Characterization of Fuel Cell Materials

Project ID FC020

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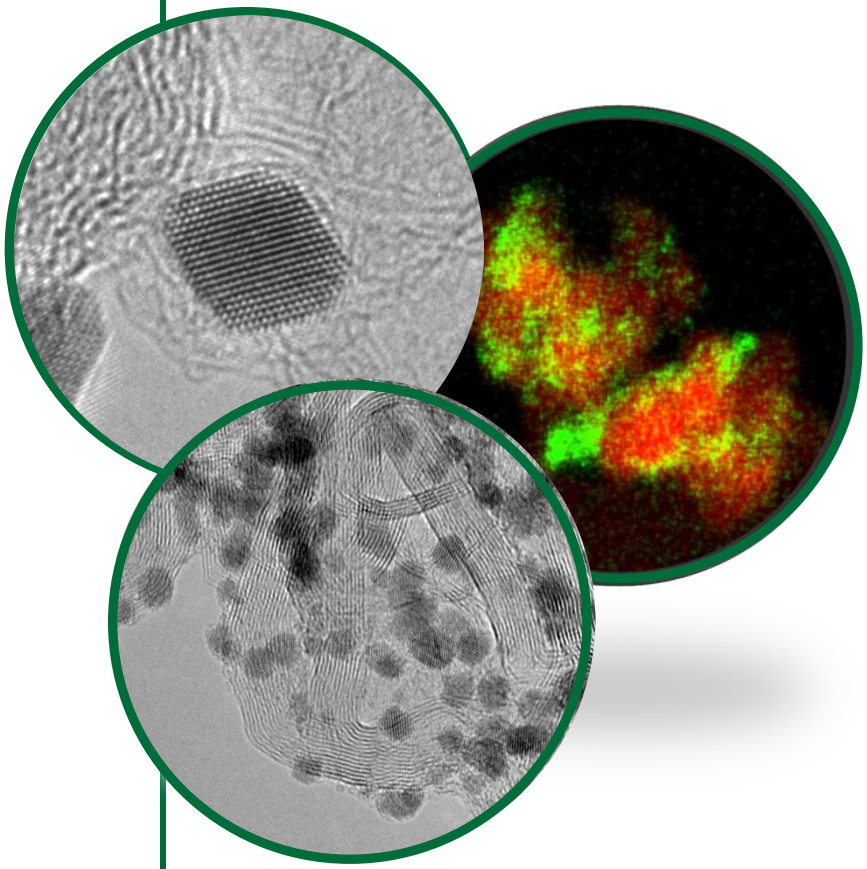
2013 DOE Annual Merit Review
May 14, 2013



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U.S. DEPARTMENT OF ENERGY

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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 FY12 - $600k (~1.5 FTE)
- Funding in FY13 - $500k (~1.25 FTE)

Barriers

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

Partners

- Los Alamos National Laboratory
- General Motors
- 3M
- Automotive Fuel Cell Cooperation (AFCC)
- Ballard
- Nissan Technical Center North America
- Nuvera Fuel Cells
- University of Tennessee
- Brookhaven National Laboratory
- Florida Solar Energy Center
- Colorado School of Mines
- UTC Power
- 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-to-Å scale characterization of 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/input from members of the fuel cell community
- Integrate microstructural characterization within 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

Relevance – ORNL Collaborates With Many External Partners To Address Critical Fuel Cell Issues

component durability

- *LANL (sub) – Durability Improvements through Degradation Studies*
- *LANL – Accelerated Testing Validation*
- *Nuvera Fuel Cells – SPIRE Project*
- *Nissan TCNA – Catalyst support durability*
- *UTC Power (sub) - Improved Accelerated Stress Tests Based on FCV Data*
- *3M and AFCC – NSTF durability testing*

novel catalysts and supports

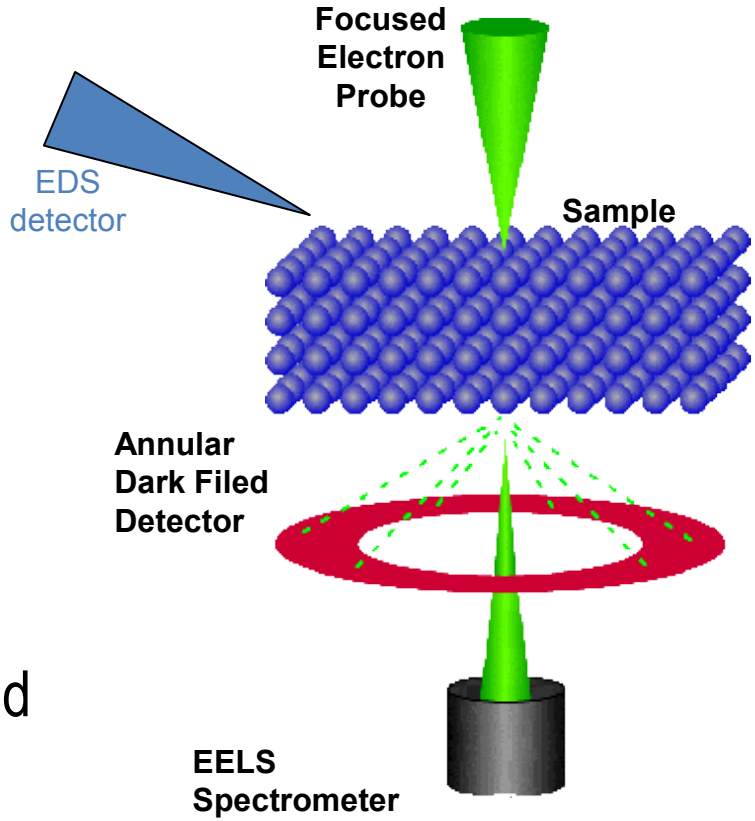
- *LANL (sub) – The Science and Engineering of Ultralow PGM Catalysts*
- *NREL (sub) – Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes*
- *UTC Power – Pt nanowire catalysts*
- *3M – NSTF alloy cathode catalysts*
- *LANL – Engineered Nano-scale Ceramic Supports for PEM Fuel Cells*
- *LANL – Advanced Materials and Concepts for PORtable Power Fuel Cells*
- *ANL (sub) – Nanosegregated Cathode Catalysts with Ultra-low Pt Loadings*
- *3M (sub) – Durable Catalysts for Fuel Cell Protection During Transient Conditions*
- *3M (sub) – High-Performance, Durable, Low Cost MEAs for Transportation Applications*

ionomer studies

- *GM - ionomer layers/films on model substrates; ionomer distribution(s) within catalyst layers*
- *Ballard – ionomer distributions as a function of carbon support type and Pt loading*
- *LANL – varying ionomer solvents (catalyst layers and membranes)*

Approach: Use Advanced Microscopy to Investigate Structure and Composition of Fuel Cell Materials and Correlate Observations With Performance

- Apply state-of-the-art electron microscopy techniques for the characterization of MEA material constituents:
  - Catalyst nanoparticles – composition, chemistry, size, and morphology
  - Polymer - membrane and 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 – FY12 and FY13

- **FY12 Milestones:**
  - ✧ Report results from combined XPS/TEM/STEM study of ionomer degradation in PEM fuel cells MEAs as a function of aging protocol *Completed*
  - ✧ Publish results from fundamental study of Pt/graphene nucleation & growth as related to Pt supported on carbon blacks *Delayed to 6/13*
- **FY13 Milestones:**
  - ✧ Report results of model Pt-ionomer study with GM; to be conducted using ORNL's unique low-voltage microscope (equipped with EELS) and XPS to establish critical Pt-ionomer interactions and ionomer chemistry-composition as a function of ionomer thickness/loading. *Completed*
  - ✧ Publish results summarizing imaging-based methods developed to quantify amount of Pt loss/degradation occurring via dissolution/migration and nanoparticle coalescence *On Track 8/13*

Technical Accomplishments and Progress Have Been Focused on Topics of Interest to the FC Community (Collaborators, Tech Team, and FY12 AMR Reviews)

Past AMR presentations have highlighted ORNL research specific to:

- Membrane characterization
- Electrode architecture optimization
- Sub-Å-scale catalyst nanoparticle studies
- Mechanisms of carbon corrosion

ORNL has continued to focus resources on these topics, but has undertaken several new initiatives:

- Quantifying cathode degradation, esp. carbon corrosion
- Characterization of ionomer films
- In-situ microscopy technique development

Recommendations From Presentation to USCAR Fuel Cell Tech Team in October 2012

component durability

Explicit measurements of graphite oxide content including a quantification of graphite oxide content are needed to be able to correlate graphite oxide formation to performance loss and degradation mechanisms.

ionomer studies

The Tech Team believes the catalyst ionomer imaging work is very important and suggests increasing its priority.

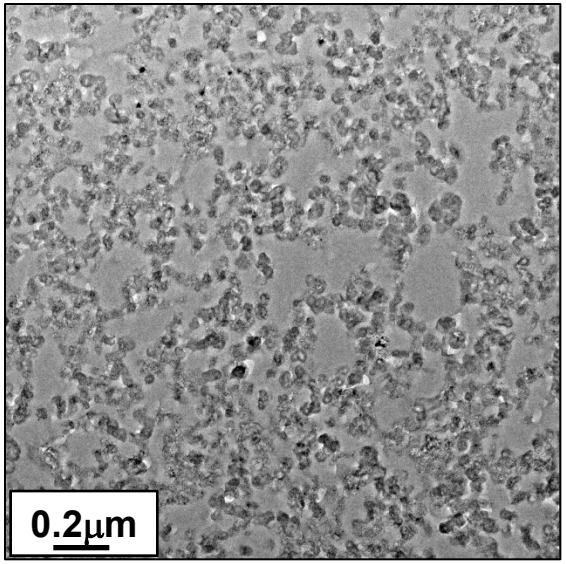
Consistent with 2012 AMR Reviewer Comments

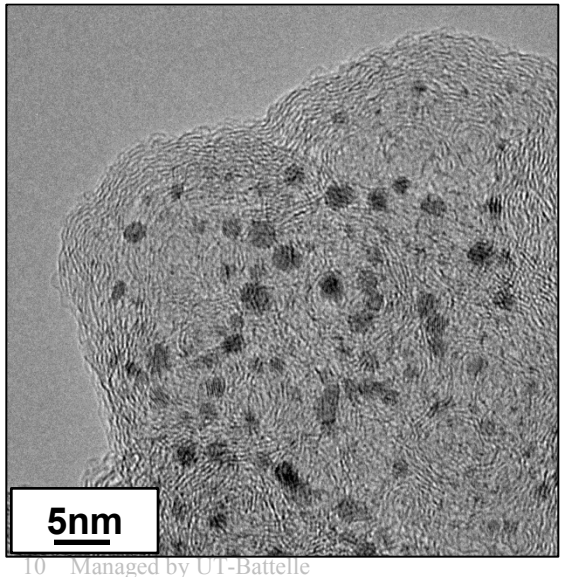
Technical Accomplishment: Understanding Effect of Cathode Carbon Corrosion on MEA Performance

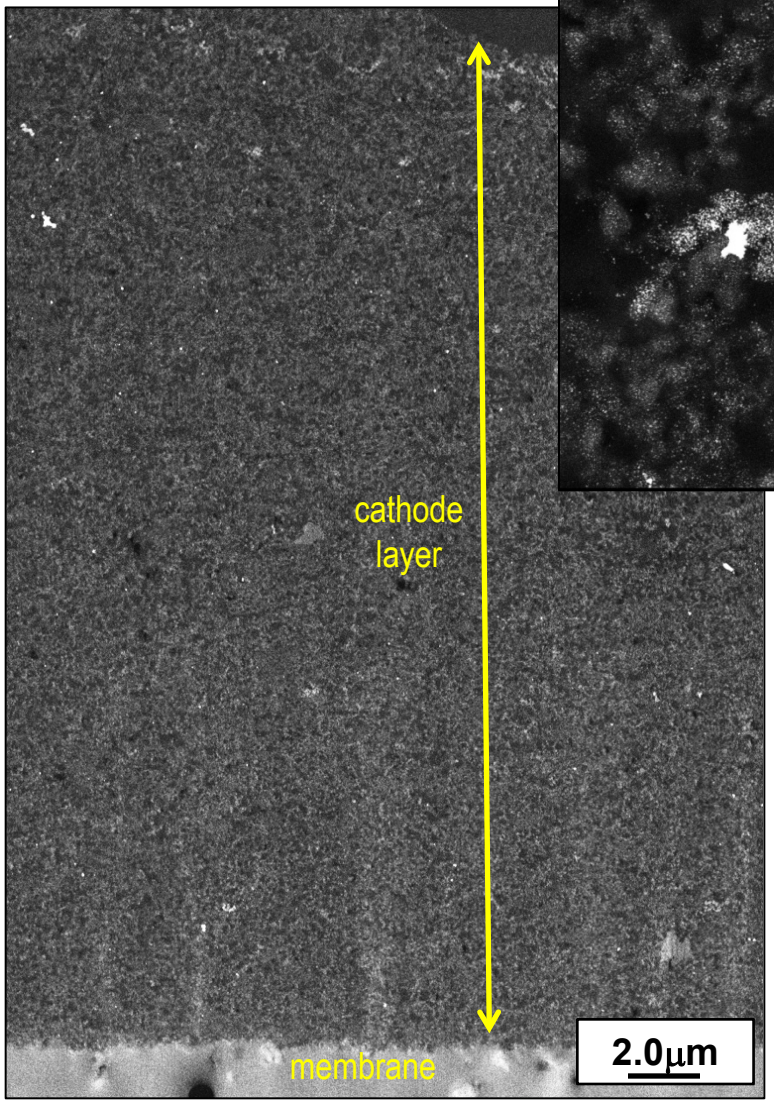
Collaboration with LANL to QUANTIFY carbon corrosion and correlate with durability and performance

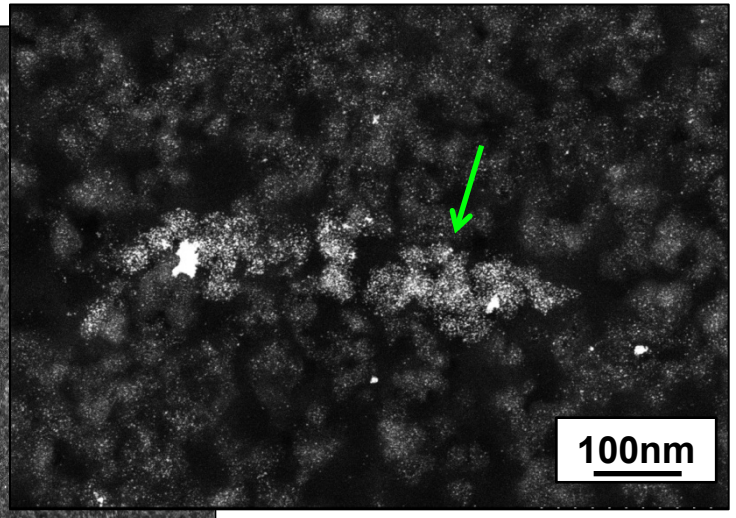
- MEAs prepared by Ion Power were subjected to carbon corrosion AST and modified US-DOE drive cycle tests at LANL:
  - 20% Pt/HSAC – 1.2V hold for **5h**, **10h**, 20h, 40h, 100h
  - 20% Pt/Vulcan – 1.2V hold for 15h, **25h**, **50h**, 400h
- After each test, ultramicrotomed MEA cross-sections were examined via TEM and HAADF-STEM
- Chopped cathode powders (with MPL and membrane carefully removed) were analyzed by XPS
- Extensive image analysis of cathode porosity, carbon support structure, and Pt particle distributions were quantified from TEM/STEM images

Technical Accomplishment: Understanding Effect of Cathode Carbon Corrosion on MEA Performance





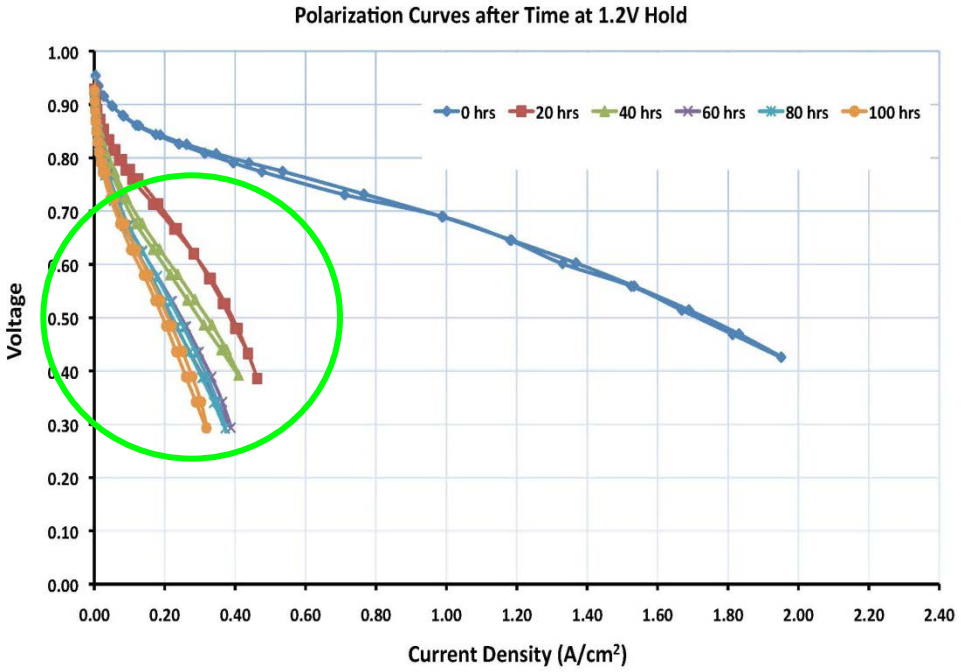


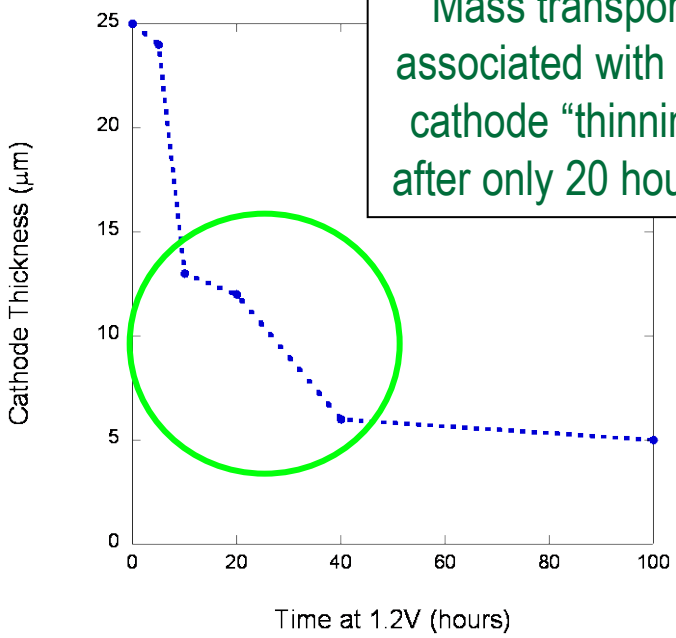


Characteristics of 'fresh' cathode layer:

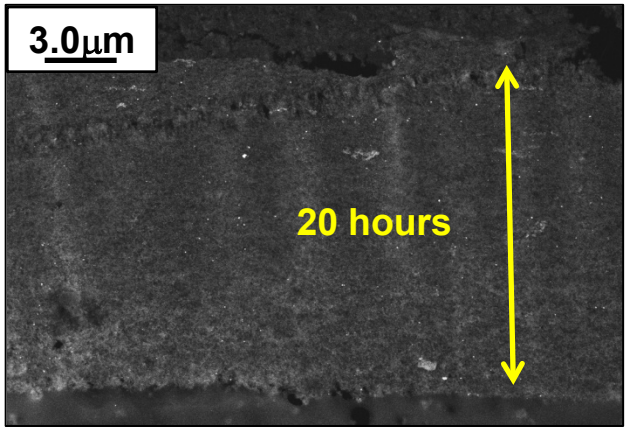
- ***25μm thick***
- ***20% Pt on high surface area carbon (HSAC)***
- ***35% open porosity***
- ***isolated regions of densely packed Pt***

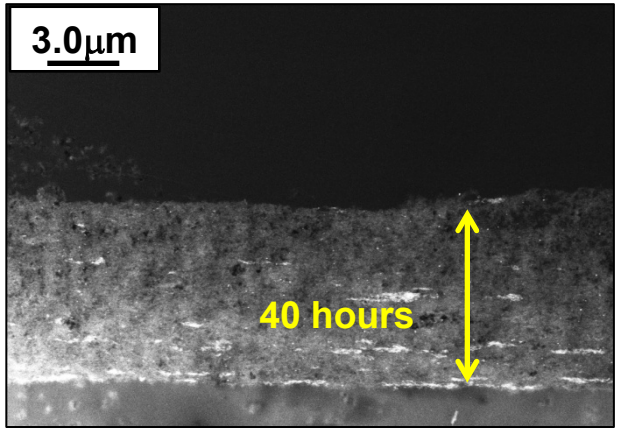
Technical Accomplishment: Understanding Effect of Cathode Carbon Corrosion on MEA Performance

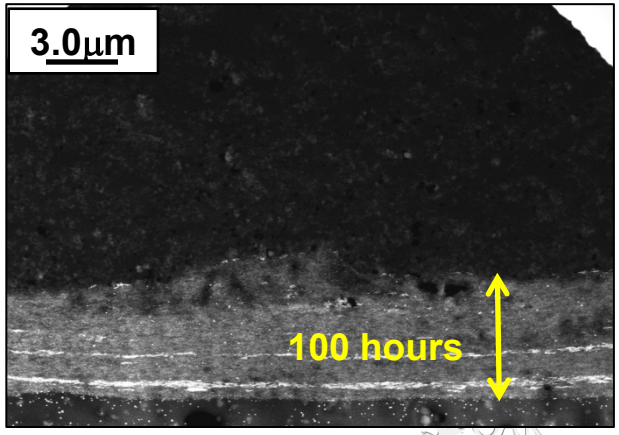




Mass transport losses associated with significant cathode "thinning" >50% after only 20 hours at 1.2V





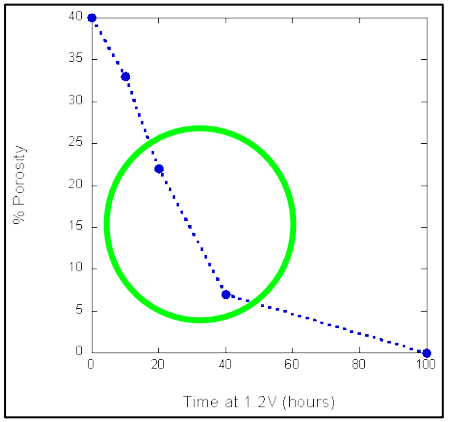


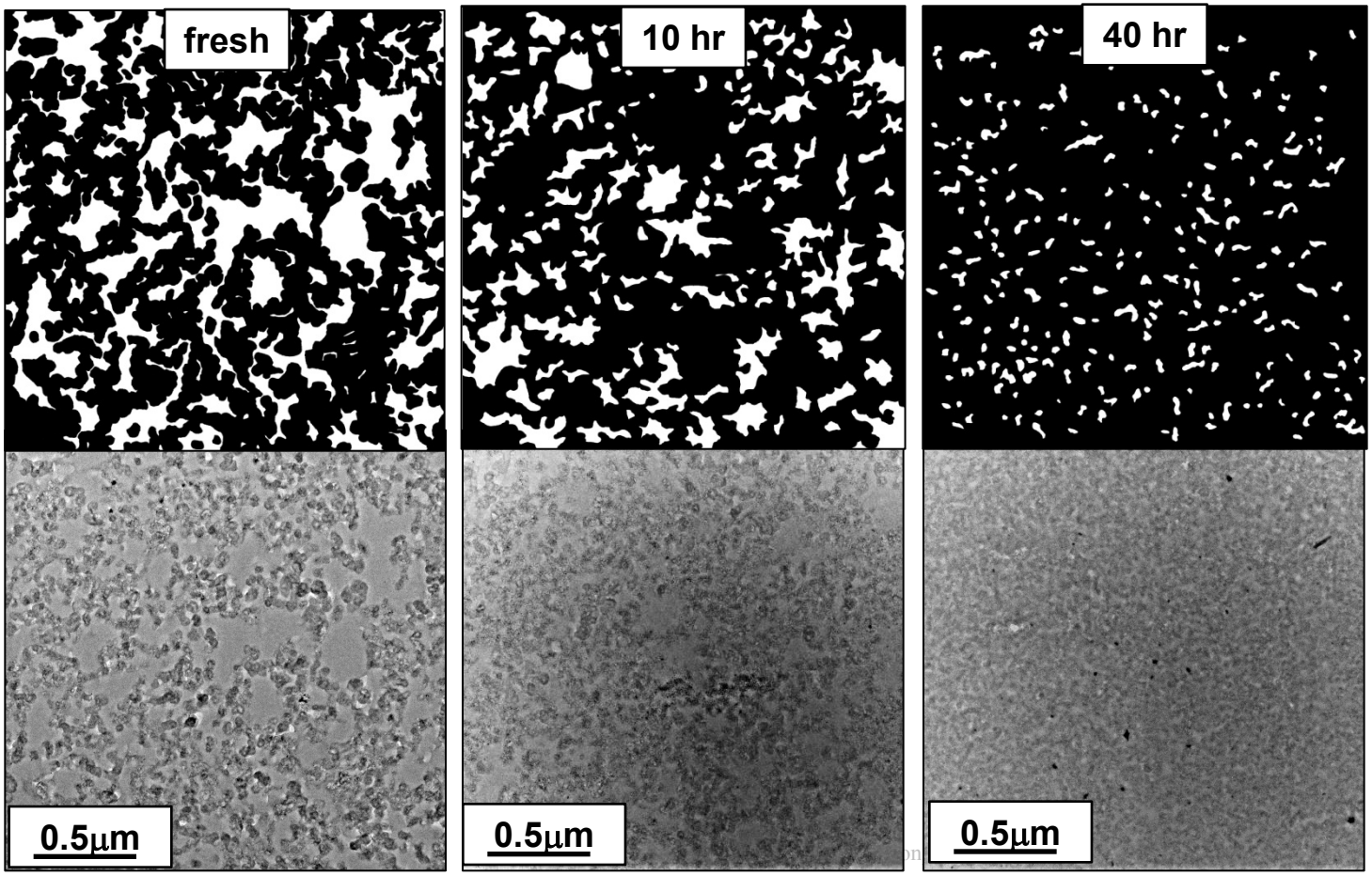
What factors contribute to cathode thinning?

Technical Accomplishment: Understanding Effect of Cathode Carbon Corrosion on MEA Performance

Factors contributing to cathode thinning?

- ***loss or change in porosity***
- carbon oxidation – CO_2 evolution
- carbon oxidation – graphite oxide formation





After 20h at 1.2V ~50% porosity loss in cathode layer

Binary images represent pore distributions after AST

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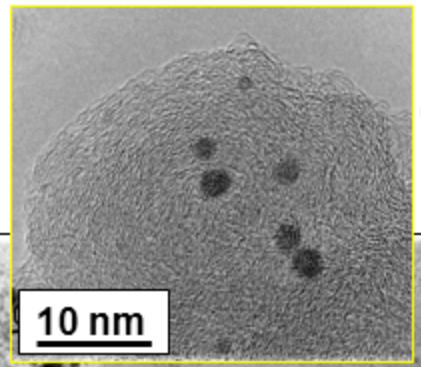
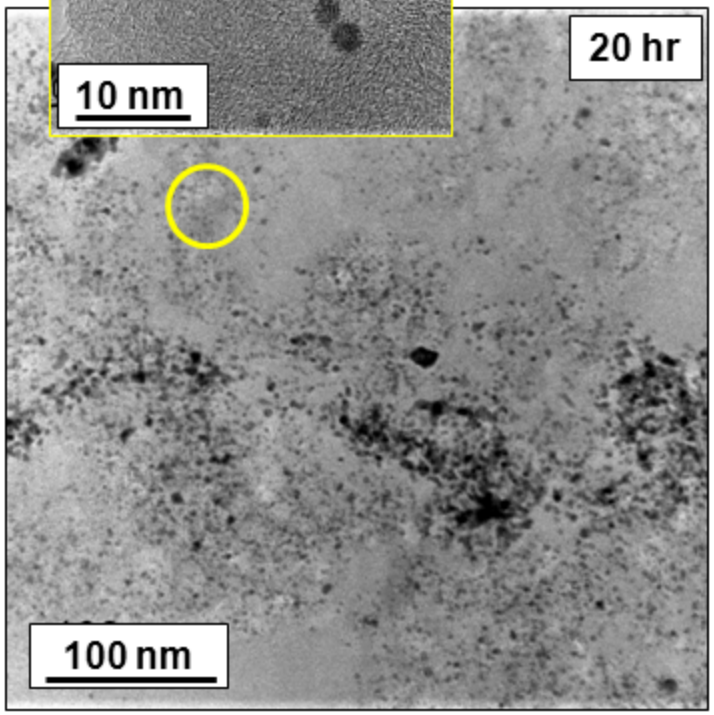
Technical Accomplishment: Understanding Effect of Cathode Carbon Corrosion on MEA Performance

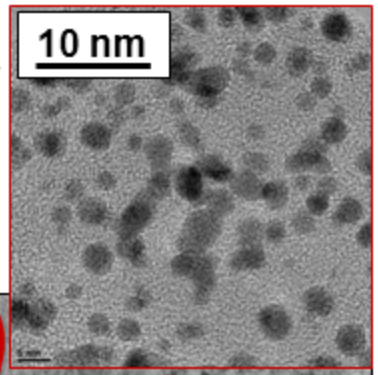
Factors contributing to cathode thinning?
- loss or change in porosity
- ***carbon oxidation – CO_2 evolution***
- ***carbon oxidation – graphite oxide formation***

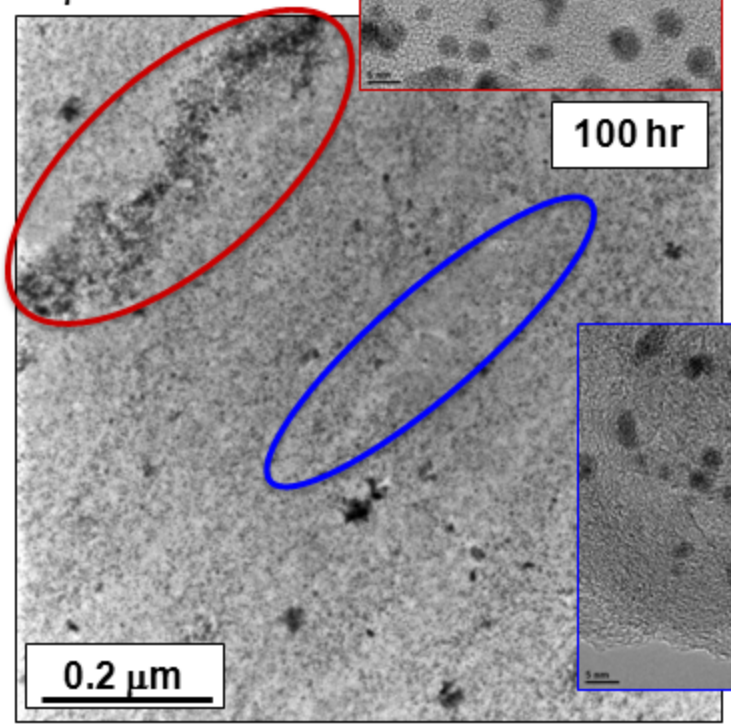
… but loss of porosity loss does not directly correlate with either CO_2 evolution or amount of oxidized carbon formed in cathode layer!

Thinned cathode is a layered structure of "bands" of graphite oxide + partially oxidized carbon + retained HSAC that can be directly correlated with Pt size and are "directional" with respect to membrane

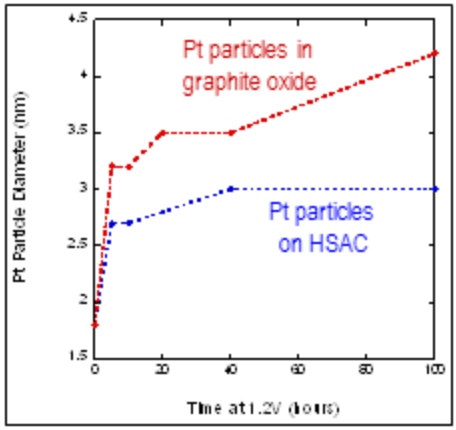


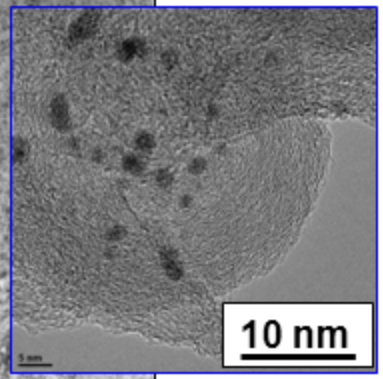






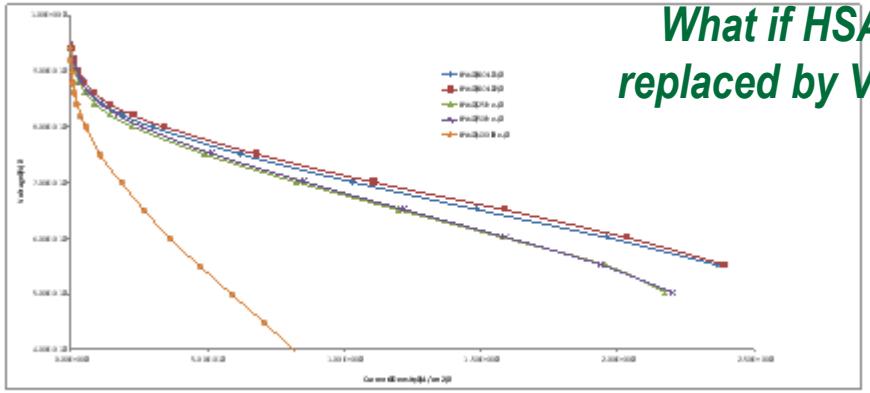
After 100 hr at 1.2V, much of the HSAC has been oxidized to form graphite oxide



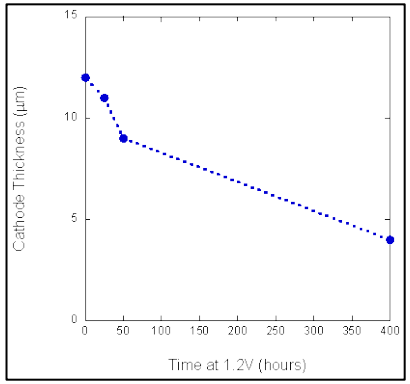


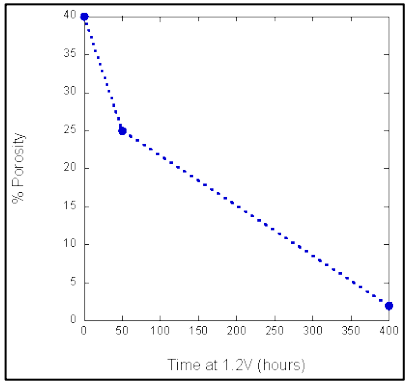
After 100 hr at 1.2V, evidence for retained meso-graphitic HSAC structure

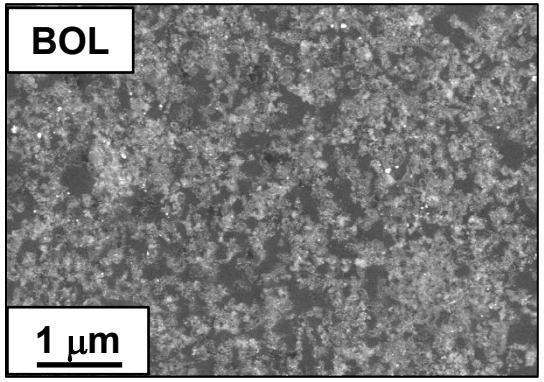
Technical Accomplishment: Understanding Effect of Cathode Carbon Corrosion on MEA Performance

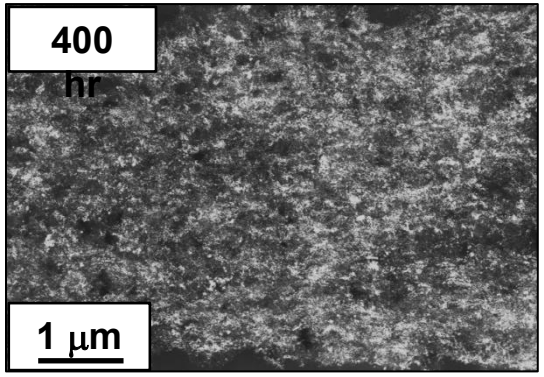


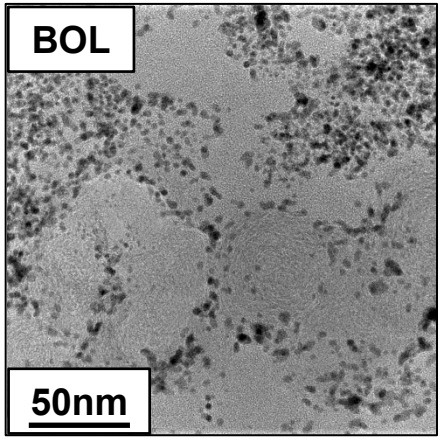
What if HSAC is replaced by Vulcan?

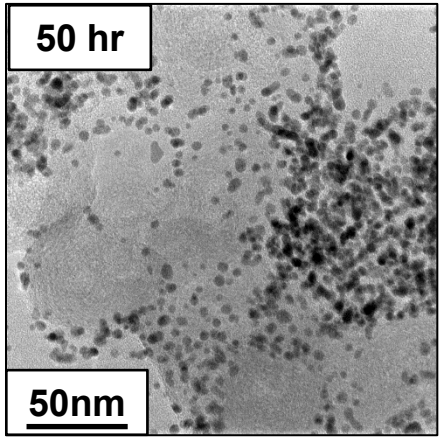


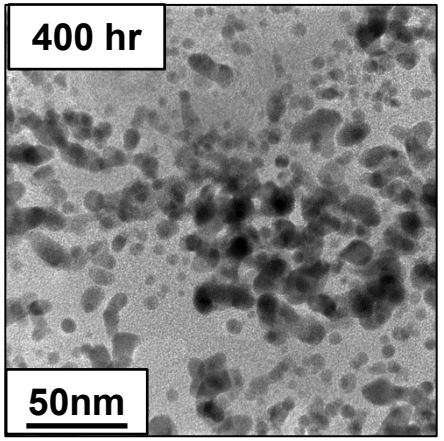




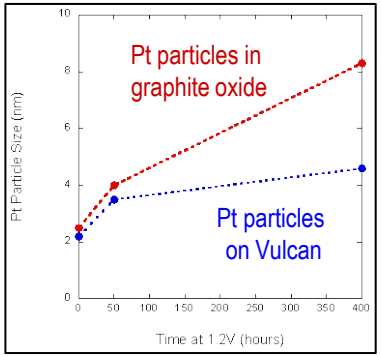


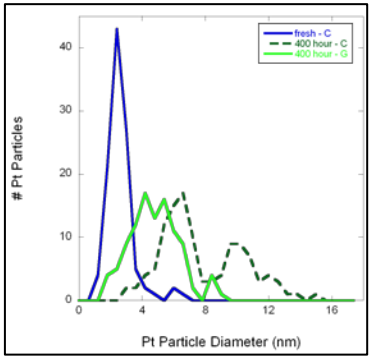






Thinned cathode exhibits a "clustered" morphology of large Pt particles associated with localized graphite-oxide formation

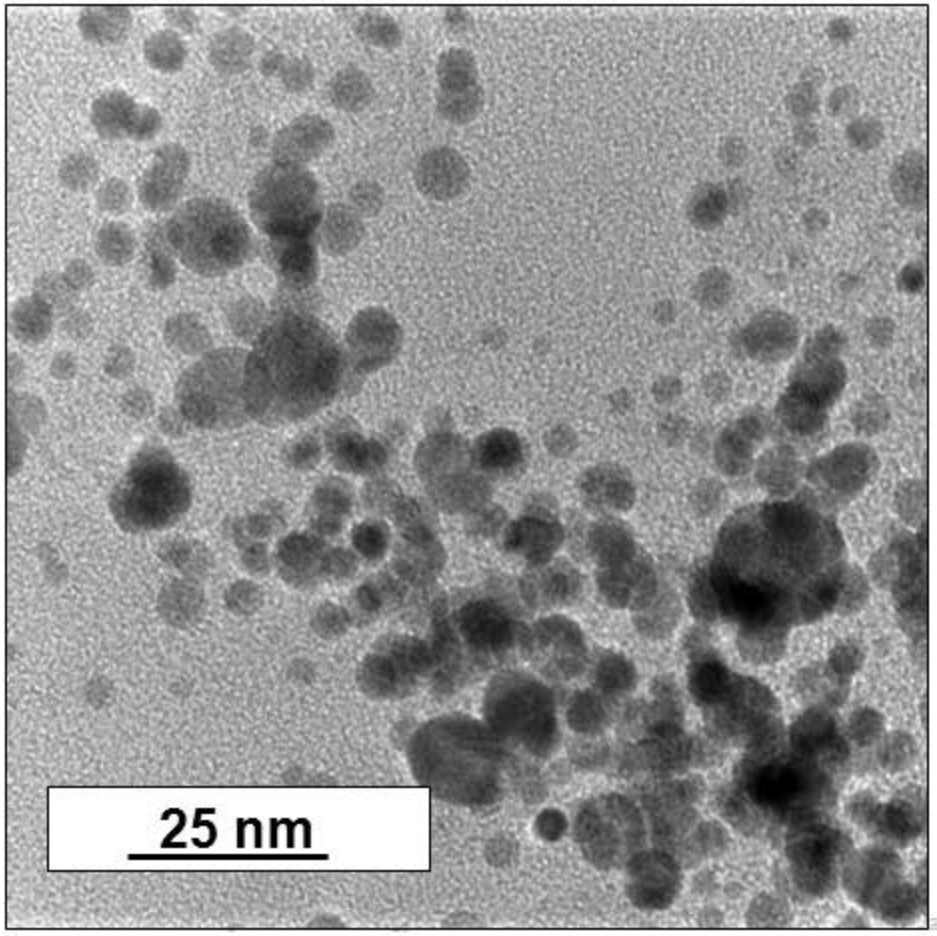




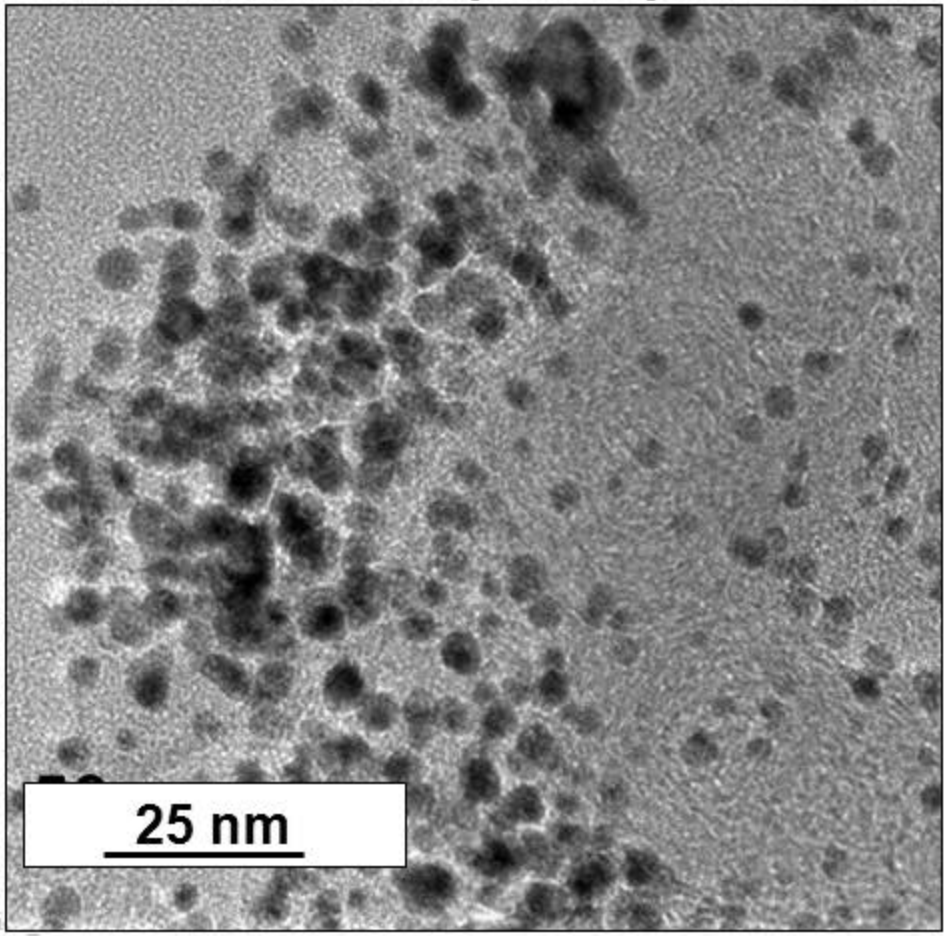
Technical Accomplishment: Understanding Effect of Cathode Carbon Corrosion on MEA Performance

Similar "mixed" carbon oxidation clusters observed for 20% Pt/Vulcan MEA subjected to modified US drive cycle testing

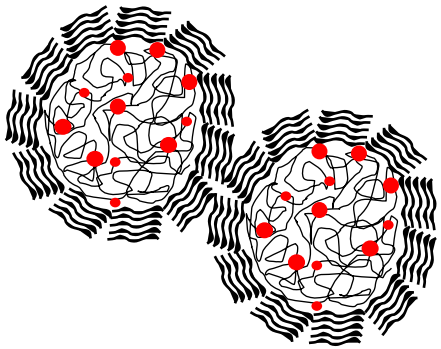
1224 hr "wet" drive cycle

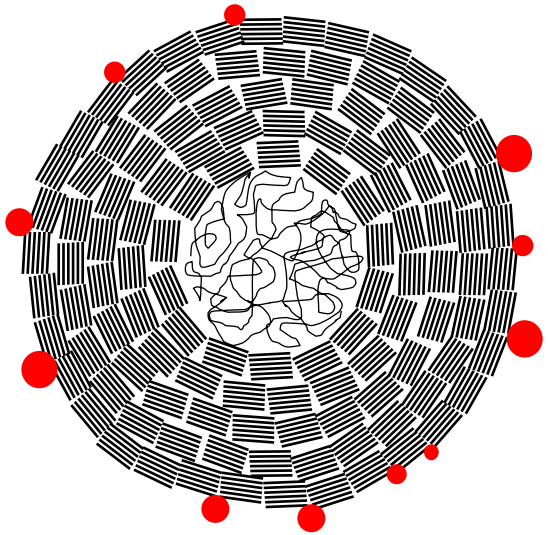


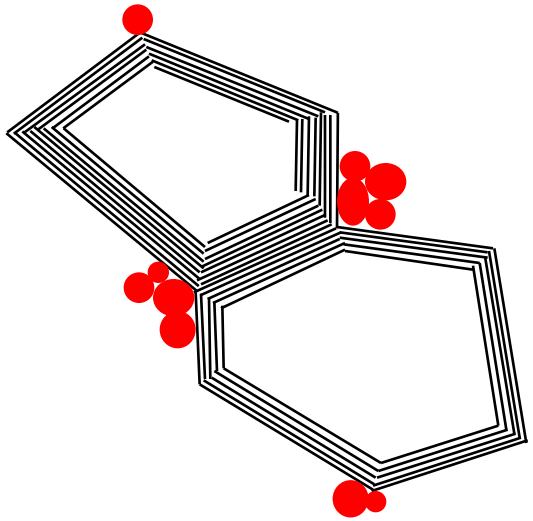
389 hr "wet/dry" drive cycle



Technical Accomplishment: Understanding Effect of Carbon Structure on Carbon Corrosion



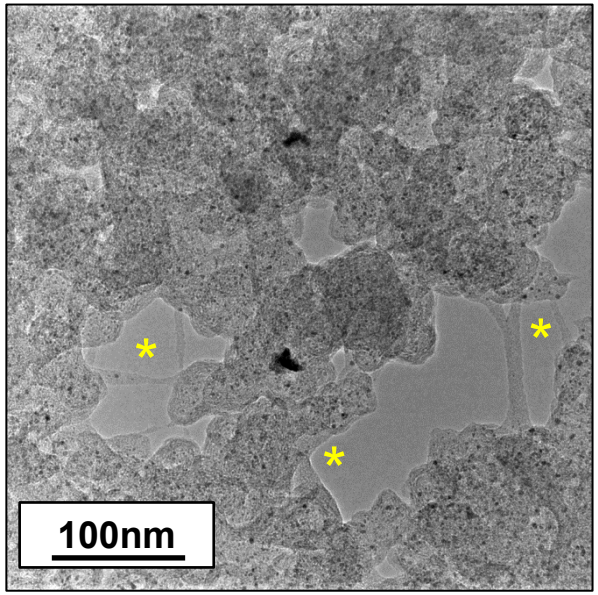


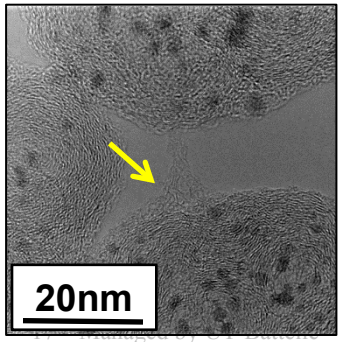


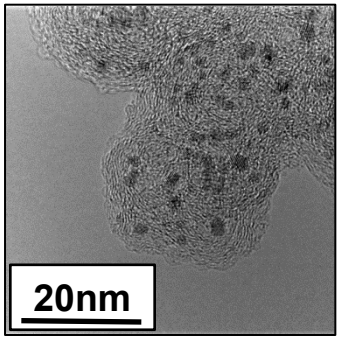
Pt/HSAC – 800-1400 m^2/g		**Pt/Vulcan** – 200-300 m^2/g		**Pt/LSAC** – 500-600 m^2/g
Highly disordered with meso-graphitic outer 'shell'		Concentric 'domain' structure with 4-5nm graphite domain size		Highly ordered/faceted graphitic 'shell' with hollow core
d_{002}	>	d_{002}	>	d_{002}
Less hydrophobic surfaces	<	Hydrophobic surfaces	<	High hydrophobicity
Pt in pores below surface		Pt on surface		Poor Pt surface dispersion

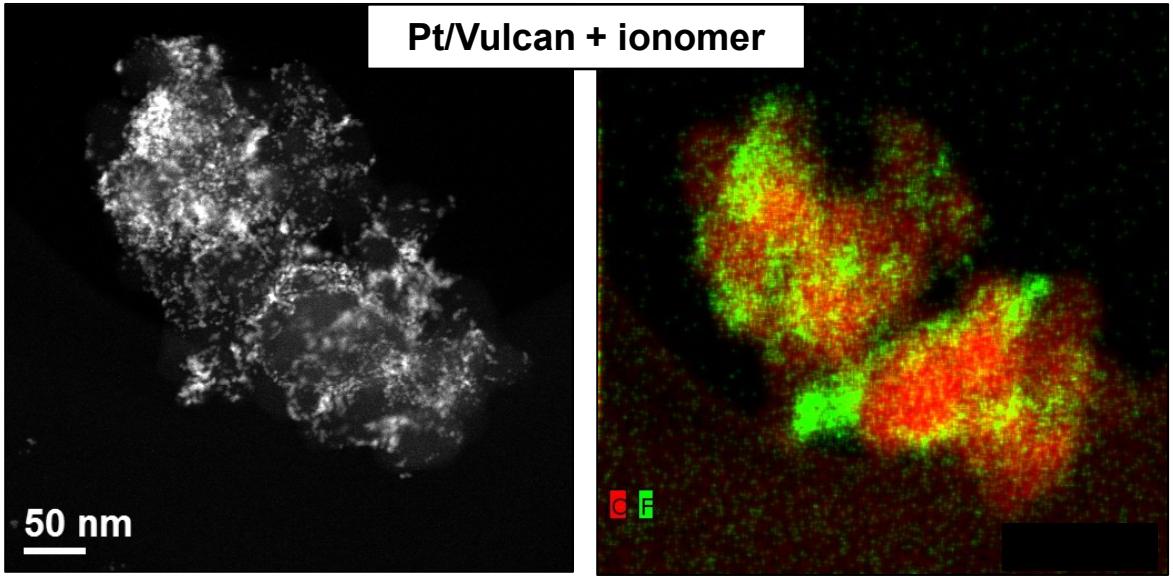
Technical Accomplishment: Microscopy and Spectroscopy of Ionomer Films

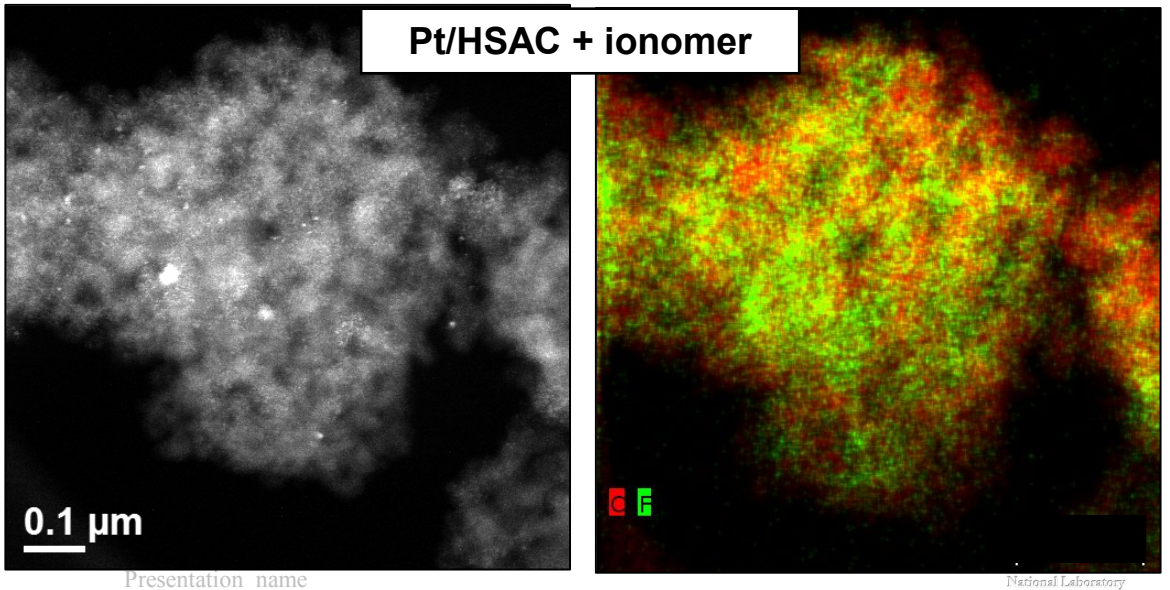
Inhomogeneous dispersion of ionomer within catalyst layer (yellow asterisk - arrows) and depends on the carbon – ionomer rarely exists as a uniform thin film on Pt/carbon surfaces









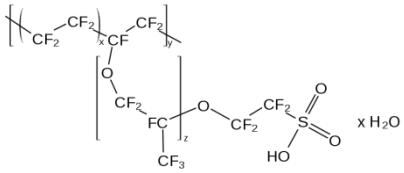


Technical Accomplishment: Microscopy and Spectroscopy of Ionomer Films on Model Substrates

Partners GM, Clarkson University, Brookhaven National Lab

Calculated atomic fractions:

F: 58.38%
C: 30.02%
S: 1.66%
O: 8.29%
H: 1.66%



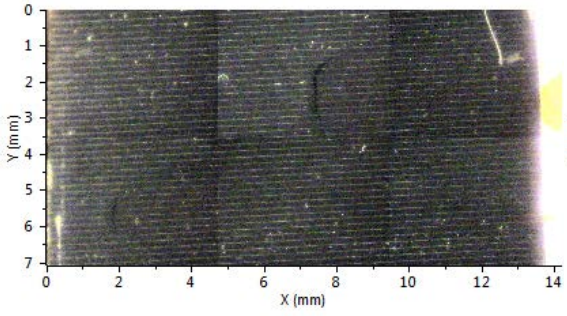
Model Systems (ionomer thick.):

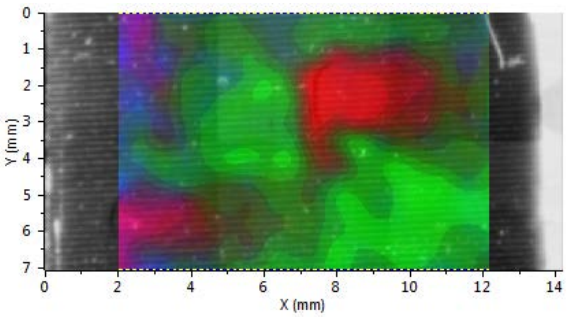
NSTF (1-4 nm)
2D Pt Array (5-40 nm)
Nanoporous Si (5-40nm)
Bulk (hundreds of nm)

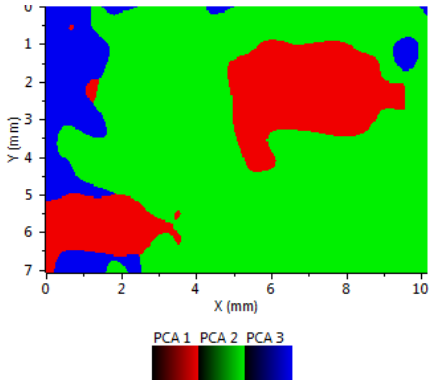
Characterization methods used:

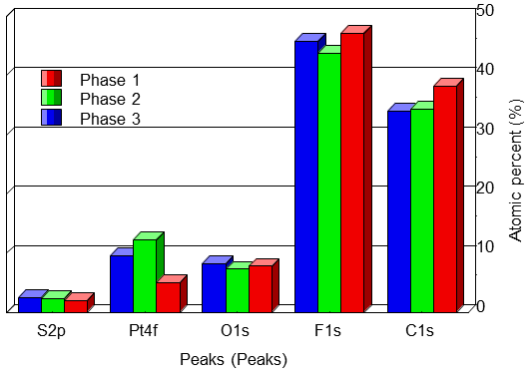
AFM
XPS
STEM

XPS of thin ionomer layers on NSTF: composition and uniformity





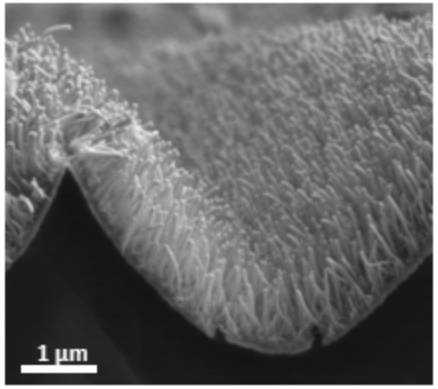


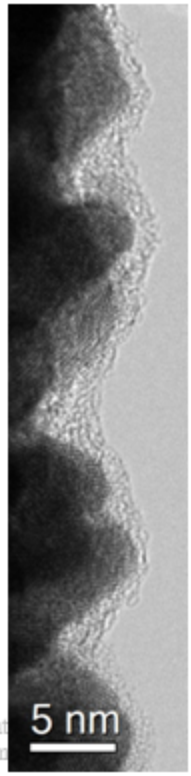


XPS Surface Composition (at.%)

Thick	C	F	C:F	Mn	Co	Pt	O	S
1nm	28.2	39.6	0.71	0.5	3.2	16.7	11.1	0.8
2nm	29.3	42.9	0.68	0.5	2.0	14.8	9.7	0.9
4nm	35.7	50.2	0.71	0.1	0.5	3.8	8.2	1.5

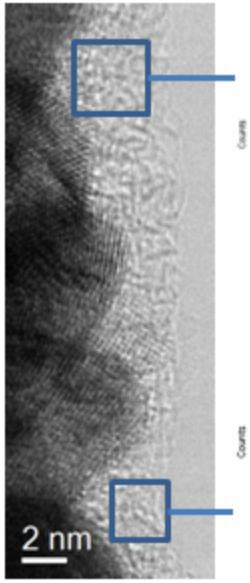
Technical Accomplishment: Microscopy and Spectroscopy of Ionomer Films on Model Substrates

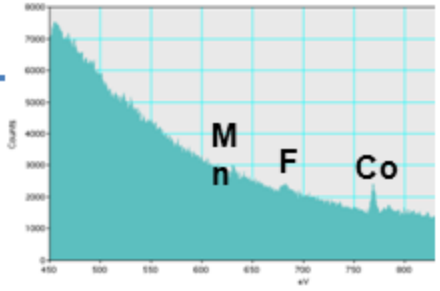


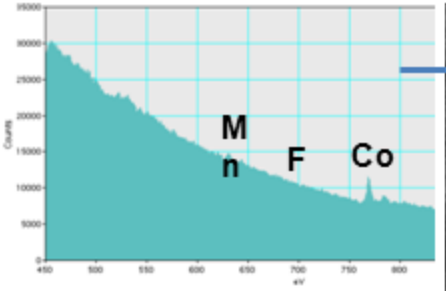


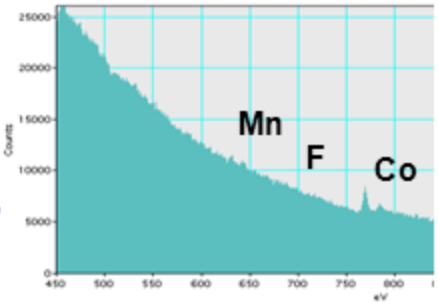
- Ionomer layer (1-2nm) visualized on NSTF surfaces by low voltage STEM.
- However, EELS unable to detect F in layers <5nm, analysis limited by electron beam damage.
- Focus turned to understanding limits of F detection and developing best practices for STEM-EELS.
- Ultimate goal to map ionomer concentration across full Pt/C electrode.

1st Scan



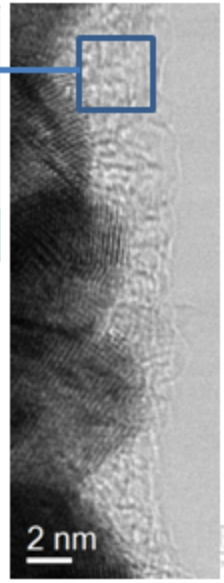




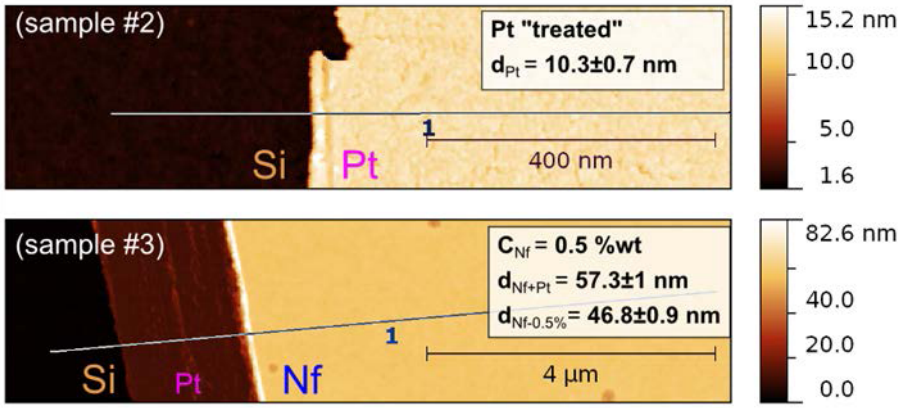


EELS spectrum from 2-3 nm thick ionomer layer. Fluorine peak is visible on first scan in thicker area, but disappears on second scan. No fluorine peak observed in first scan of thinner layer

2nd Scan

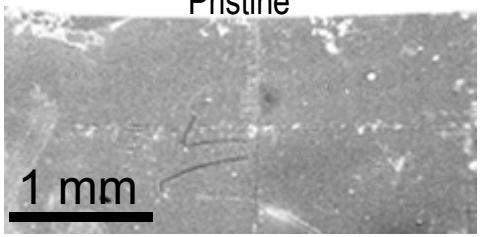


Technical Accomplishment: Microscopy and Spectroscopy of Ionomer Films on Model Substrates

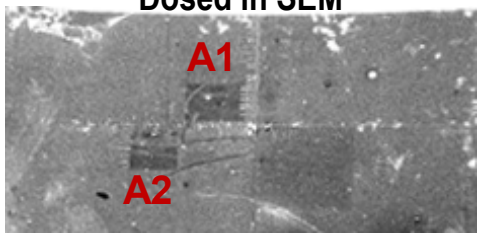


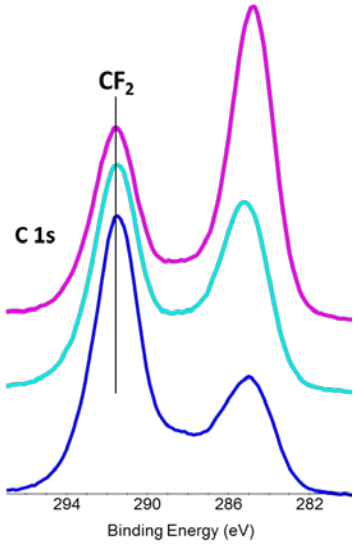
44nm Ionomer layer on 2D Pt array grown on Si

Pristine



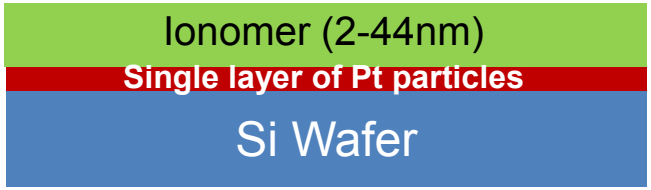
Dosed in SEM



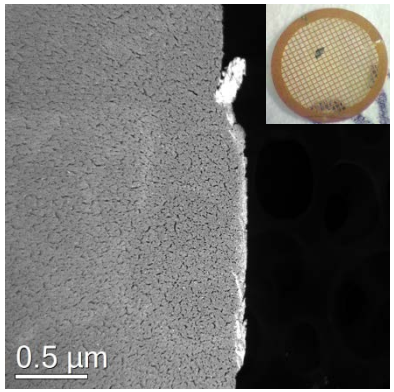


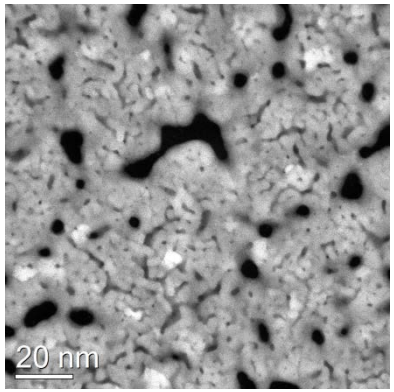
Surface Composition (at.%)

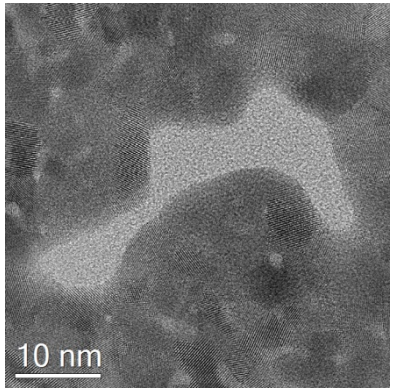
	C	F	O	Pt	Si
Nominal	42.1	47.0	9.4	0.7	0.9
Area 1	41.2	45.7	10.5	0.5	2.2
Area 2	41.8	46.6	9.4	0.4	1.8



Model structure compatible with AFM, XPS, and SEM . . . not ideal for STEM-EELS.



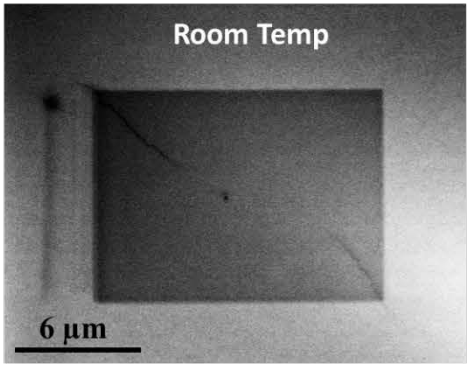


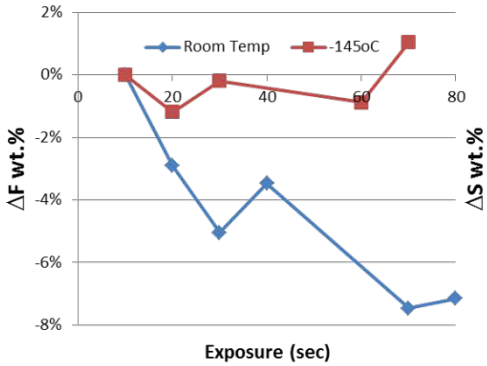


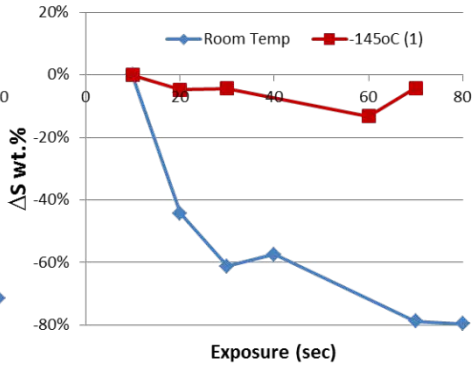
Samples not ideal for STEM-EELS analysis, since an etch in nitric acid required to remove Pt/Ionomer layer from Si.

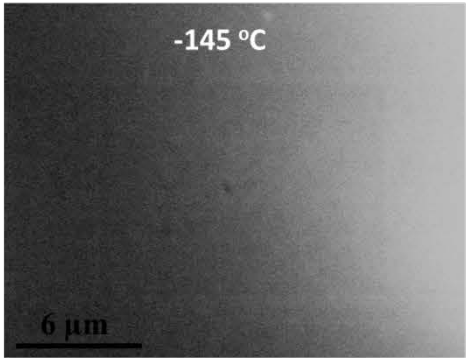
Technical Accomplishment: Microscopy and Spectroscopy of Ionomer Films on Model Substrates

In thick ionomer layers, at high dose, Cryogenic cooling has huge effect on F and S losses

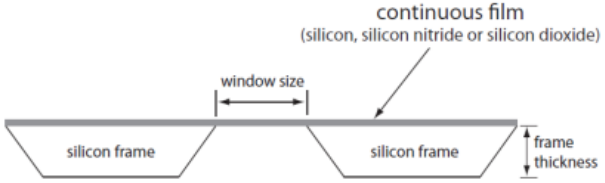




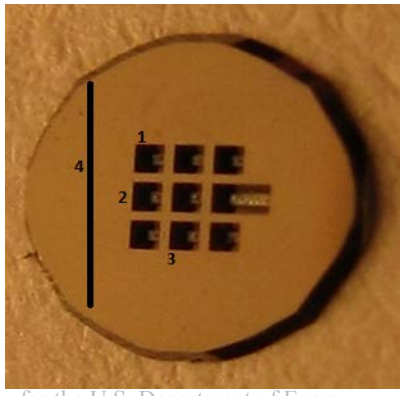


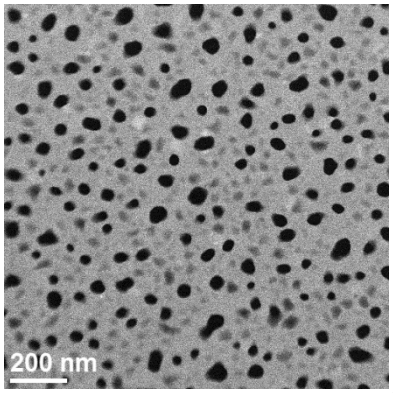


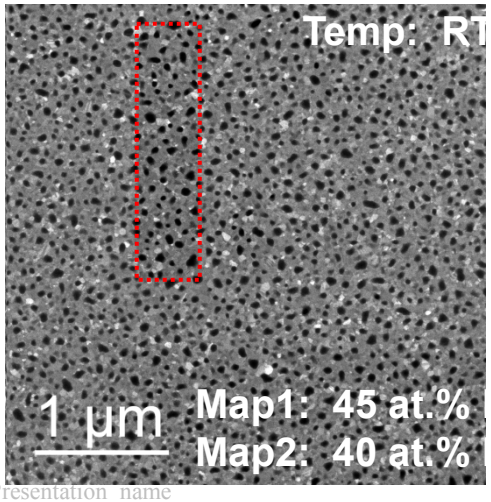
In very thin ionomer layers, at low dose, cryogenic cooling can only reduce rate of F and S losses

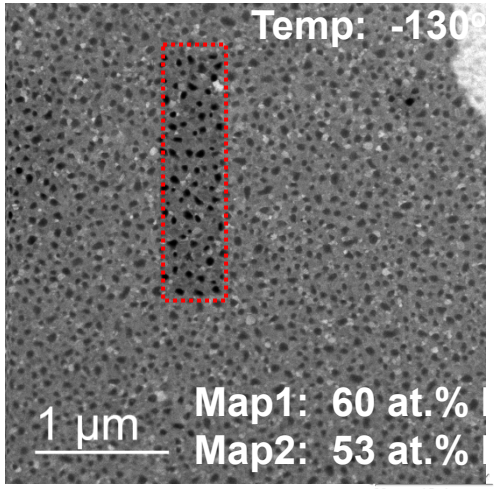


Thickness: ≈5nm Voltage: 60keV Dose: ??







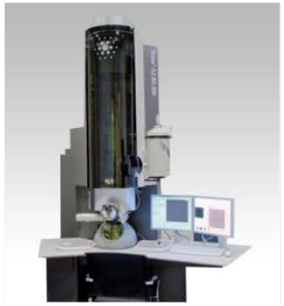


Technical Accomplishment: Enabling Catalyst Research through Large Solid Angle Silicon Drift Detectors

JEOL 2200FS

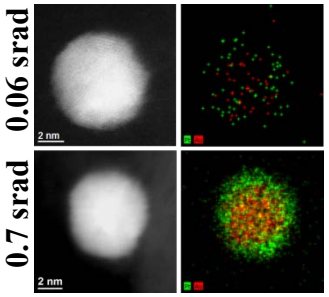
- FEG Gun
- CEOS Probe Corrector
- High resolution Pole Piece
- **Single** Bruker SDD detector
  - Active area=30 mm^2
  - **Solid angle=0.06 srad**

FEI Titan G2 80-200



- X-FEG High Brightness Gun
- DCOR probe corrector
- Analytical TWIN objective lens
- **Four** Bruker SDD Detector
  - Active area=4x30 mm^2
  - **Solid angle=0.7 srad**

PtNi Nanoparticles

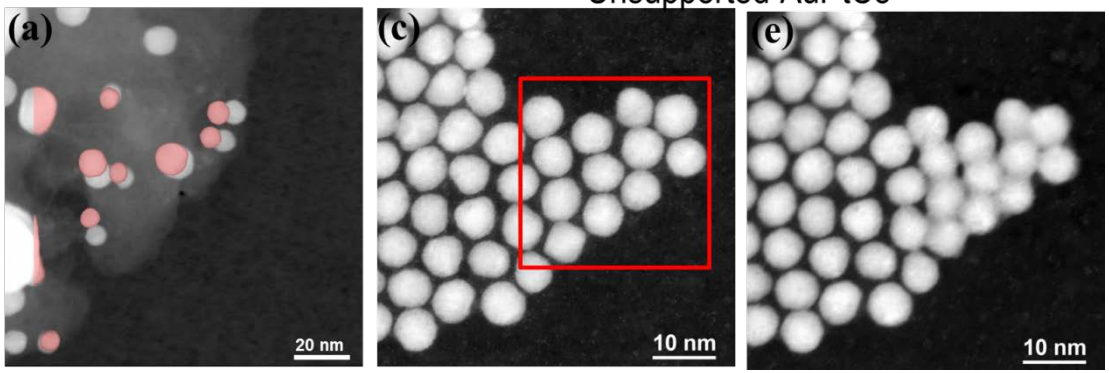


Recorded with same probe current (150 pA) and total live time (65 sec).

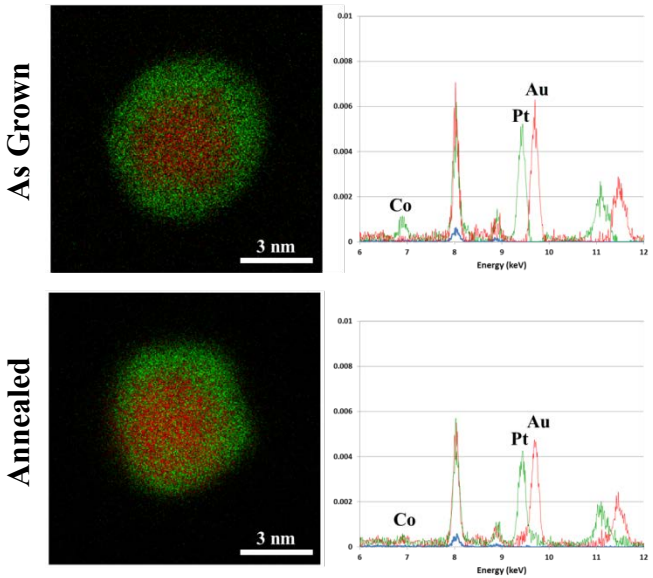
PtNi on C

Unsupported AuPtCo

200 keV



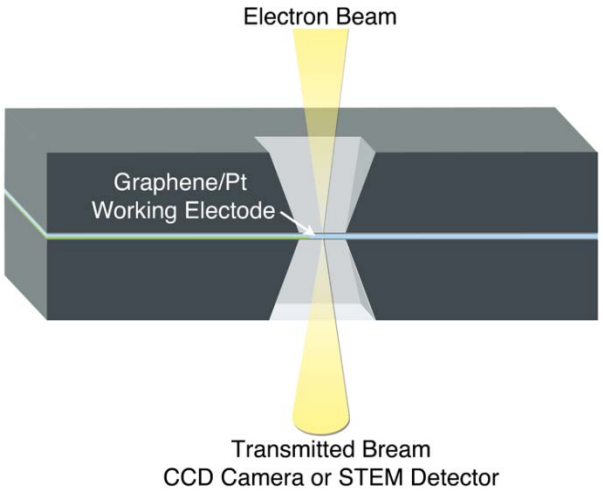
AuPtCo Nanoparticles



Most nanoparticles are unstable under large electron doses. The new generation of large solid angle annular detectors opens new possibilities in the study of dose-sensitive specimens, such as multimetallic nanoparticles. The increase in maximum detection efficiency leads to the following advantages:

- Enabling the study of beam-sensitive nanomaterials
- Better counting statistics for quantitative analysis
- Detection of elements present at very low concentrations
- Increase in sampling size

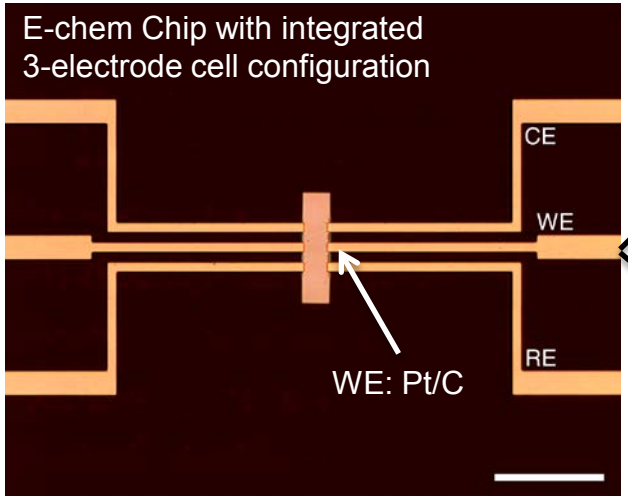
Technical Accomplishment: In-situ Characterization of Fuel Cell Degradation Mechanisms



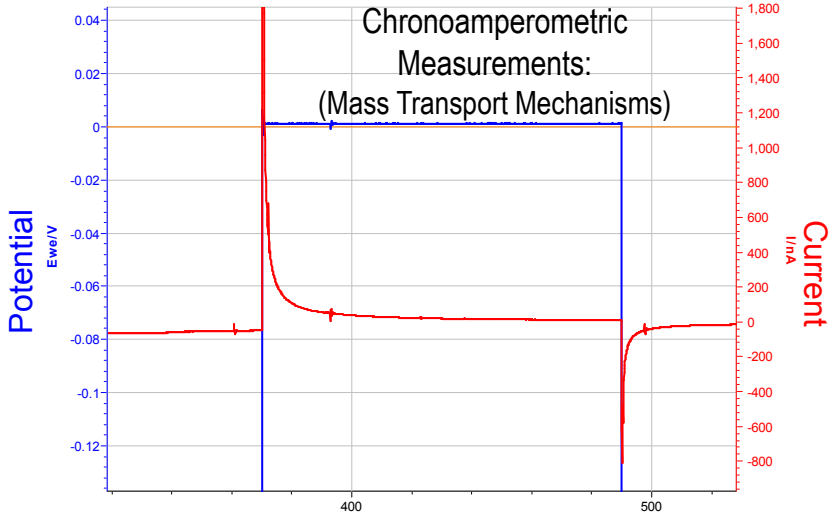
In situ Electrochemical Liquid Cell S/TEM

MEM-based microchips are used as a platform for:

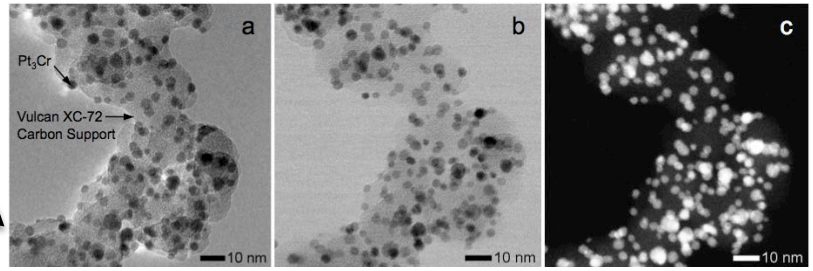
- Sealing electrodes and electrolyte between SiNx membranes
- Performing quantitative electrochemical measurements
- Simultaneous in situ imaging of electrochemical processes



Electrochemical Characterization



In situ STEM Characterization



Current efforts aimed at developing new methods to integrate electrocatalyst nanoparticles on model working electrode substrates (e.g. graphene)

In situ (S)/TEM:
(Electrocatalyst Coarsening/Dissolution/Carbon Corrosion)

Future Work

- Correlate microstructural/compositional observations with AST protocols and “real world” fuel cells, 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.
- Continue the development of in-situ electrochemical “liquid-cell” TEM/STEM as a priority for ORNL’s baseline project - this will be enabled by recent purchase of a specialized holder and hiring a new post-doc.
- Expand current ionomer studies with GM, LANL, and Ballard to specifically focus on interactions with various carbon surfaces with and without Pt.
- Continue to establish collaborations with industry, academia, and national laboratories (including access via ORNL User Facilities) to facilitate “transfer” of unique capabilities.

Project Summary

Relevance: ORNL's microscopy expertise and unique capabilities are integral to identifying materials degradation mechanisms, which are critical for developing mitigation strategies thereby enhancing stability and performance

Approach: Our approach is "unique" in that it is fully collaborative in nature and benefits the entire FC community – applying advanced microscopy methods to solve relevant FC problems is the primary goal of this project

Technical Accomplishments and Progress: We continue to listen to our partners and address important issues – during the past year we have focused on quantifying carbon corrosion and graphite oxide formation, characterizing ionomer thin films, and continued development of in-situ techniques. We continue to support the FC community with unique capabilities for microscopy evaluation of FC materials.

Collaborations: ORNL continues to establish new collaborations to provide access to unique imaging/analysis (microscopy) capabilities or to access lab (and expertise) for training.

Proposed Future Research: Our goal in the coming year will be to further establish ORNL's role as a leader in in-situ microscopy to characterize fuel cell materials, to appropriately characterize ionomer films and nanoparticles , and to provide new insight regarding ionomer interactions with catalysts and support surfaces.