UT-BATTELLE

DOE Hydrogen Program

Microstructural Characterization of PEM Fuel Cell Materials

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Project ID FC_32_More

Project Overview

Timeline

- **Project initiated in FY2000**
- **Continuous - fundamental research on microstructural characterization to improve MEA durability**

Budget

- **Funding in FY08 - $500k**
- **Funding in FY09 - $538k**

Barriers

- **Fuel Cell Barriers Addressed**
  - **A: Durability**
  - **B: Cost**
  - **C: Performance**

Partners

- **Los Alamos National Laboratory**
- **Argonne National Laboratory**
- **Brookhaven National Laboratory**
- **3M Company**
- **University of Texas, Austin**
- **University of Houston**
- **University of Connecticut**
- **Rensselaer Polytechnic Institute**
- **Arkema**

ORNL Research Objectives

- Identify and optimize novel high-resolution imaging and compositional/chemical analysis techniques for characterization of the material constituents comprising PEM fuel cell MEAs (catalyst, support, membrane)
  - μm- to nm-scale - FEG-SEM (bulk)
  - nm-scale to sub-Angstrom imaging and compositional analysis - TEM/STEM and HAADF (Z-contrast) -STEM
  - 3D image reconstruction (tomography)
  - In-situ (liquid) microscopy
- Apply these analytical and imaging techniques for the evaluation of microstructural and microchemical changes that determine fuel cell stability
- Elucidate microstructure-related degradation mechanisms contributing to PEM fuel cell performance loss

Milestones

- FY08 Milestones:

  – Publish results for STEM analysis of bimetallic cathode catalysts *Completed*

  – Continue study of the mechanisms of carbon support oxidation/corrosion *Delayed, still in progress*

- FY09 Milestones:

  – Publish results for AC-STEM analyses of Pt-based catalyst stability during in-situ heating *Completed*

  – Complete study of in-situ carbon support oxidation/corrosion under relevant PEMFC operating conditions and report results *Delayed, still in progress*

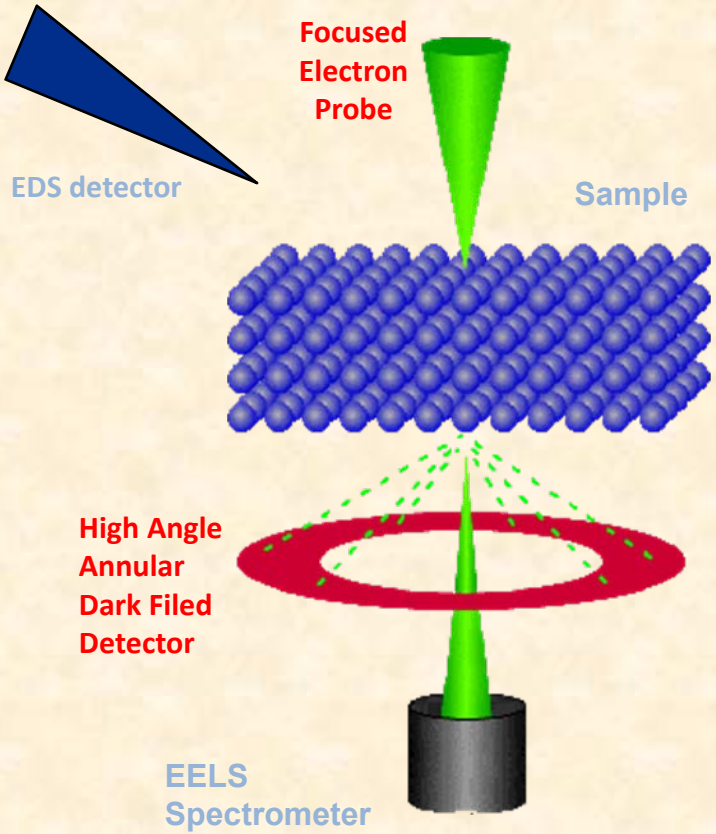
Approach: Use Advanced Imaging and Compositional Analysis Techniques to Evaluate Atomic-Scale MEA Microstructures

- Apply state-of-the-art electron microscopy techniques for the analysis of MEA material constituents:
  - High-resolution FEG-SEM - Hitachi NB5000 dual-beam FIB
  - High-resolution FEG-TEM/STEM imaging (*sub-nm-scale*) - Hitachi HF-3300
  - High-angle annular dark field (HAADF) imaging (Z-contrast) in an aberration-corrected STEM (*sub-Ångström scale*) - JEOL 2200FS-AC
- Collaborate with industry, academia, and national laboratories to make these techniques (and expertise) available to correlate structure and composition with MEA processing and/or life-testing studies

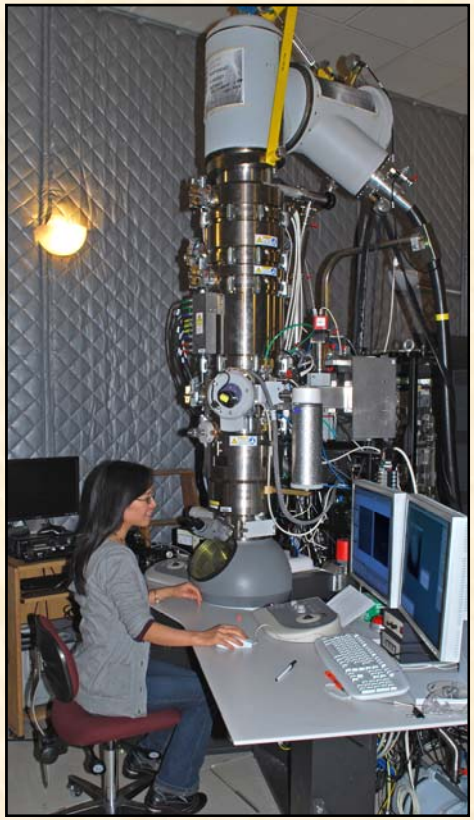
Technical Accomplishments and Progress

- Acquired and evaluated Si drift detector (SDD) for use on the JEOL 2200 aberration-corrected STEM for Ångström-scale compositional analysis
- Acquired and proof-tested *in situ* (liquid) electron microscopy holder
- Application of electron tomography to study catalyst particle distributions
- Developed ultra-low angle microtomy to study through-thickness chemical nature of polymer membranes and MEAs

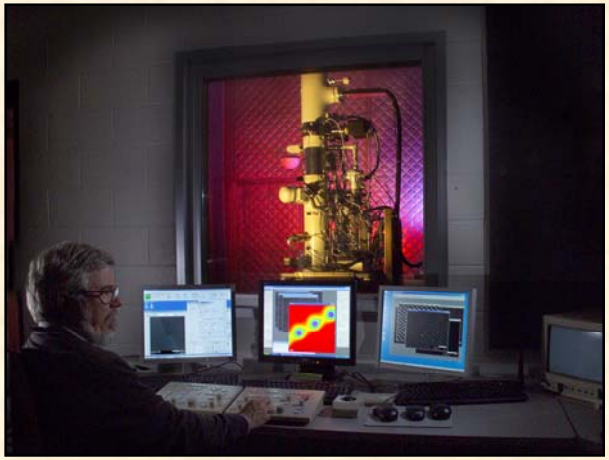
Sub-Ångström Resolution Imaging And Analysis Is Accomplished Via Aberration-Corrected STEM



- HAADF STEM - image contrast variations arise because of atomic number (Z) differences between the (~0.7Å image resolution)
- Aberration-corrector forms a sub-Ångström probe
- EDS detector for high-spatial-resolution compositional analyses

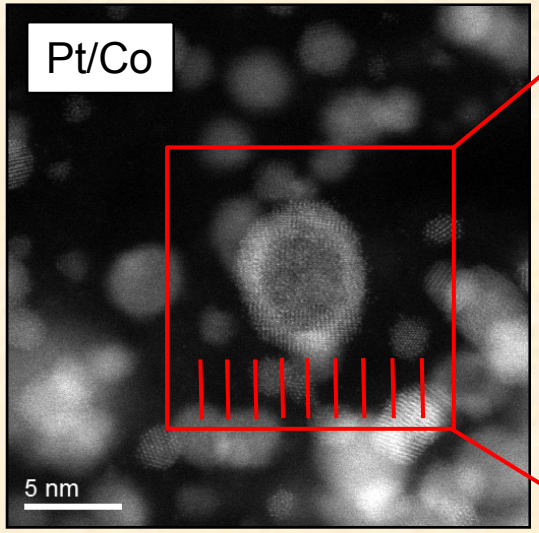


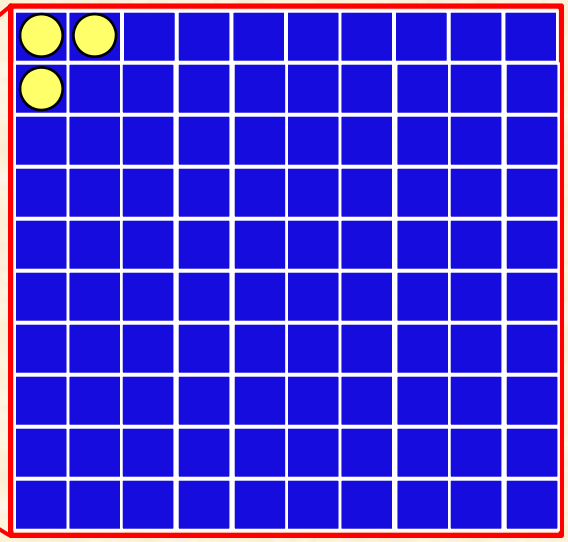
FEI Titan 80-300 TEM/STEM
with CEOS aberration-corrector



JEOL 2200FS FEG-TEM/STEM
with CEOS aberration-corrector

Compositional Analysis Of Core-Shell Nanoparticles <10 nm Diameter Is Challenging

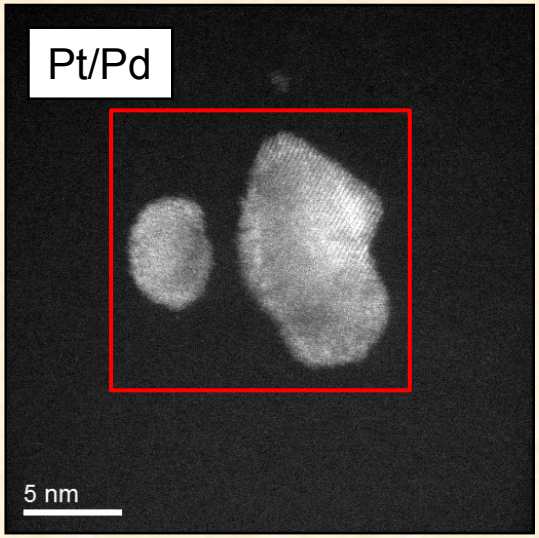




= 1.5 nm

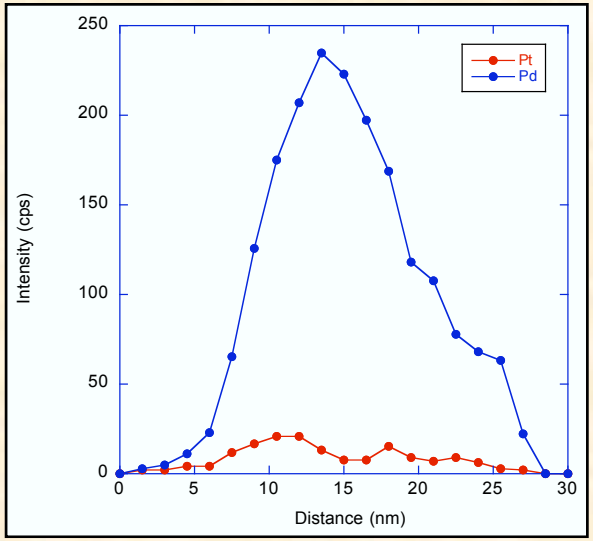
Spectrum images acquired using a "conventional" STEM equipped with a FEG are limited by a probe size of 1.2-1.5 nm –minimum step (pixel) used for EDS mapping is ≥1.5 nm

A 15 nm X 15 nm = 10 pixel X 10 pixel = 100 data points



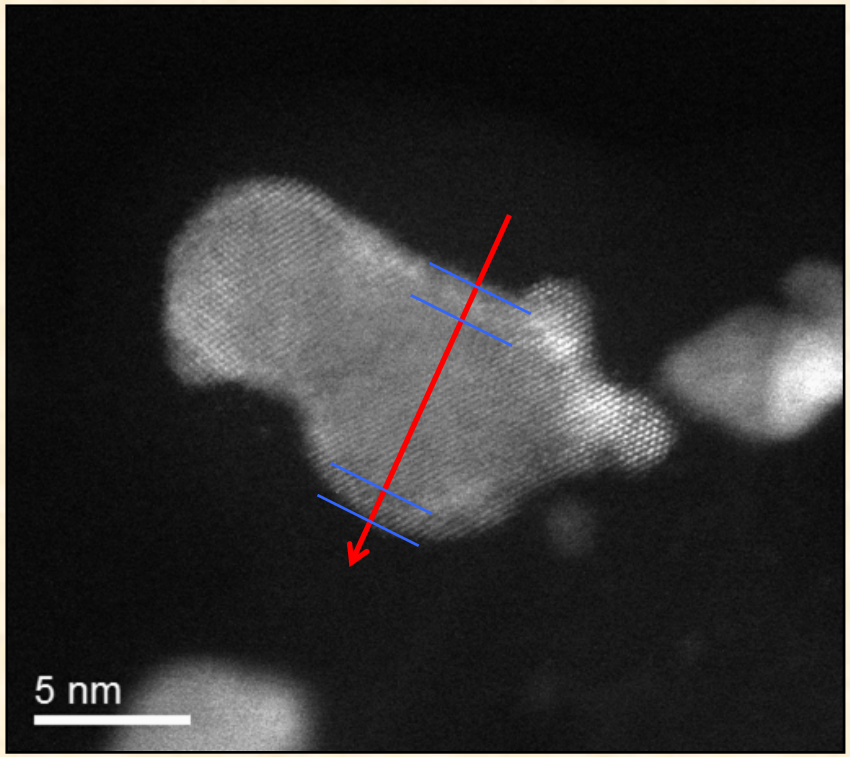
- For larger particles with well-defined shells, a 1.5 nm spatial resolution may be sufficient to define core and shell

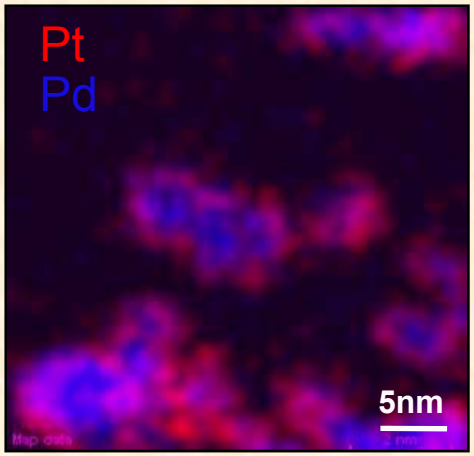
- For nanoparticles ≤10 nm or those with very thin shell structures, a higher spatial resolution is required

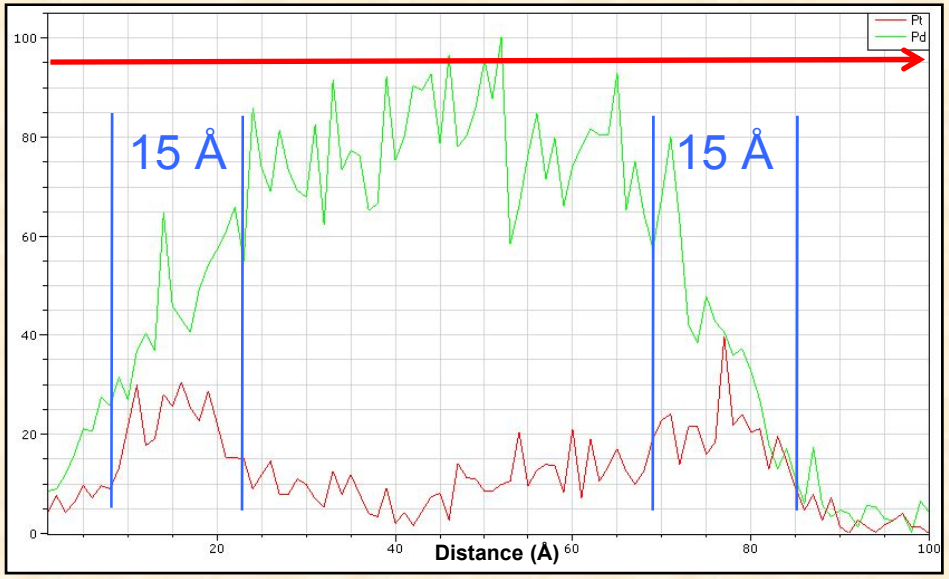


Ångström-scale Compositional Analysis Is Performed Using A Silicon Drift Detector (SDD) On An Aberration-Corrected STEM

Ångström-scale microanalysis (~5X increase) is possible using aberration-corrected STEM





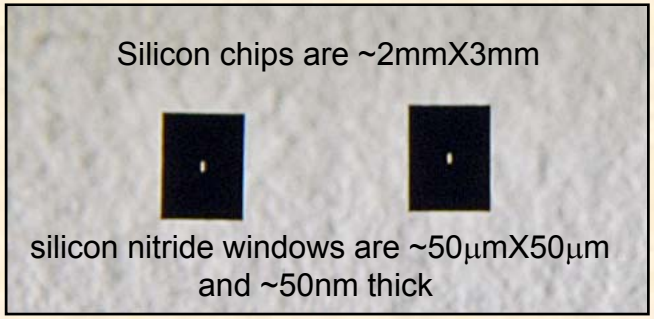


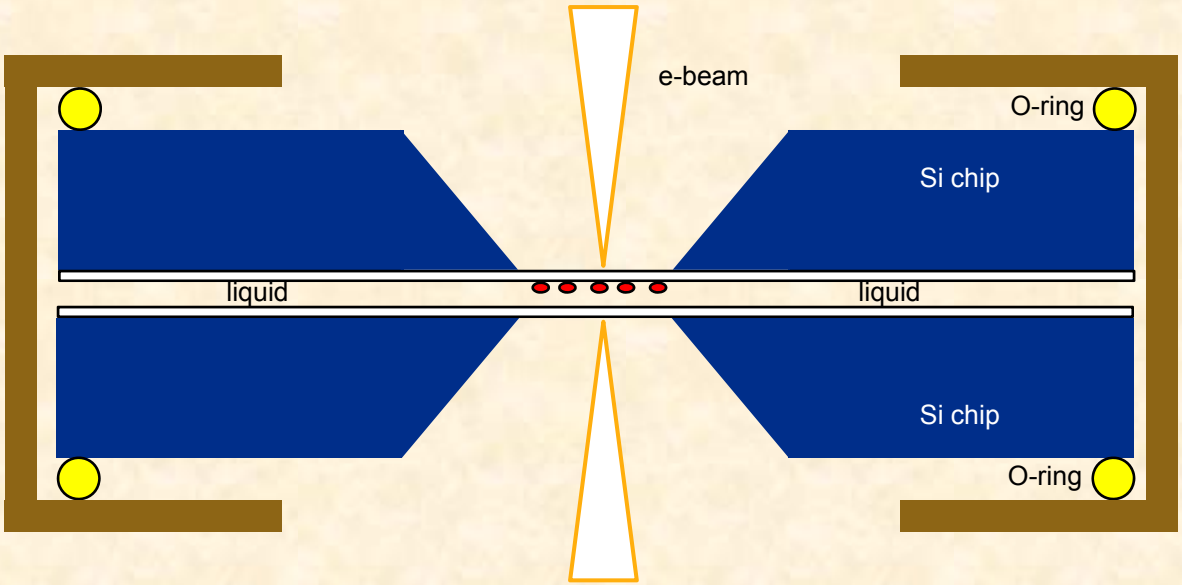
SDD On TEM/STEM Is A New Technology – Many Issues Are Yet To Be Resolved

- Acquisition parameters to optimize count rate (inherently low for nanoparticles!) while still maintaining fine-probe size (~1-2 Å), high beam current, and preventing structural damage to particle
- Specimen drift and contamination build-up are serious issues, especially when long data acquisition is required

In Situ Microscopy for PEM Fuel Cell Research at the nm-Scale – Current Status

A microscope holder with a liquid flow cell has been designed in collaboration with Hummingbird Scientific; delivered in January 2009





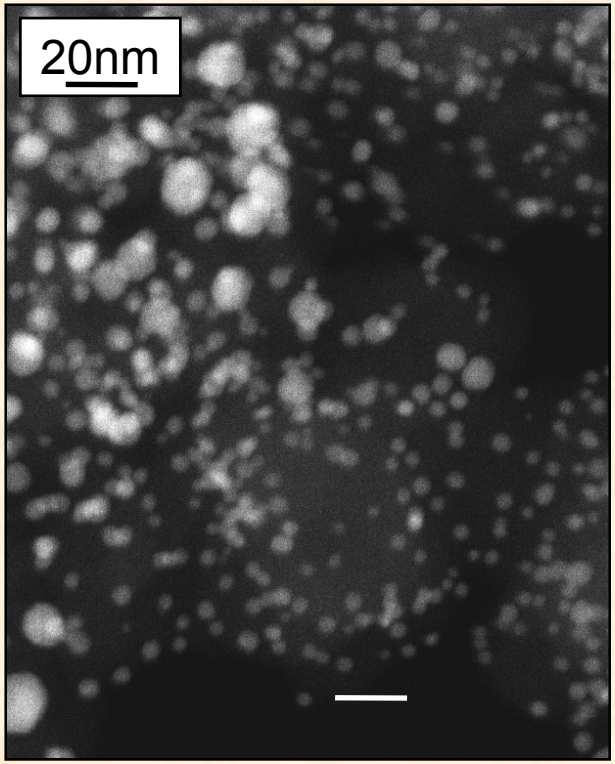
Sample is "immersed" in a conducting liquid layer ~5-10μm thick, creating multiple liquid-solid interfaces

Silicon nitride windows are electron transparent – resolution depends on:

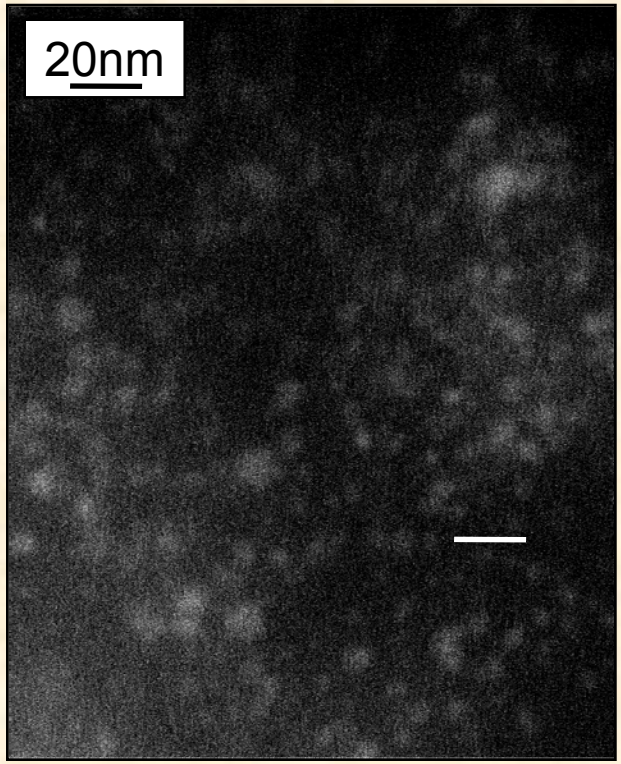
- scattering in liquid
- thickness of liquid layer
- window thickness/area

In Situ Liquid STEM – Pt_3Cr/Vulcan

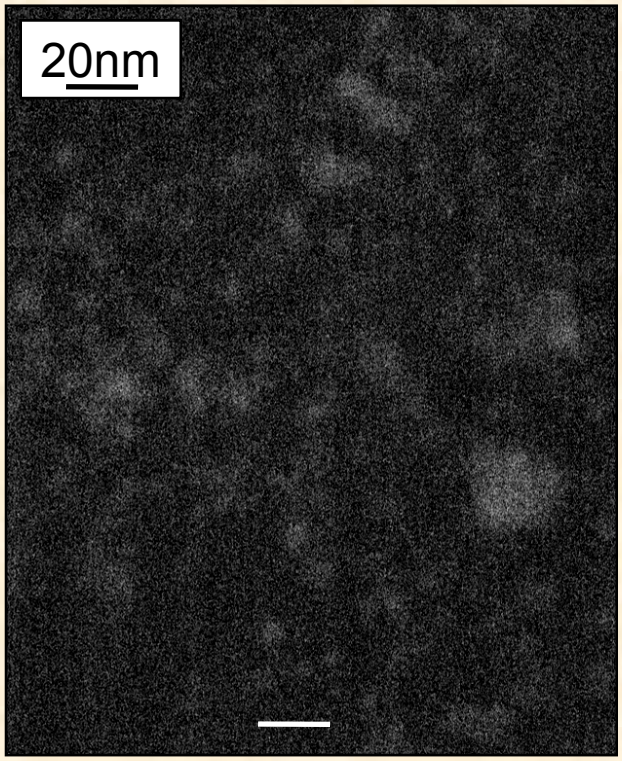
HAADF imaging of Pt_3Cr nanoparticles in 7-9μm thick water layer @ 300kV demonstrates ~3nm resolution



Pt_3Cr nanoparticles in vacuum (standard STEM imaging conditions)



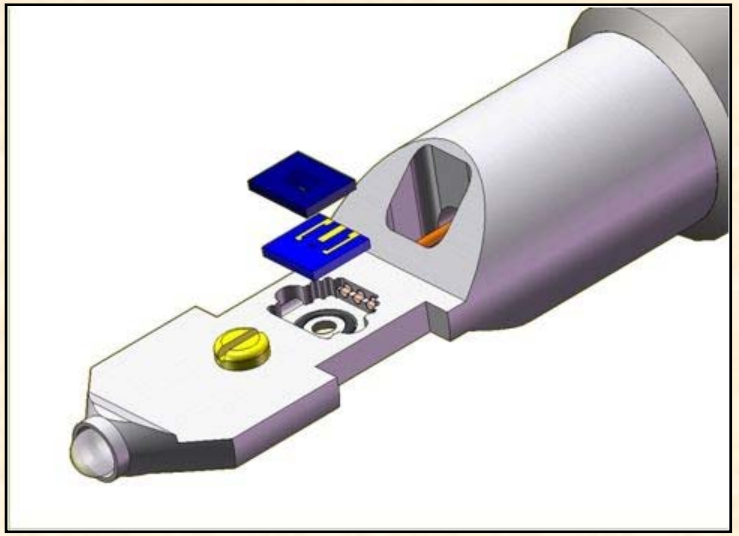
Pt_3Cr nanoparticles imaged through two SiN windows (gap filled with air)



Pt_3Cr nanoparticles in 7-9μm thick water layer (gap filled with water)

In Situ Liquid STEM – What's Next?

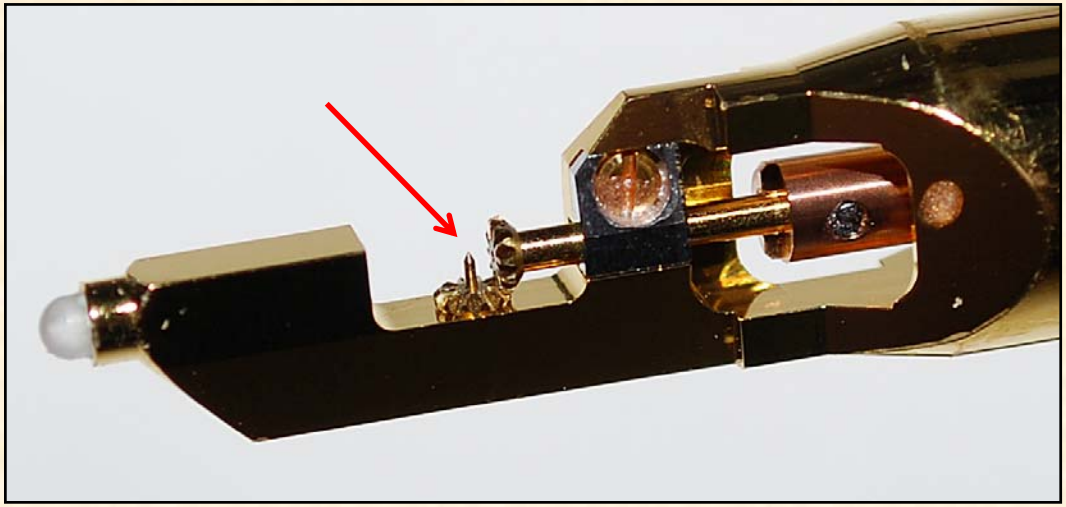
- Maximize image resolution:
  - Decreased window thickness
  - Decreased window "viewing" area to prevents window bulging
  - Decreased gap/layer thickness (using spacers)
- Add critical capabilities:
  - Potential cycling (electrical contacts)
  - Efficient current collection
  - Low temperature heating
- Rapid image recording



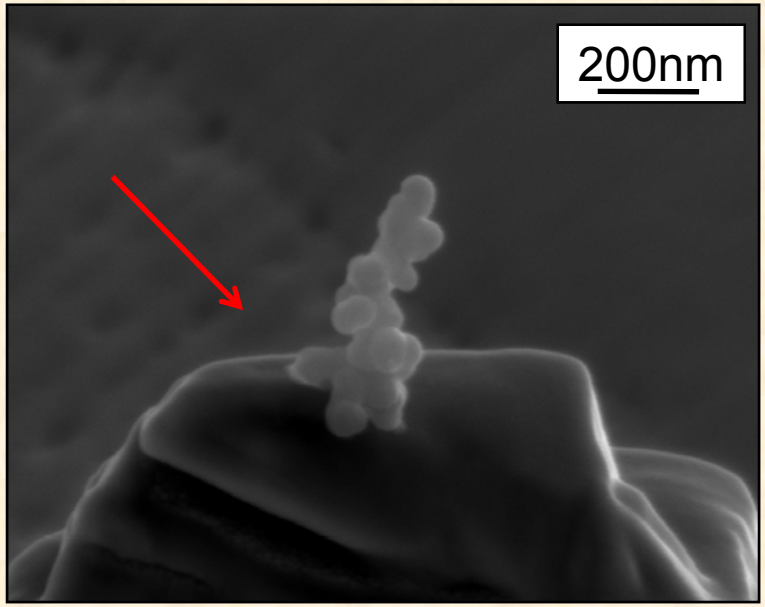
Chip/window design is critical to success!

Electron Tomography Is Being Used To Evaluate 3D Structure Of Fuel Cell Materials

Electron tomography can be conducted in 2 ways:
- tilt series – difficult to tilt sample >60°
- sample rotation – rotate 360° with no tilting

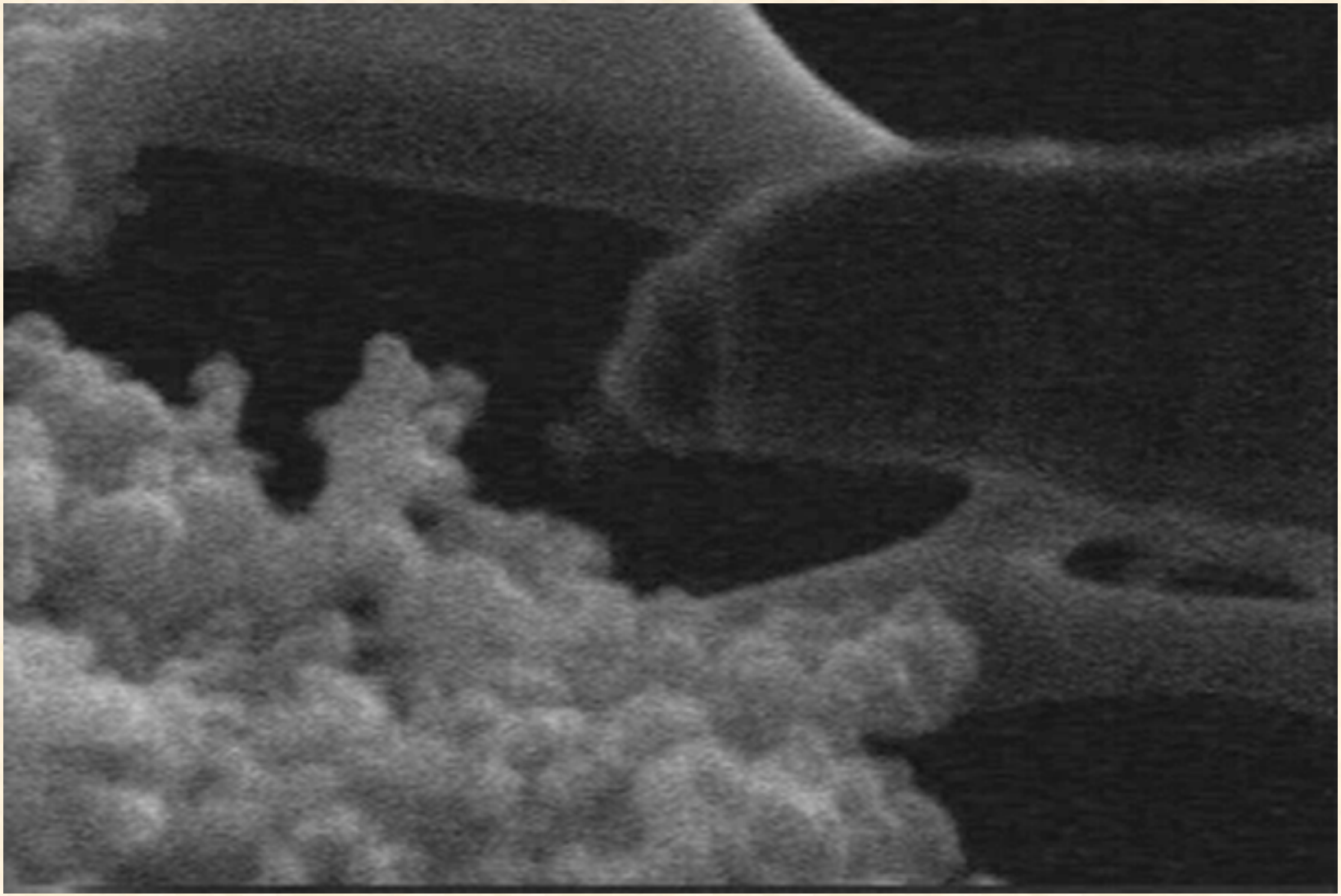


New tomography - 360° rotation "micropillar" holder is compatible with several Hitachi microscopes



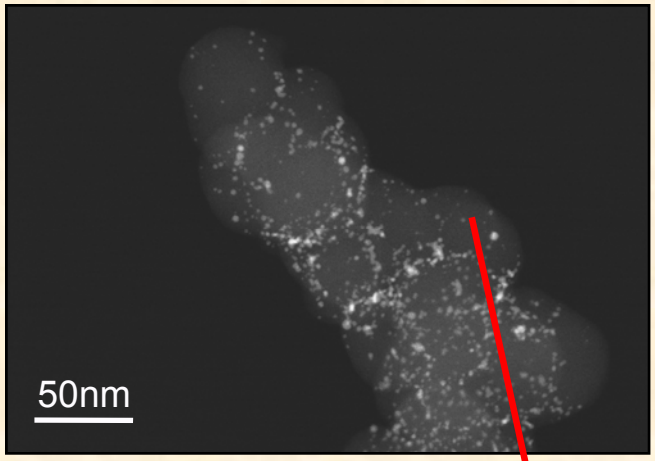
Sample is placed on surface of micropillar for microscopy (SEM, TEM, STEM)

Samples Are Placed On The Micropillar Using Micromanipulators In A Dual-Beam FIB

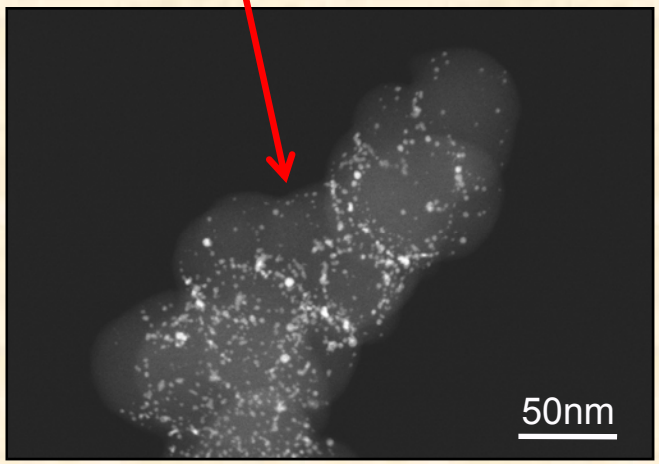


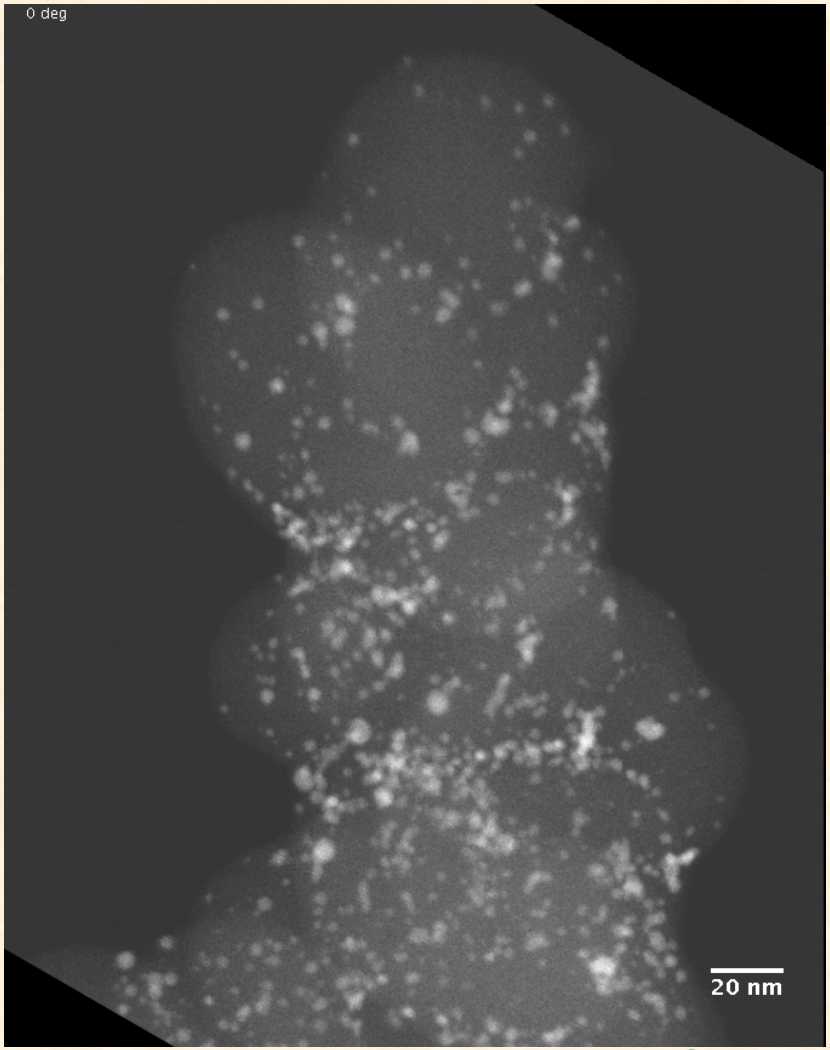
Micropillar Is Rotated 360° - Images Acquired At Different Intervals During Rotation Allow For Complete Viewing Of All Surfaces

HAADF STEM imaging of Pt on Vulcan



Micro-pillar rotated 180°

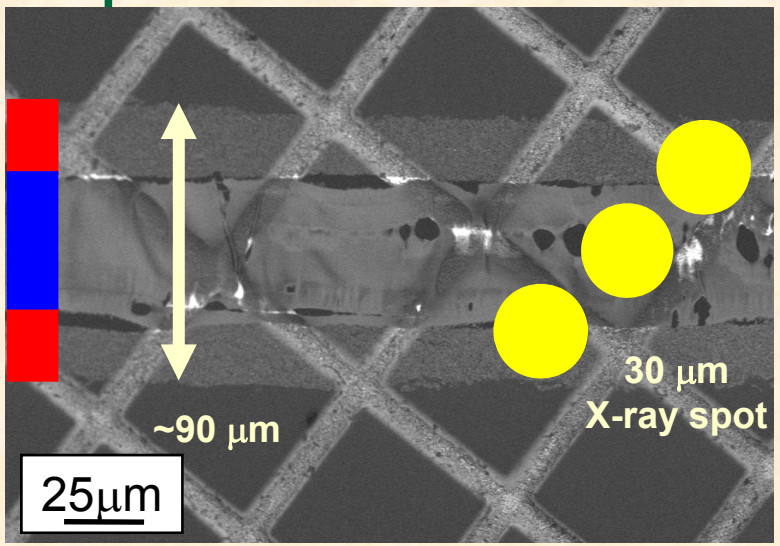




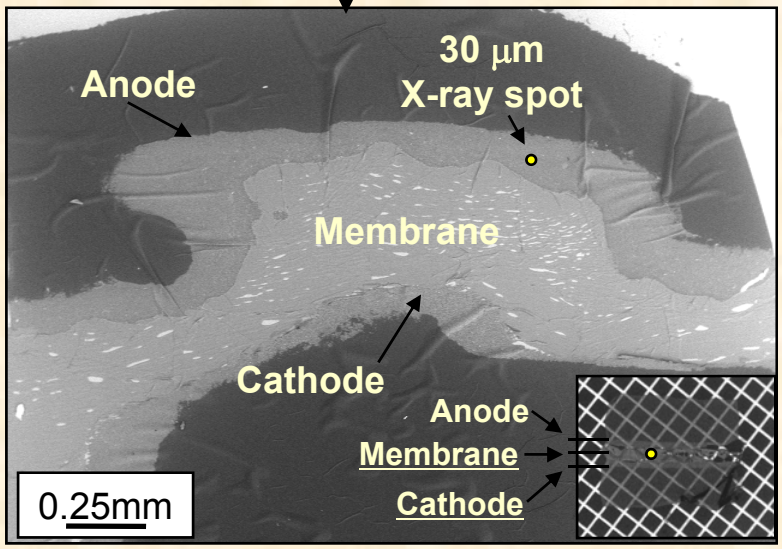
Ultra-Low Angle Microtomy (ULAM)
A Unique Membrane/MEA Preparation For XPS

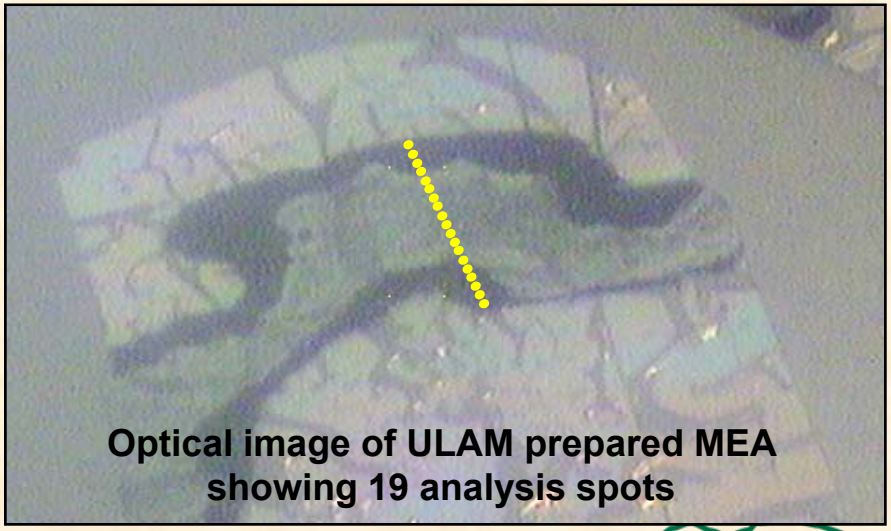
Challenge: Determine variations in chemistry across a 100 μm thick MEA using a 30 μm diameter x-ray probe!

SEM image of MEA prepared using cross-sectional microtomy



SEM image of MEA prepared via ULAM. Inset is the same cross-sectioned MEA, but at the same magnification as the ULAM sample





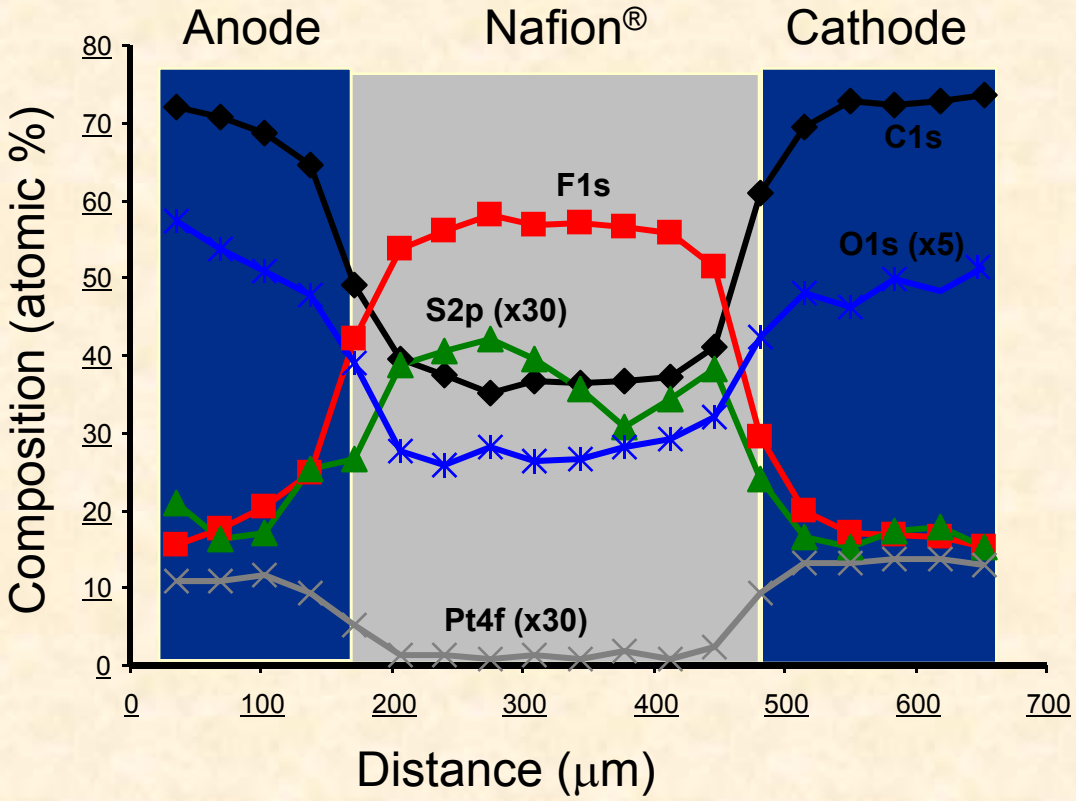
Optical image of ULAM prepared MEA showing 19 analysis spots

ULAM - Results From XPS MEA Line-Profile

Composition (at.%)

	C1s	F1s	S2p	O1s
Nafion® Film	34.0	56.5	1.6	7.9
ULAM Sample*	36.2	57.1	1.2	5.5

*Average of values from points 7-12 below



The table compares the composition of a as-received Nafion® film to Nafion® membrane within the ULAM-prepared sample - technique is not effecting the material.

The results of the full line profile show (1) change in the C/F ratio from the outer edge of the anode toward the membrane; (2) constant C/F ratio within the cathode; and (3) a decrease in the S content within the membrane as the cathode is approached. This last observation may indicate the position of the "Pt band." No significant Pt was detected at this point, but it is probably below the XPS detection limit.

Future Work

- Continue to evaluate and add capabilities to the *in situ* liquid holder for near live-time, nm-scale microscopy of PEM fuel cell material constituents operated under relevant operating conditions – liquid electrolytes, temperature, potential cycling, etc.
- Further develop tomography methods for characterizing fuel cell materials (catalyst particle coalescence, carbon support degradation, etc.)
- Continue to establish collaborations with industries, universities, and national laboratories (including access via ORNL User Facilities) to facilitate “transfer” of unique capabilities.
- Support new DOE projects with microstructural characterization and advanced characterization techniques.

Summary

- Several new collaborations have been established during the past year that have "taken advantage of" the unique imaging (microscopy) capabilities at ORNL:
  - Work-for-Others (proprietary research)
  - Shared Research Equipment (SHaRE) User Program (non-proprietary research) - University of Houston, University of Texas, University of Connecticut, Rensselaer Polytechnic Institute
  - Baseline PEM-MEA Characterization Program (non-proprietary)
- Progress to date to develop *in situ* liquid STEM as a viable technique to follow degradation of PEMFC materials has been slower than expected in – several critical issues have yet to be resolved
- Addition of SDD technology to high spatial resolution STEM will enable <2Å compositional analysis - optimization of data collection parameters will be ongoing