UT-BATTELLE

DOE Hydrogen Program

Microstructural Characterization of PEM Fuel Cell MEAs

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

Project ID FC9

Project Overview

Timeline

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

Barriers

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

Budget

- Total Funding to date - ~$1.9M
- Funding in FY07 - $300k

  plus $400k capital towards purchase of new $2M TEM
- Funding in FY08 - $500k

  (additional funding in FY08 to support in-situ microscopy development for PEMFCs)

Partners

- Los Alamos National Laboratory
- Argonne National Laboratory
- Brookhaven National Laboratory
- 3M Company
- Cabot Superior MicroPowders
- United Technologies Research Ctr
- Honda Research Institute
- Rensselaer Polytechnic Institute
- Arkema

ORNL Research Objectives

- Identify high-resolution imaging and compositional/chemical analysis techniques for characterization of the material constituents comprising PEM fuel cell MEAs
  - μm- to nm-scale using FEG-SEM (bulk)
  - nm-scale imaging using TEM/STEM (atomic)
  - Z-contrast sub-A structure imaging using HAADF-STEM
  - nm-scale 3D depth-profiling and image reconstruction
  - In-situ 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

- FY07 Milestones:
  - Initiate a new collaboration with an industrial/university/laboratory partner to conduct durability studies *Completed*
  - Initiate study of the mechanisms of carbon support corrosion *In progress*

- FY08 Milestones:
  - Publish results for STEM analysis of bimetallic cathode catalysts *Completed*
  - Continue study of the mechanisms of carbon support oxidation/corrosion *In progress*

Carbon support corrosion continues to be an area of interest. Techniques are being developed to evaluate this phenomenon using in-situ microscopy.

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 S4800
  - High-resolution FEG-TEM/STEM imaging (*sub nm-scale*) - new Hitachi HF-3300
  - High-angle annular dark field (HAADF) imaging (Z-contrast) in an aberration-corrected STEM (*sub-A 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

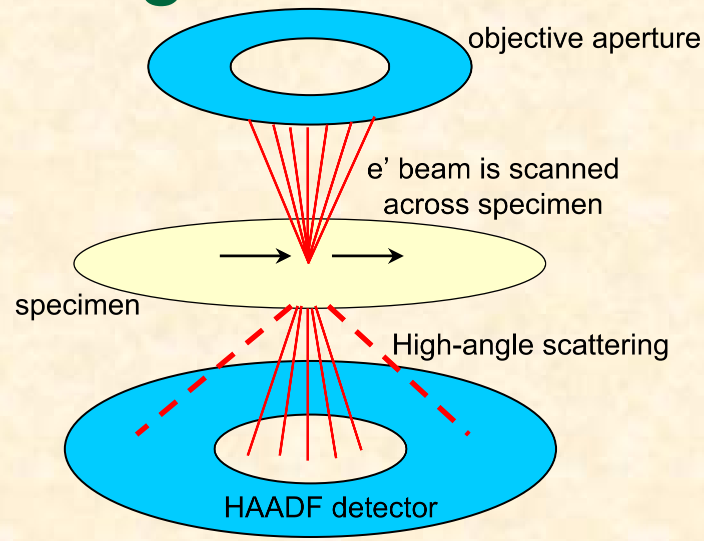
- Advanced the HAADF-STEM technique to studying fuel cell (cathode) catalysts
- Increased external collaborations using the unique microscopy characterization facilities at ORNL
- Initiated first stages of *in situ* microscopy holder development
- Applied 3D depth-profiling STEM and image reconstruction to study catalyst and support structures

HAADF, Or Z-Contrast, STEM Is Used to Image Catalyst Particles At Sub-Ångström Resolution

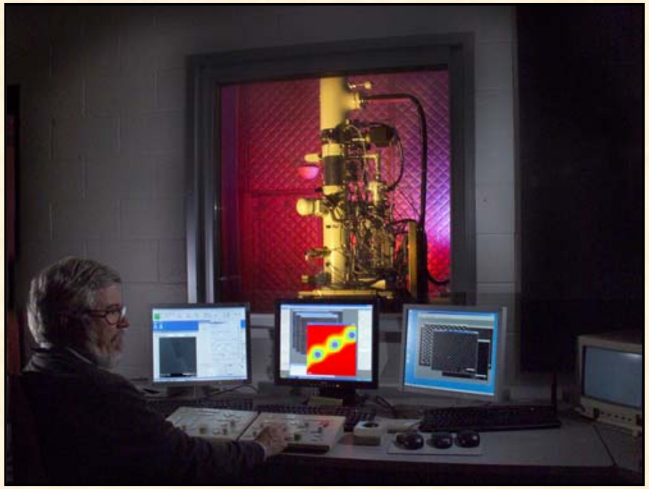
Image contrast variations arise because of atomic number (Z) differences between the elements - individual atoms comprising the particle's crystal lattice can be identified. For catalyst characterization:

(*i*) high-Z particles (Pt-based catalysts) supported on a low-Z substrate (carbon) and

(*ii*) alloy catalyst particles that are comprised of elements having a fairly large Z difference (Pt-Co, Pt-Cr, Pt-Ni, Pt-Ru, Pt-Pd, etc.)

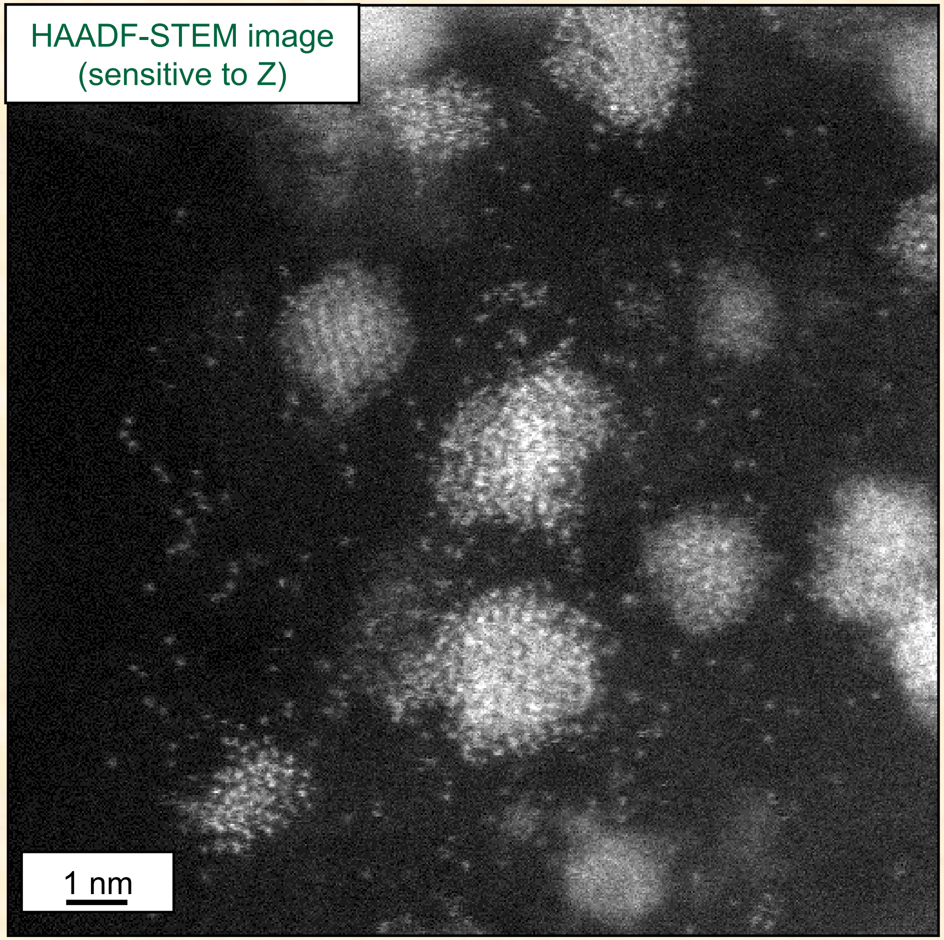


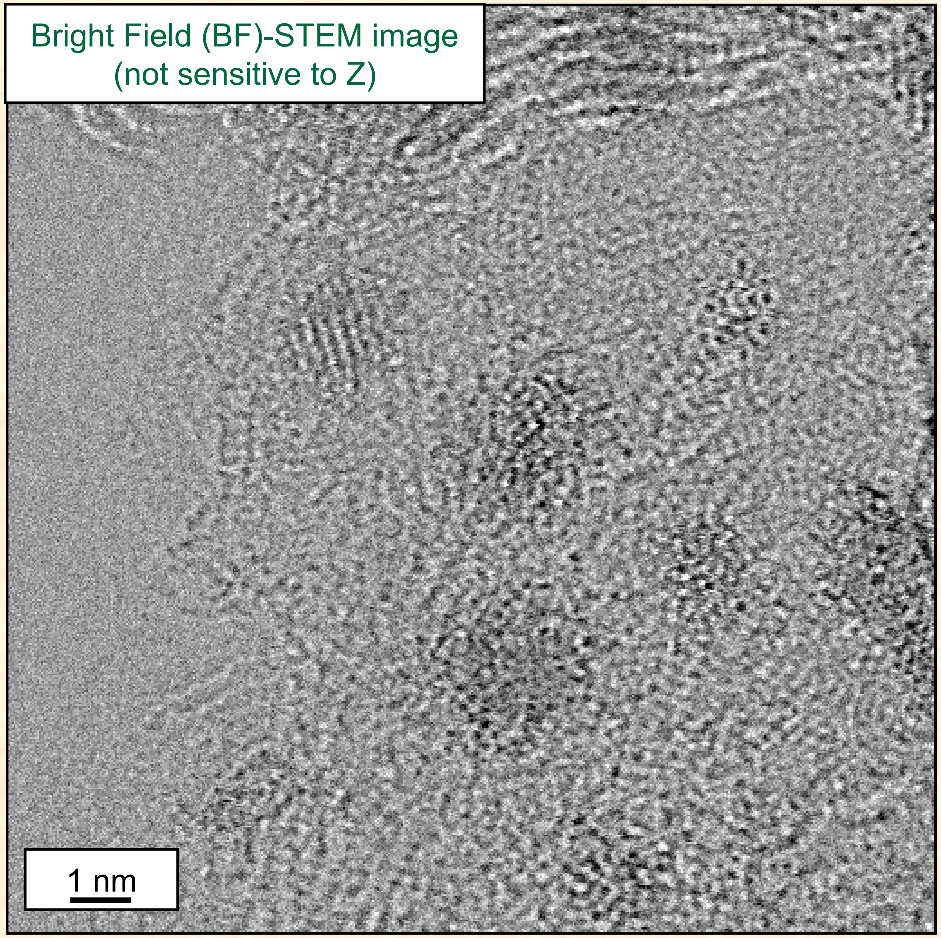
High-angle scattering depends on Z and the image contrast (intensity) will vary as Z^2



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

There is a Direct Correlation Between BF-TEM/STEM and HAADF-STEM Images Since Both are Acquired Simultaneously





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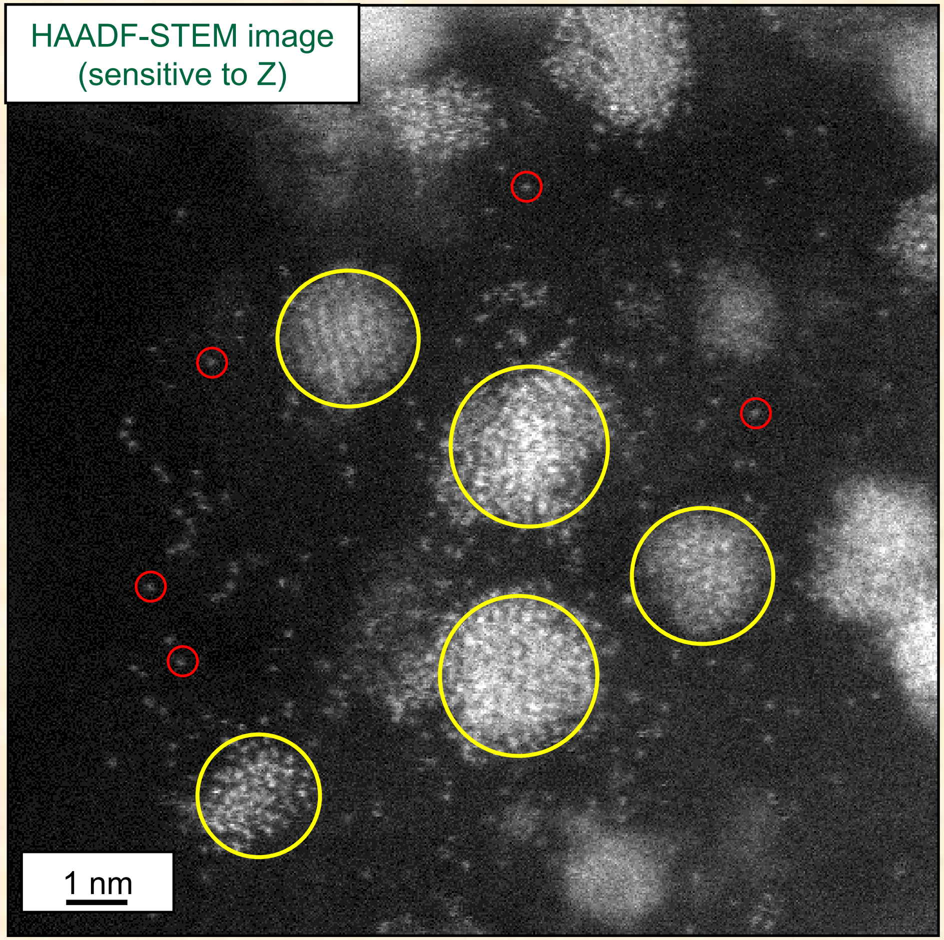
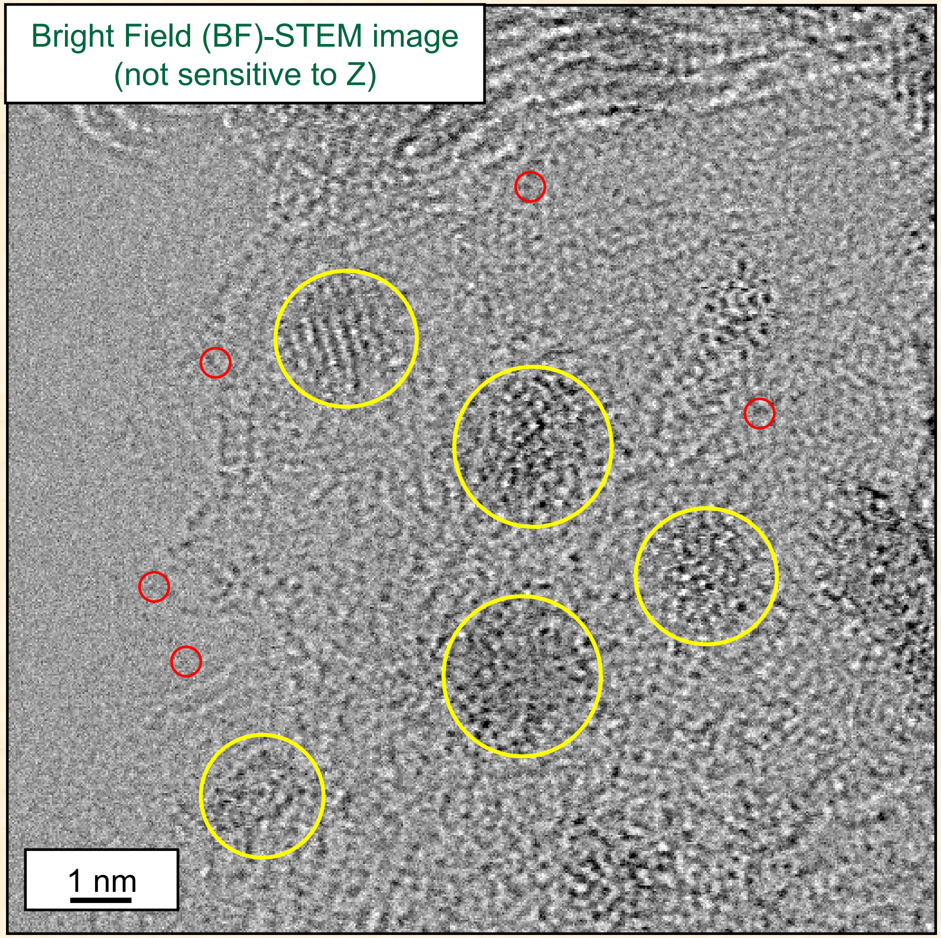
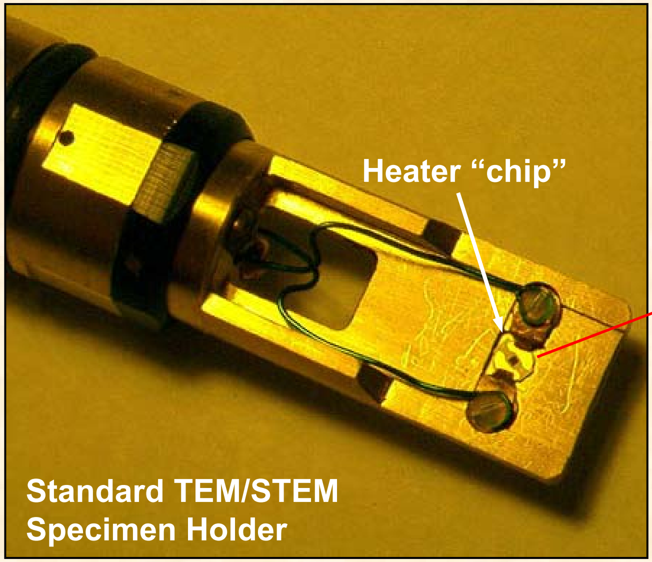
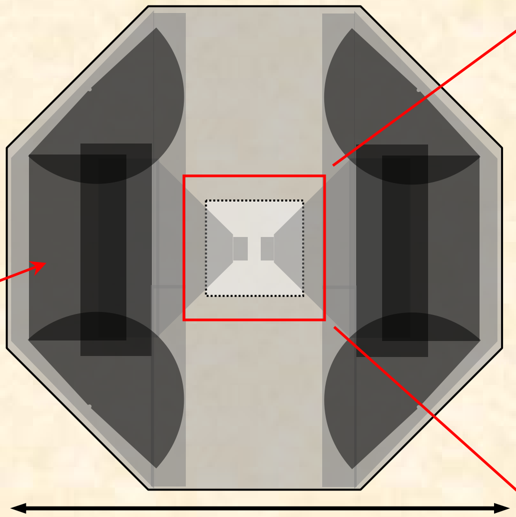
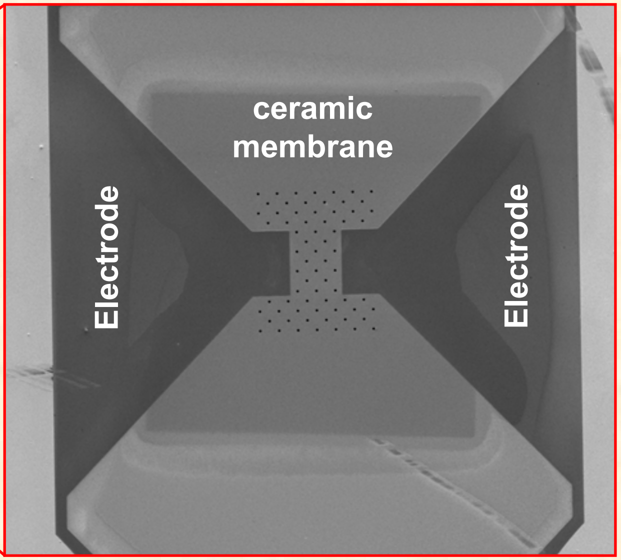




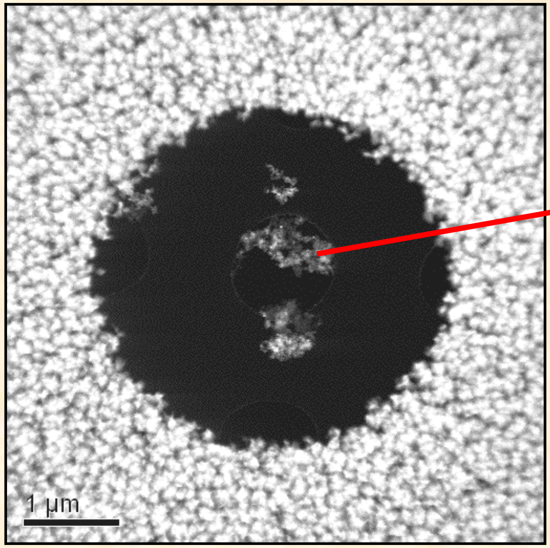
TEM/STEM Heating Holder for In-Situ Microscopy

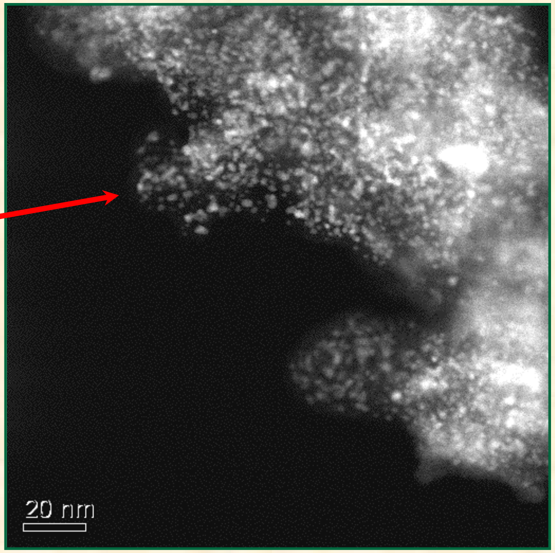






Protochips Co. provides novel heating elements based on semiconductor technology.

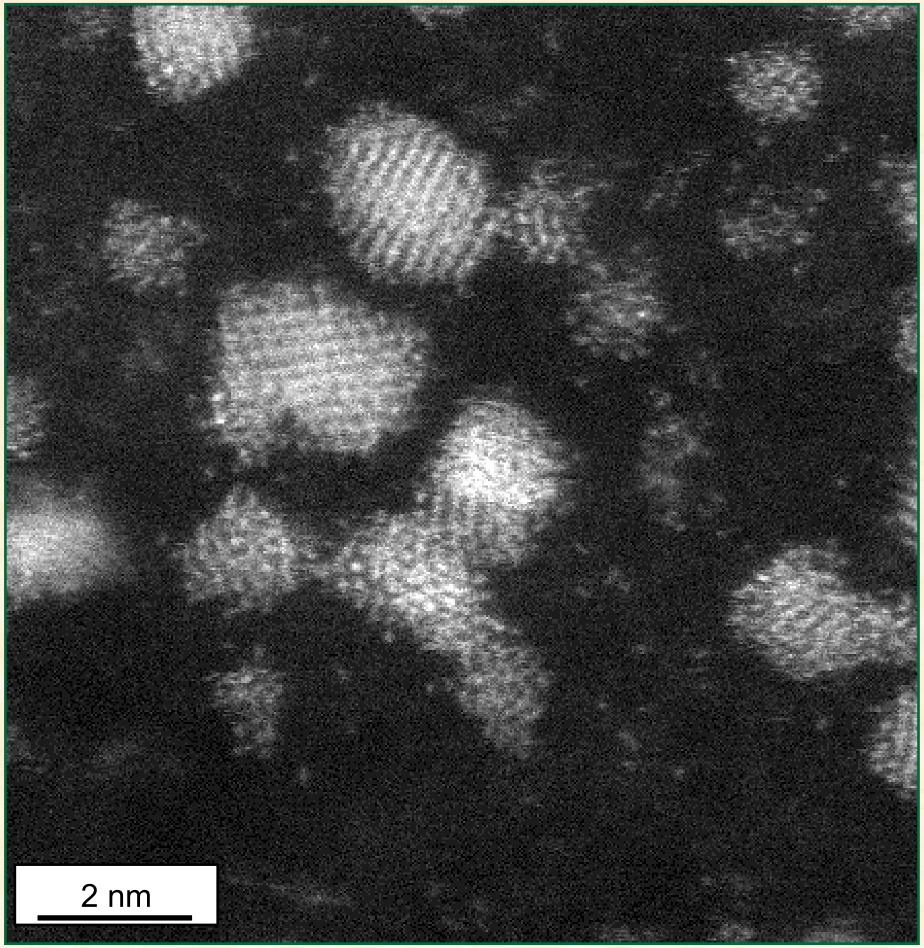


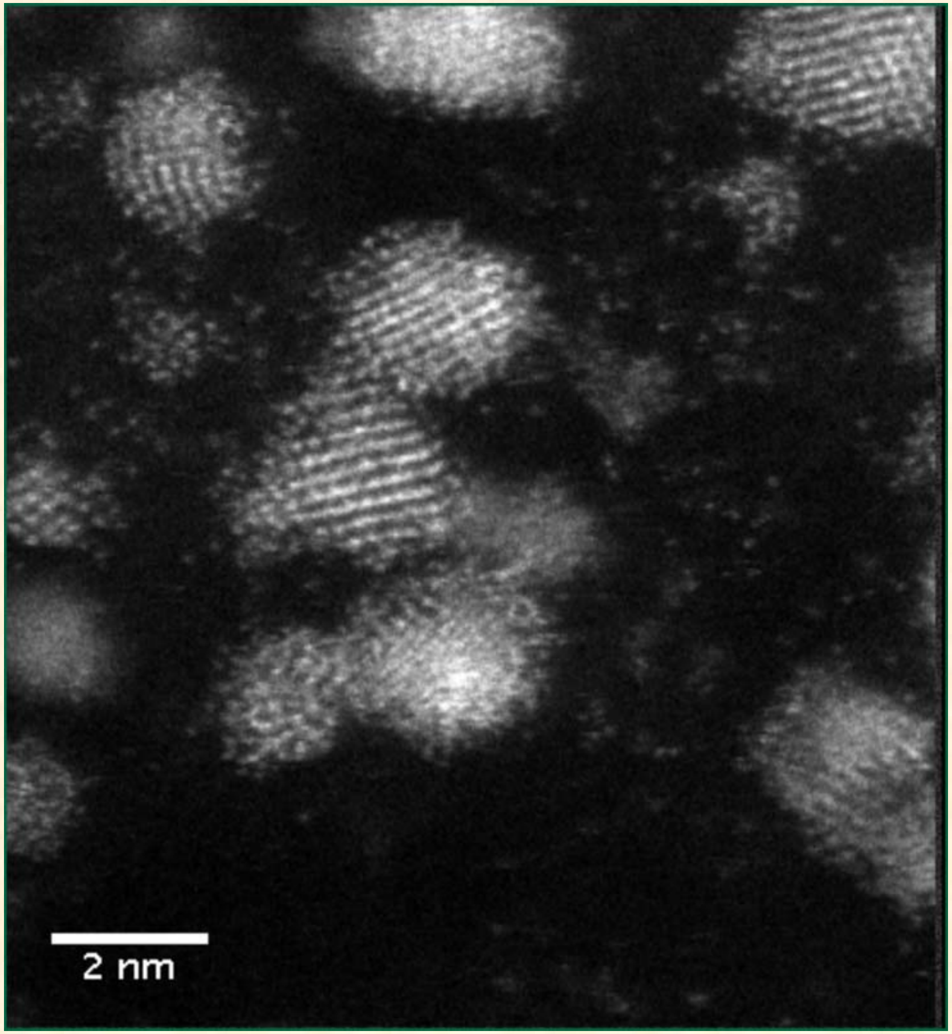


Pt/C Heated In-Situ To 150°C:

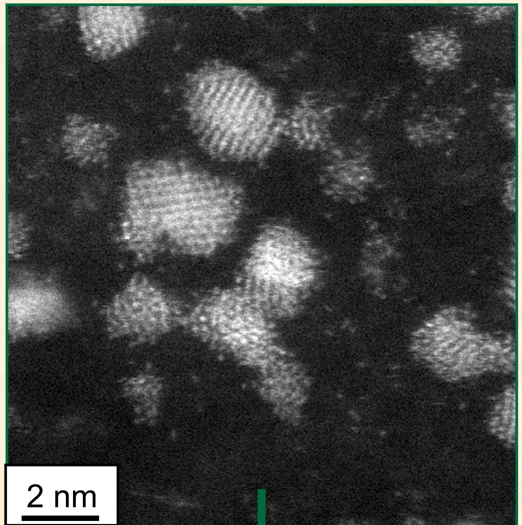
8 X 1.5 min hold
3 X 12 min hold
1 X 24 min hold

Starting Pt particle size/dispersion

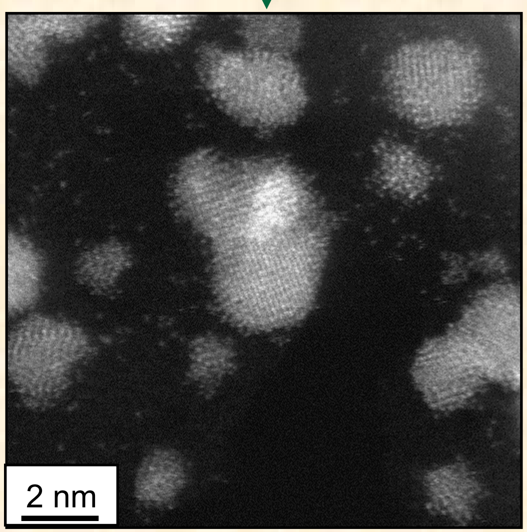




Pt Particle Coalescence Observed During Heating Pt/C for Only 48 min @150°C

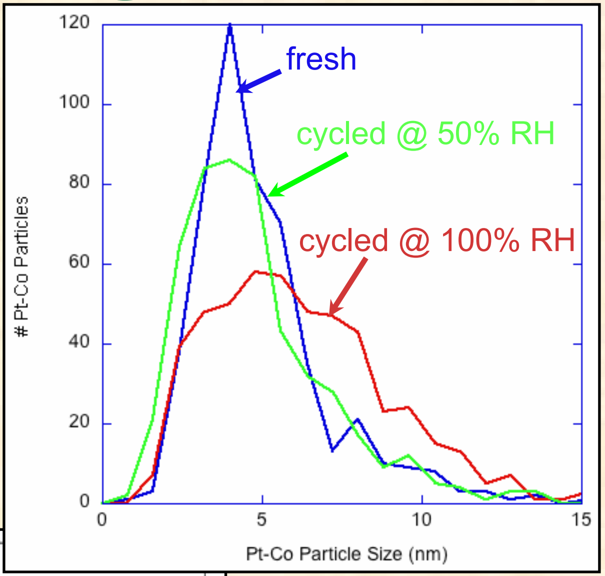


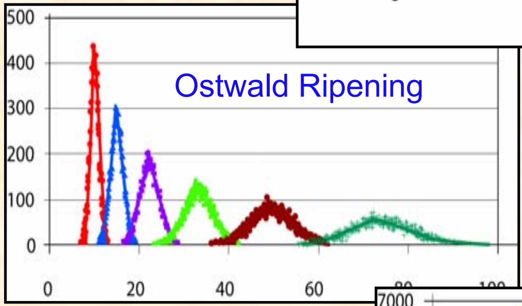
48 min @ 150°C



Low-temp behavior of Pt on Carbon:

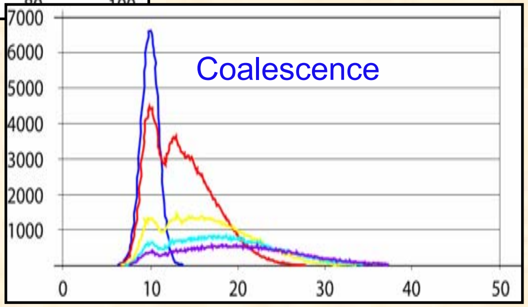
- Pt particles ***do not*** dissolve and move atomically across the carbon surface to deposit on nearby particles.
- Pt particles move across carbon surface and coalesce with nearby particles forming larger single crystal particles





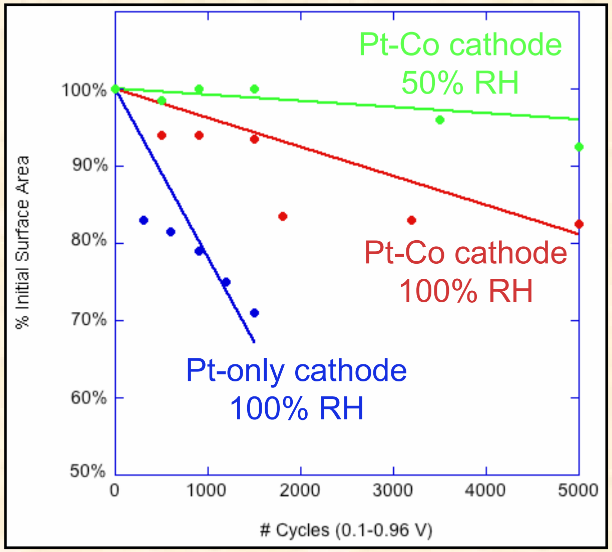
What is next:

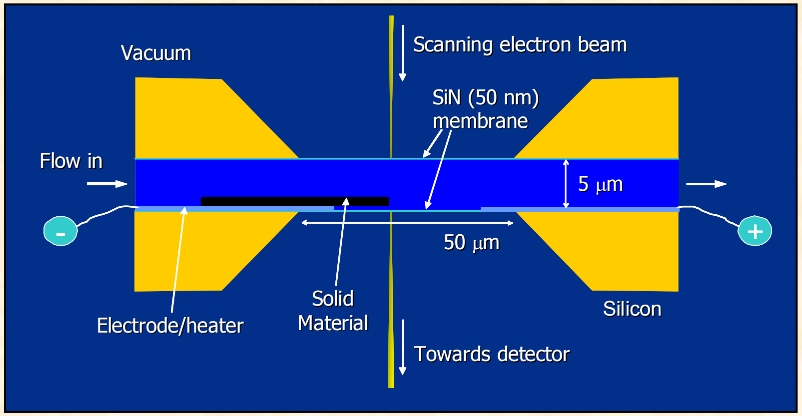
-statistical analysis of particle size and interparticle distances on relationship to particle coalescence
-effect of humidity, potential, etc. on coarsening mechanism and rate of coarsening



In Situ Microscopy for PEM Fuel Cell Research at the nm-Scale - Several Paths Forward

- Pt-Co exhibits lower loss of surface area compared with Pt during potential cycling
- Higher %RH enhances particle growth



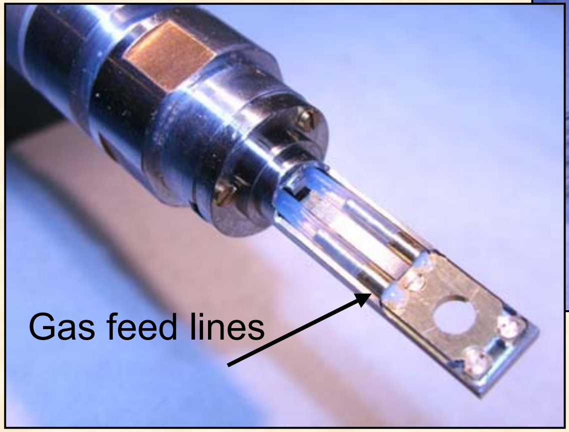


Develop specialized holders for fuel cell materials based on an initial design for imaging particles in liquid H_2O:

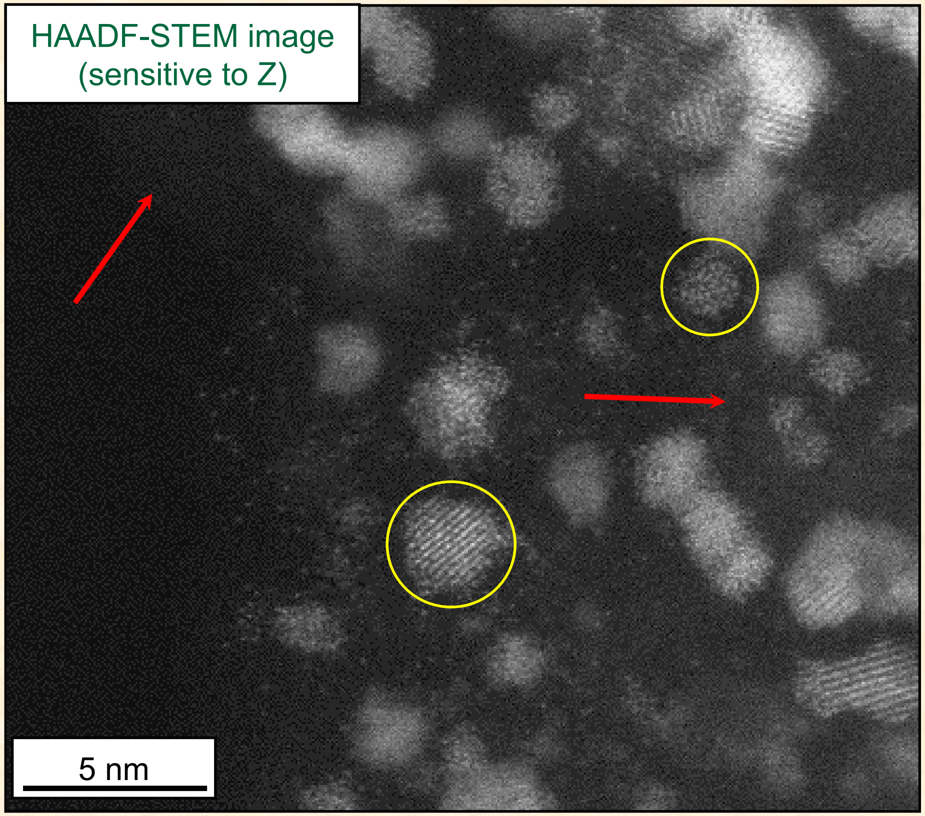
- variable liquid and gas flow rates
- variable temperature (cryo-1000°C)
- potential cycling

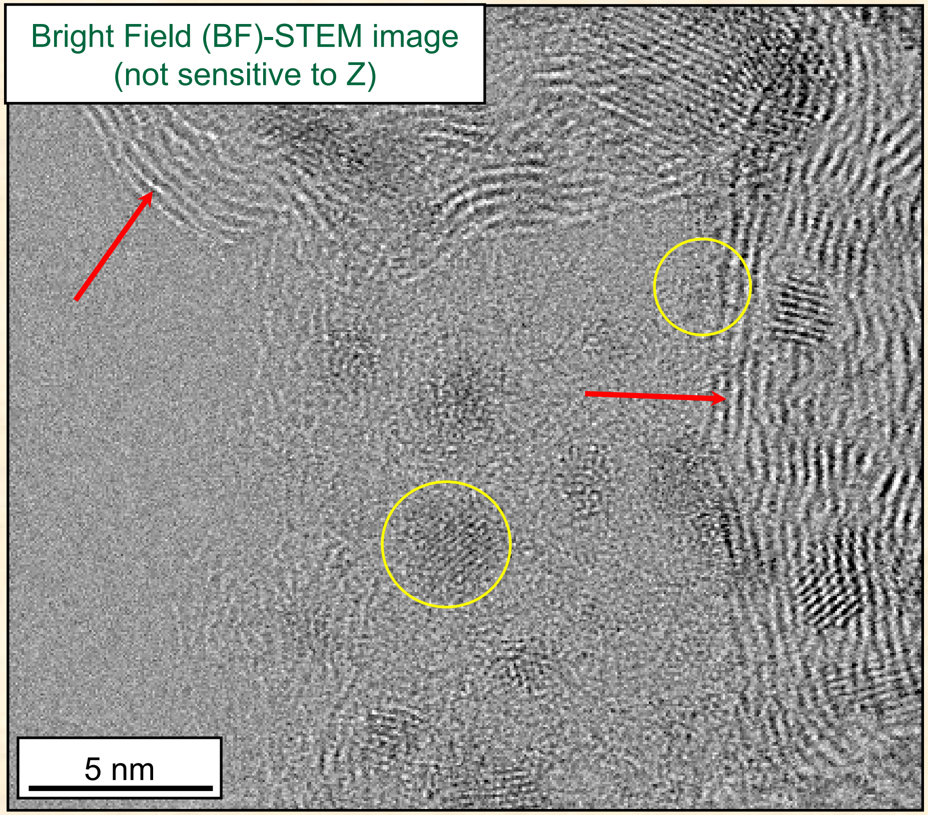
Potential Research Areas:

- Near live-time imaging of:
  - surface reactions
  - catalyst coarsening/migration
  - carbon corrosion
- Hydrophilicity/hydrophobicity (GDL, MPL components)
- STEM 3D imaging; i.e., through-thickness reconstruction



Simultaneous Acquisition of HAADF and BF STEM Images Provides Structural Information Regarding Catalyst AND Support



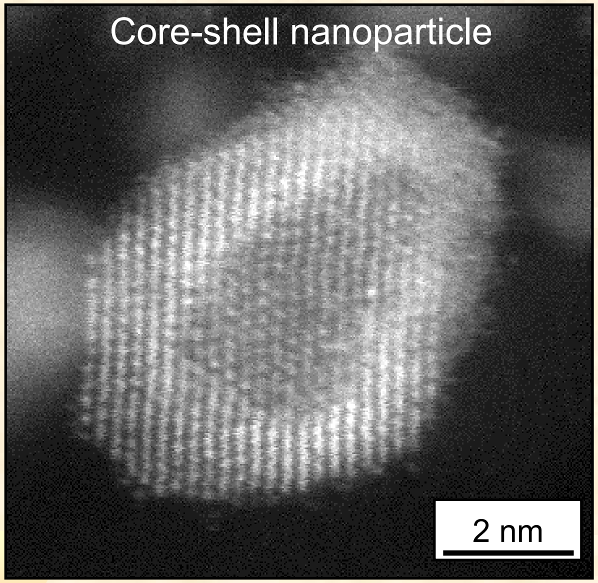


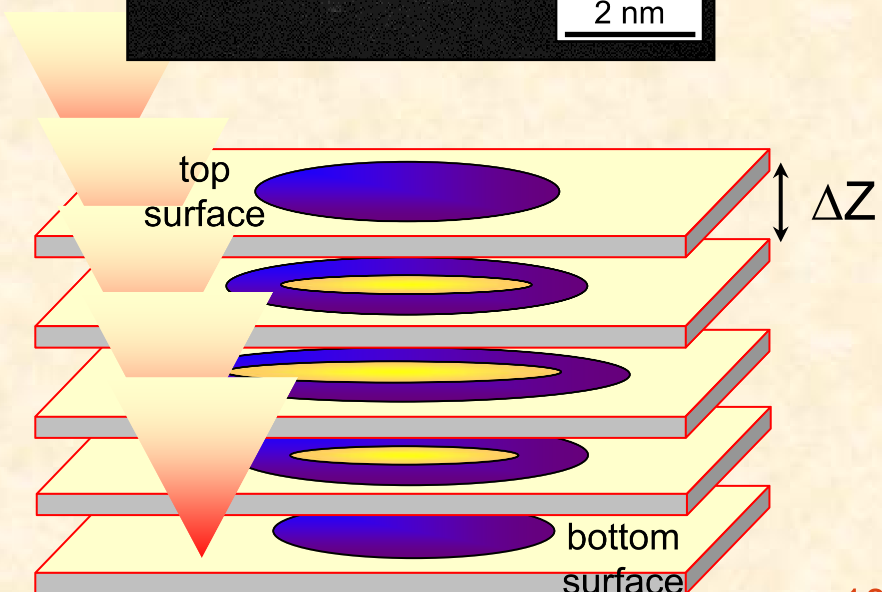
HAADF STEM used to image the structure of high-Z catalyst nanoparticles on carbon

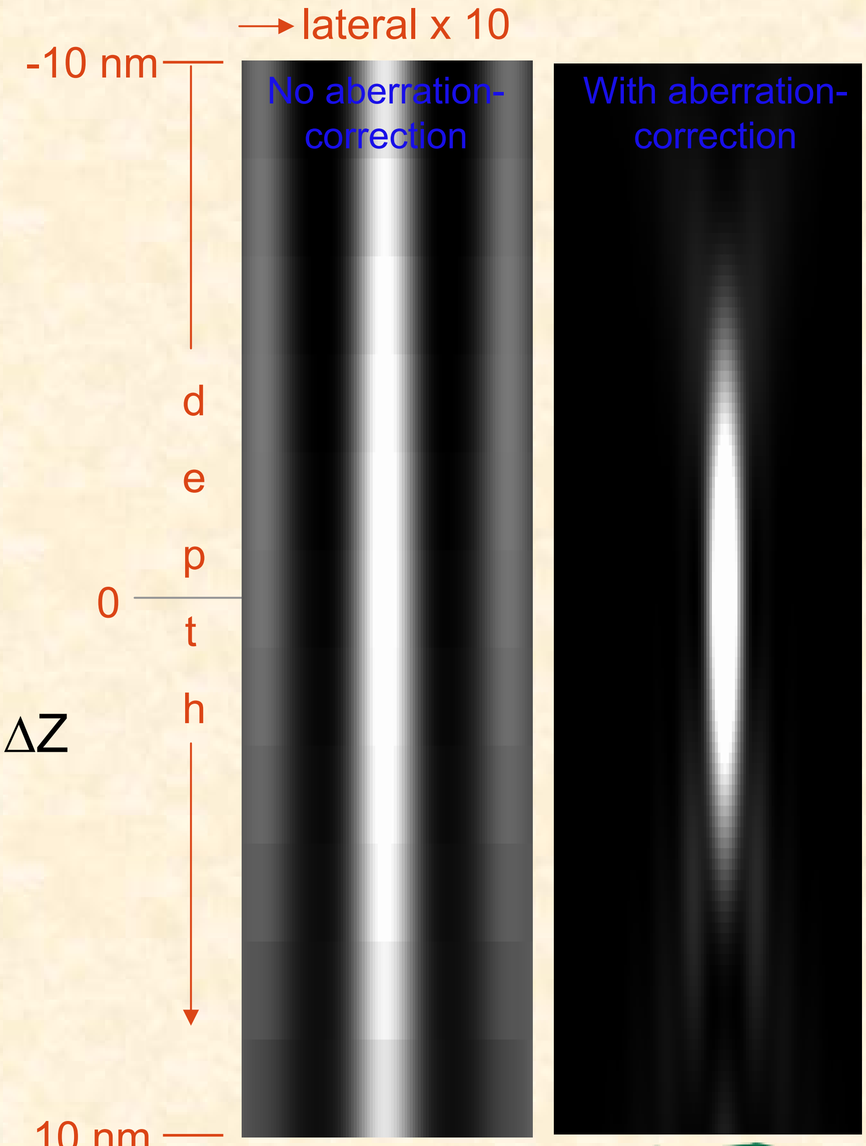
BF STEM used to image the structure of the carbon support (note 0.34nm graphite lattice)

ORNL Research is Focused on Depth-Sectioning Through Nanoparticles and 3D Reconstruction

3D STEM: depth-imaging “through” the thickness of a particle

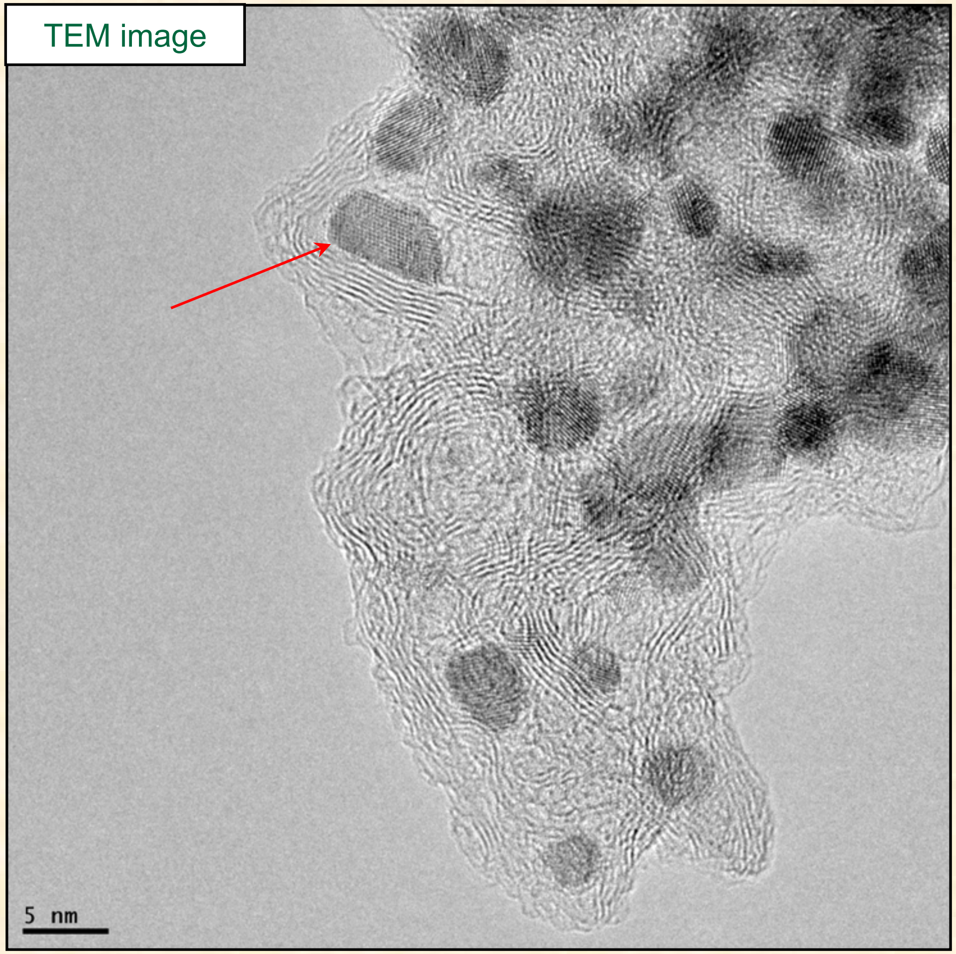


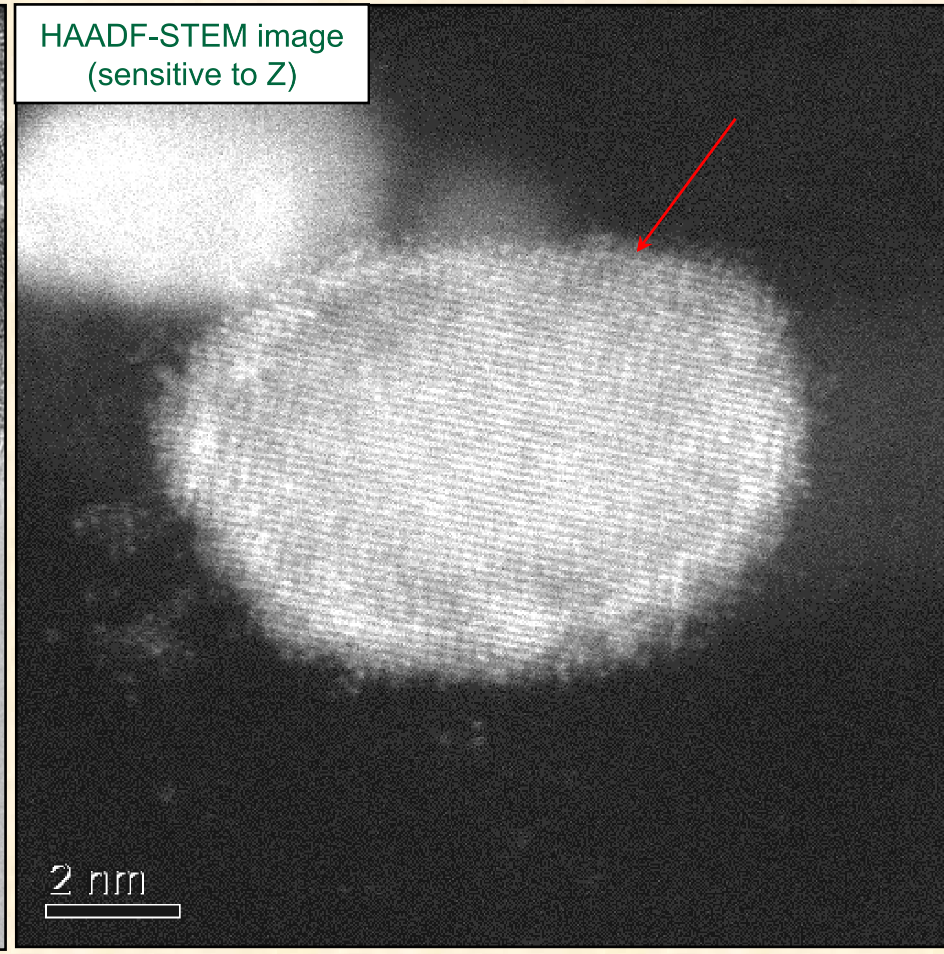




Slide courtesy of S.J. Pennycook, ORNL

Microstructure of BNL's Pt(ML)/Pd Catalyst

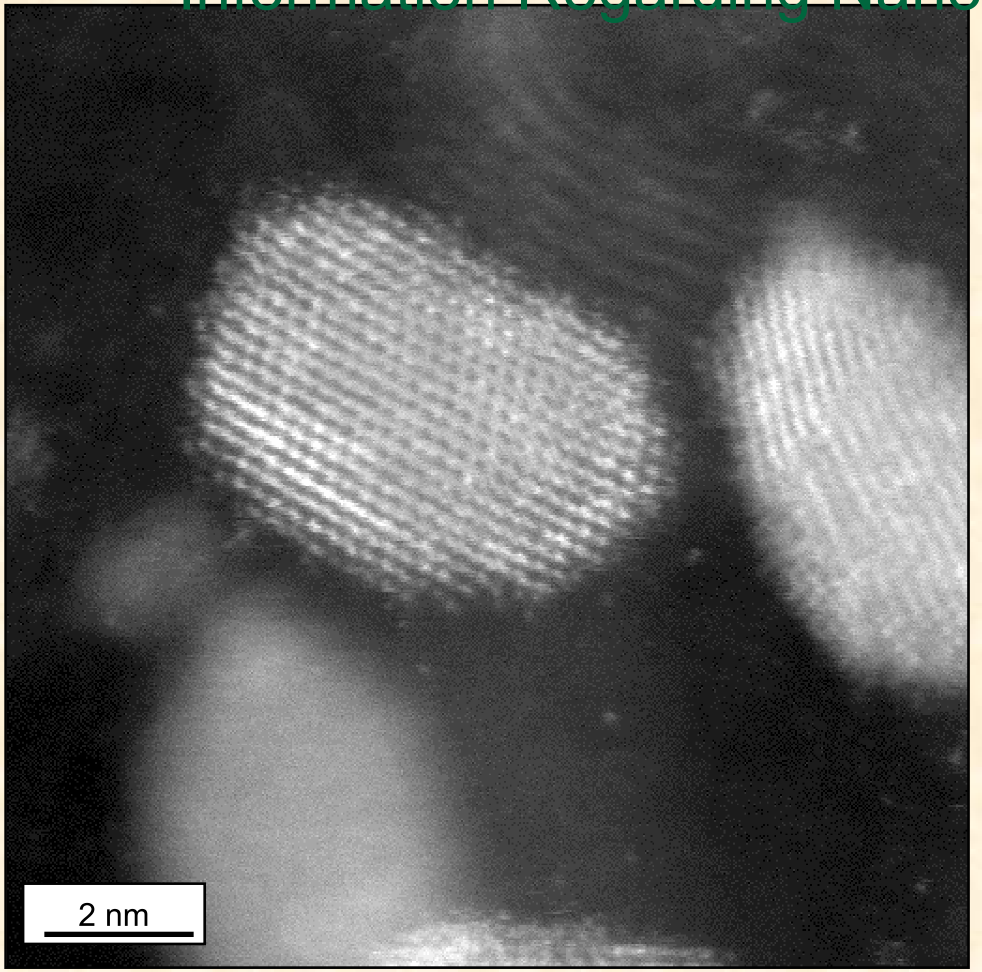


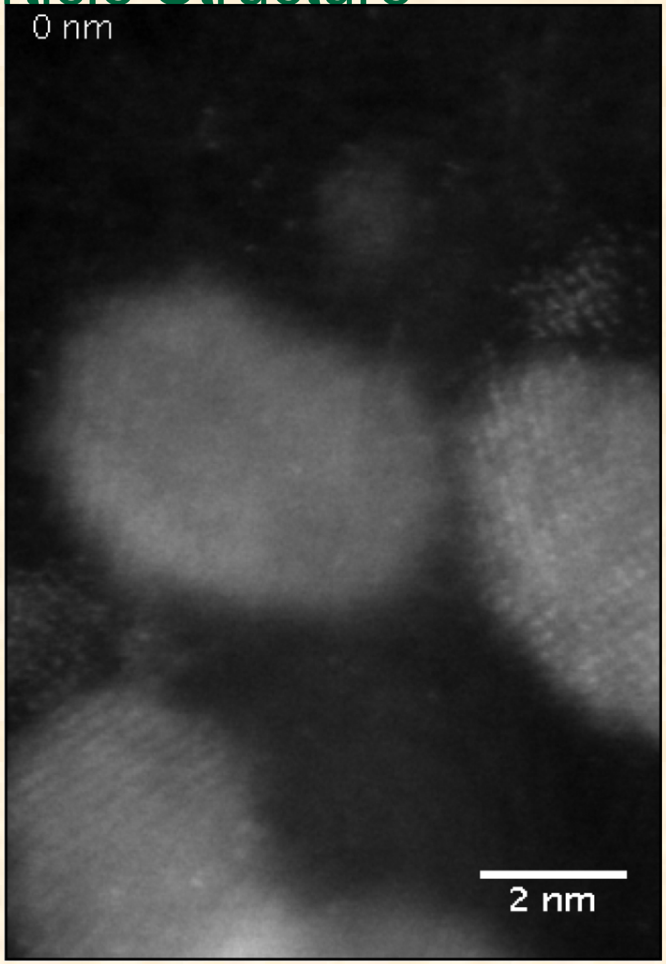


Pd nanoparticles typically exhibit an elongated morphology and have a significant area of contact with the carbon support

BNL's Pt(ML)/Pd Catalyst Particles Exhibit a Well-Defined Core-Shell Structure.

Through-Focal Imaging (3D) Can Provide Additional Information Regarding Nanoparticle Structure





Future Work

- Continue to take necessary steps to design, develop, and implement an *in situ* holder for near live-time, nm-scale microscopy of PEM fuel cell material constituents under relevant operating conditions - temperature, potential cycling, humidity.
- Statistical analysis of catalyst nanoparticle coalescence (with and without ionomer) as a *f*(T,RH,V).
- Design *in situ* experiments to understand mechanisms of carbon support degradation.
- Further develop the 3D STEM technique for catalyst nanoparticles.
- Continue to establish collaborations with industries, universities, and national laboratories (including access to ORNL User Facilities) to facilitate "transfer" of unique capabilities.
- Support new DOE projects with microstructural characterization and technique development.

Summary

- Many 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, RPI
  - Baseline PEM-MEA Characterization Program (non-proprietary)
- Significant progress is being made in developing *in situ* STEM as a viable technique to follow degradation of PEMFC materials (step-by-step approach)
- 3D STEM and image reconstruction is an extremely useful technique to look at the tomography of bulk agglomerates as well as individual nanoparticles