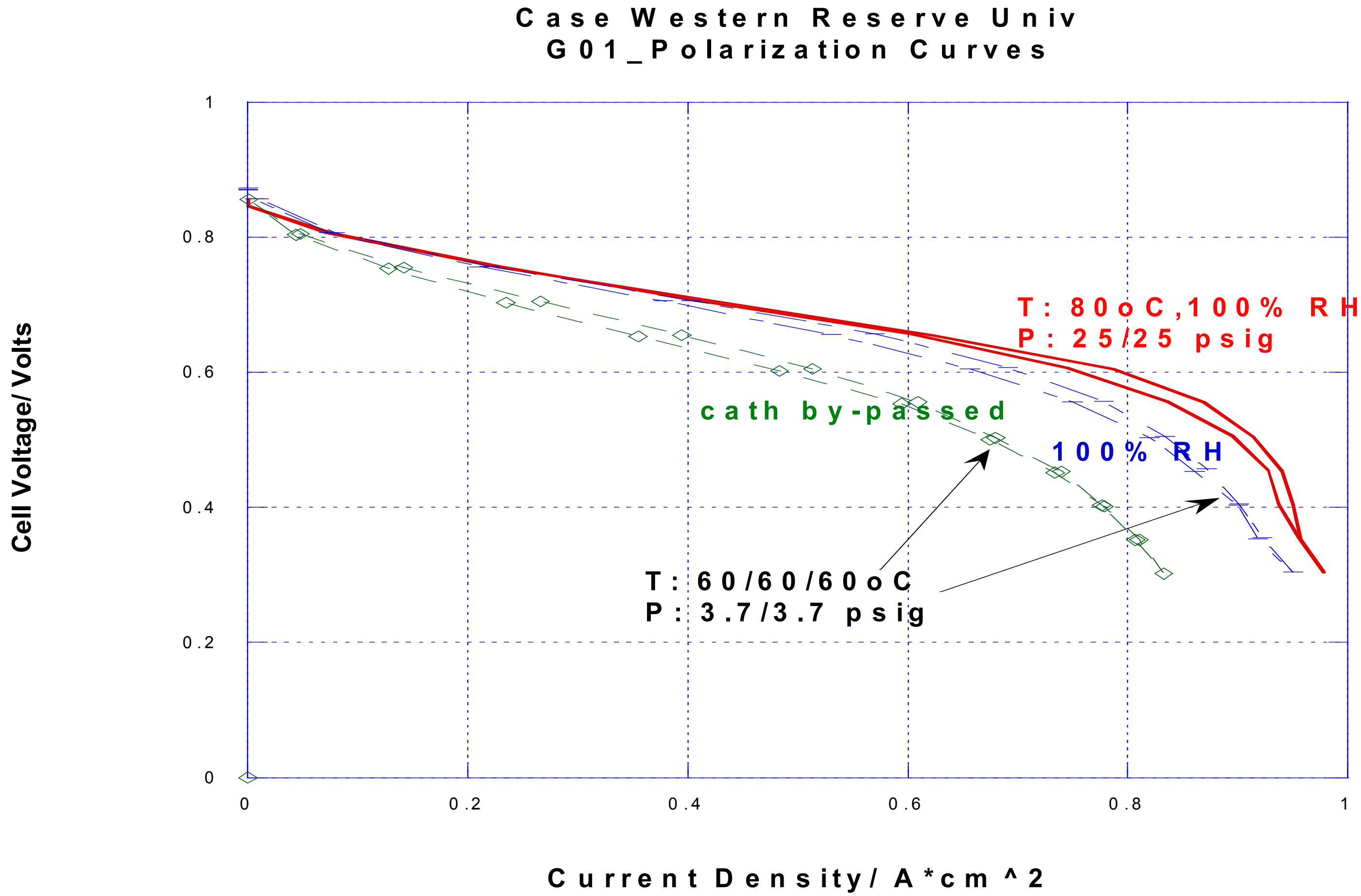
Case Western Reserve University



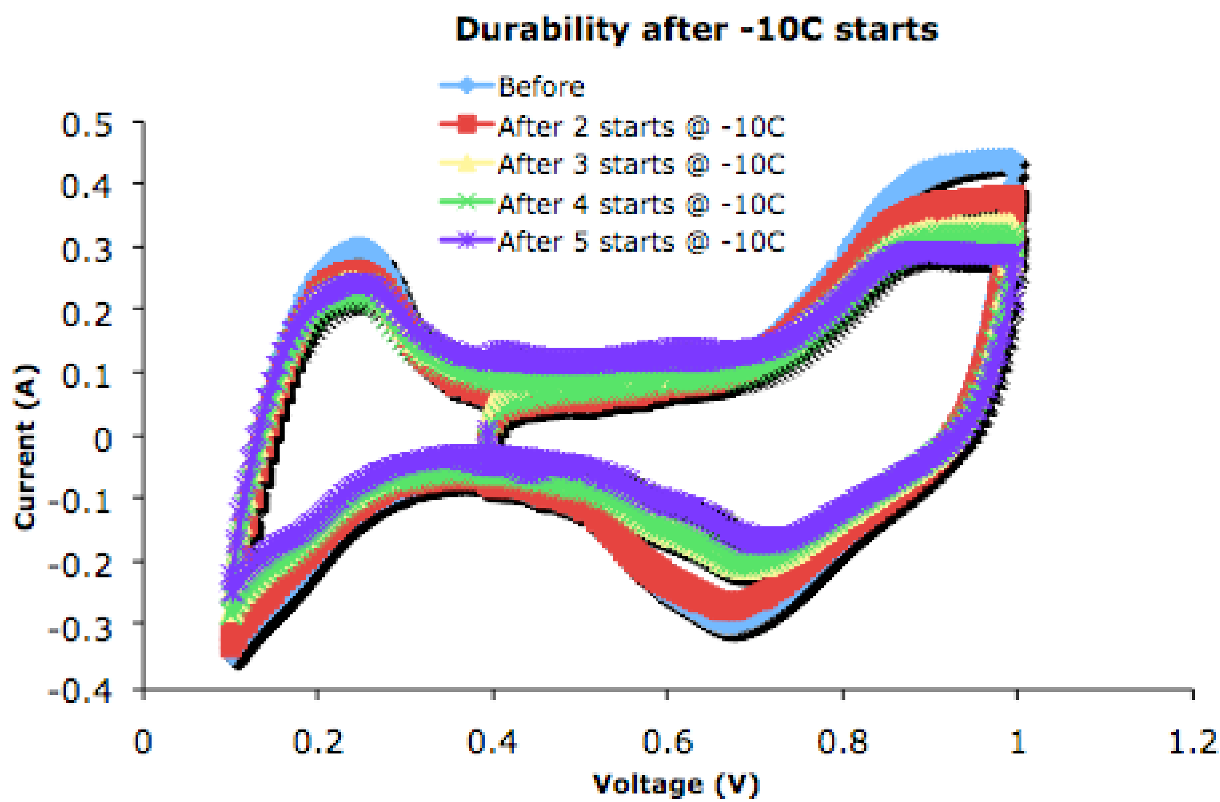
- Significantly higher H_2 cross-over measured in the CWRU sample (3-5 times)
- Low OCV typical of high H_2 cross-over
- CWRU cell operated with descent performance even at low T, pressure and/or RH

Nuvera PEM Freeze Workshop

Los Alamos presented their results on the “Performance and Durability of PEM Fuel Cells Operated at Sub-Freezing Temperatures”

Los Alamos demonstrated loss in cathode catalyst surface area with repeated isothermal cold starts at sub-freezing temperatures. This loss was a function of MEA preparation method.

Los Alamos coordinated a breakout session and provided valuable input on single cell testing and location of ice formation.



HyCell Energy, LLC
Pedicab Engineering Study

Task:

Provide Fuel Cell expertise/guidance

Approach:

1.Research the existing FC stack and its viability/compatibility for the intended purpose.

2.LANL scientists will summarize their findings and recommendations

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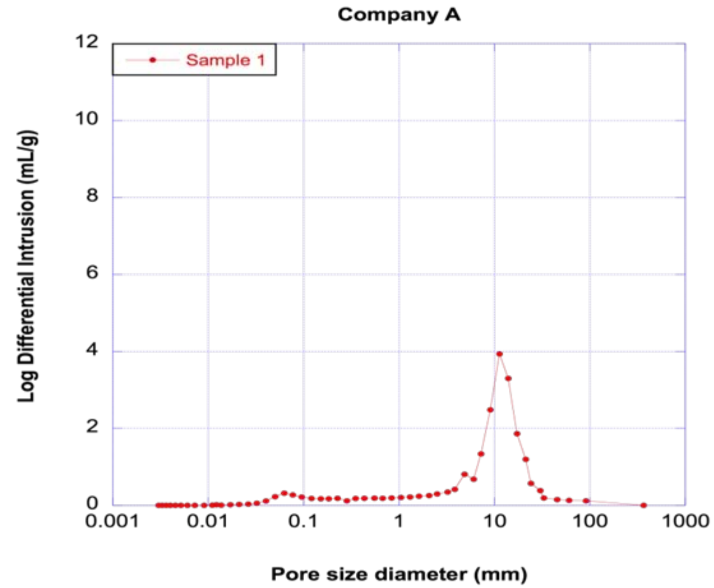
Mercury Intrusion Porosimetry (MIP) Gas Diffusion Backing Measurements

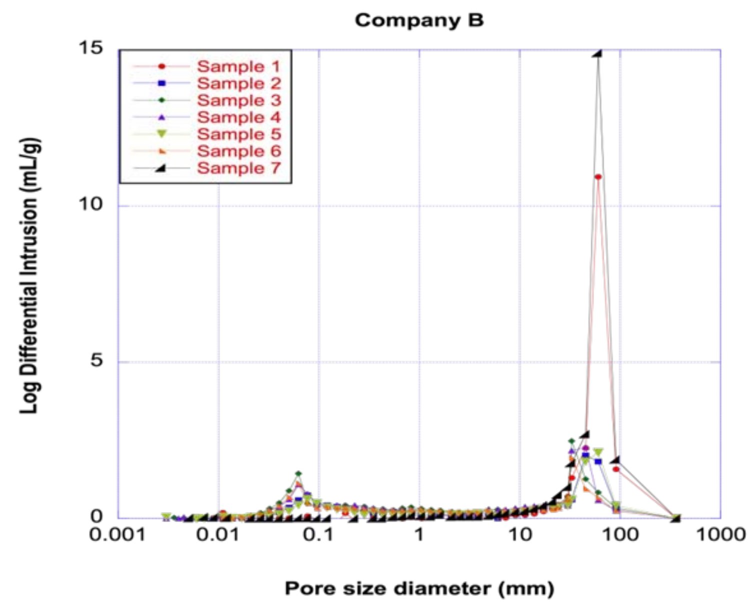
Task:

Provide Mercury Intrusion Porosimetry (MIP) results for several different manufactured GDL backings

Approach:

1. *14 samples from 6 manufacturers were provided*
2. *LANL scientist conduct measurements and provide results*





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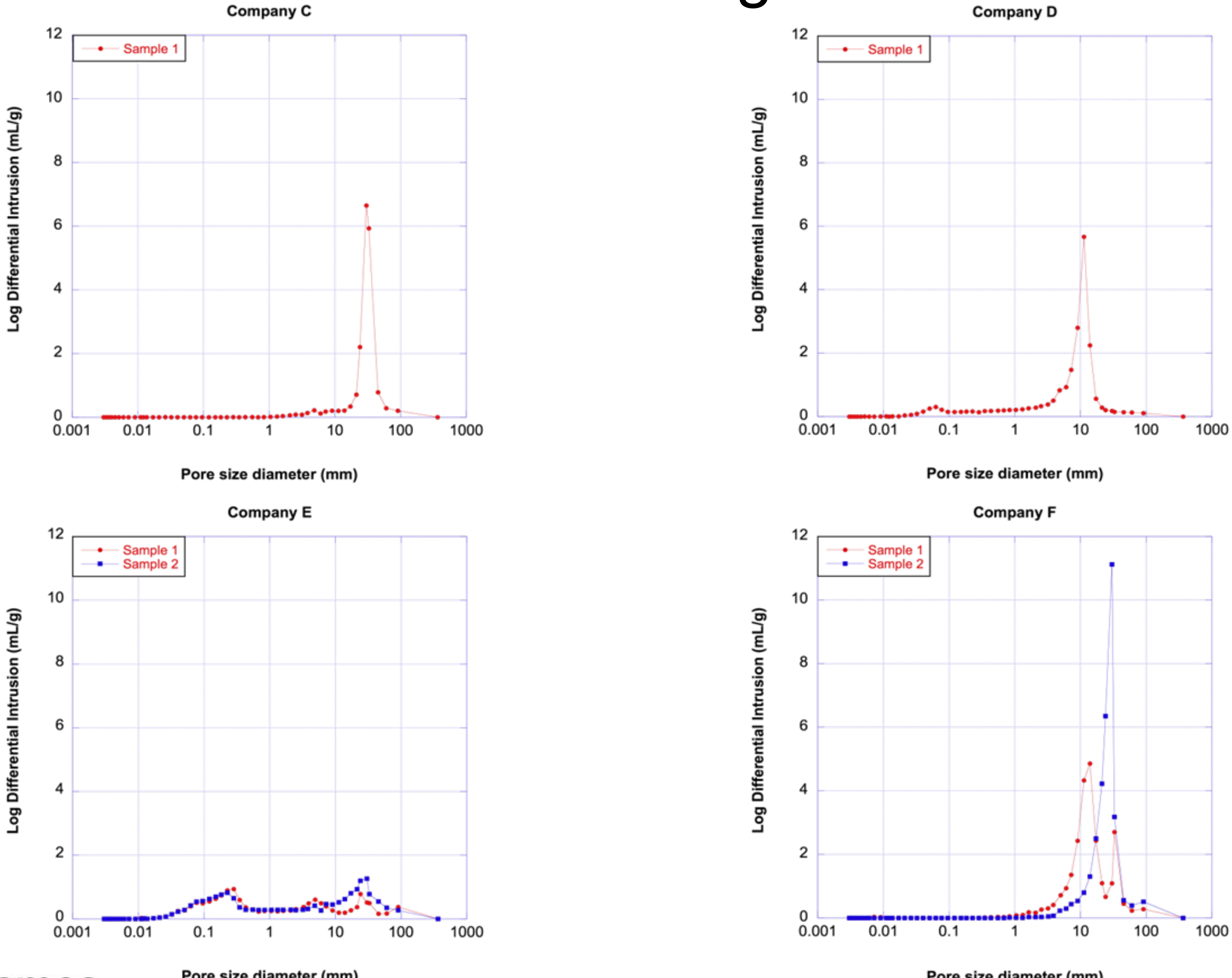
Mercury Intrusion Porosimetry (MIP) Gas Diffusion Backing Measurements



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NIST-Metrology Group

Task:

Investigate cell-to-cell performance with a commercially available CCMs and/or possible in-house testing issues.

Approach:

1.LANL scientist visited test site to observe test facility and testing /analytical equipment

2.LANL scientist provide testing guidance as necessary; pointing out best test practices

3.NIST will provide a CCM sample for testing at LANL's facility

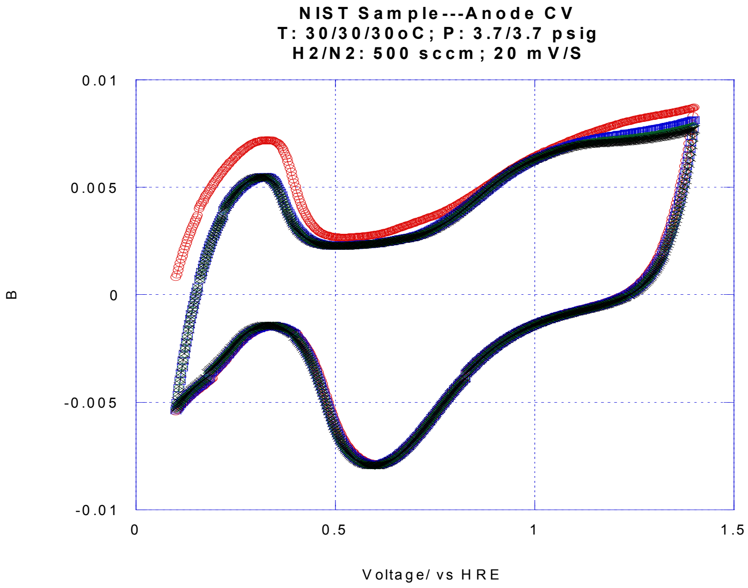
4.Summary and report to be sent to NIST

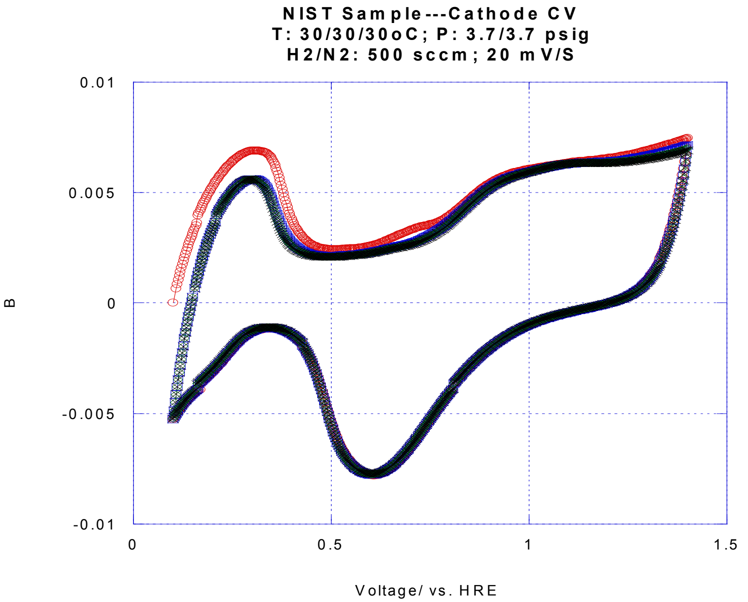
NIST-Metrology Group

NIST Visit:

1. *Testing and analytical equipment was adequate*
2. *Gases: H_2/Air/N_2: concerned with quality of gases*
3. *Limited to daytime testing*
4. *Cell performance decreased after each reconditioning*

NIST-Tests Results





- Initial CVs show normal behavior with little to no H_2 cross-over;
- Low cross-over further confirmed
- EASA nearly identical as expected considering identical Pt loadings

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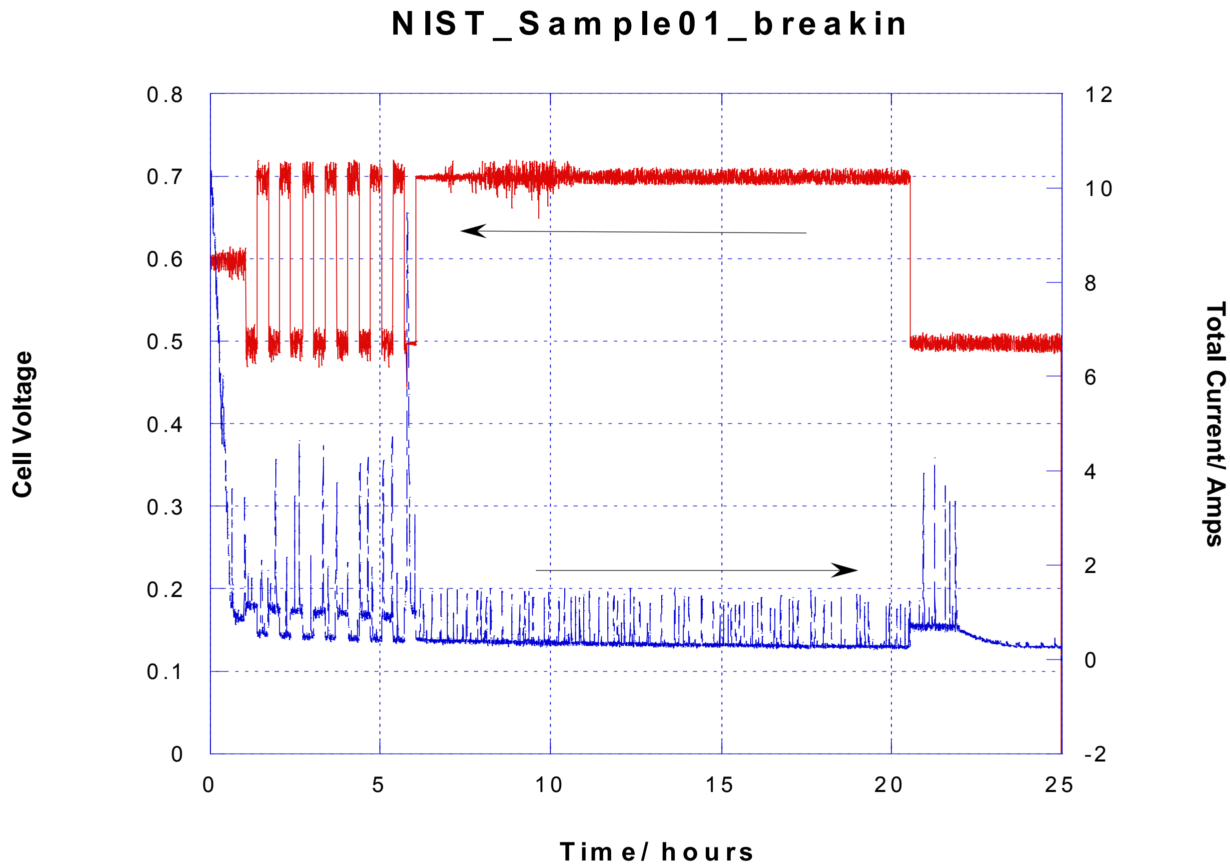
NIST-Results cont'd



Initial break in results were not as we would of expected, the break-in could not be carried out fully. After hours of undesirable results, we disassembled and…

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NIST-Results Problem

A hole developed sometime during the testing

Possibilities:

1.Location of hole may suggest materials issue; typical hole formations occur at the gas inlets.

2.Pin-hole formations possible during assembly of CCM possible when utilizing paper gas diffusion backings. (not likely)

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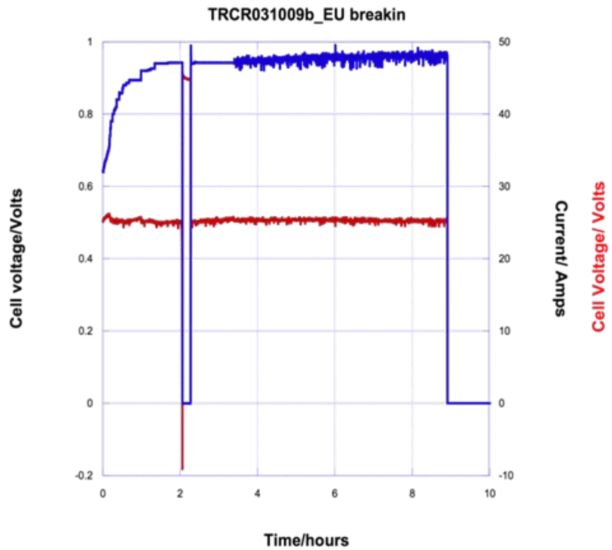
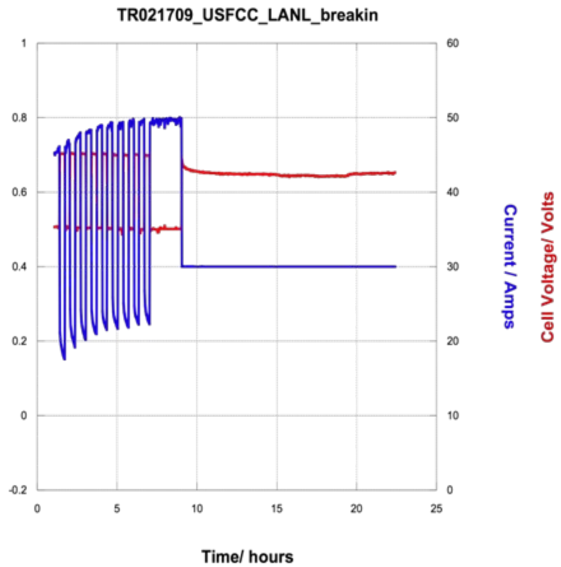
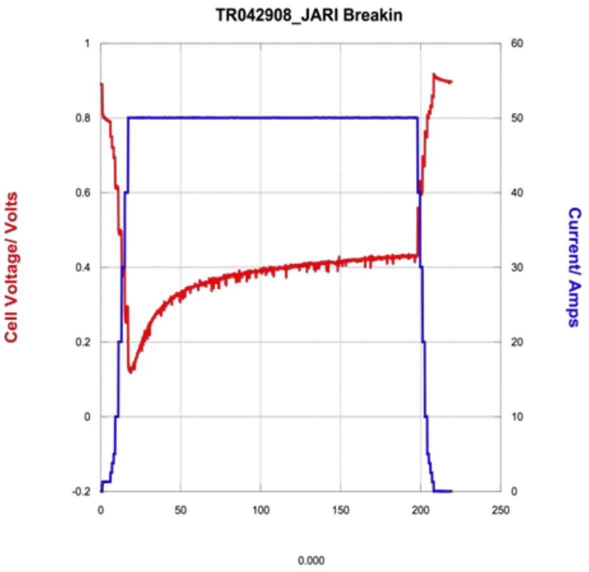
Evaluating Standard Procedures

LANL used three different protocols (EU, JARI, USFCC/LANL). Korea and China to be tested after protocols are received.







Testing at the low Pt loadings (DOE targets) are continuing until other protocols are received. These results reflect anode and cathode loadings of 0.1 & 0.2 mg Pt/cm^2, respectively.

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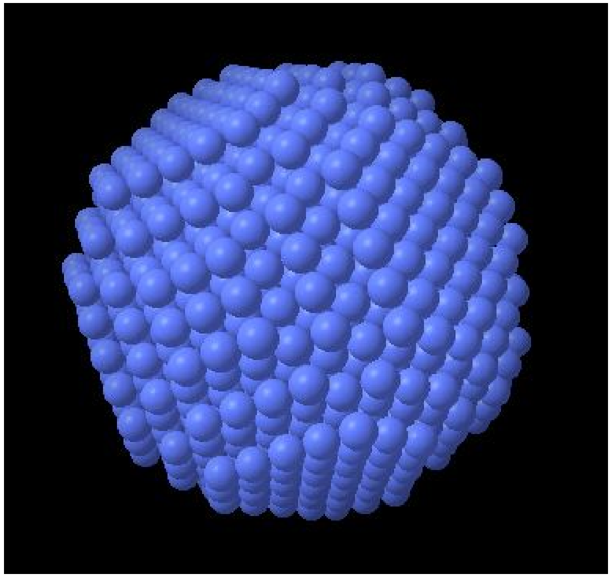
Fuel Cell Nano-Catalysts Materials

- New catalysts such as Pt-Pd core shell
- Higher Pt loading Pt-C
- Unsupported Pt-C

- Composition
- Crystal Structure
- Crystal size distribution
- Reactivity



Pt small crystal model

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Characterization Techniques

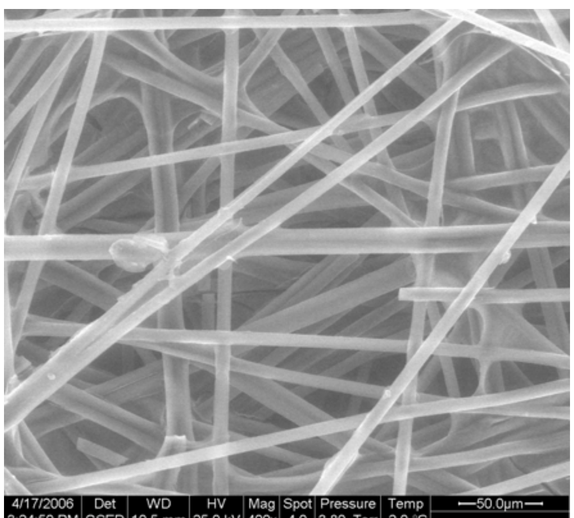
- Microscopic
  - TEM, ESEM, AFM-STM, X-Ray Microscopy, Neutron Imaging (NIST)
- Macroscopic
  - Structure
    - XRD, XAFS (Stanford,ANL)
  - Chemical analysis
    - XRF, Laser Ablation ICP-MS, XANES, EDX
- Surface and Thermodynamics
  - Hg Pore, BET Gas Adsorption, TGA-(TBD) DSC-MS

GDL Imaging (ESEM)

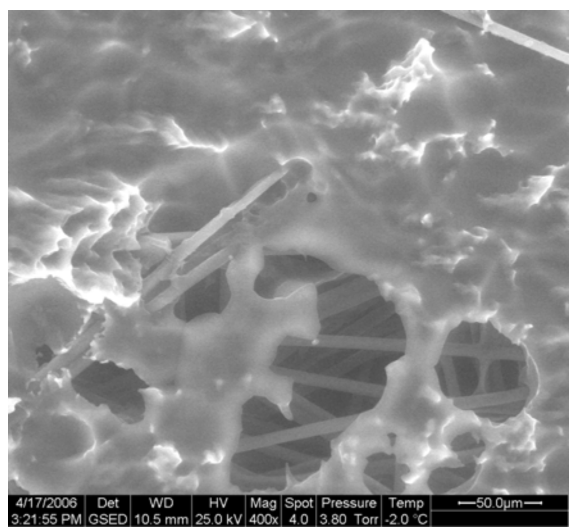
- *Ex situ* monitoring of ice formation
- Control of P_{H2O}(0-100% RH) and T (-10˚C to +40°C) during imaging
- Freeze/thaw cycling at various RH while imaging

- Mount samples in cross-section (stage being machined)
- Examine interfaces during freeze/thaw cycling (GDL/MEA; catalyst/membrane)

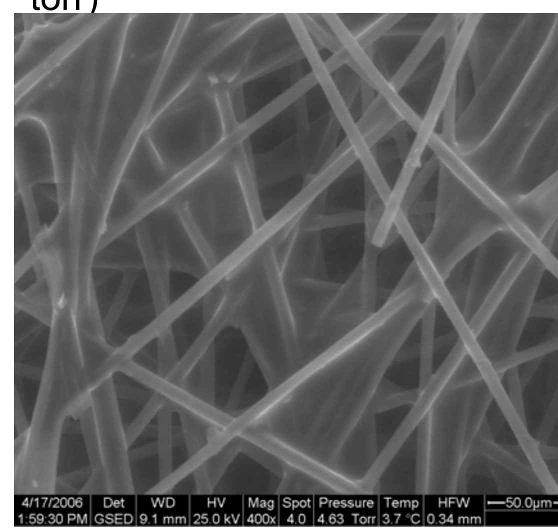
Untreated GDL (SGL)



Ice (T = -2°C; P_{H2O} = 3.8torr)



Water (T = 3.7°C; P_{H2O} = 4.63 torr)



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X-ray Fluorescence Spectroscopy

- Nondestructive
  - Insensitive to bounding environment
  - No sample preparation
  - Sensitivity to $\mu g/cm^2$
- Spatial resolution with mapping stage
- Use Fundamental Parameters Model for matrix corrections
  - Fit multilayer systems also
- Accurate catalyst loading and impurity detection

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Diffraction and X-ray Fluorescence, Hg Porosimetry

Crystal structure, Pt particle size, Alloy composition Pt/C ratio, Pt loading, impurities catalyst loss

Surface area and pore size distribution

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X-ray Whole Pattern Fitting Method

- Convolute instrument broadening, crystallite scattering, crystallite size and strain and background to calculate the diffraction pattern
- Perform least squares fit iteratively to minimize difference between observed and calculated pattern
- Programs
  - SHADOW, Snyder and Howard
  - GSAS, Von Dreele and Larson
- Very accurate unit cell determinations
- Amorphous material fractions may estimated
- Sample displacement errors can also be corrected

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Warren-Averbach Fourier Analysis

- Remove instrumental effects by Fourier deconvolution
- Represent X-ray peak profiles in reciprocal space by Fourier series

$$F(s) = \sum_{L=-\infty}^{\infty} \{A_L \cos(2\pi(s - s_0)L) + B_L \sin(2\pi(s - s_0)L)\}$$

$$s = \frac{2\sin\theta}{\lambda}$$

- Real (cosine) coefficients are used in Warren Averbach analysis to separate size and strain

$$A_L = A_L^{size} A_L^{strain}$$

  - Approach gives area weighted crystallite sizes
- Bertaut demonstrated second derivative of the Fourier coefficients contained the crystallite size distribution
- MudMaster-Eberl (direct transform) WINFIT-by Krumm PSF fitting

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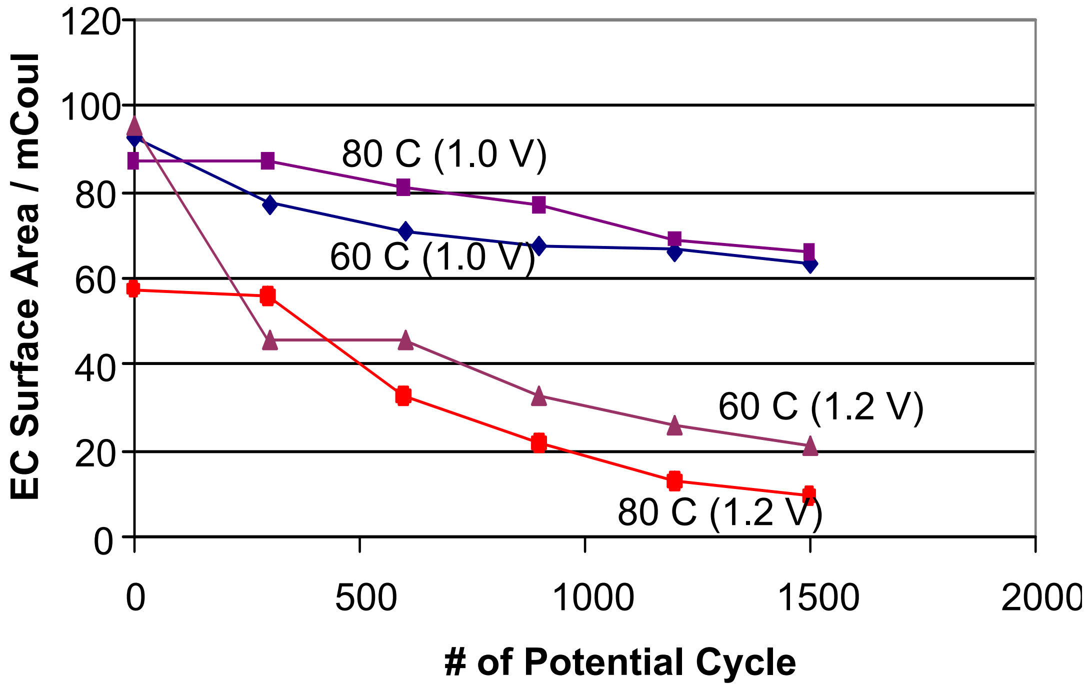
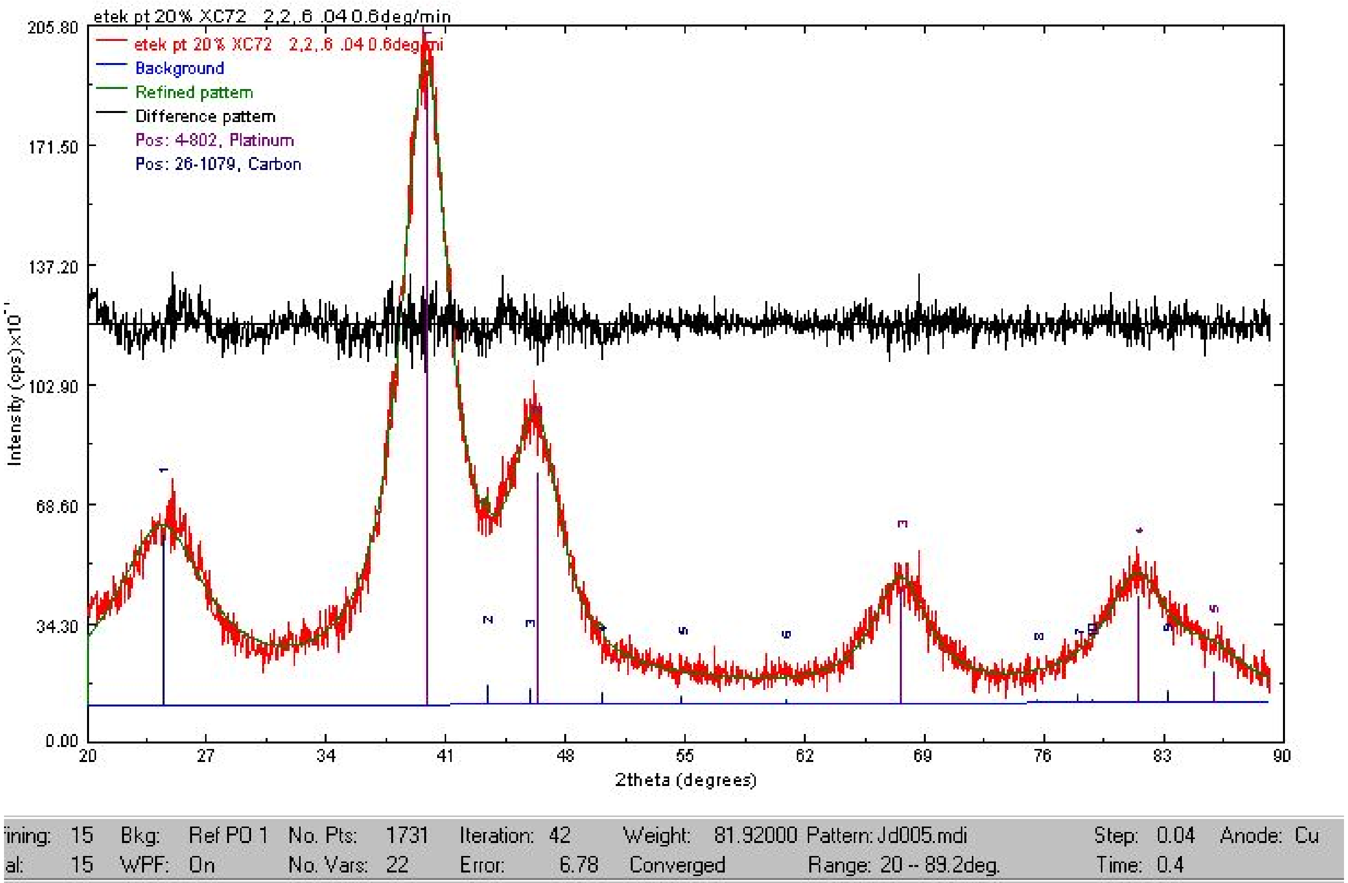
Electrochemical Surface Area Loss

- No net mass loss of catalyst
  - Total loadings the same <u>before and after</u> cycling confirmed by XRF
- Catalyst particle growth?



X-Ray Whole Pattern Fitting



- ETEK Pt 20% -C sample ~20 Å vol weighted size
- a=3.9261 (0.00068)Å

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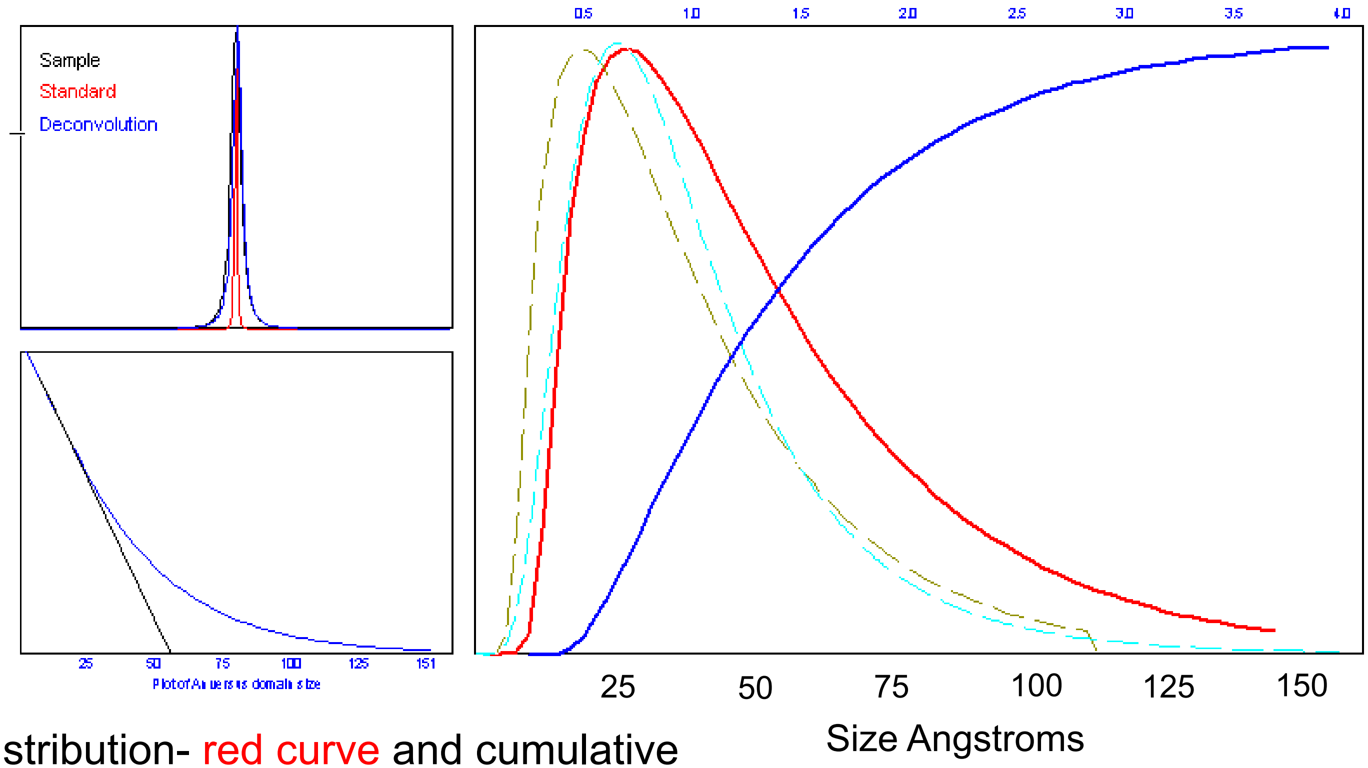
Crystallite Size Pt-Cathode Cycled 0.1-1.2 V



- Particle size distribution- red curve and cumulative distribution-blue curve
- For cathode sample cycled to 1.2 volts
- Crystal size 60 Å average from distribution
- Crystal size 78 Å average volume weighted
- Max crystal size ~150Å

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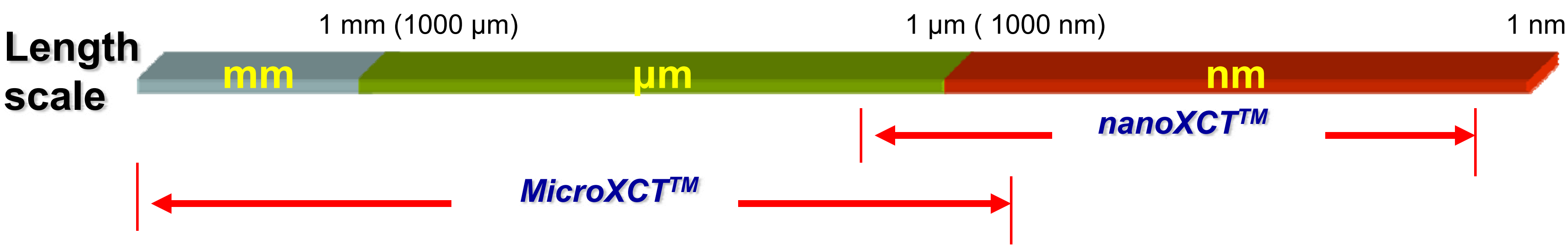
X-ray CT Microscopes

Imaging resolution with length scale from several mm to sub 30 nm



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MicroXCT™
3D X-ray Microscope

- Cross-sectioning soft materials for SEM/TEM is difficult
    - microtoming or freeze fracturing usually employed
    - Dehydration of samples in vacuum systems is also a problem
- CT "Virtual cross sectioning" preserves delicate microstructures
- Large numbers of "cross sections" may be studied
- W target used for good penetration no thinning required

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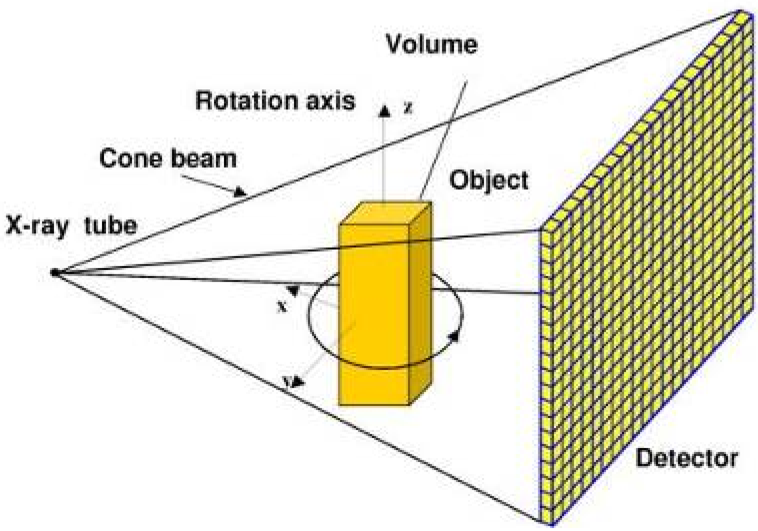
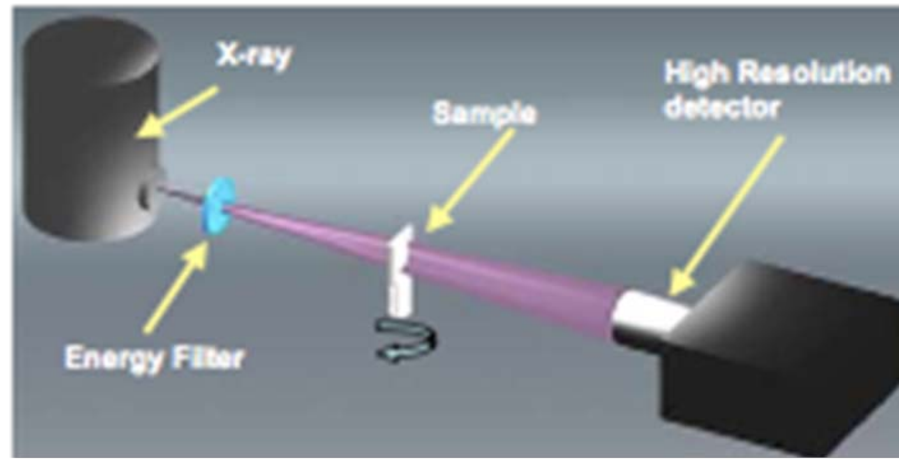
Differences Between
Conventional CTs and Xradia CT





Conventional CTs: Simple Projection geometry with Flat panel detector to achieve magnification and resolution

Xradia proprietary optics with high resolution & high contrast detector system

High Resolution & High Contrast

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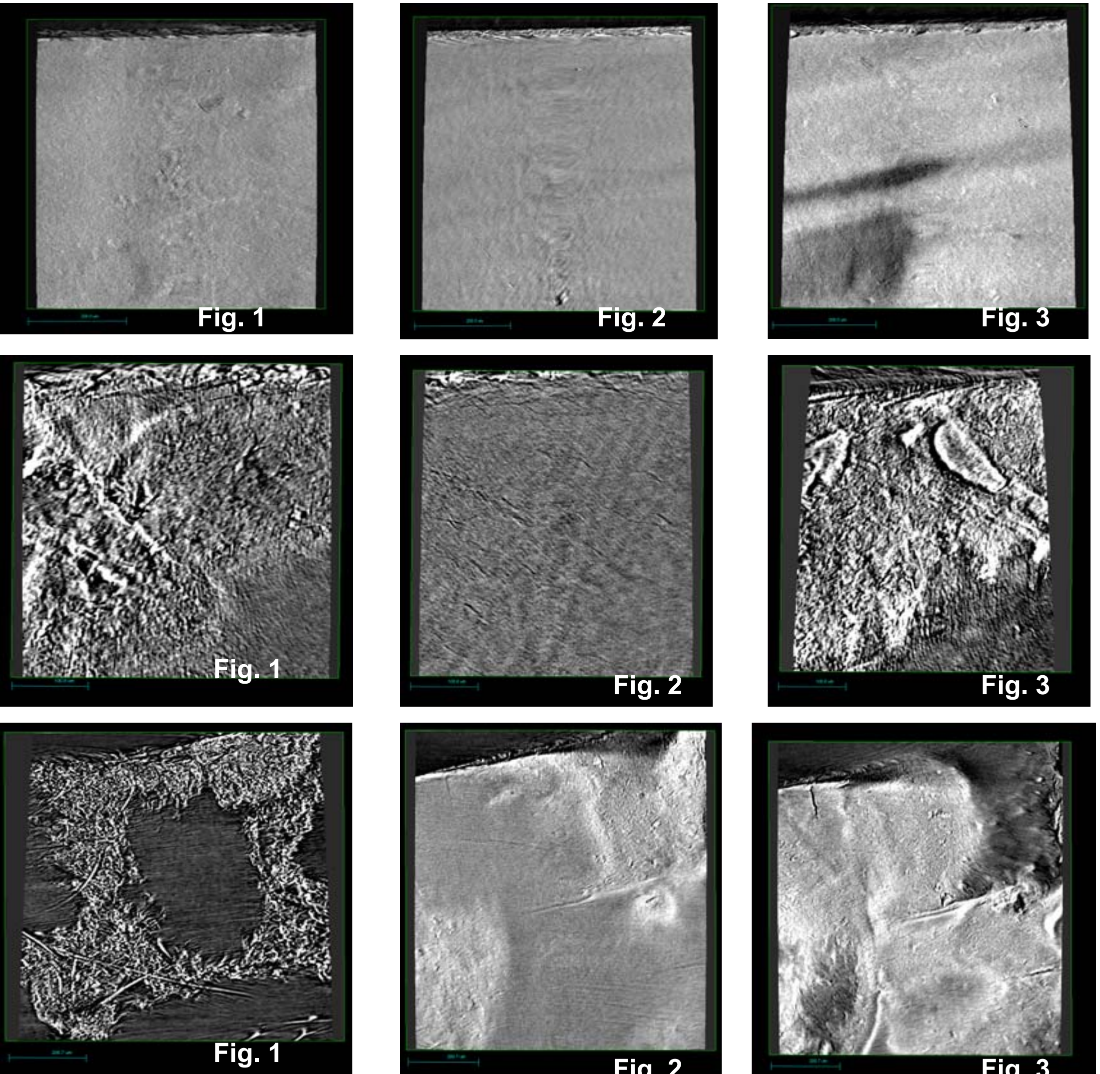
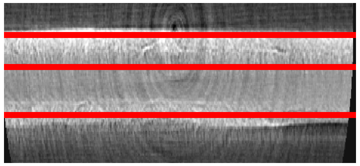
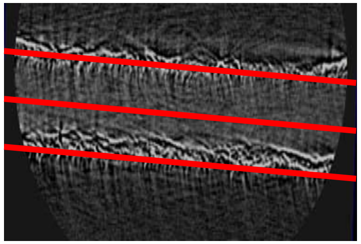
Comparison of Nafion®
Fuel Cell Membranes(#1, #2 and #3).



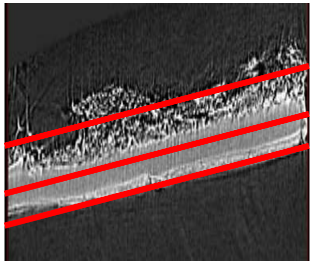
Membrane 1. unused fuel cell membrane



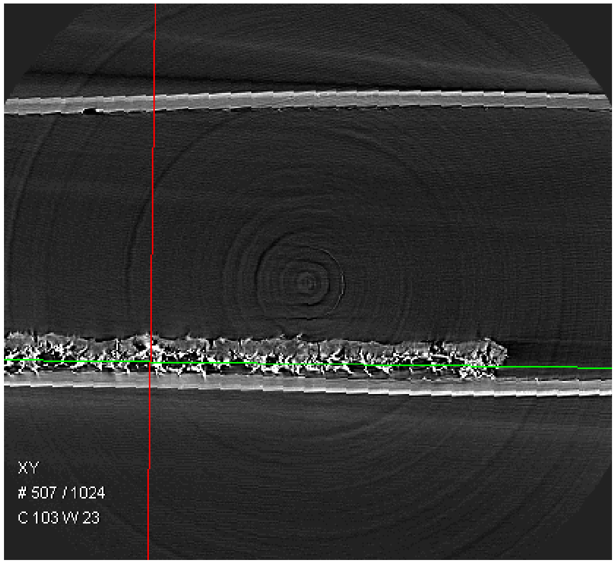
Membrane 2. went through a cycle test until failure.

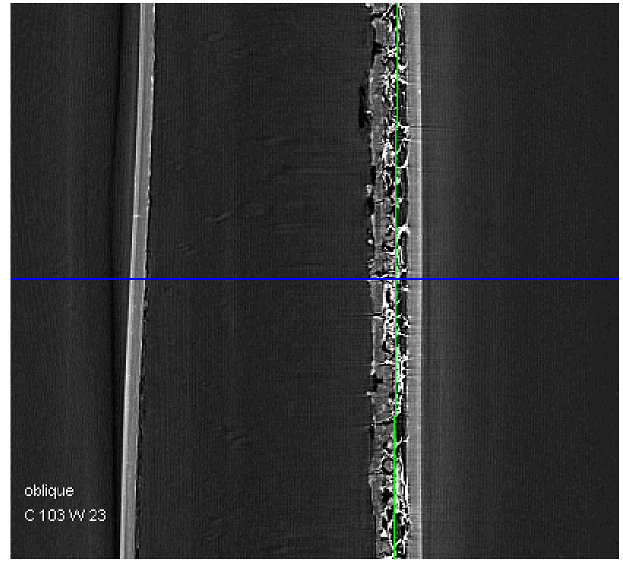


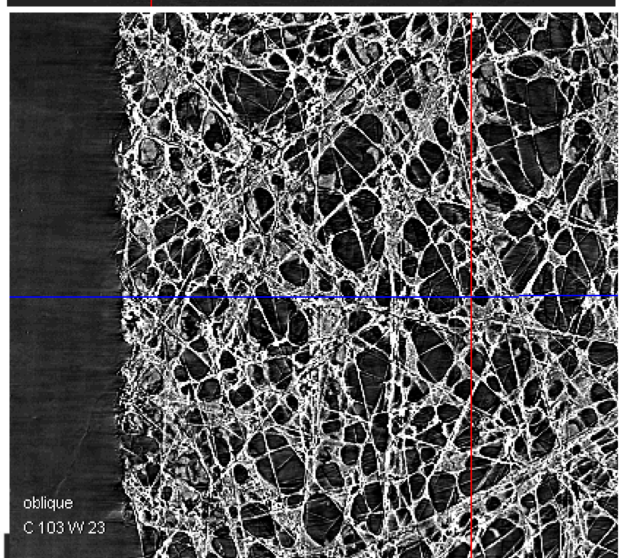
Membrane 3. went through a cycle test and start stops.

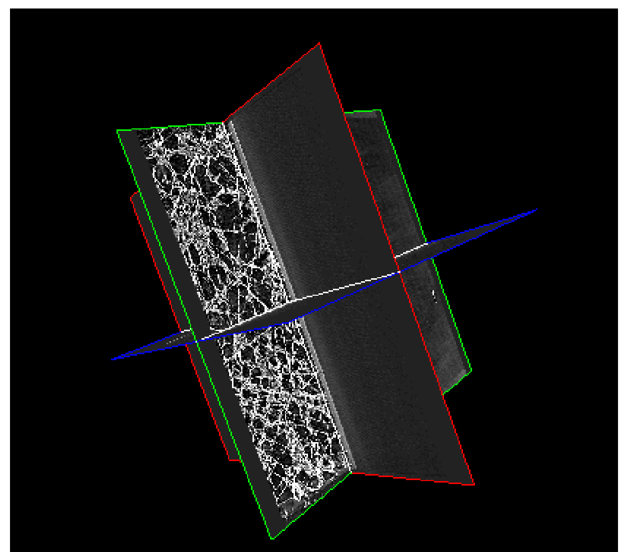


SGL GDL Imaging









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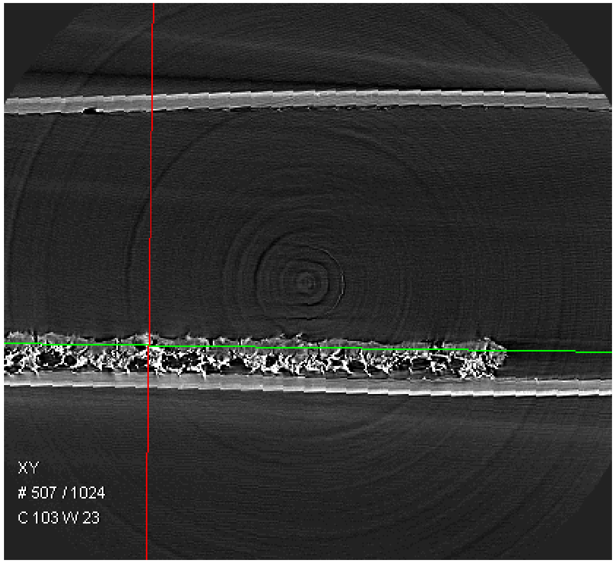
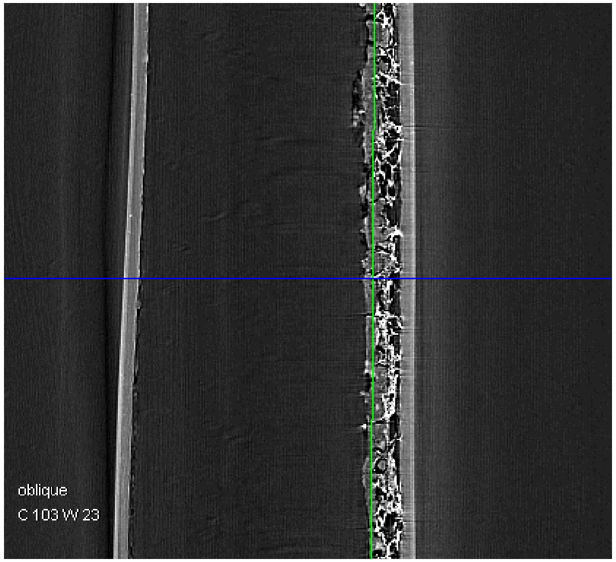
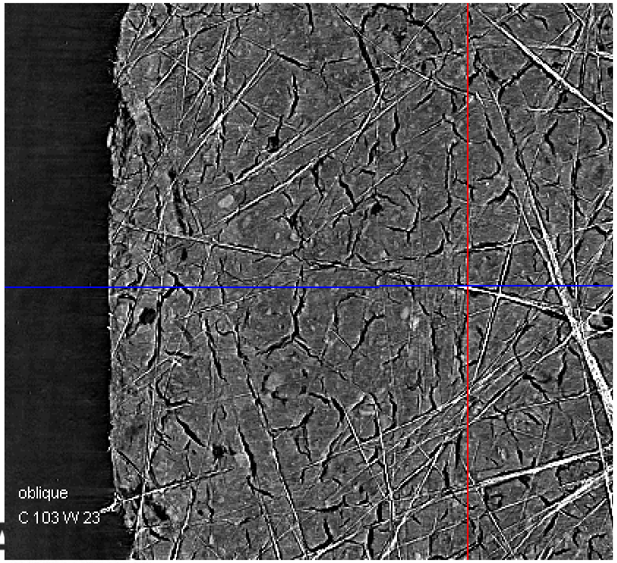
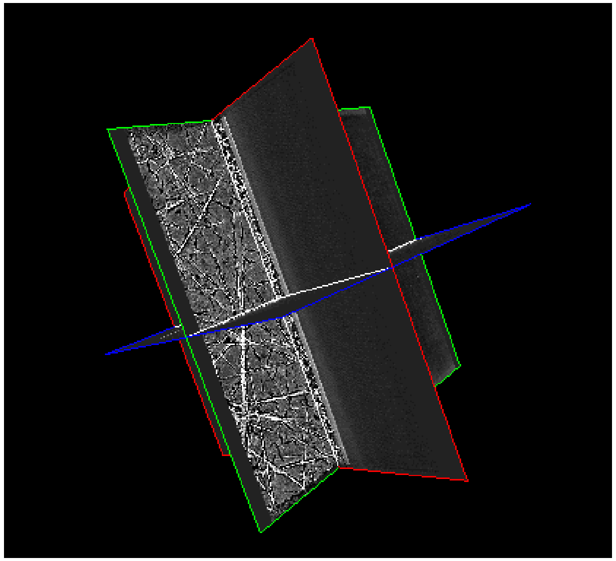
SGL GDL Microporous Layer









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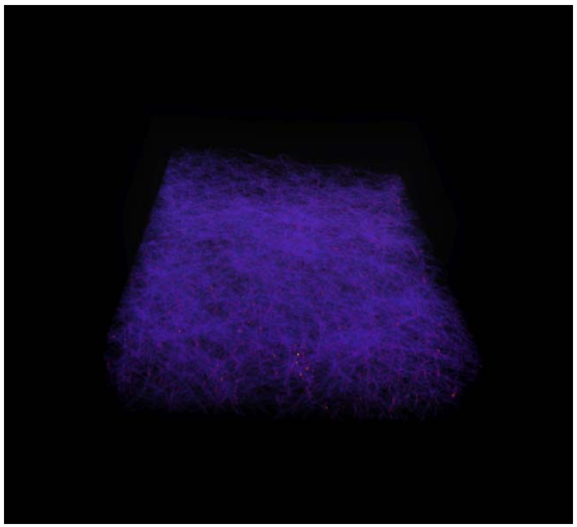
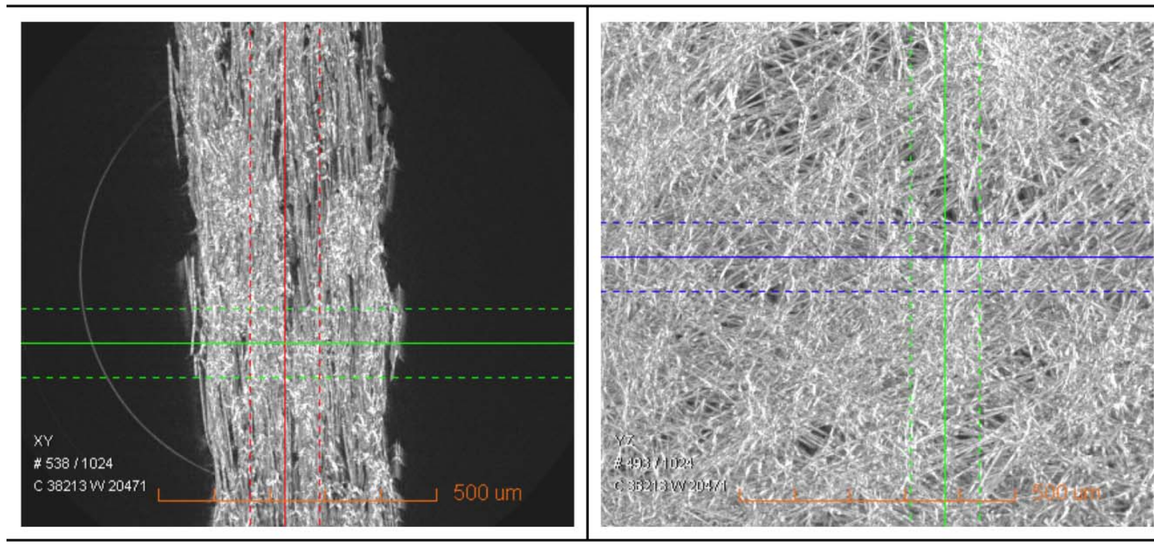
Toray GDL





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LANL Fuel Cell Training Class
October 2008

LANL MEA Fabrication Process
Hands-on PEM Fuel Cell Testing
Several Demonstrations using Different Analytical Techniques
Multiple Fuel Cell Presentations presented by LANL Scientist

Participants from industries, national labs, and universities

Upcoming 2009 Class TBA
Ask me about registering

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