Characterization of Fuel Cell Materials

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June 9, 2010

Project ID FC020

Project Overview

Timeline

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

Budget

- **Funding in FY09 - $500k**
- **Funding in FY10 - $583k**

Barriers

- **Fuel Cell Barriers Addressed**
  - **A: Durability**
  - **C: Performance**
  - **G: Start-up/Shut-down Time and Energy/Transient Operation**

Partners

- **Los Alamos National Laboratory**
- **Argonne National Laboratory**
- **3M Company**
- **UTC Power**
- **Cabot Superior Micropowders**
- **Naval Research Laboratory**
- **Honda Research Institute**
- **Jet Propulsion Laboratory**
- **University of Houston**
- **University of Illinois - Chicago**
- **Rensselaer Polytechnic Institute**

Relevance - ORNL Research Objectives

- Identify and optimize novel high-resolution imaging and compositional/chemical analysis techniques, and unique specimen preparation methodologies, for the μm-Å-scale characterization of the material constituents comprising fuel cells (catalyst, support, membrane)
- Apply advanced analytical and imaging techniques for the evaluation of microstructural and microchemical changes that correlate with fuel cell performance
- Elucidate microstructure-related degradation mechanisms contributing to fuel cell performance loss
- MAKE TECHNIQUES AND EXPERTISE AVAILABLE TO FC RESEARCHERS OUTSIDE OF ORNL!

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

- Apply state-of-the-art electron microscopy techniques for the analysis of MEA material constituents:
  - Catalyst nanoparticles
  - Membranes
  - Carbon supports
  - GDLs/MPLs

- Collaborate with industry, academia, and national laboratories to make these techniques (and expertise) available to correlate structure/composition with MEA processing and/or life-testing studies

Milestones

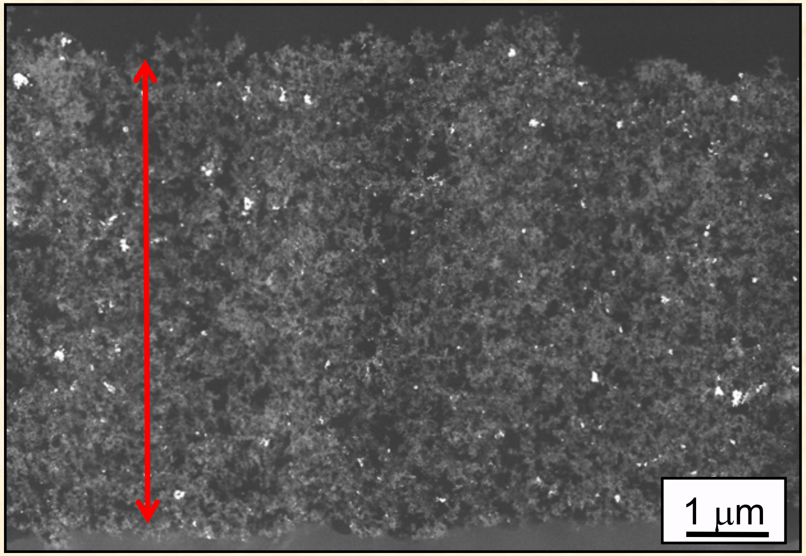
- FY09 Milestones:
  - Publish results for AC-STEM analyses of Pt-based catalyst stability during in-situ heating *Completed*
  - Complete study of the mechanisms of carbon support oxidation/corrosion under relevant PEMFC operating conditions and report results *Completed*
- FY10 Milestones:
  - Establish "baseline" design for window/chips for *in-situ* electrochemical cell for STEM imaging/analysis *Completed*
  - Publish results of preliminary *in-situ* STEM catalyst degradation study *In Progress*

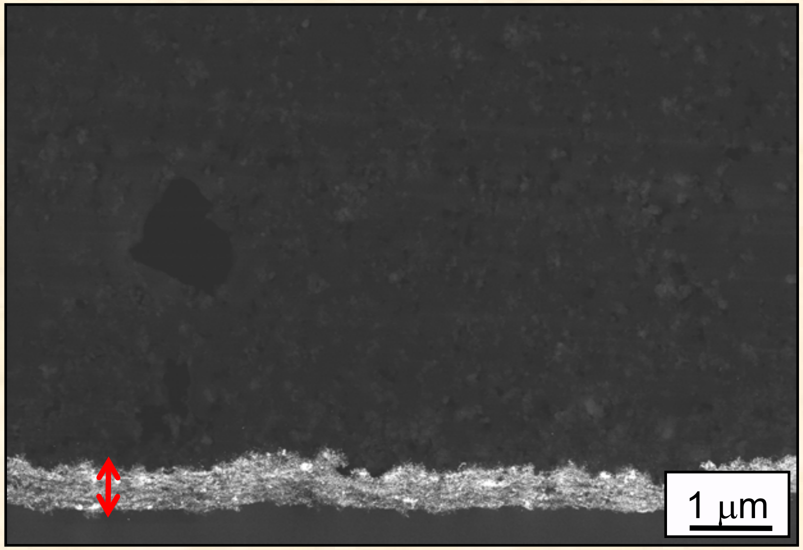
Technical Accomplishments and Progress

- Investigated carbon-support corrosion mechanisms in electrochemically-aged MEAs
- Studied Pt migration as a function of aging protocols
- Applied advanced statistical analysis techniques to evaluate Å-scale elemental/compositional analyses of catalyst nanoparticles (Multivariate Statistical Analysis – Principal Component Analysis)
- Continued development of liquid STEM technique to characterize PEMFC materials constituents during operation – many obstacles encountered!

Technical Accomplishments and Progress

Understanding Mechanisms of Carbon Corrosion at Cathode





During electrochemical aging under adverse conditions (>OCV; start-up/shut-down cycles; H_2 fuel starvation), the cathode can collapse/compress/thin resulting in major implications for:

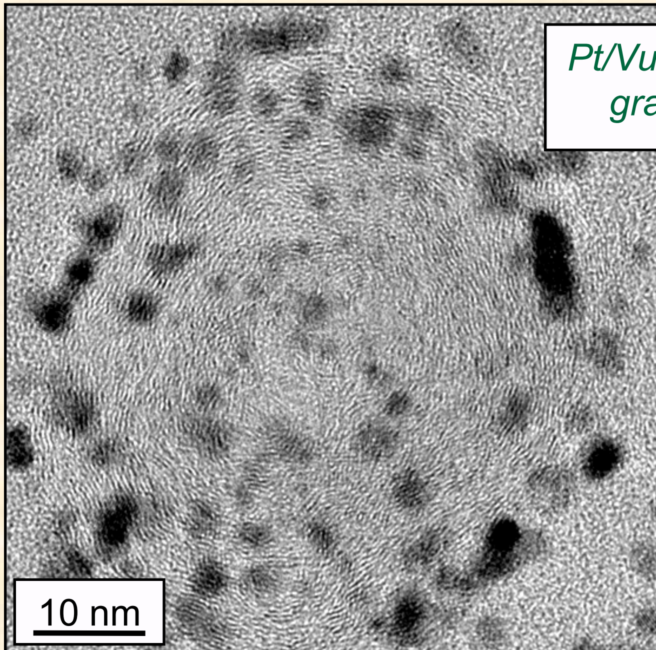
- loss of catalyst electrochemically active surface area (Pt EASA)
- loss of catalyst support (carbon) due to enhanced electrochemical oxidation
- loss of porosity for gas transport to reactive sites
- implications for water management

Recent publications suggest that:

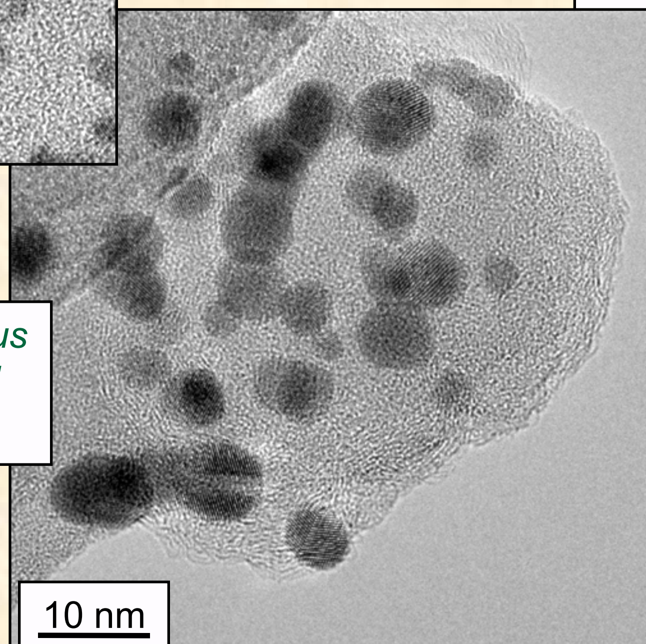
- severe oxidation of carbon results in LITTLE/NO carbon support remaining in cathode
  $C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$ (carbon loss and CO_2 evolution)
- Pt is “detached” from support

Technical Accomplishments and Progress

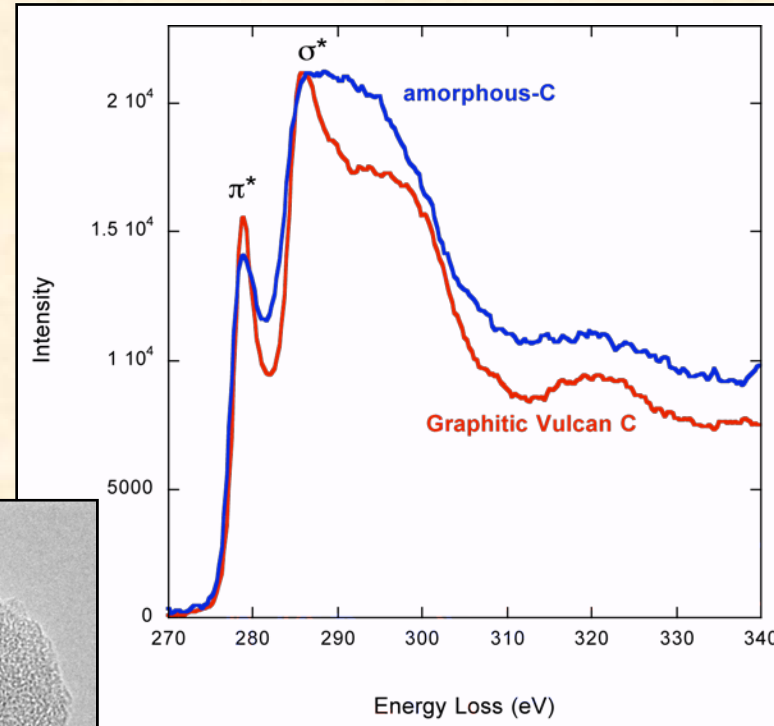
Understanding Mechanisms of Carbon Corrosion at Cathode



Pt/Vulcan – virgin MEA graphitic structure



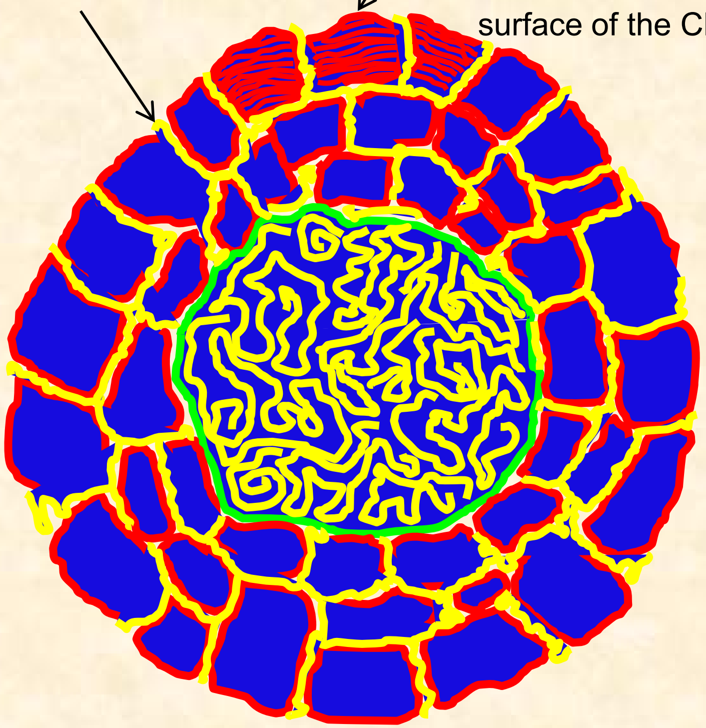
Pt/Vulcan –amorphous carbon in collapsed cathode



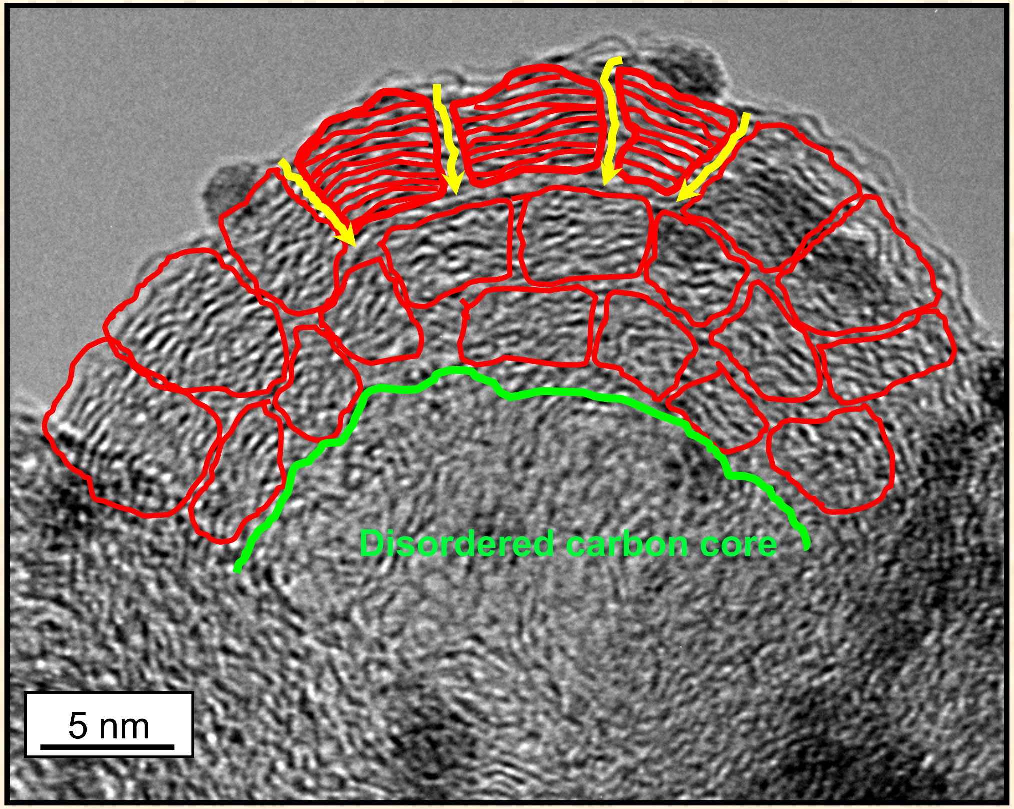
Corrosion of carbon black at cathode:

- *some loss of carbon via oxidation to CO_2*
- *oxidation resulting in amorphous "glassy" carbon*
- *sintering of glassy carbon particles*
- *extreme Pt coarsening – Pt particles remain attached to glassy carbon*

Technical Accomplishments and Progress
Understanding Mechanisms of Carbon Corrosion at Cathode



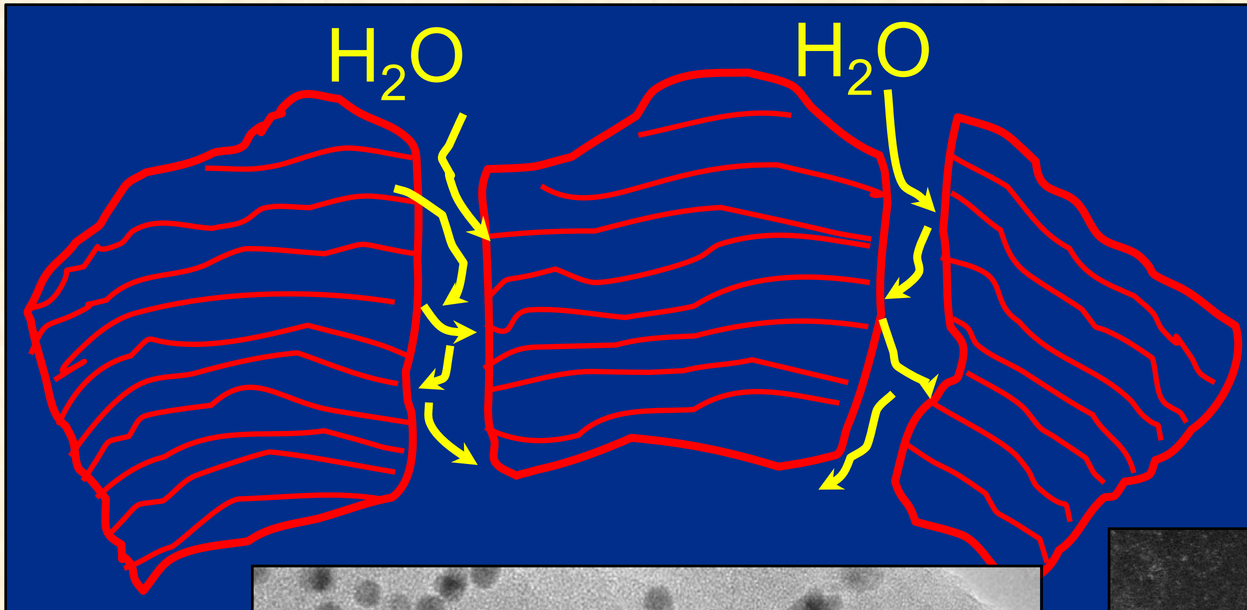
Structure Of Vulcan Support



The amount of disordered carbon within a CB particle is ~20% for both the domain boundaries + central core (Zerda, et. al., *Carbon* **38** (2000) 355). The surface roughness is limited to 1-2 graphite $d_{(0002)}$ (~0.6 nm) where domains meet at the disordered boundaries.

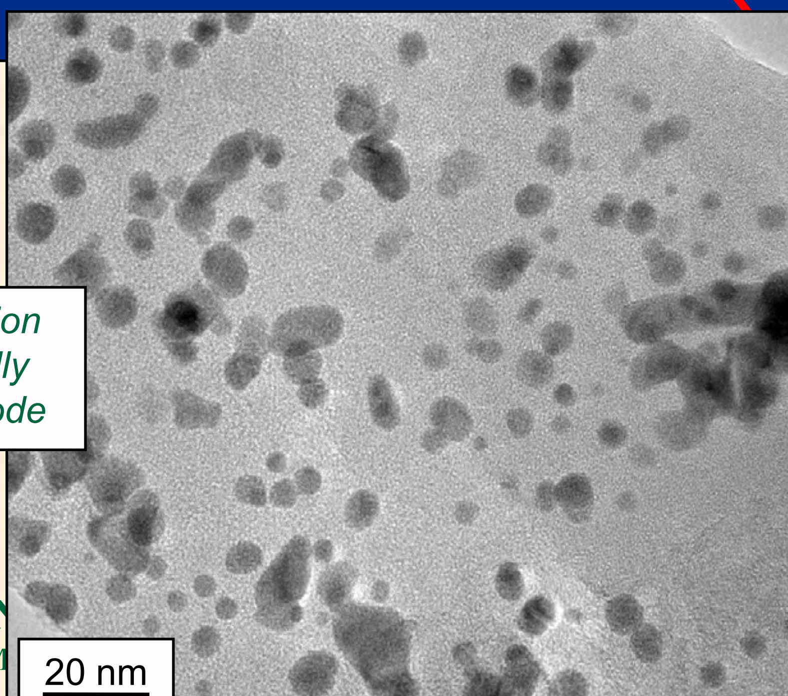
"Mosaic-domain structure"
Oberlin, in Chemistry and Physics of Carbon **22** (1965) 1
Huttepain and Oberlin, *Carbon* **28**[1] (1990) 103

Technical Accomplishments and Progress
Understanding Mechanisms of Carbon Corrosion at Cathode

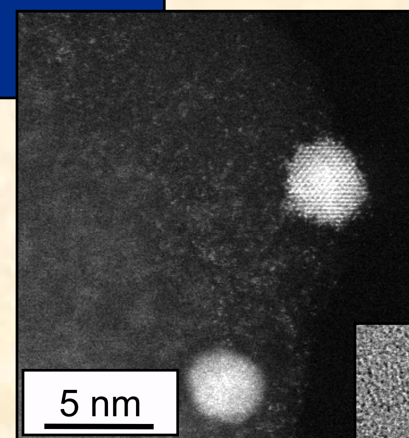


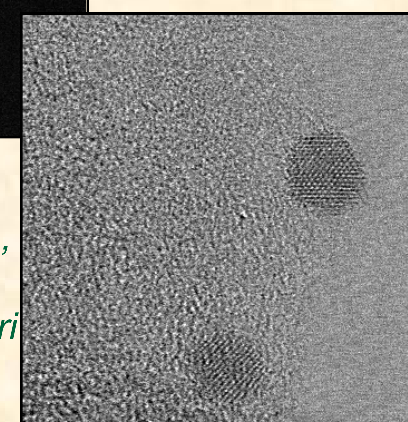
Reactivity on basal plane surface-terminating sites is very low

Reactivity of disordered carbon between graphitic domains (singly-bonded carbon end sites) is much higher.



Carbon oxidation results in a fully densified cathode





Impurities (glass-formers such as Ca, Si) can accelerate amorphization/sinteri ng

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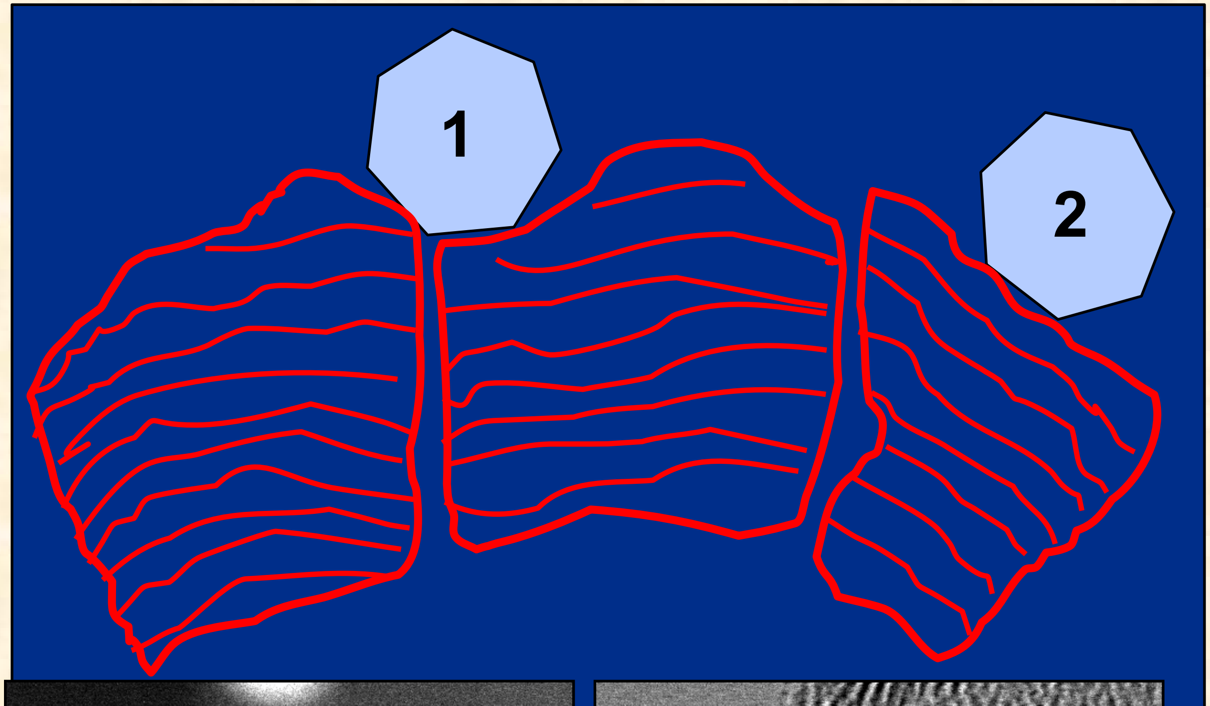

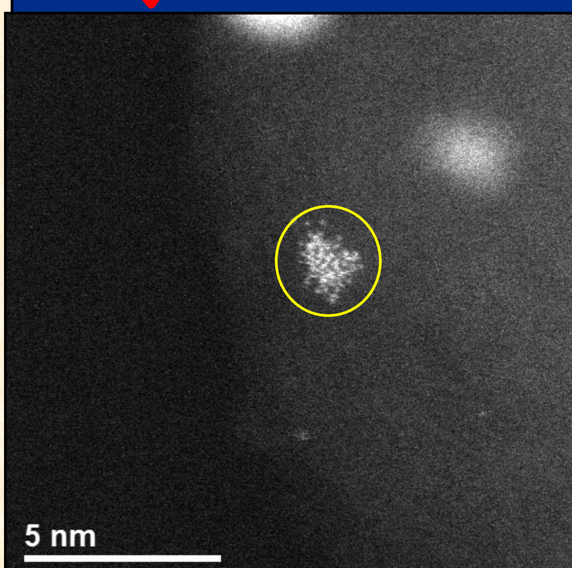

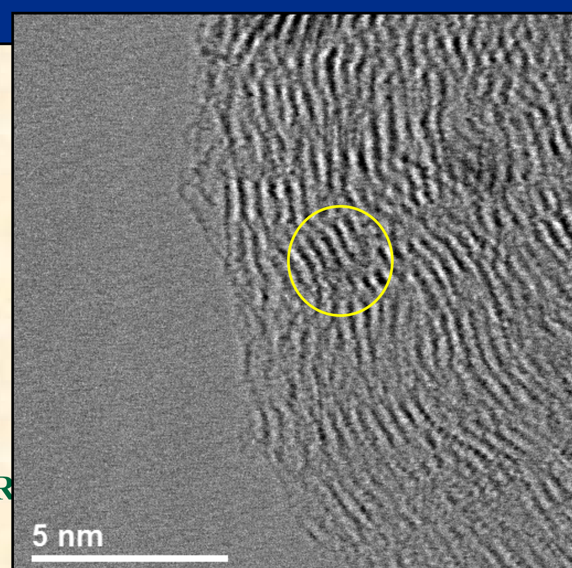

Nucleation of Pt On Vulcan Surface

1 – *Pt nucleates preferentially at disordered regions between graphitic domains:*

- *Pt anchored by oxygen-containing functional groups on basal plane edges*

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2 – *Pt nucleates preferentially on surfaces of graphitic domains*

- *Pt anchored by* π *sites on basal plane surfaces*

Indications are that Pt nucleates on the π sites on basal plane surfaces, which would leave disordered channels open to surface

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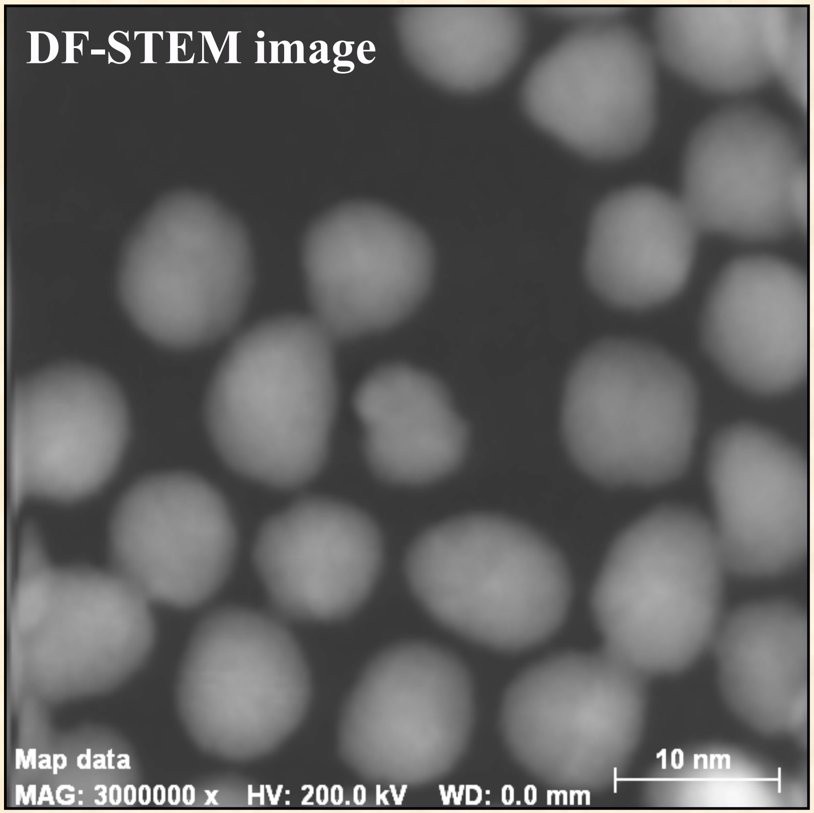
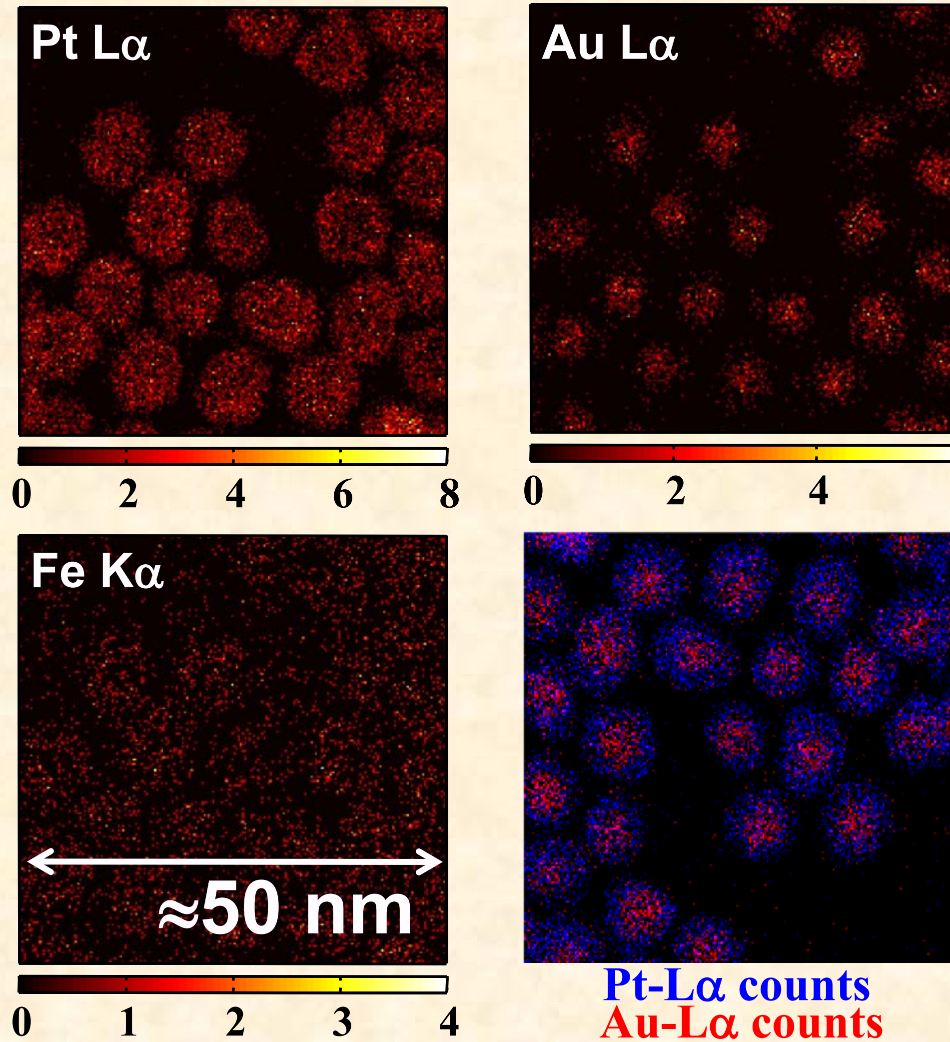
Technical Accomplishments and Progress

Using Statistical Data Analysis Methods For Nanoparticle Analysis
Multivariate Statistical Analysis – Principal Component Analysis



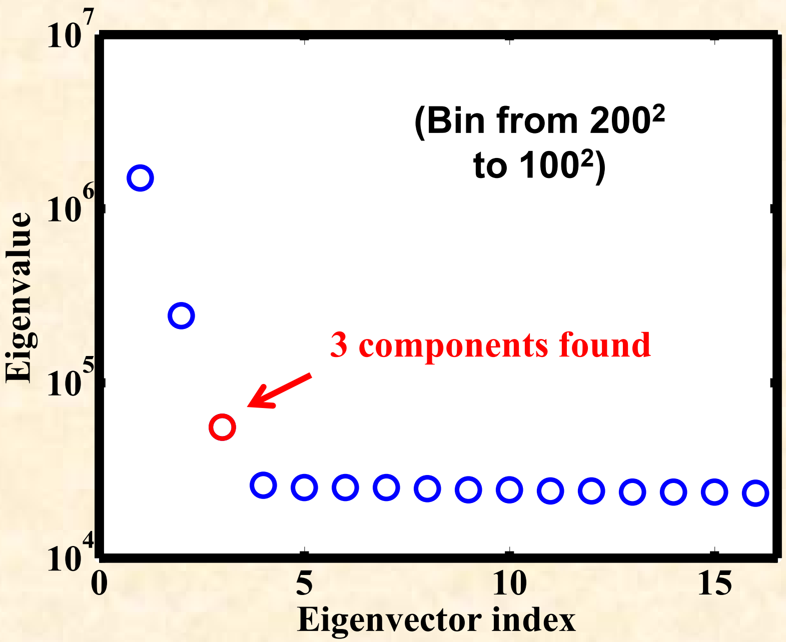
"Raw" EDS data
Pt-shell/Au-core structure evident but association of Fe not clear



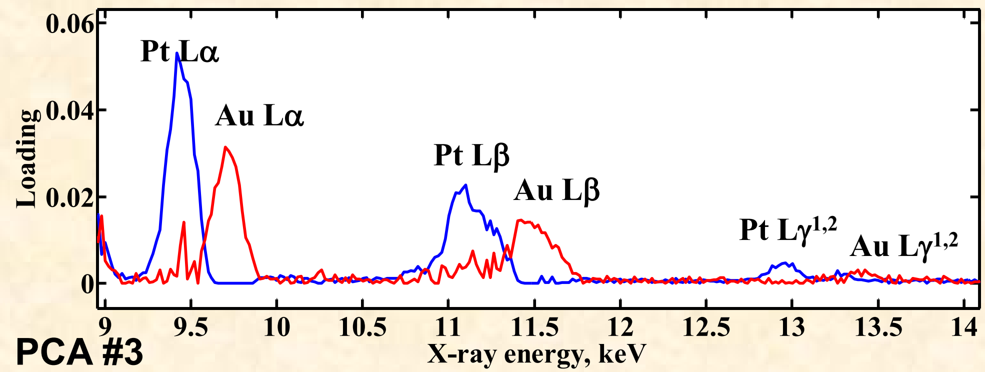
Technical Accomplishments and Progress

Using Statistical Data Analysis Methods For Nanoparticle Analysis

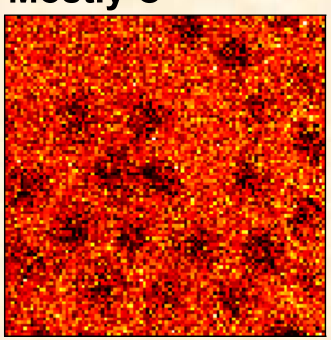
Multivariate Statistical Analysis – Principal Component Analysis



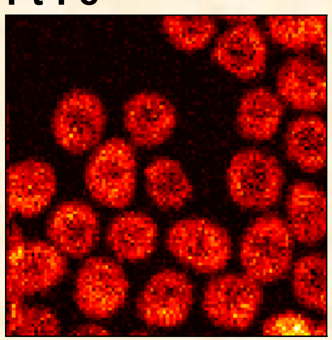
PCA/MVSA allows for an “unbiased” analysis of the data to extract the primary elements and their primary lociation within the structure of the nanoparticle



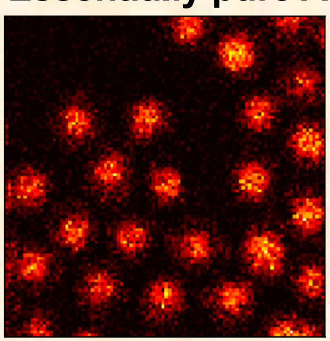
PCA #1
Mostly C

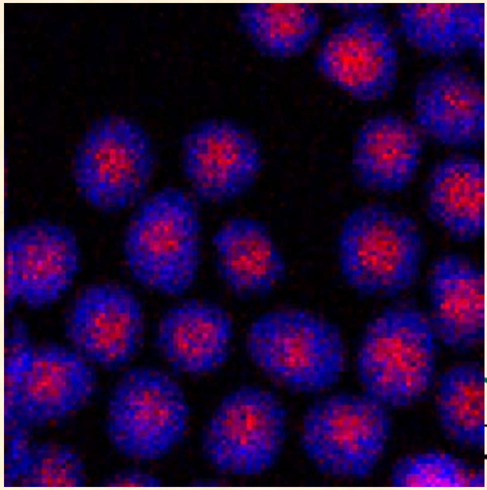


PCA #2
Pt-Fe

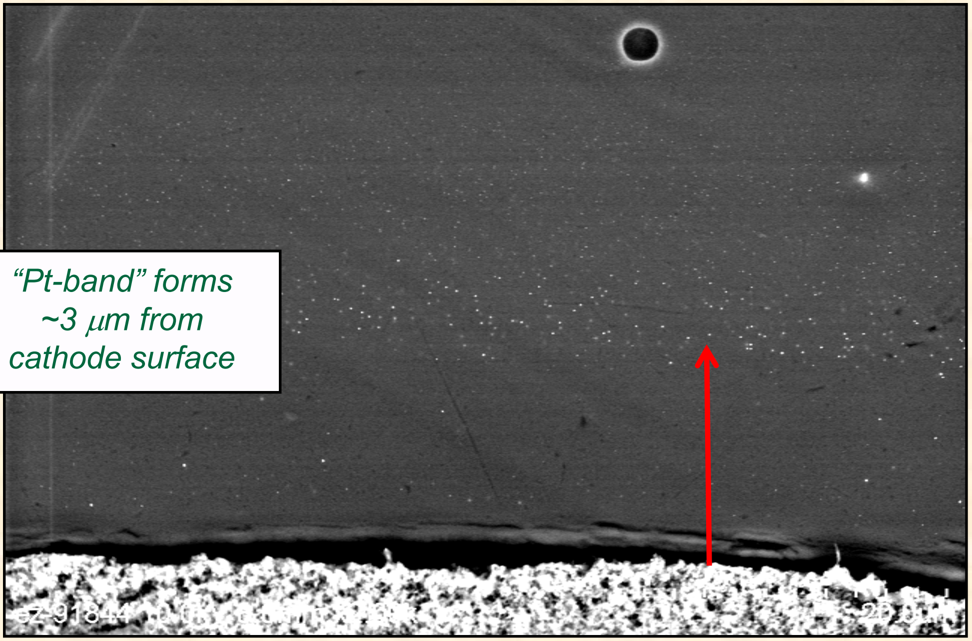


PCA #3
Essentially pure Au

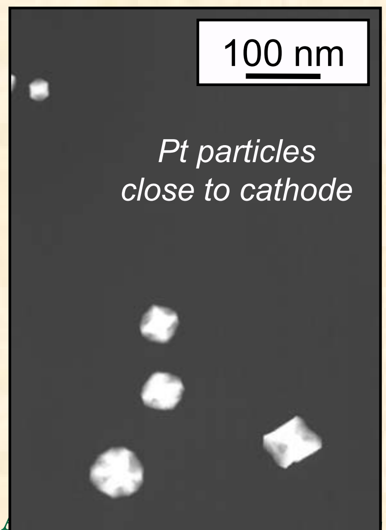


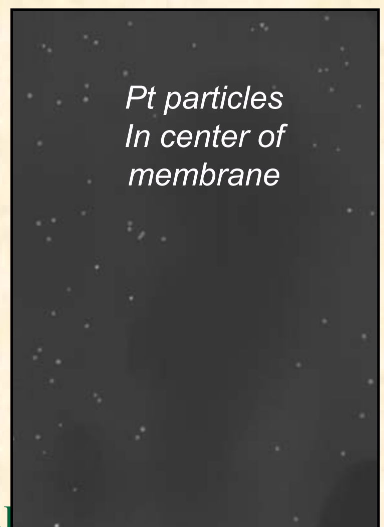


Technical Accomplishments and Progress
Pt Migration From Cathode Into Membrane

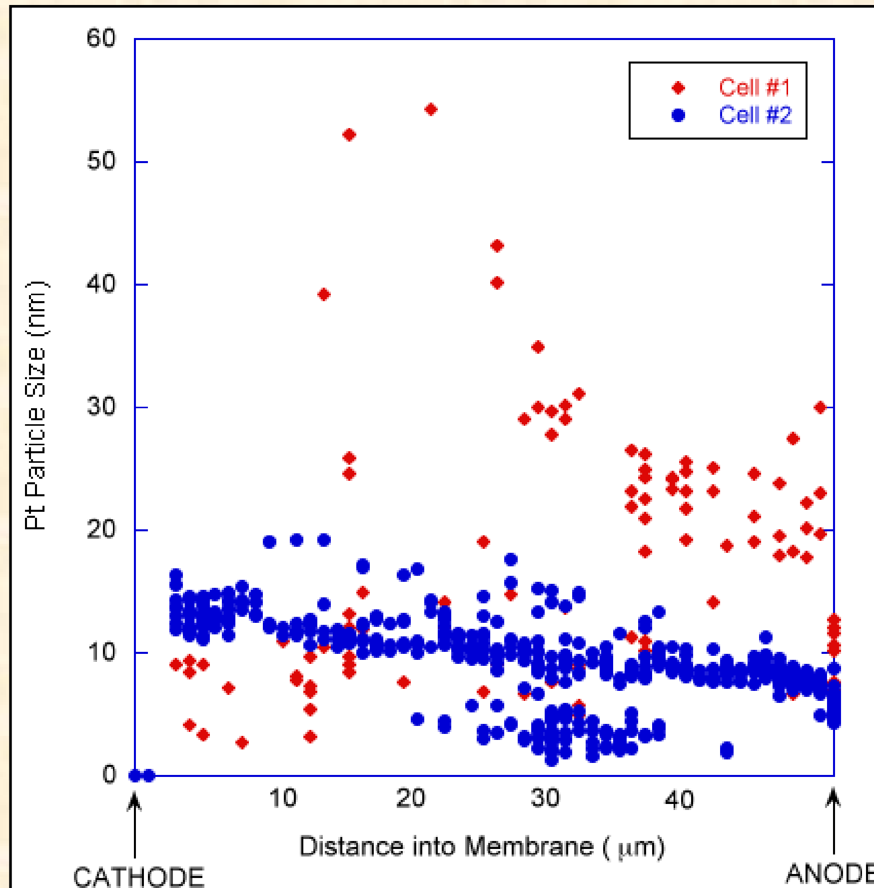


"Pt-band" forms ~3 μm from cathode surface





So-called "Pt-band" refers to the highest concentration of Pt particles that precipitate out in membrane at some distance from cathode surface: *Pt migration profiles are much more complicated and are comprised of numerous "Pt-bands" of different size Pt particles distributed across the membrane*



Future Work

- Correlate microstructural/compositional observations with AST protocols (automotive and stationary), especially related to catalyst coarsening & migration, carbon corrosion, membrane degradation
- Apply novel statistical analysis techniques to new catalyst compositions, both as-processed and aged/tested
- 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.
- 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)
- MVSA/PCA is being applied “routinely” to analyzing compositions/distributions of elements comprising catalysts
- New insight into understanding carbon corrosion mechanisms and Pt migration will enable strategies for improved material stability to be studied/implemented