

Characterization of Fuel Cell Materials

Project ID FC020

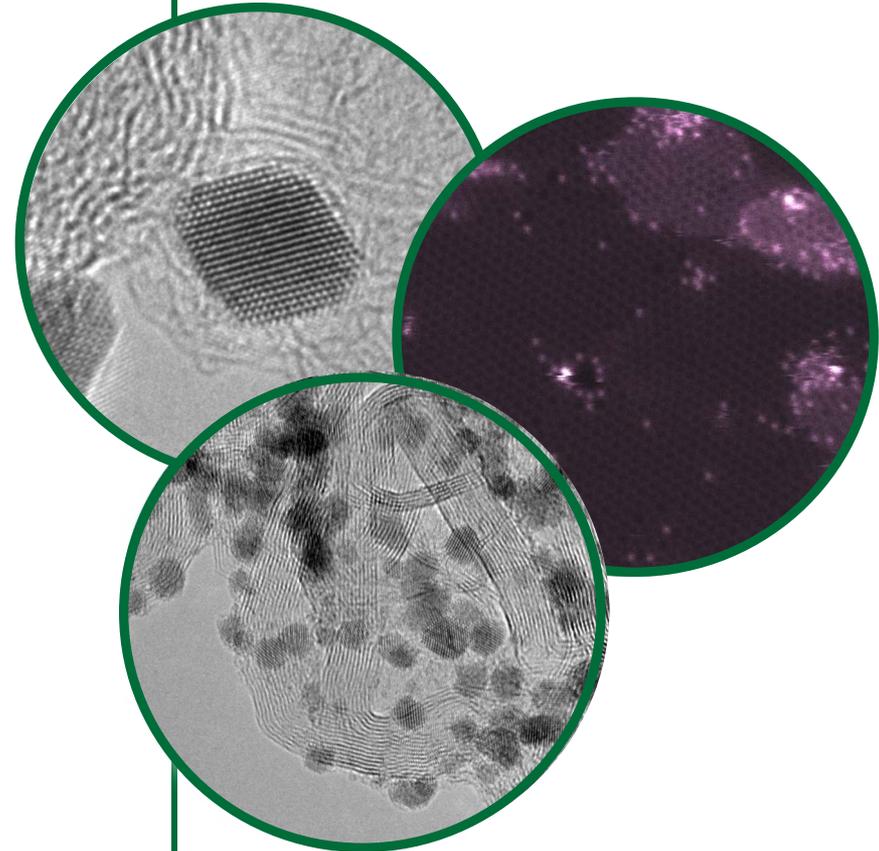
PI: Karren L. More

Juan Carlos Idrobo, Miaofang Chi,
Kelly Perry, Dave Cullen, Harry Meyer,
and Shawn Reeves

*Oak Ridge National Laboratory
Oak Ridge, TN*

*2011 DOE Annual Merit Review
May 12, 2011*

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Project Overview

Timeline

- Project initiated in FY2000
- *Continuous* - fundamental research on the microstructural characterization of fuel cell materials to improve durability

Budget

- Funding in FY10 - \$580k (~1.5 FTE)
- Funding in FY11 - \$580k (~1.5 FTE)

Barriers

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

Partners

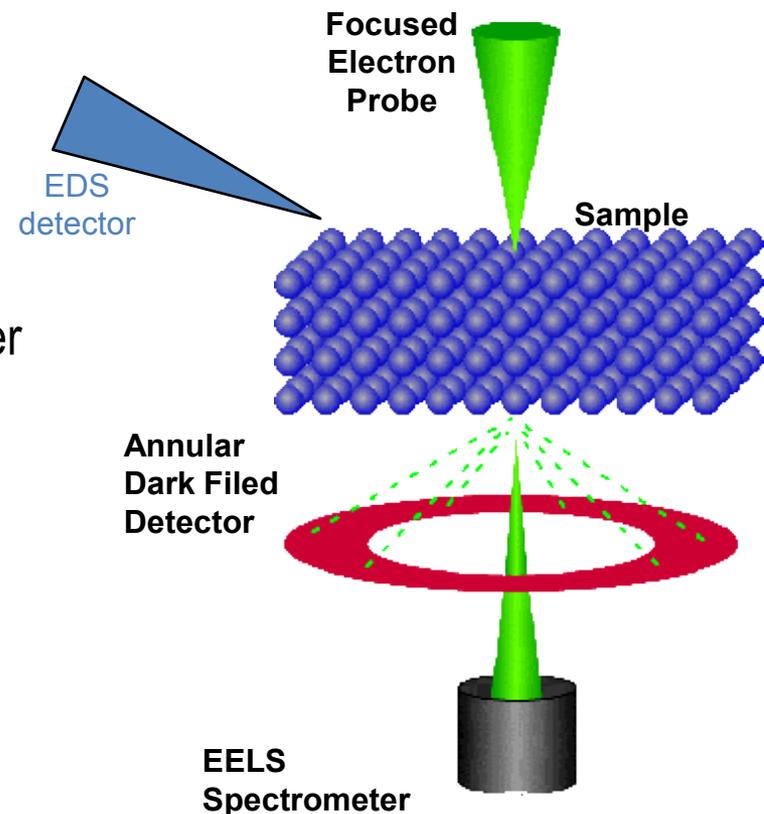
- Los Alamos National Laboratory
- Brookhaven National Laboratory
- Lawrence Berkeley National Laboratory
- GM
- Nissan Technical Center North America
- Naval Research Laboratory
- Proton Energy
- Fuel Cell Energy
- University of Tennessee
- University of New Mexico
- Brown University
- The Netherlands guy
- Fuel Cell Cubic, Japan
- Additional DOE project collaborations: LANL, ANL, NREL, 3M, and UTC Power. Results from these studies are NOT included in this project summary.

Relevance - ORNL Research Objectives

- Identify, develop, and optimize novel high-resolution imaging and compositional/chemical analysis techniques, and unique specimen preparation methodologies, for the μm - \AA -scale characterization of the material constituents comprising fuel cells (catalyst, support, membrane)
- Understand fundamental relationships between the material constituents within fuel cell MEAs and correlate these data with stability and performance as per guidance of the entire fuel cell community
- Integrate microstructural characterization with other DOE projects
- Apply advanced analytical and imaging techniques for the evaluation of microstructural and microchemical changes to elucidate microstructure-related degradation mechanisms contributing to fuel cell performance loss
- **MAKE CAPABILITIES AND EXPERTISE AVAILABLE TO FUEL CELL RESEARCHERS OUTSIDE OF ORNL – THIS IS THE MOST IMPORTANT ASPECT OF ORNL'S RESEARCH!**

Approach: Use Advanced Microscopy To Address Fundamental Questions Regarding Materials Behavior

- Apply state-of-the-art electron microscopy techniques for the characterization of MEA material constituents:
 - Catalyst nanoparticles – composition, chemistry, and particle morphology
 - Polymer - membrane and electrode re-cast ionomer
 - Catalyst support materials
 - MEAs/GDLs/MPLs
- Collaborate with industry, academia, and national laboratories to make capabilities and microscopy expertise available to correlate structure/composition with MEA processing and/or life-testing studies



Milestone Schedule – FY10 and FY11

- 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 *Completed*

- FY11 Milestones:

- ✧ Report results from a progressive study of the mechanisms of carbon corrosion as a result of transient FC operation. *Completed*
- ✧ Report results of cathode corrosion monitored using the *in-situ* electrochemical cell for the HR-TEM/STEM *On Track*

Technical Accomplishments and Progress Have Been Focused On Several Topics Of Interest To The FC Community (partners and FY10 AMR reviewers)

- Characterizing the ionomer distribution and changes during durability testing
- Membrane “structure” and chemistry
- Fundamental Pt nucleation and growth mechanisms and Pt-support interactions (C-based supports)

These topics, and identifying the means by which to characterize them, have been raised as “priorities” by numerous collaborators in the FC community and by last year’s AMR and Tech Team reviewers.

Several research investigations have been minimized as a result of previous reviews:

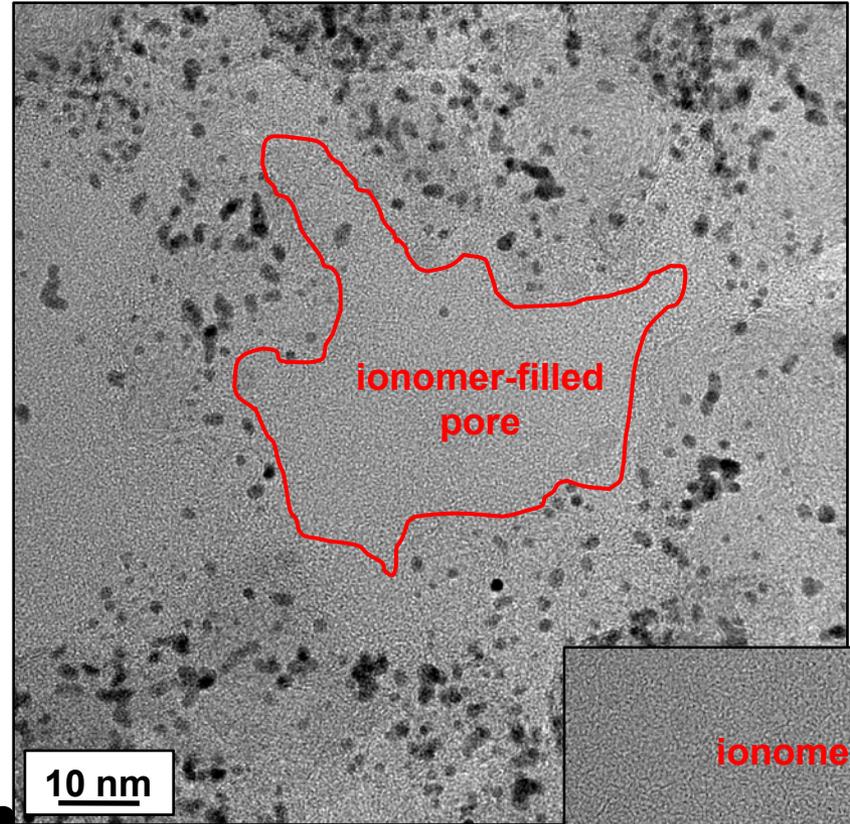
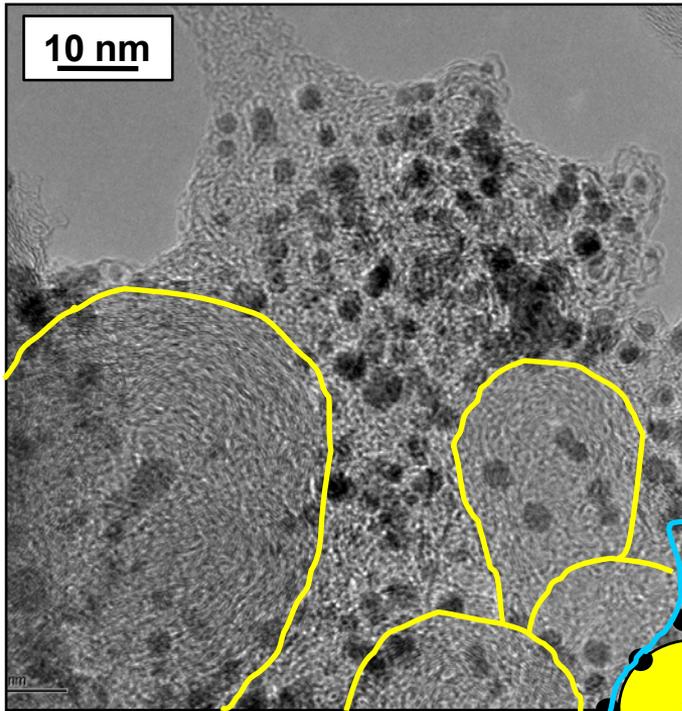
- Statistical analysis of EDS data via MVSA-PCA
- In-situ electrochemistry of FC materials (effort significantly reduced)

Technical Accomplishment: Characterizing The (Recast) Ionomer Within Electrodes

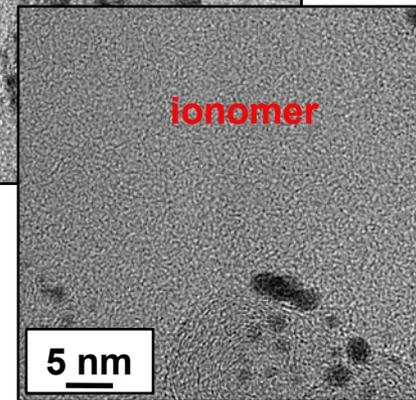
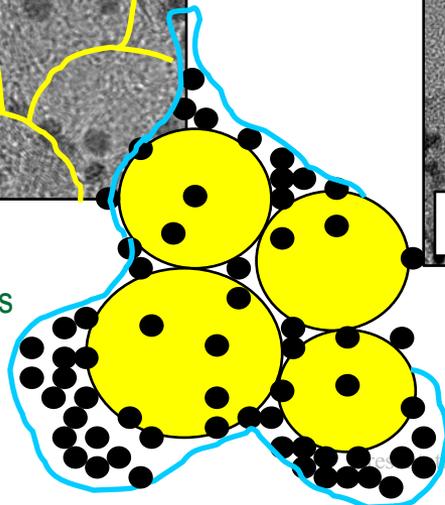
Characterizing the ionomer film within the electrode structure is extremely difficult because “isolating” the ionomer is virtually impossible!

Non-homogeneous ionomer distributions observed.

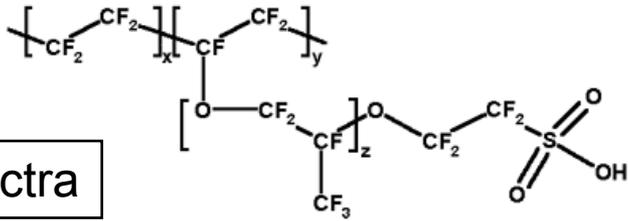
To isolate ionomer regions, electrodes were prepared such that the pores were filled with ionomer:
61wt% ionomer mixed with Pt/C decal-electrodes



The ionomer tends to reside in “pockets” with high catalyst densities

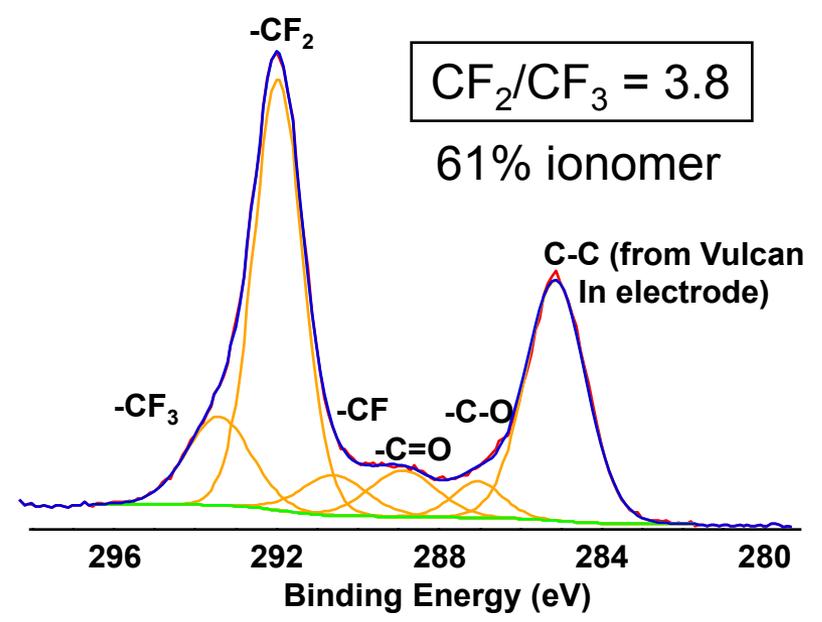
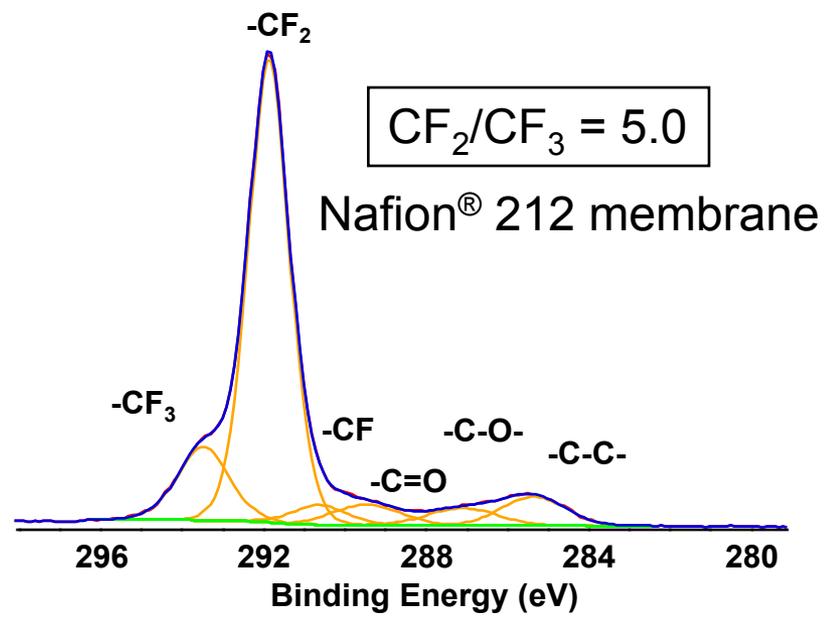


Technical Accomplishment: Characterizing The (Recast) Ionomer Within Electrodes



C1s spectra

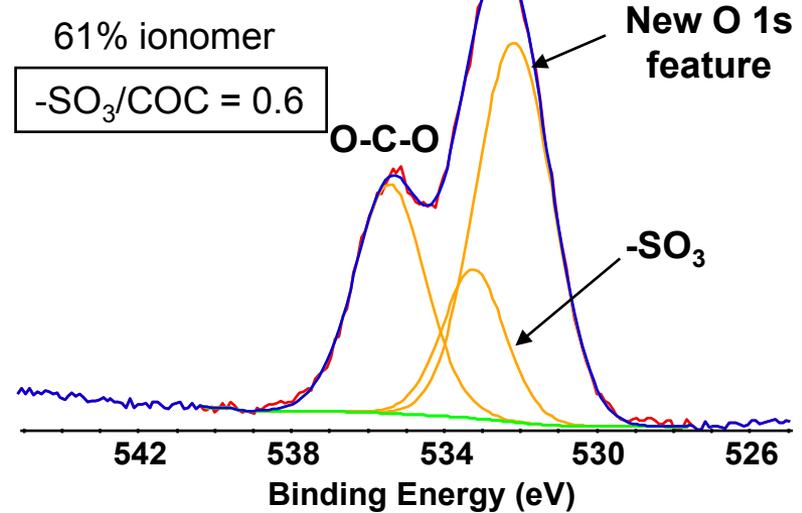
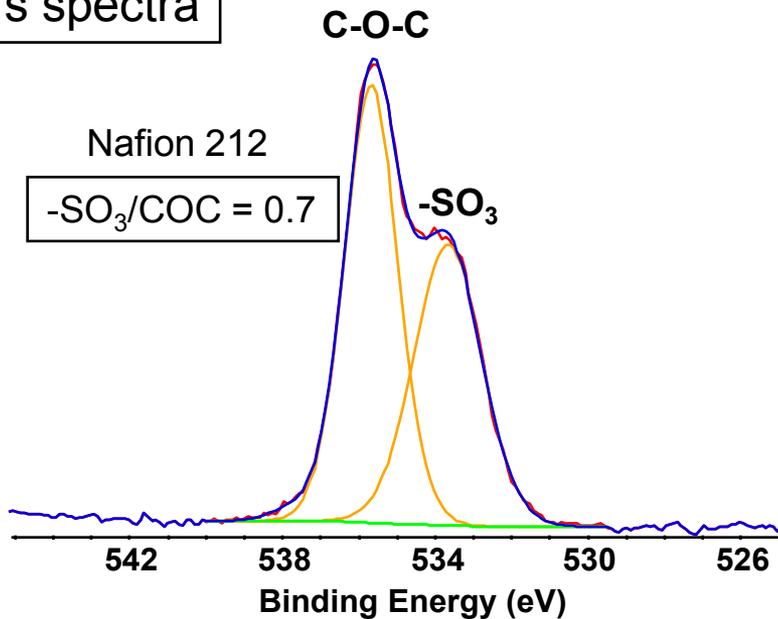
Nafion® Composition (at.%) XPS				
	C	F	O	S
Nafion® 212	33.2	59.9	5.8	1.1
61wt% ionomer	39.2	48.3	9.6	1.0



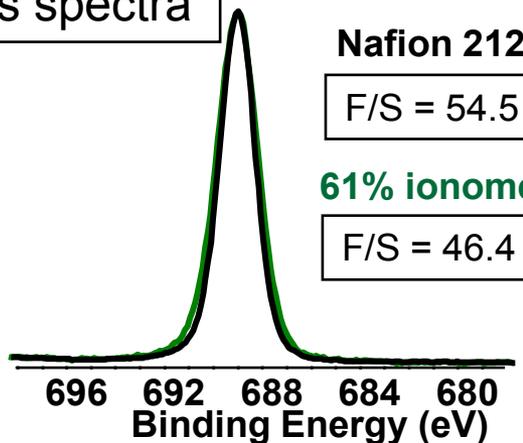
The Nafion® membrane exhibits more CF₂-type (PTFE) bonds and has higher fluorine and oxygen contents than the recast ionomer (XPS data collected from “inside” the electrode).

Technical Accomplishment: Characterizing The (Recast) Ionomer Within Electrodes

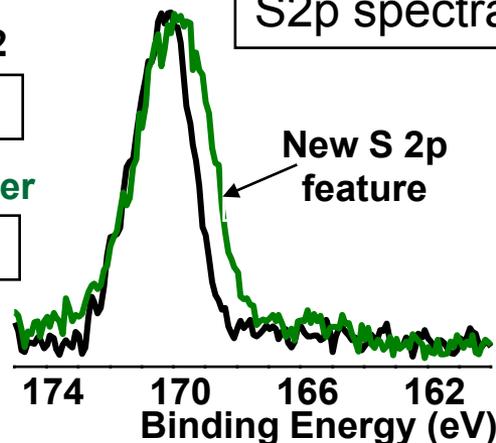
O1s spectra



F1s spectra

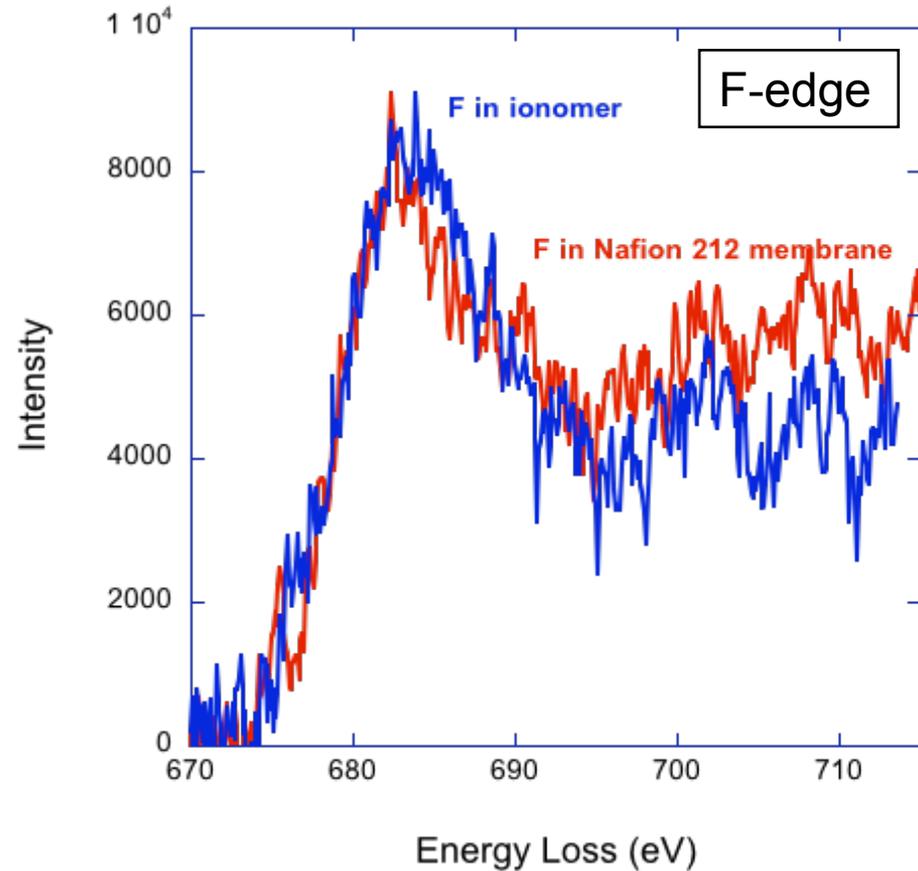
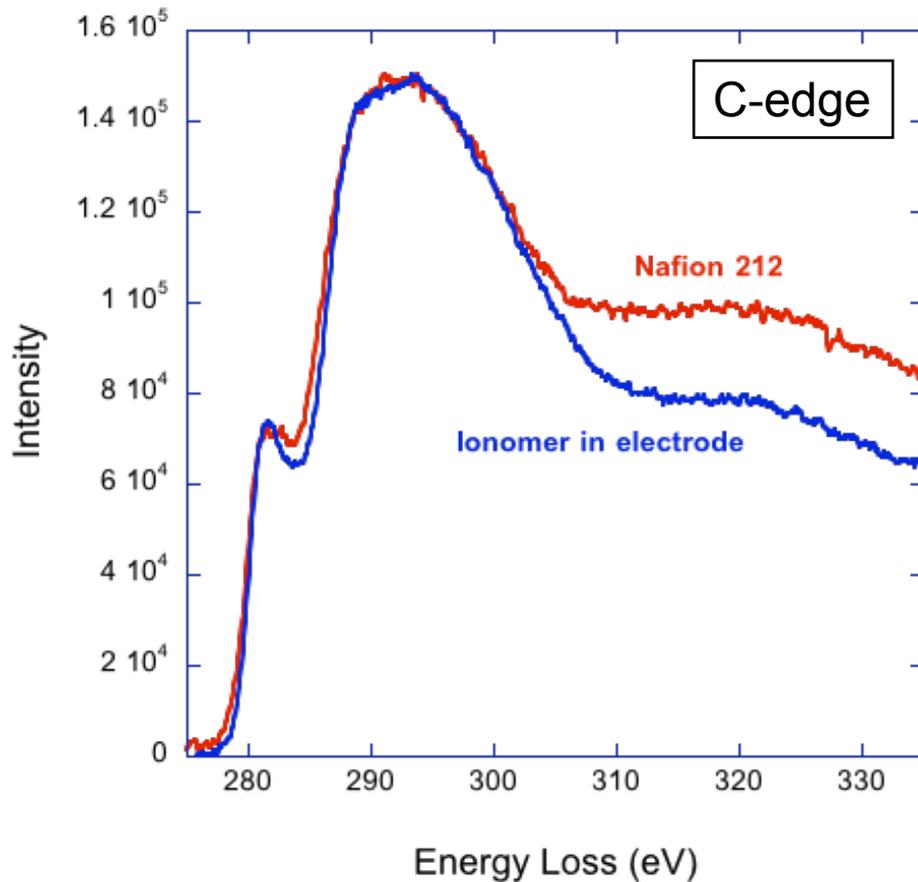


S2p spectra



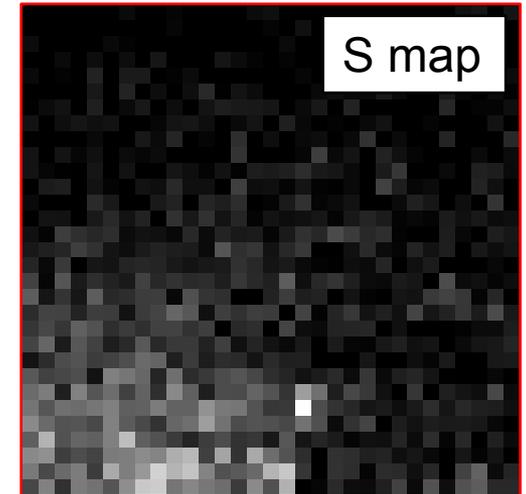
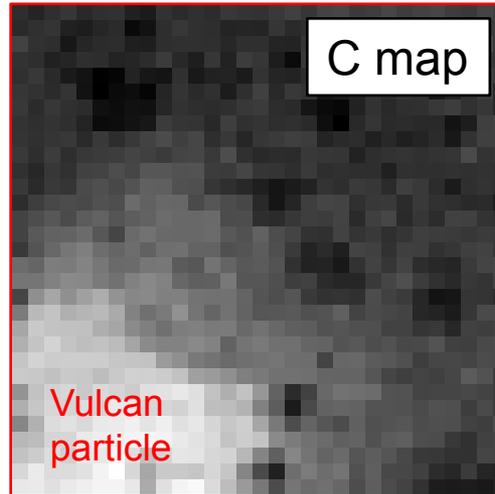
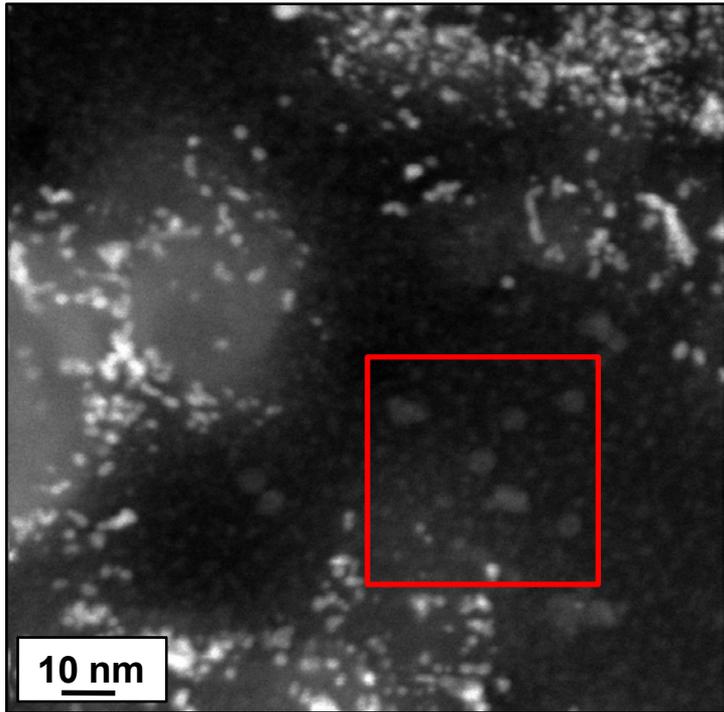
O1s and S2p exhibit new bonding configurations interpreted as side-chains no longer bonded to the polarizing C-F backbone structure. F 1s is broadened in the 61% ionomer consistent with loss of uniformity in sulfonate bonding sites.

Technical Accomplishment: Characterizing The (Recast) Ionomer Within Electrodes

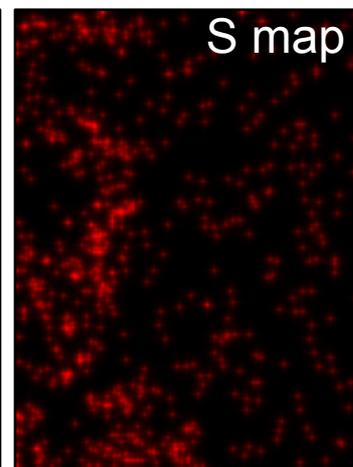
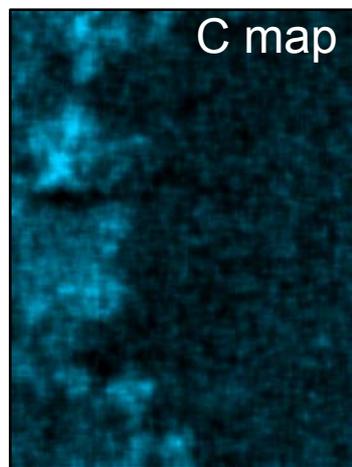
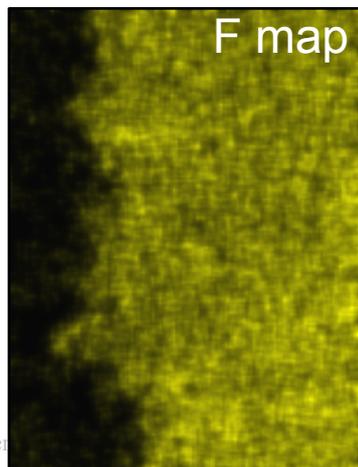
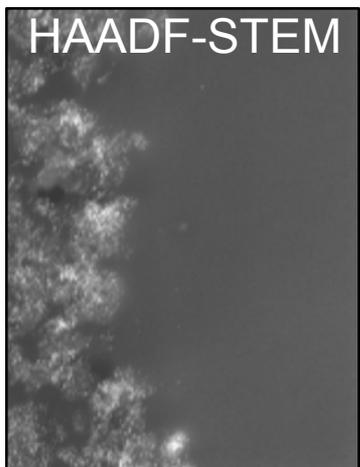


Carbon and Flourine edges exhibit some differences and are consistent with XPS data

Technical Accomplishment: Characterizing The (Recast) Ionomer Within Electrodes And Nafion Membranes

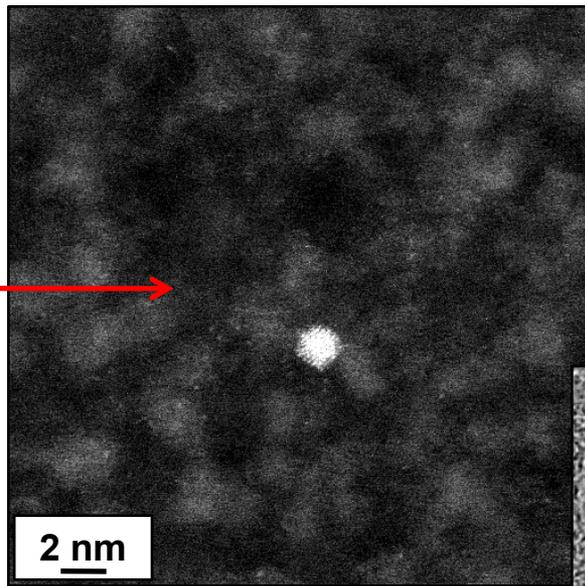
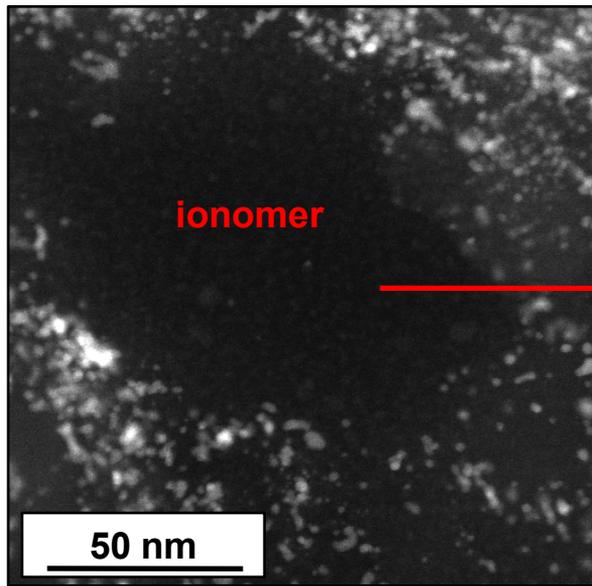


EELS spectrum imaging data from 61wt% ionomer sample – Low levels of sulfur was consistently associated with Vulcan Pt/CB regions within the electrode structure

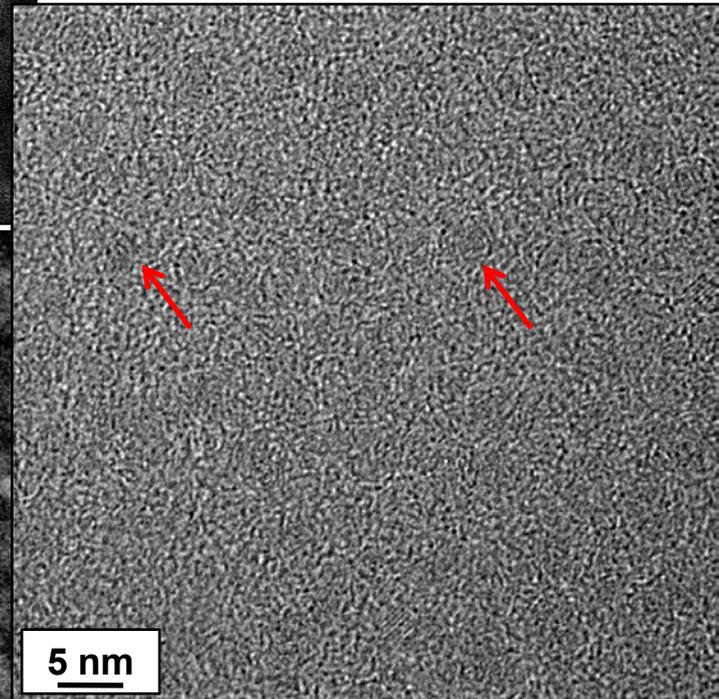
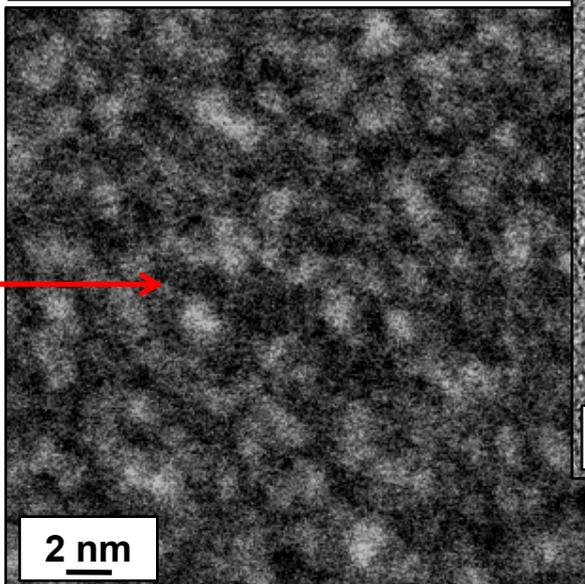
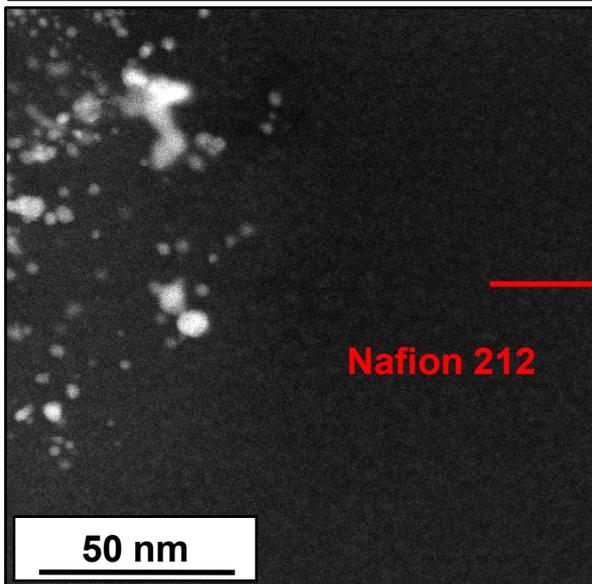


EDS data from MEA with Nafion 212 also showed that sulfur was highest at the Vulcan Pt/C regions in the electrode.

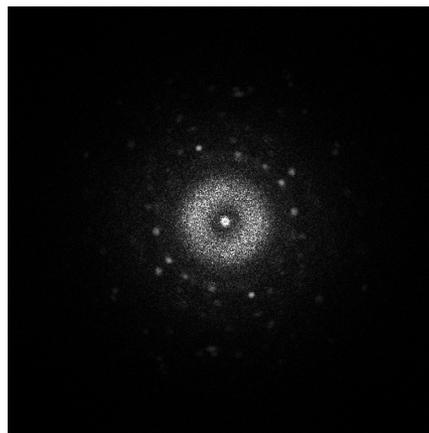
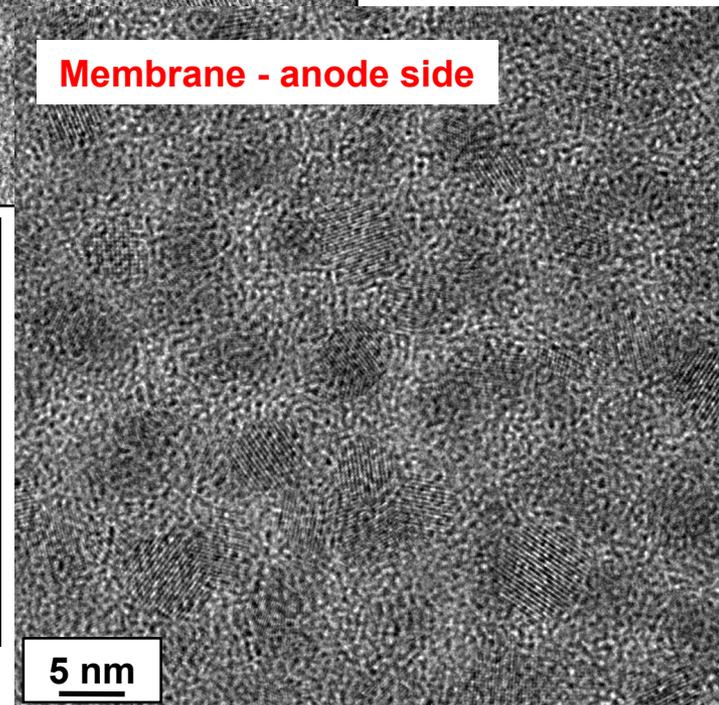
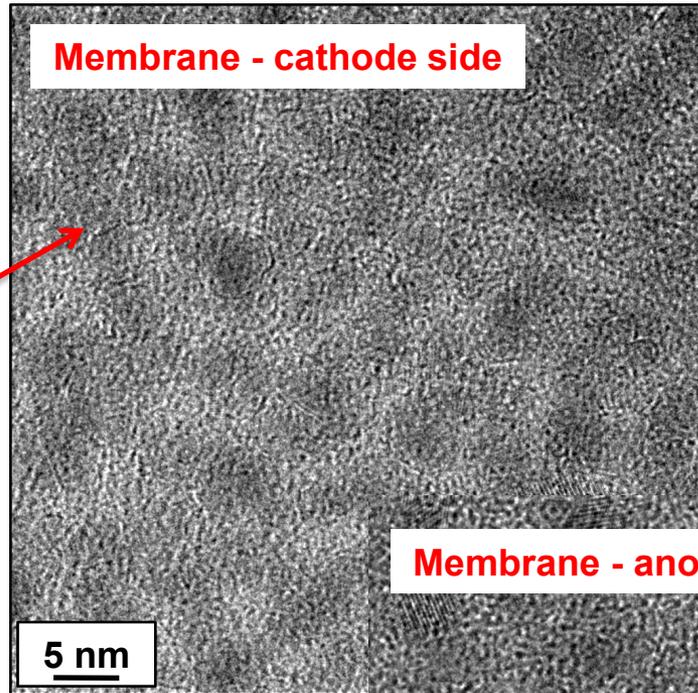
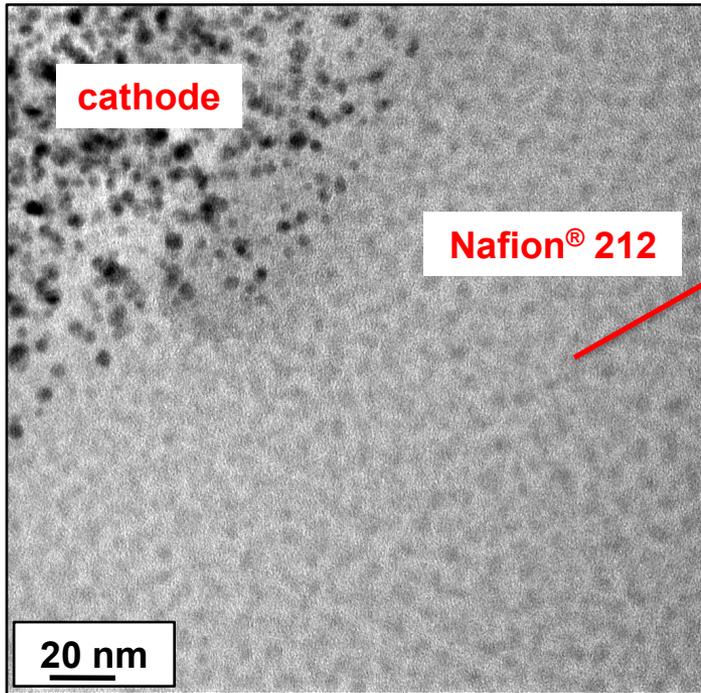
Technical Accomplishment: Characterizing The (Recast) Ionomer Within Electrodes And Nafion Membranes



HAADF-STEM images of the ionomer regions in “filled” electrode and of Nafion 212 membrane show evidence for compositional variations (high- and low-intensity), consistent with F-rich domains (2-4 nm) in a fluorocarbon matrix. This has been termed “nanoscopic phase separated morphology”



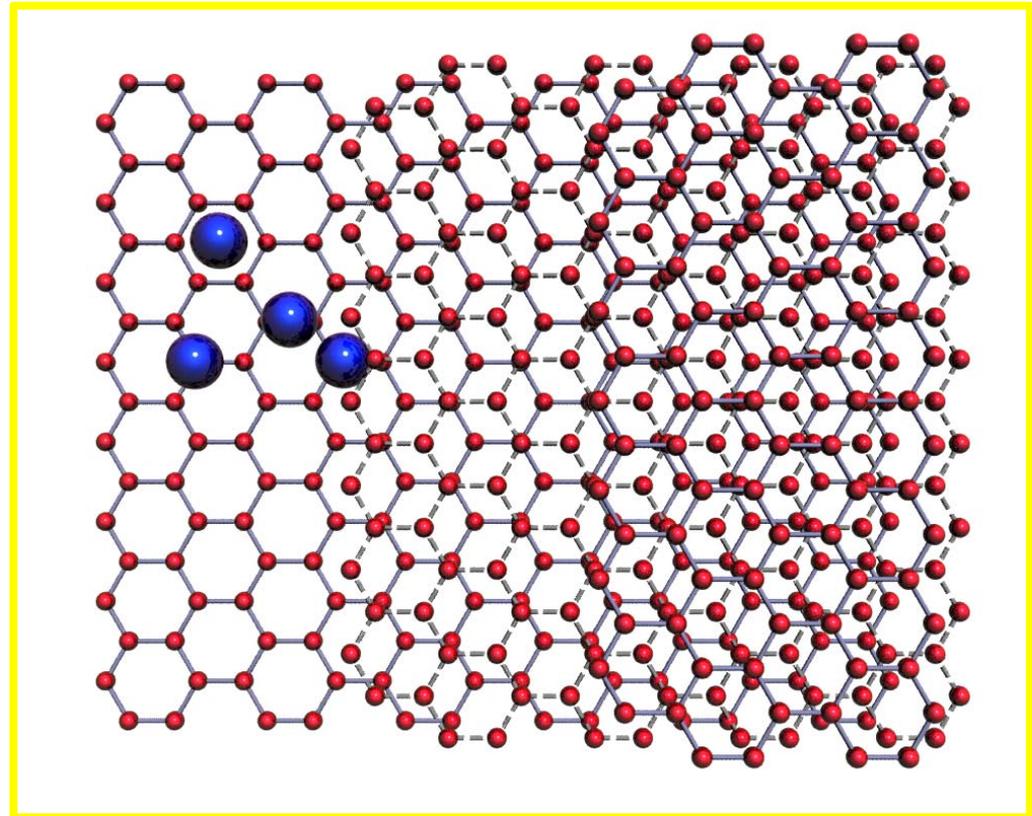
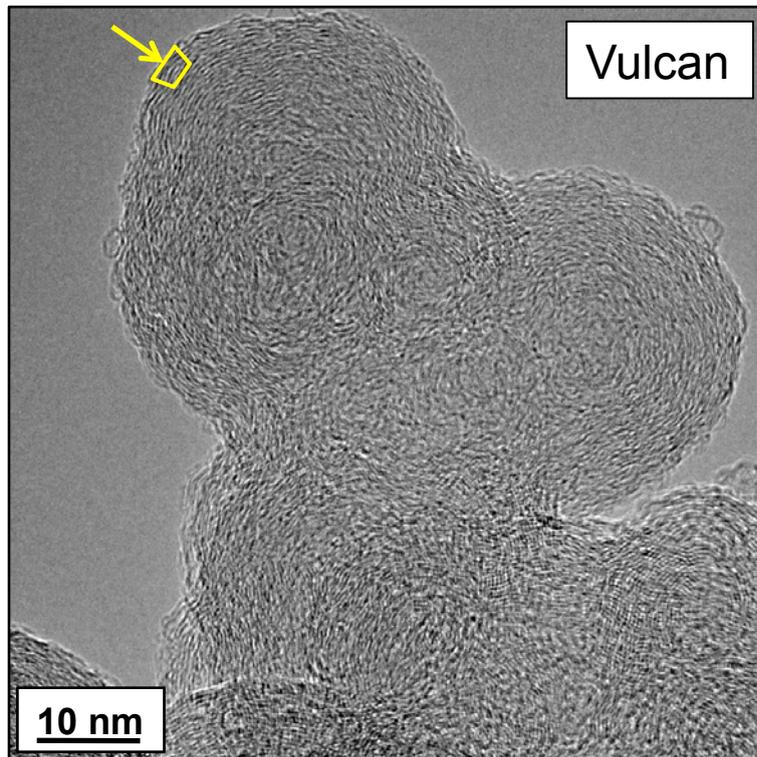
Technical Accomplishment: Characterizing The (Recast) Ionomer Within Electrodes And Nafion[®] Membranes



PTFE crystallite growth and increased crystallization observed after short-time (301h) cycling (0.1-1.0V) across entire Nafion[®] 212 membrane thickness.

Technical Accomplishment: Investigating Pt Nucleation & Growth On “Typical” C-Supports Via Use Of Graphene

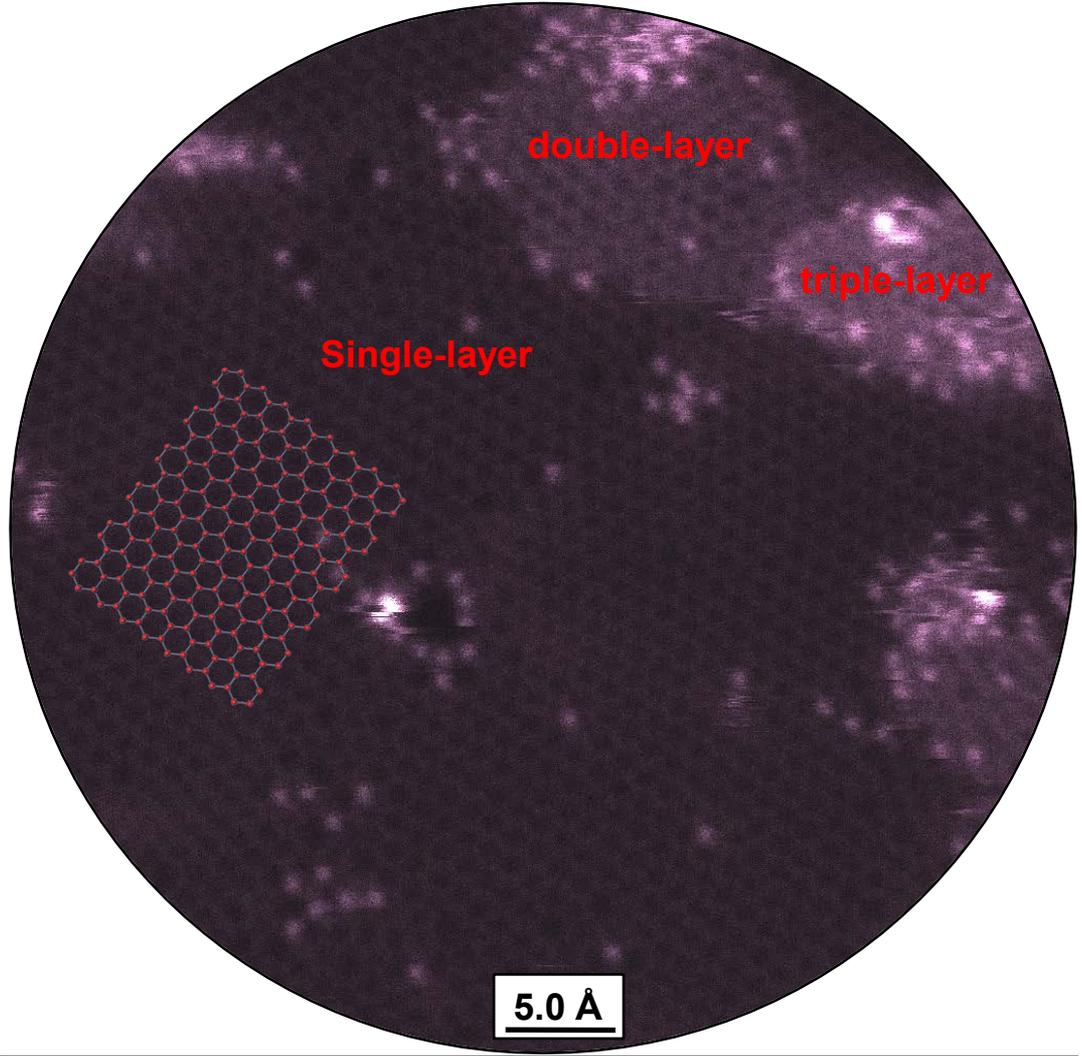
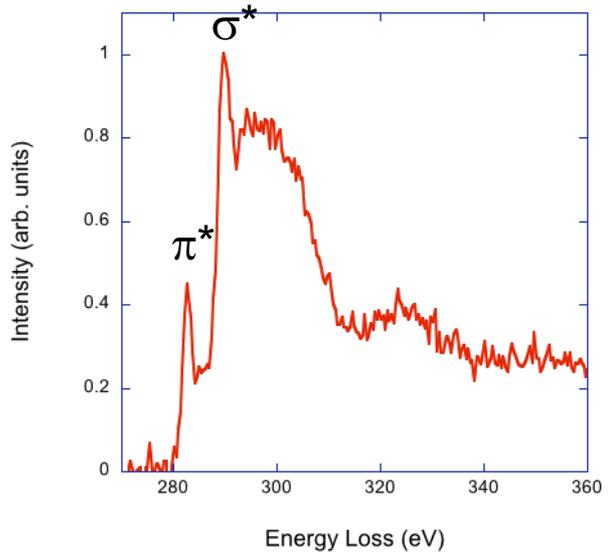
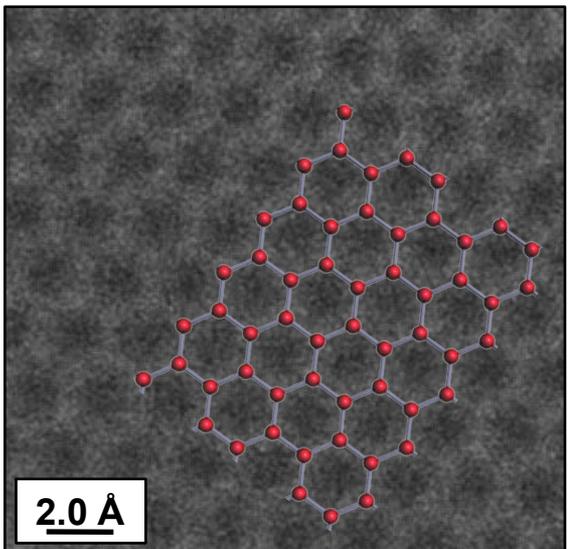
Since all nanostructured carbon materials have “graphene-based” structures, graphene nanosheets/films can be used to model the carbon surfaces and identify preferred nucleation sites for Pt on carbon surfaces (CNTs, CNFs, CNHs, etc.)



Most carbon black surfaces are comprised of small (4-5nm) highly-(002)-textured graphitic crystallites (domains) with many defects and surface steps - meso-graphitic or turbostratic structure

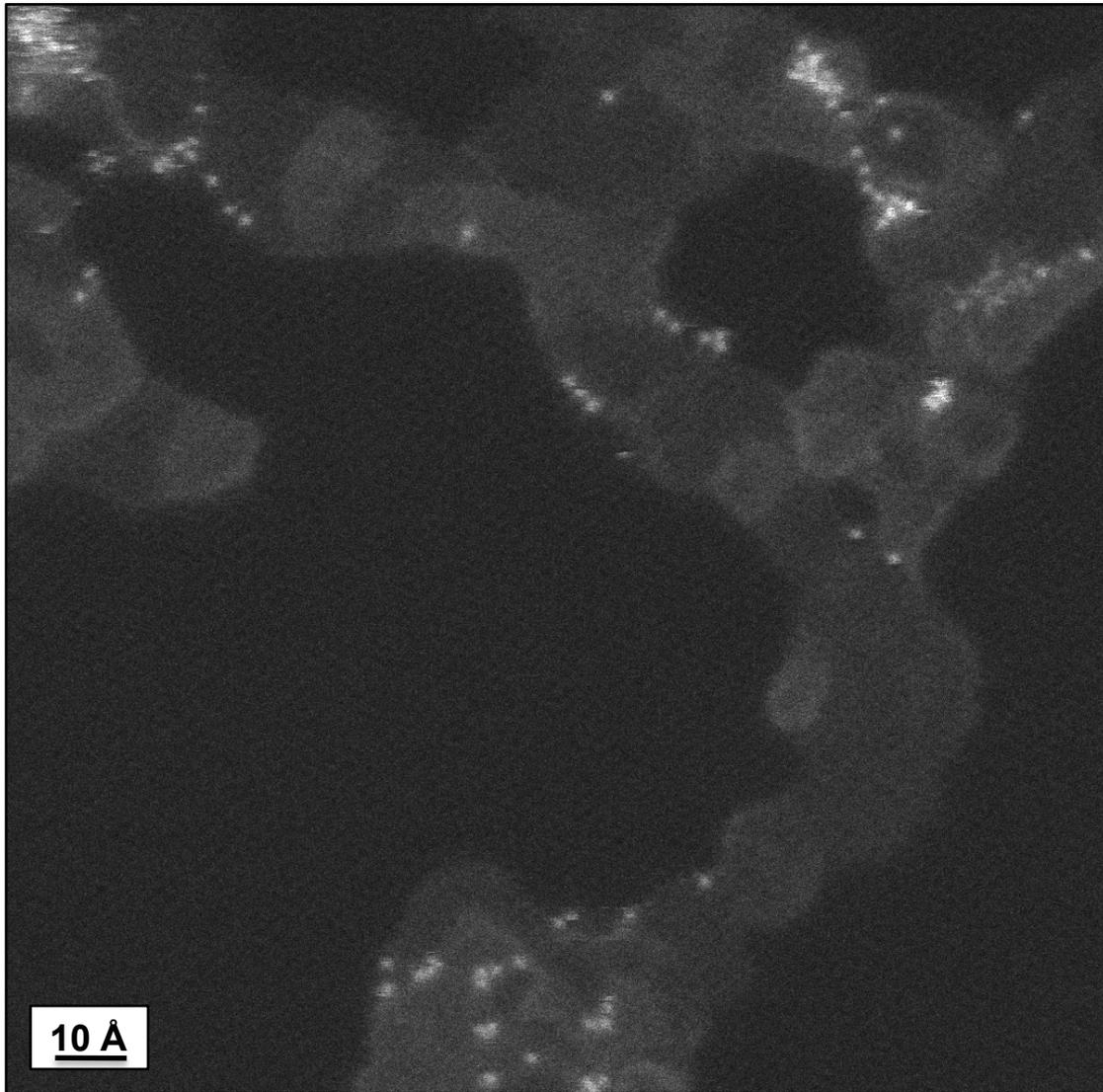
Single, double, and triple-layered graphene sheets exhibit areas of sp^2 -bonded carbon and “edge sites” where layers overlap

Technical Accomplishment: Investigating Pt Nucleation & Growth On “Typical” C-Supports Via Use Of Graphene



Single, double, and triple-layered graphene sheets exhibit areas of sp^2 -bonded carbon and “edge sites” where layers overlap

Technical Accomplishment: Investigating Pt Nucleation & Growth On “Typical” C-Supports Via Use Of Graphene

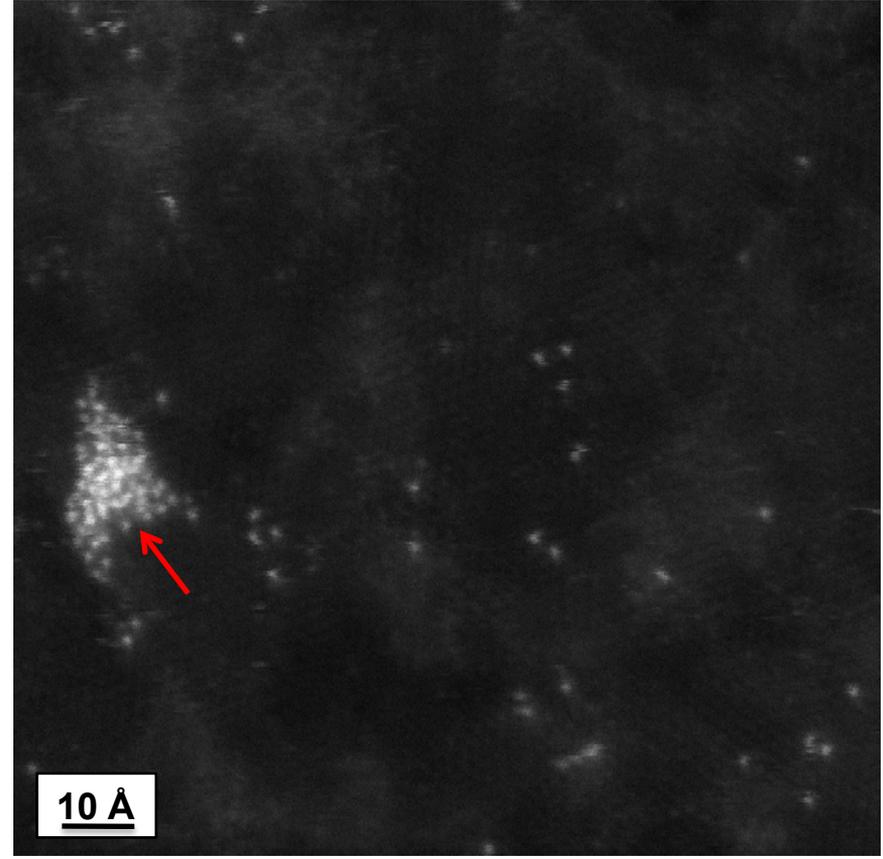
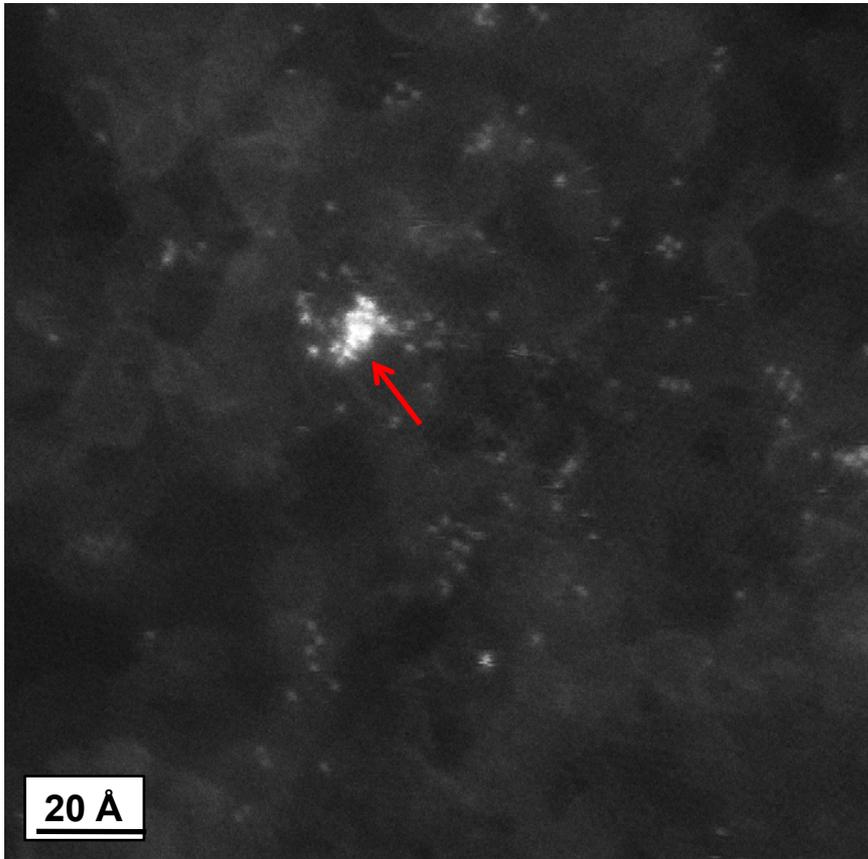


Single Pt adatoms were deposited across the surface of the graphene.

Pt atoms were found ONLY at the edges of overlapping graphene layers.

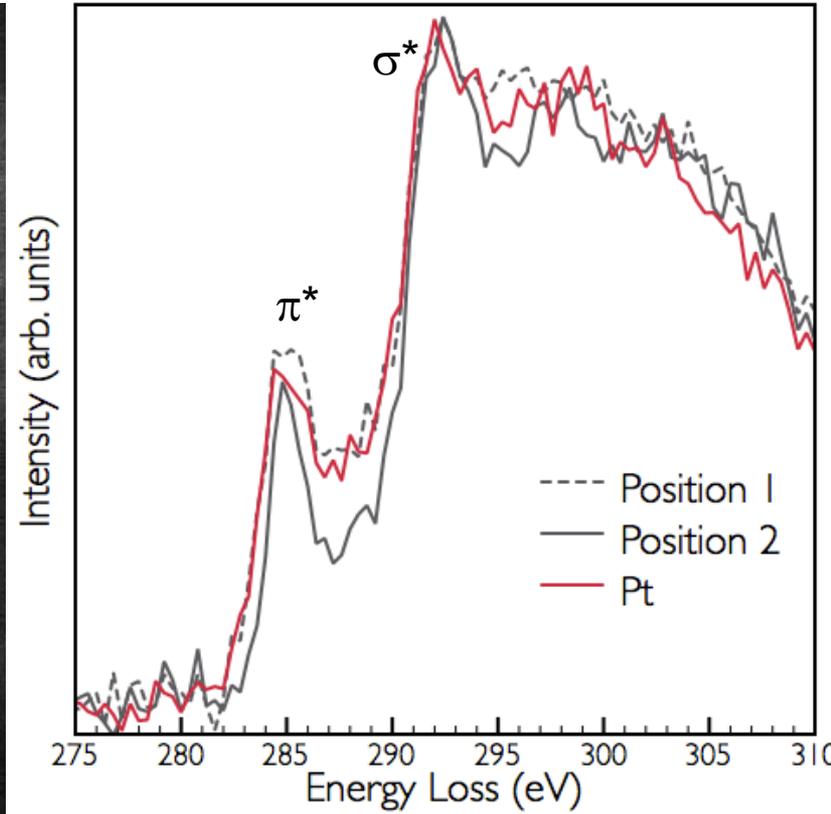
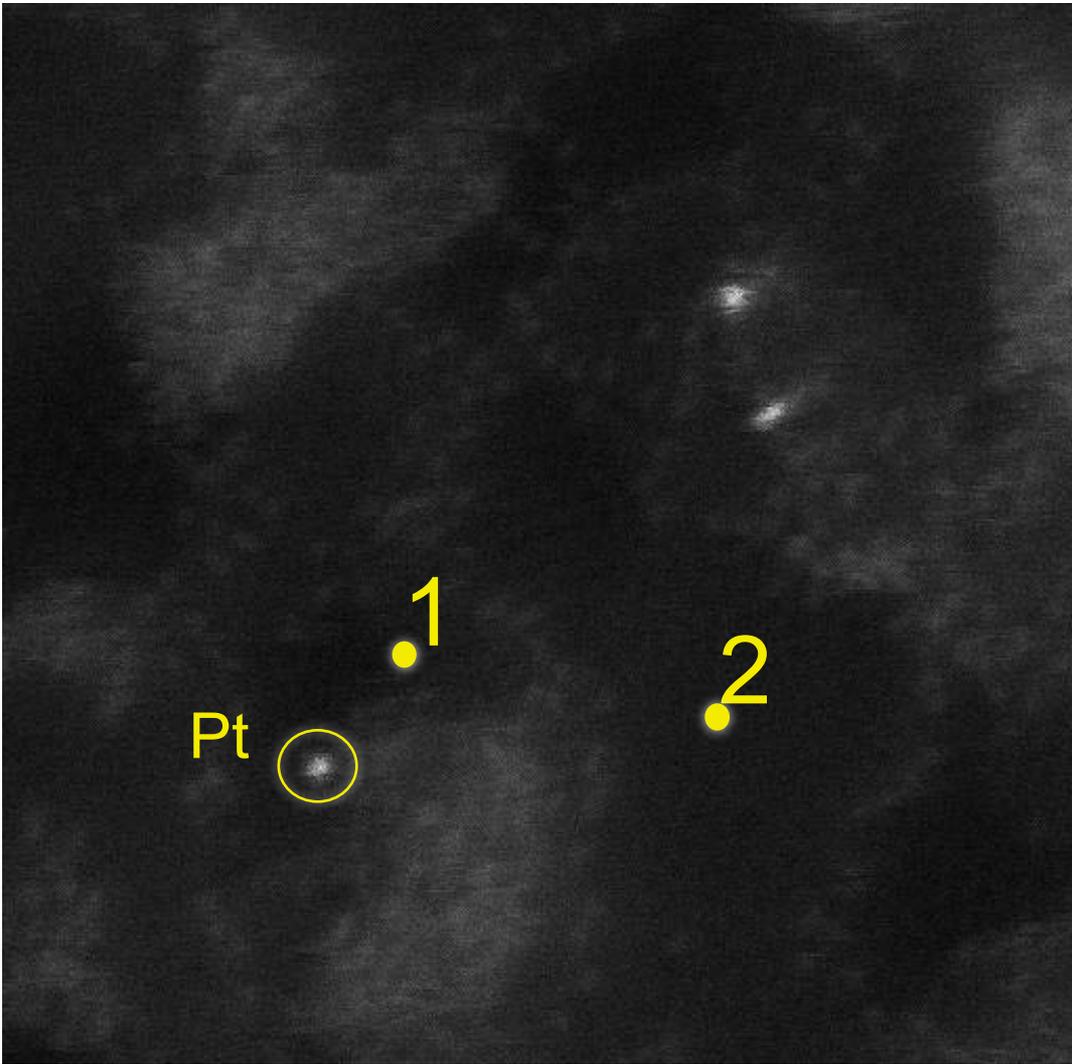
Binding energy is relatively high since Pt “stays put” during 24 hr heat treatment @ 400°C

Technical Accomplishment: Investigating Pt Nucleation & Growth On “Typical” C-Supports Via Use Of Graphene



Single Pt adatoms and Pt clusters were consistently associated with edge sites where multiple layers overlapped.

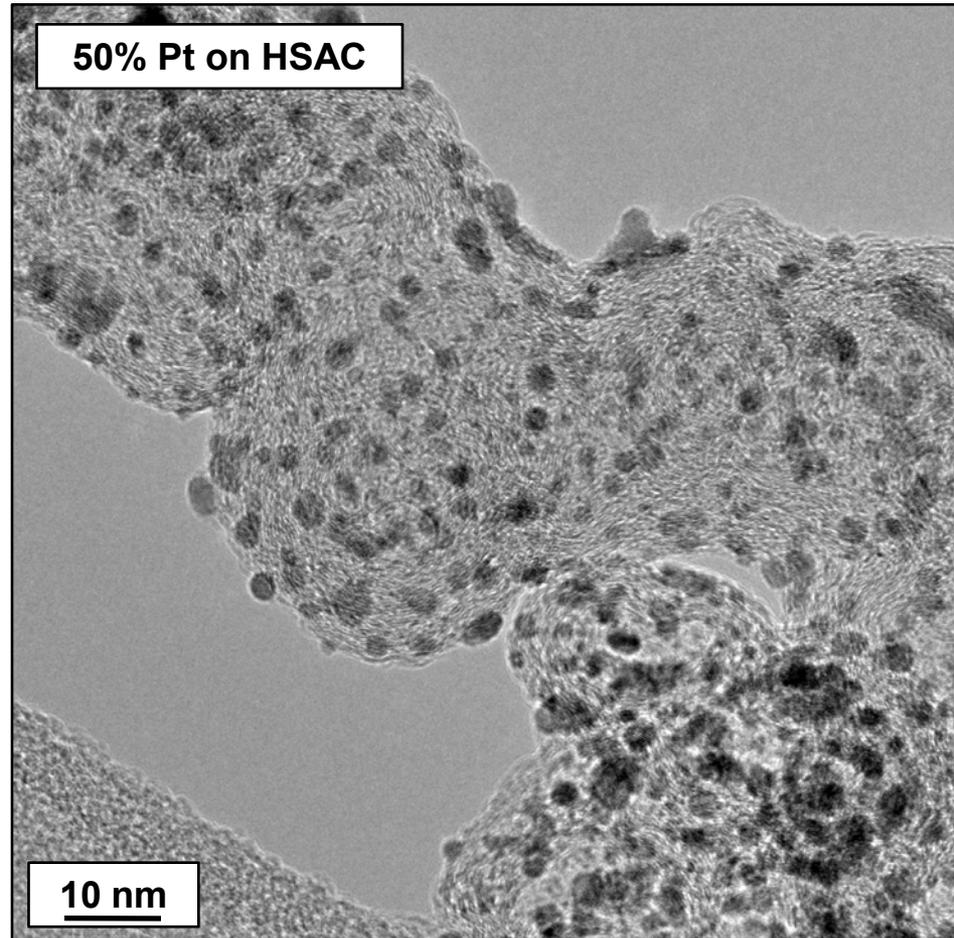
Technical Accomplishment: Understanding Pt Nucleation & Growth On Carbon Supports



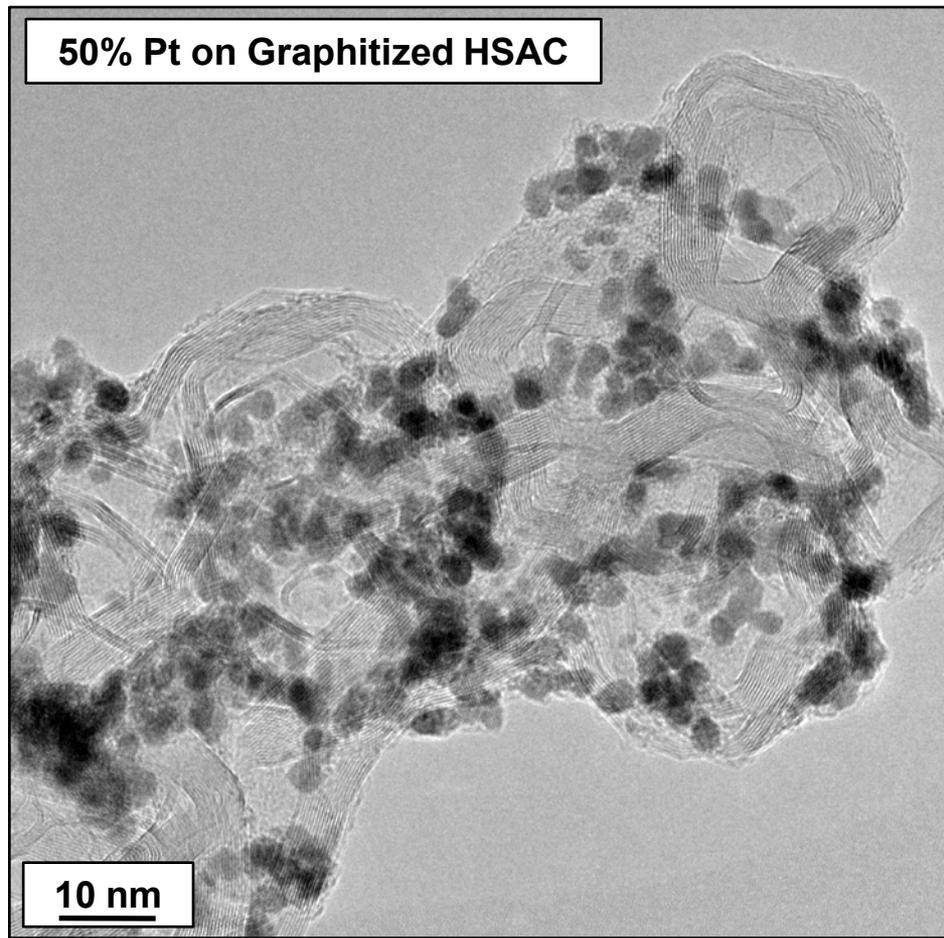
Pt atoms do not affect the fine-structure (bonding) of the carbon, but do not deposit on the sp^2 -bonded regions of the graphene

Technical Accomplishment: Understanding Pt Nucleation & Growth On Carbon Supports

50% Pt on HSAC



50% Pt on Graphitized HSAC



Pt nanoparticles nucleate uniformly across highly-defective surfaces of HSAC – once graphitized (fewer surface defects), Pt nucleates predominantly at regions "between" carbon particles rather than on graphite surfaces

Technical Accomplishment: Understanding Pt Nucleation & Growth On Carbon Supports

50% Pt on Vulcan

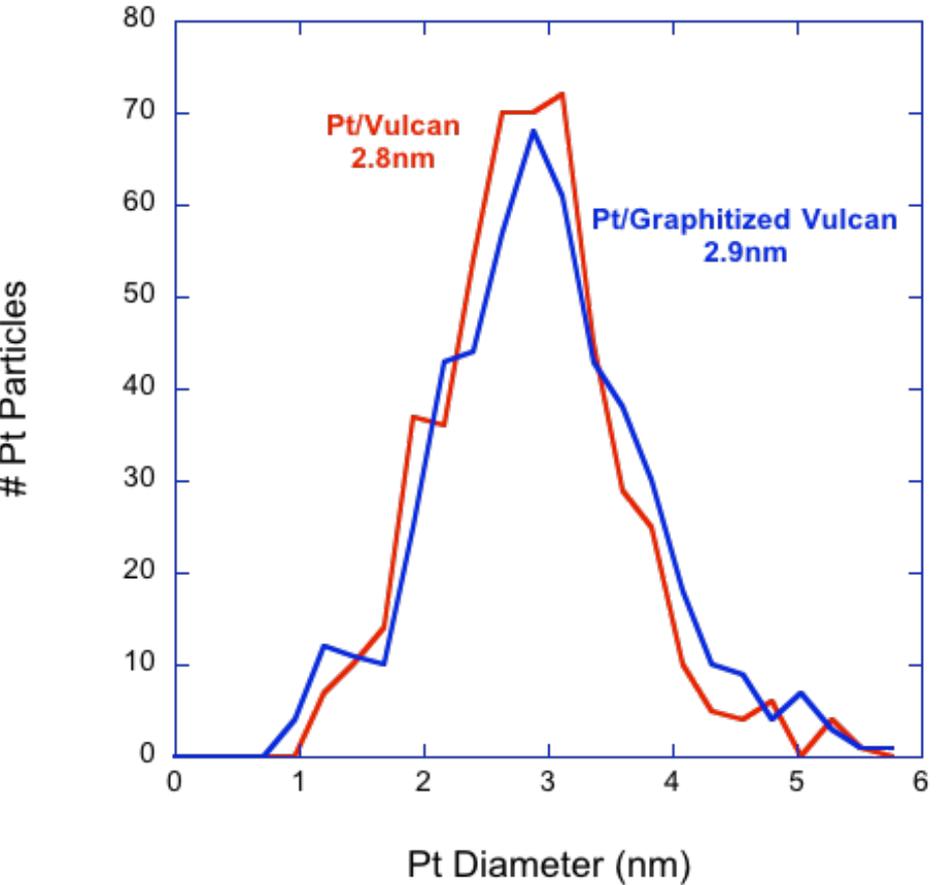
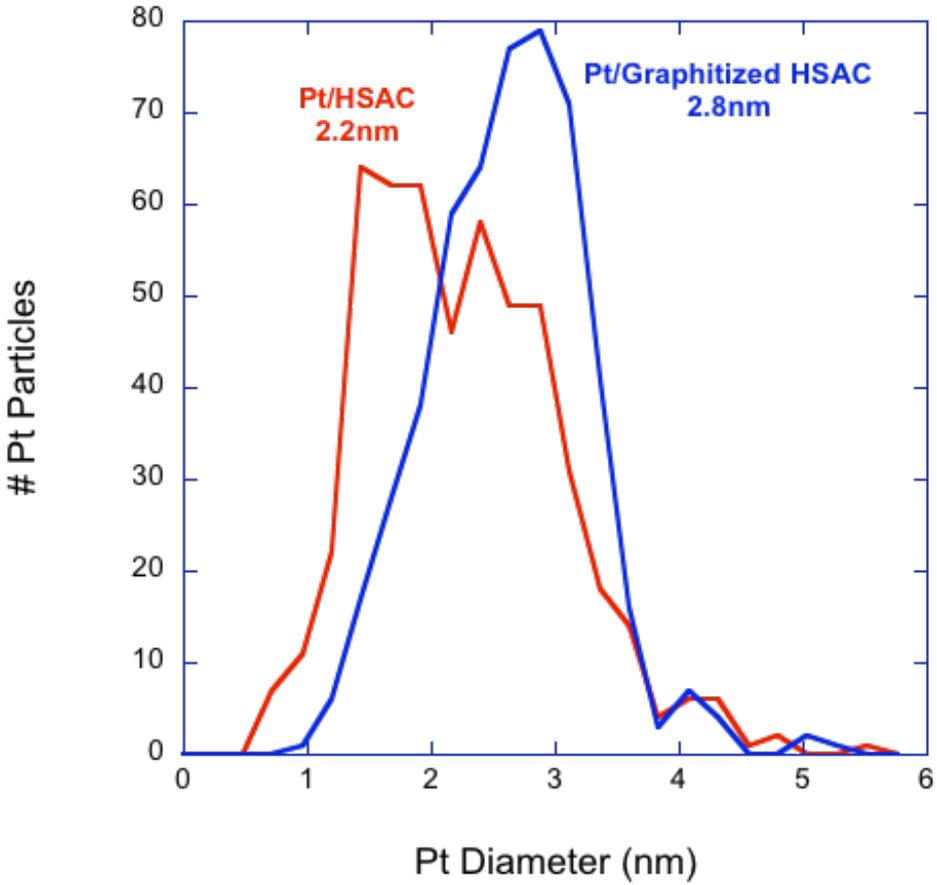
10 nm

50% Pt on Graphitized Vulcan

10 nm

Pt nanoparticles nucleate uniformly across highly-defective surfaces of Vulcan – once graphitized (fewer surface defects), Pt nucleates predominantly at regions “between” carbon particles or at graphite folds rather than on flat graphite surfaces

Technical Accomplishment: Understanding Pt Nucleation & Growth On Carbon Supports



Pt size distributions changed significantly for HSAC as a function of support graphitization, whereas Pt size distribution remained the same on Vulcan as a function of support graphitization.

Collaborations Established For Baseline Project

Collaborations with ORNL are focused (1) direct collaborations under baseline project to enable further understanding, (2) via user programs at ORNL, or (3) focused research under separate DOE projects.

- **Los Alamos National Laboratory** – durability studies (ASTs); FC materials for portable power applications; ionomer studies; alternative supports
- **Brookhaven National Laboratory** – characterization of novel monolayer catalysts and catalysts for methanol oxidation
- **GM** – durability-tested MEAs to identify degradation mechanisms
- **Nissan Technical Center North America** –TKK catalysts deposited on graphitized supports
- **Naval Research Laboratory** – characterization of novel Ta-phosphate films to stabilize Pt on carbon
- **Proton Energy Systems** - MEAs for electrolyzers
- **Fuel Cell Energy** – characterization of new membranes
- **University of Tennessee** – ionomer studies
- **University of New Mexico** – understanding Pt coarsening mechanisms
- **Brown University** – characterization of novel bi- and tri-metallic catalysts
- **Energy Center of The Netherlands** – specimen preparation and characterization of MEAs
- **Fuel Cell Cubic, Japan** – visiting scientist from FC-Cubic to collaborate on materials characterization
- **Additional DOE project co-collaborations with LANL, ANL, NREL, 3M, and UTC Power. Results from these studies are NOT included in this project summary**

Proposed Future Work

- Correlate microstructural/compositional observations with AST protocols (automotive and stationary), especially related to catalyst coarsening & migration, carbon corrosion, membrane degradation – this is a continuing priority of this research program and has been part of ongoing and proposed “future” research each year.
- Acquire the proper series of durability-tested MEAs to further understand the degradation of polymer electrolytes (membrane and ionomer in electrode) using a combination of characterization techniques as described in this presentation
- Correlate observations of Pt nucleation & growth to long-term stability via in-situ gas heating experiments
- 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

- New insight into morphology of Nafion membranes reveals 2-4nm F-rich domains that undergo increased crystallization during aging; crystallites are consistent with PTFE. Microstructure is “consistent” with models that have described a “nanoscopic phase-separated morphology”
- The ionomer phase within electrodes exhibits some small structural and chemical differences compared with Nafion membranes – sulfur exhibits some degree of “segregation” to carbon surfaces and lower overall fluorine content
- Pt has been clearly shown to deposit-nucleate preferentially at graphite/graphene edge-sites (defects) and is very stable at these sites.
- Several new collaborations have been established during the past year that have accessed the unique imaging (microscopy) capabilities at ORNL or have visited the lab for training:
 - Work-for-Others (proprietary research)
 - Shared Research Equipment (SHaRE) User Program and the HTML User Program (non-proprietary research)
 - Baseline PEM-MEA Characterization Program (non-proprietary)