Characterization of Fuel Cell Materials

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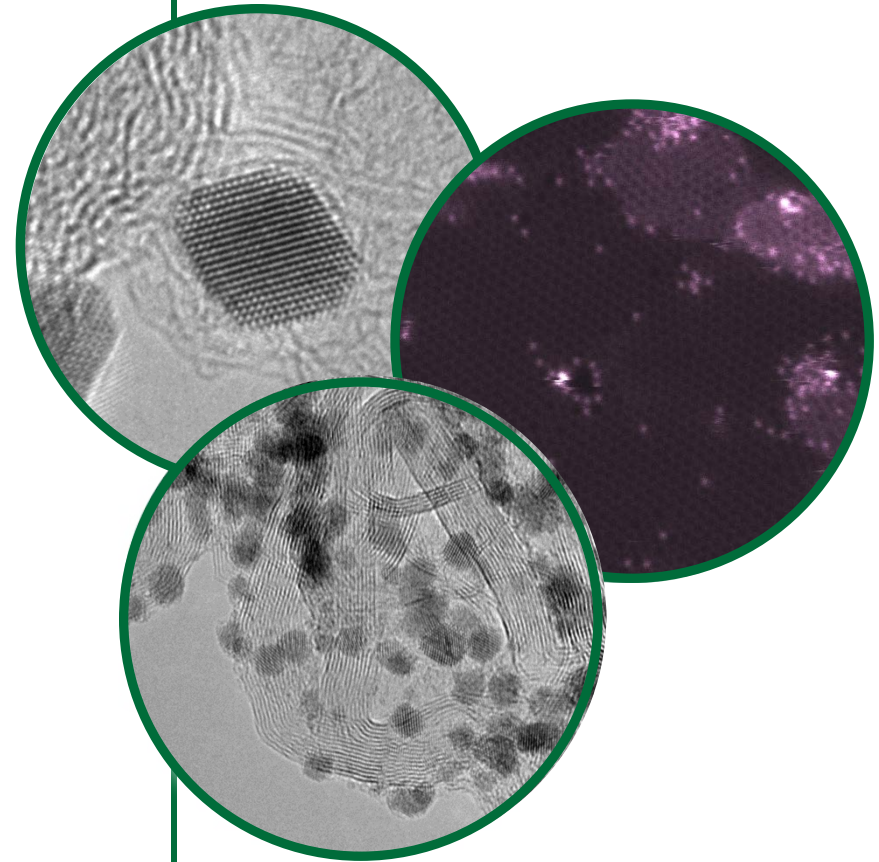
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6064

2014 DOE Annual Merit Review
June 19, 2014

Project ID FC020

U.S. DEPARTMENT OF **ENERGY**

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Project Overview

Timeline

- **Project initiated in FY2000**

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

Budget

- **Funding in FY13 - $600k (~1.5 FTE)**

- **Funding in FY14 - $600k (~1.25 FTE)**

Barriers

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

Partners/Collaborators

- **Los Alamos National Laboratory**

- **General Motors**

- **3M**

- **Automotive Fuel Cell Cooperation (AFCC)**

- **Ballard**

- **Nissan Technical Center North America**

- **Ford Motor Co.**

- **University of Tennessee**

- **Argonne National Laboratory**

- **CEA-Grenoble, France**

- **IRD Fuel Cells**

- **Fuel Cell Energy**

- **McMaster University, Canada**

- ***Additional DOE project collaborations: LANL, ANL, NREL, and 3M. Results from these studies are NOT included in this project summary***

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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

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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*
- *Nissan TCNA – Catalyst support durability*
- *UTC Power (sub) - Improved Accelerated Stress Tests Based on FCV Data (project ended)*
- *3M and AFCC – NSTF durability testing*
- *Fuel Cell Energy – novel membrane and MEA characterization*

novel catalysts and supports

- *LANL (sub) – The Science and Engineering of Ultralow PGM Catalysts*
- *NREL (sub) – Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes*
- *LANL (sub) – Non-Precious Metal Fuel Cell Cathodes: Catalyst Development and Electrode Structure Design*
- *3M – NSTF alloy cathode catalysts*
- *Ford Motor Co. – novel carbon supports*
- *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 electrodes*
- *Ballard – ionomer distributions as a function of carbon support type and Pt loading*
- *CEA-Grenoble – characterization of ionomer distributions within catalyst layers*
- *McMaster University – STXM characterization of ionomer distributions in catalyst layers*

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 from μm-to-Å-scale:

  - Catalyst nanoparticles and catalyst NSTF – composition, chemistry, size, and morphology
  - Re-cast ionomer within catalyst layers
  - 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

cathode

membrane

anode

20 μm

1 nm
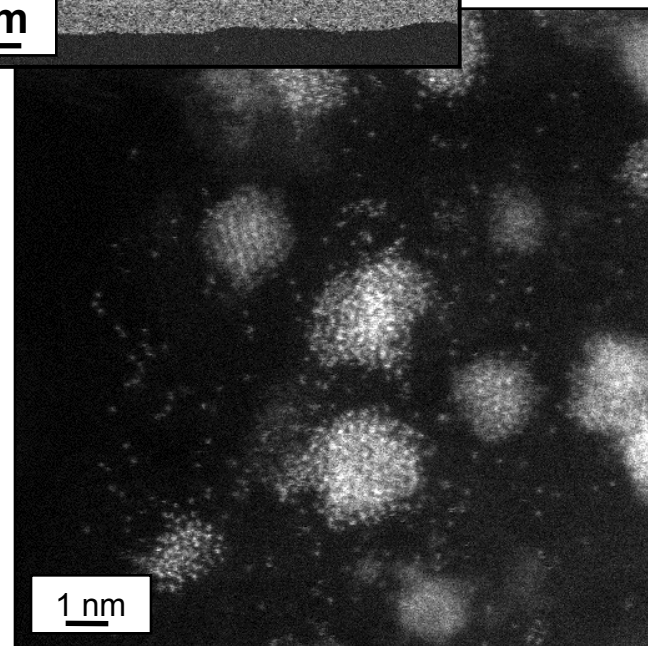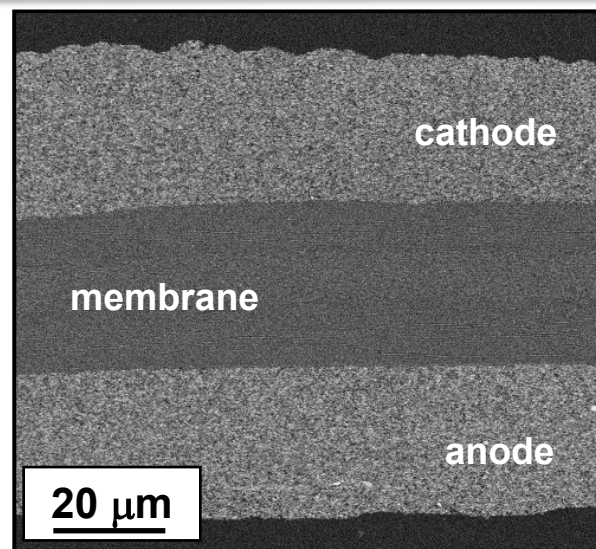
Milestone Schedule – FY13 and FY14

- ## 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.*Completed*

- ## FY14 Milestones:

  - ✧ Initiate new collaboration with an industrial partner to characterize novel/new catalyst and/or catalyst support structures.   *Completed*

  - ✧ Complete parametric study of ionomer thin films with General Motors and collaboratively publish results. This study will establish baseline conditions to quantitatively assess ionomer structure and composition in an electron microscope.   *Completed*

  - ✧ Establish electrochemical conditions for potential cycling and potential holds for in-situ microscopy liquid cells to study Pt coarsening and carbon corrosion in real time.   *In Progress*

  - ✧ Complete report summarizing tomography characterization results to study NSTF catalyst degradation during MEA aging.   *In Progress*

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Technical Accomplishments and Progress: Responses to 2013 Year Reviewer Comments

- *FY13 Reviewer Comment*: Besides continuing the very successful work, the researchers plan to correlate the knowledge to experimental data from fuel cell testing. This takes the work to a next, higher stage. As for the observed compression of the catalyst layers, it is recommended the project put in effort regarding understanding the mechanism of densification in detail. This might open up new options of carbon modification other than the already-identified Pt on low surface area carbon (LSAC).

  - *FY14 response*: consistent with recommendation above, work has been done to provide insight regarding compression/densification in terms of catalyst dispersion and accelerated carbon corrosion.

- *FY13 Reviewer Comment:* The electrode structure (catalyst + ionomer) can be significantly different depending on formation (coating, spraying, etc.), and it may be necessary to examine the as-made, pre-conditioned, and used MEAs to ascertain the structure as it exists during actual fuel cell operation.

  - *FY14 response*: we have made significant progress in identifying proper conditions for evaluating ionomer within catalyst layers and characterizing ionomer distributions after aging.

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Technical Accomplishments and Progress:
Work Focused on Topics Prioritized by FC Community
(Collaborators, Tech Team, and FY13 AMR Reviews)

Past AMR presentations have highlighted ORNL research specific to:

- Sub-Å-scale alloy catalyst nanoparticle characterization

- Understanding carbon corrosion mechanisms

- Pt dissolution/migration and coarsening studies

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

- Ionomer distribution/quantification within catalyst layers

- In-situ microscopy

- Compaction/compression effects in cathode layers

- Catalyst dispersion

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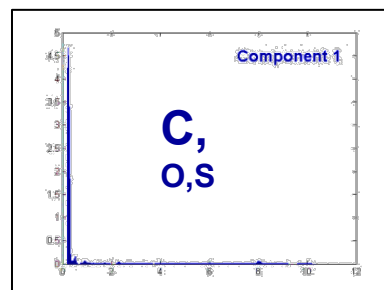**Ultimate goal – <u>quantitative</u> study of ionomer distributions (through-electrode loadings)**

No ionomer

1μm

100nm

0.5-5.0nm ionomer layer

1μm

100nm

50 nm

5 nm

2 nm

a

b
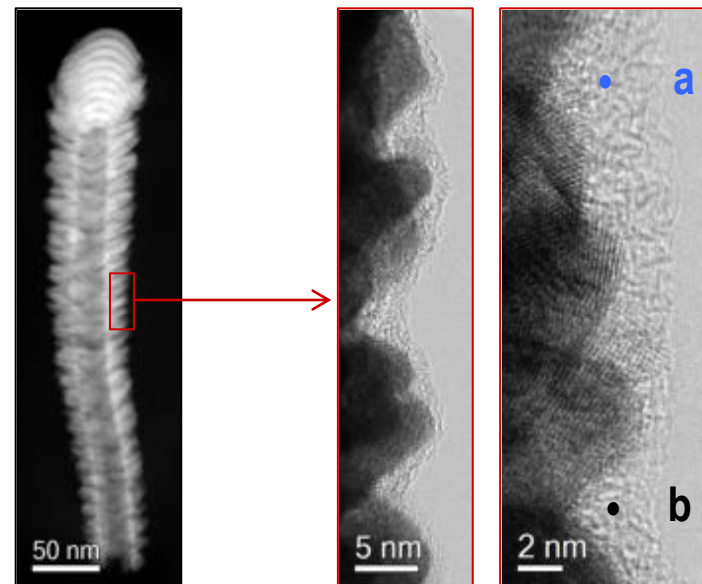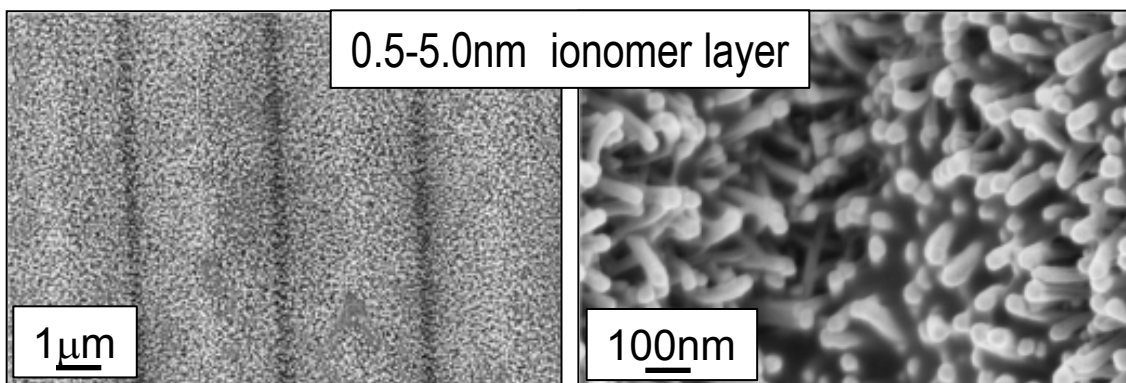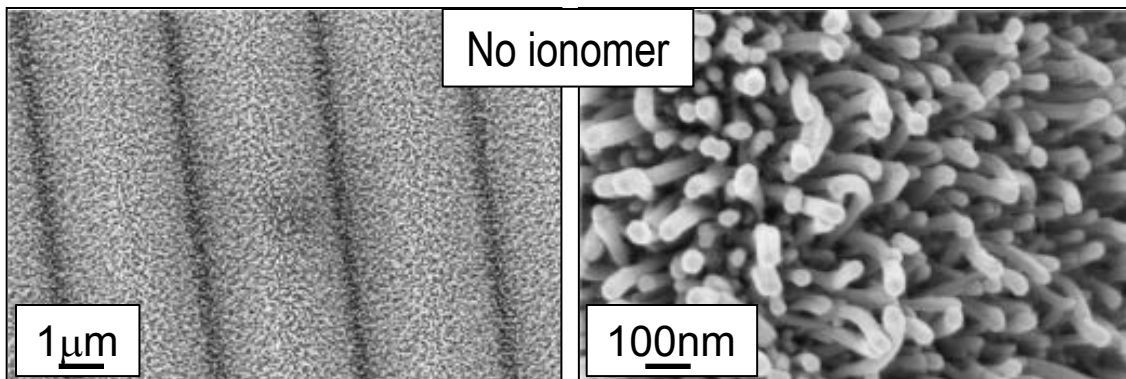
- **Ionomer films imaged on PtCoMn NSTF low voltage STEM.**
- **EELS unable to detect F in films <5nm thick - analysis limited by electron beam damage.**
- **Focus turned to understanding limits of F detection and developing best practices for STEM-EELS+EDS analysis.**
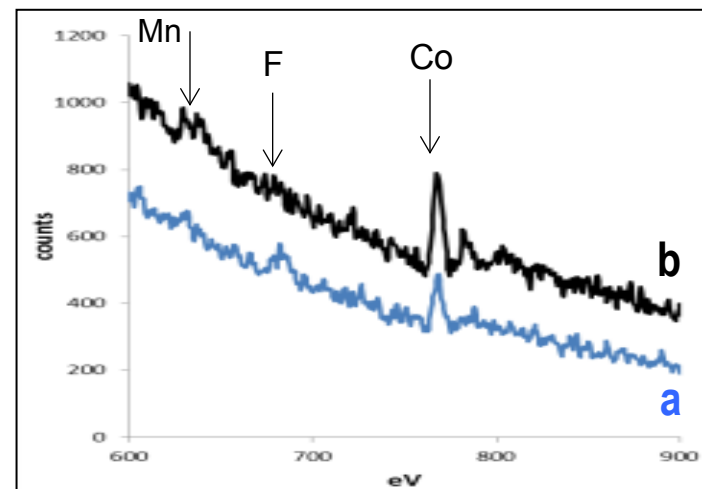
Mn F Co

b

a

Technical Accomplishments and Progress:
Characterization of Ionomer Films and Distributions

Slightly thicker ionomer films used to determine proper conditions for microanalysis

3mm TEM disk

200nm
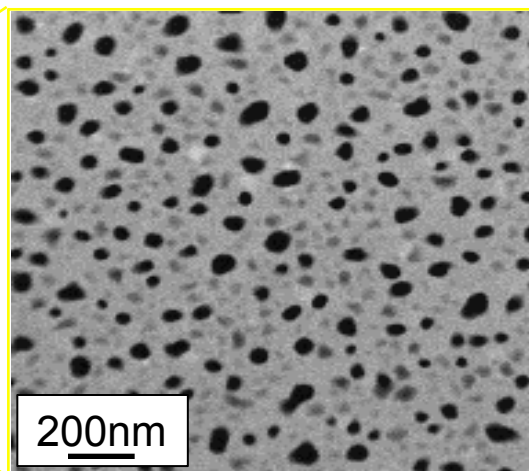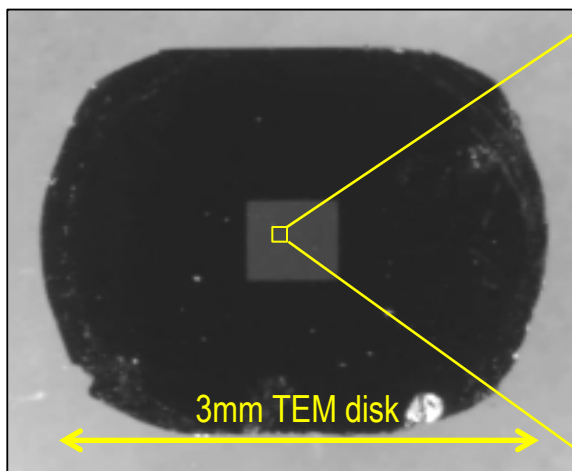
~5-25nm thick ionomer films were spin-coated across nanoporous Si

Ionomer films were studied at 60-200kV at both RT and LN$_2$ using various electron doses
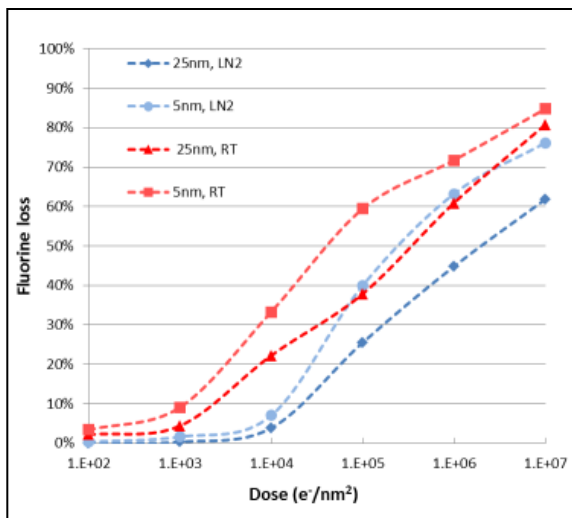
Flourine loss as a function of electron dose @ 60kV during STEM-EELS
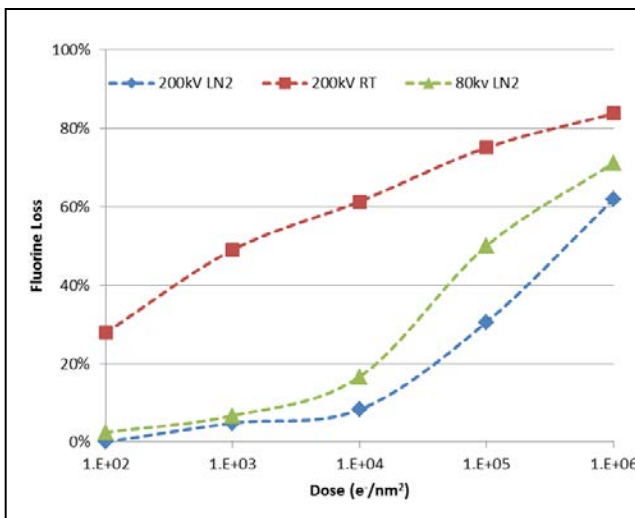
Flourine loss as a function of voltage and specimen cooling during STEM-EDS

Results demonstrate that LN$_2$ cooling and film thickness have pronounced effects on F-loss for both EELS and EDS data acquisition.

A 2-3X order of magnitude decrease in electron beam damage can be achieved by using LN$_2$ cooled specimens and higher microscope operating voltages

Technical Accomplishments and Progress:
Characterization of Ionomer Films and Distributions

Quantitative STEM study of ionomer distributions (through-electrode loadings)

- *Two different electrodes preparation methods (target I/C=1 and 50% Pt/C):*
  - *Catalyst-coating-on-decal (CCD)*
  - *Catalyst-coating-on-diffusion-media (CCDM)*

- *"Lessons learned" from model ionomer layer systems applied to quantify ionomer distribution (through-electrode loadings) and minimize F-loss* ⟶ *LN$_2$-cooling and low electron doses*

50% Pt/V and I(Nafion®)/C = 1.00
nPrOH:H$_2$O::3:1 w/w ; MRC105 w/MPL

CCD (I/C 0.964)
CCDM (I/C 0.568)

$y = -0.0174x + 0.6322$
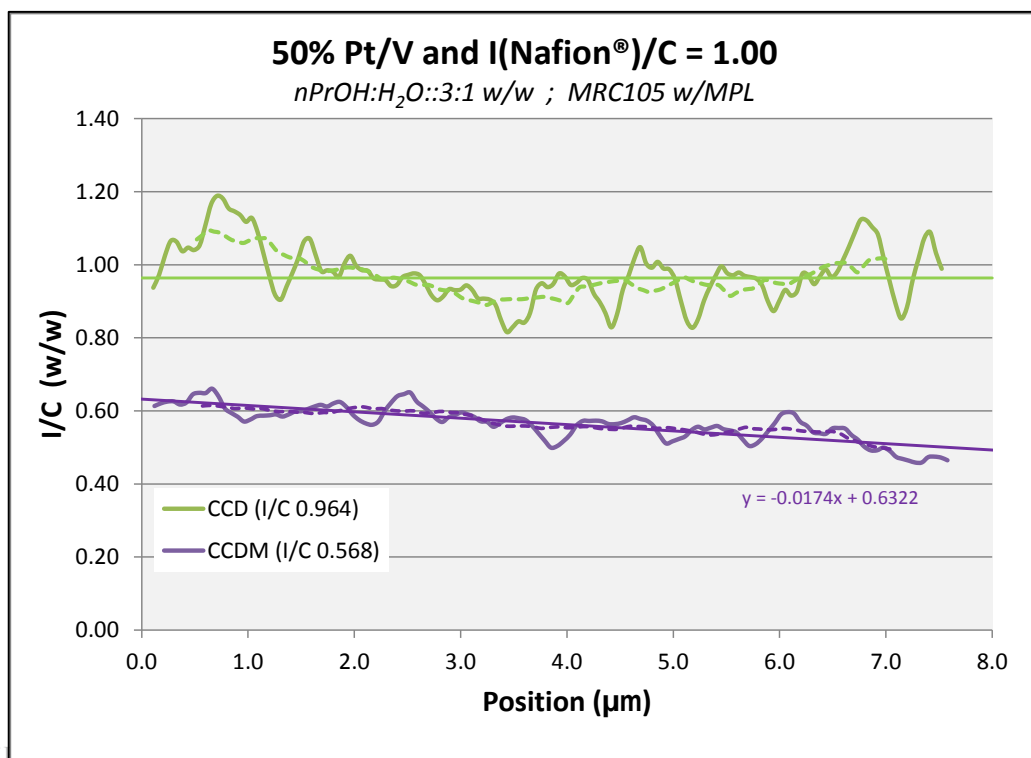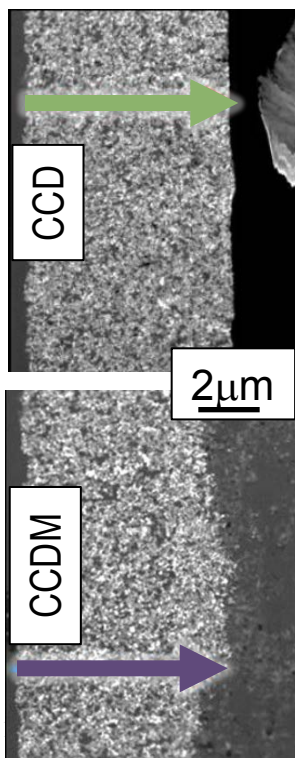
- *CCD electrode exhibits a "bowed" ionomer profile.*

- *CCDM electrode exhibits a linearly sloped ionomer profile, with a lower I/C at the diffusion media interface due to some drainage of ionomer into diffusion media.*

- *Ionomer distributions can be quantified using STEM by mitigating beam damage effects.*

- *Results are comparable in spatial resolution with STXM performed using synchrotron.*

Technical Accomplishments and Progress:
Characterization of Ionomer Films and Distributions

## *Increasing resolution to map ionomer distributions on a finer scale*

Before analysis — 200nm

After analysis — 200nm

Component 2: **F, O,** S, Ca

Component 1: **C,** O, S

Component 3: **Pt**

PCA map
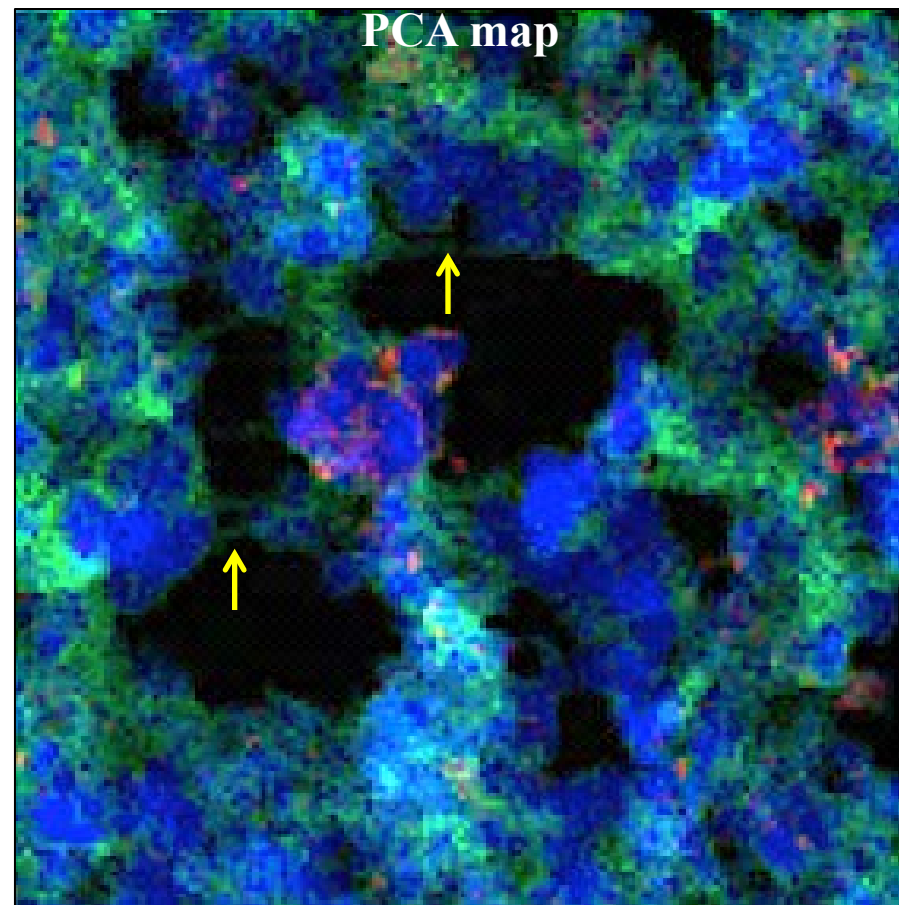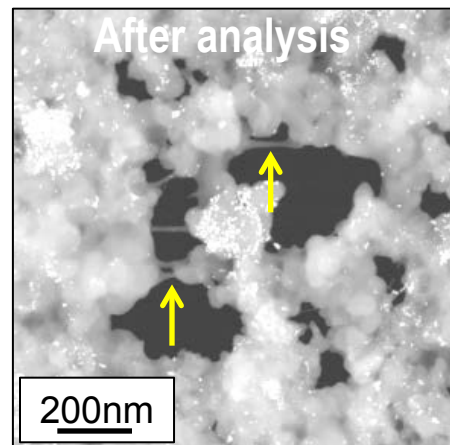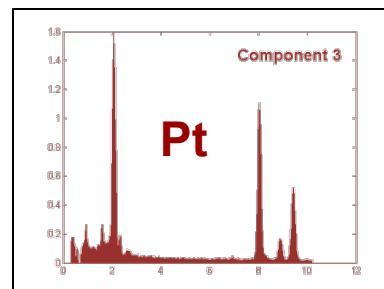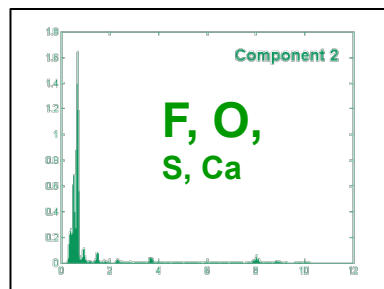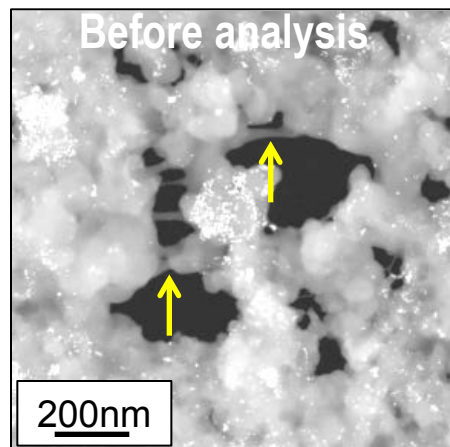
EDS maps acquired in an FEI Osirus equipped with large solid-angle SDD with pixel size of 5nm, 200kV operating voltage, LN_2 cooling, and electron dose of $4X10^6$ e^-/nm^2. MVSA-PCA methods applied to "denoise" spectra.

Thin ionomer layers are clearly resolved!

Increasing resolution to map ionomer distributions on a finer scale
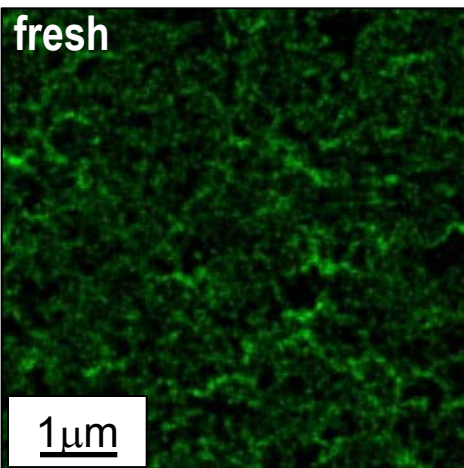
EDS maps acquired in an FEI ChemiSTEM equipped with large solid-angle SDD – pixel size of 5nm, 200kV operating voltage, LN_2 cooling, and electron dose of 1×10^6 e^-/nm^2.

Distribution of ionomer within fresh electrode varies with carbon support.

Stability of ionomer also varies with carbon support (400hrs @ 1.2V).
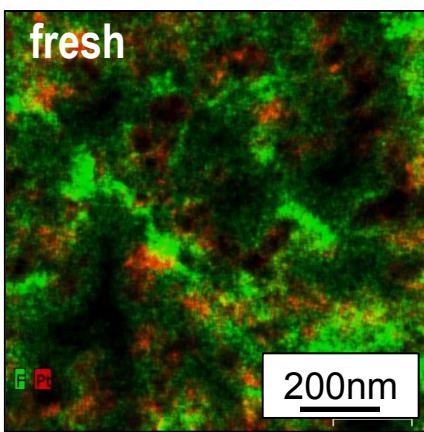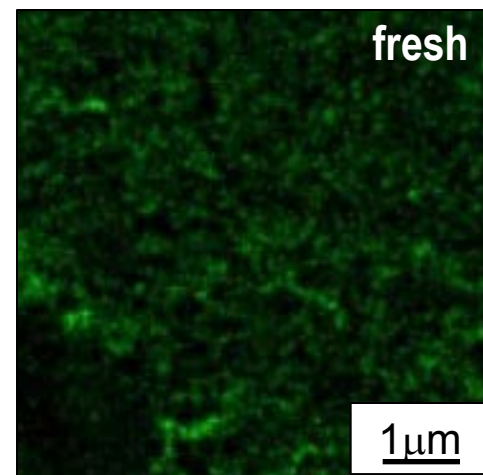
Pt/Vulcan
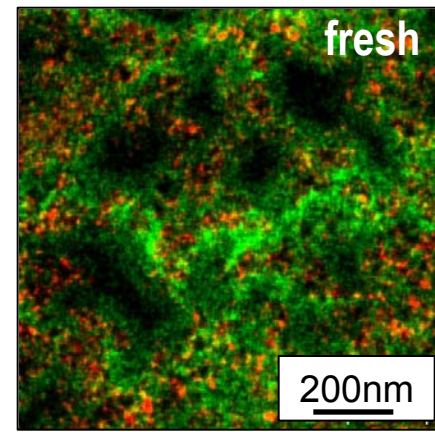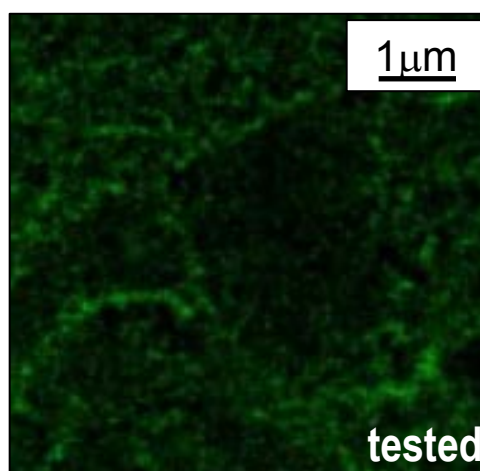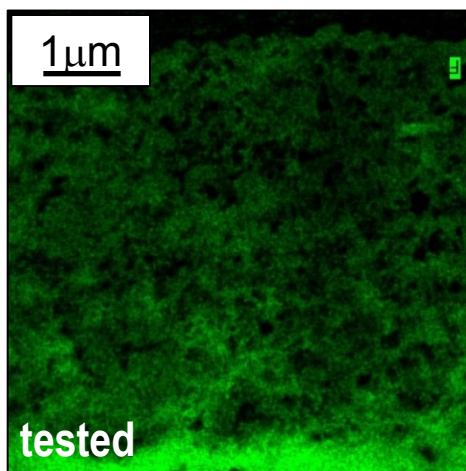
Pt/LSAC

Technical Accomplishment (FY13): Understanding Effect of Cathode Carbon Corrosion on MEA Performance
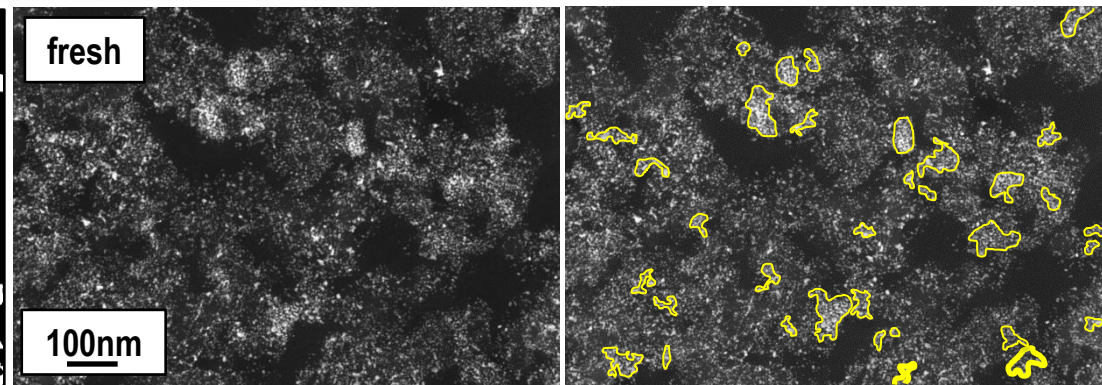
What if HSAC is replaced by Vulcan?
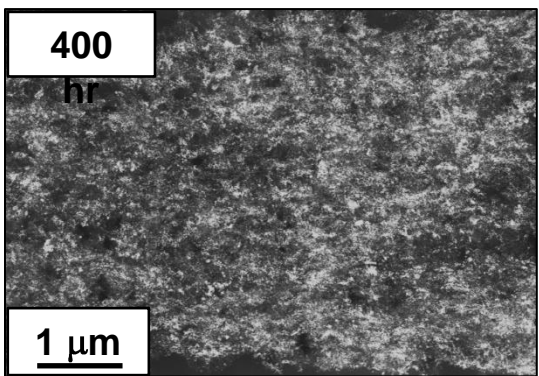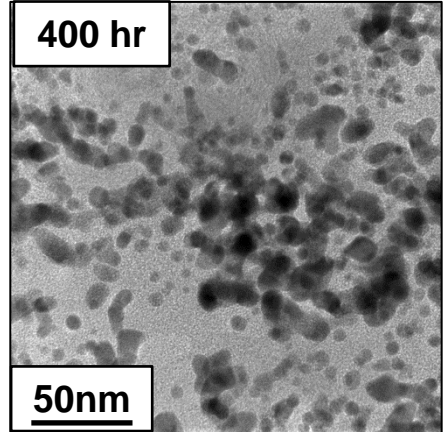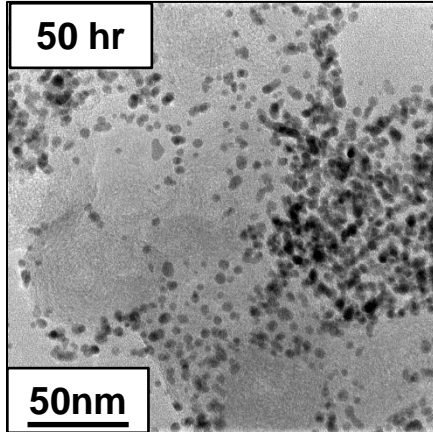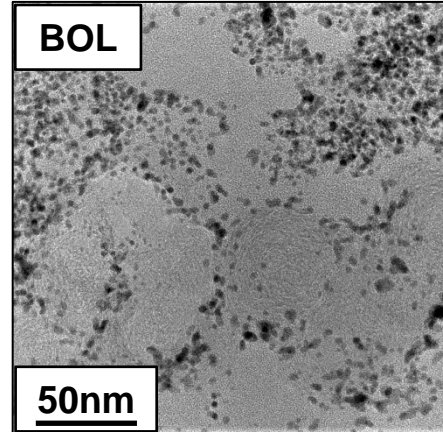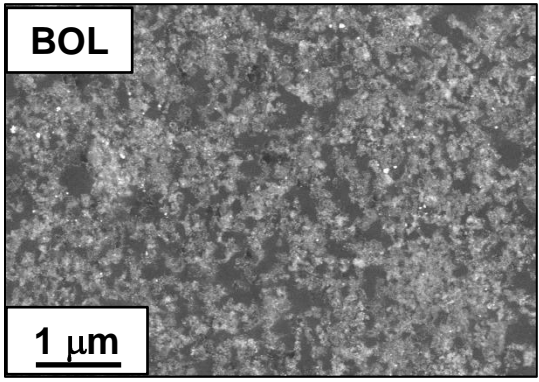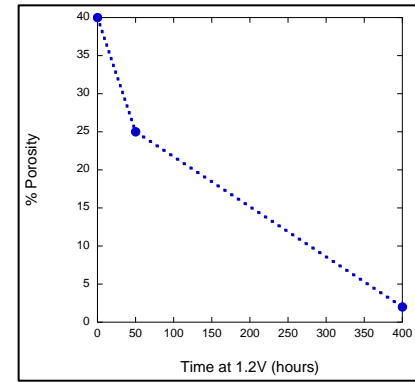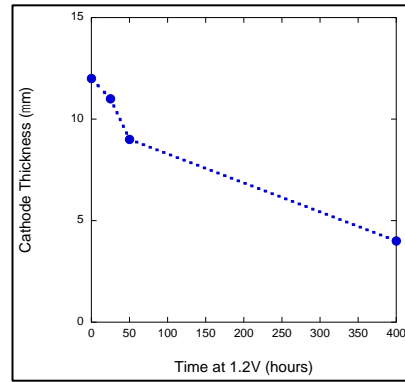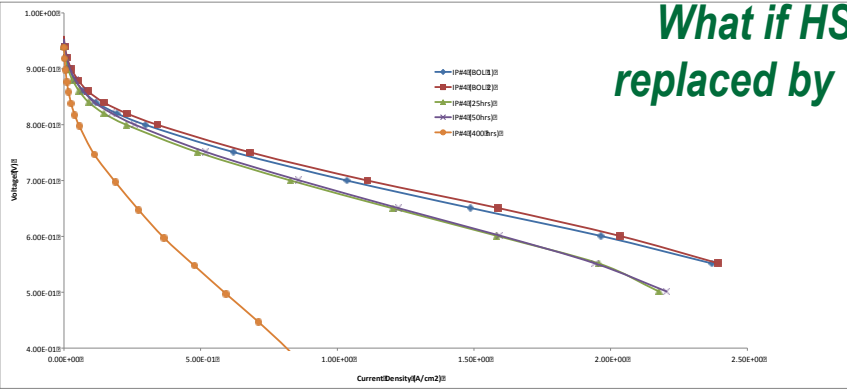
Thinned cathode exhibits a "clustered" morphology of large Pt particles associated with localized graphite-oxide formation
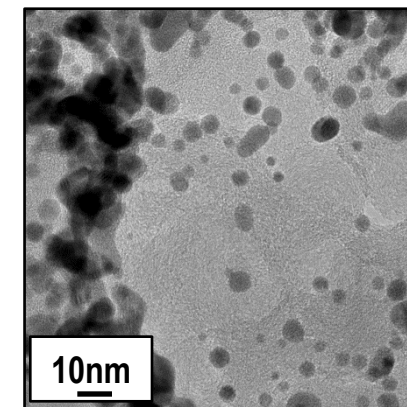
for the U.S. Department of Energy
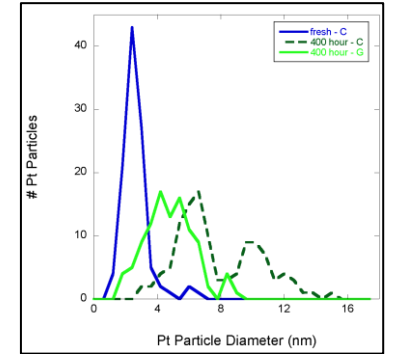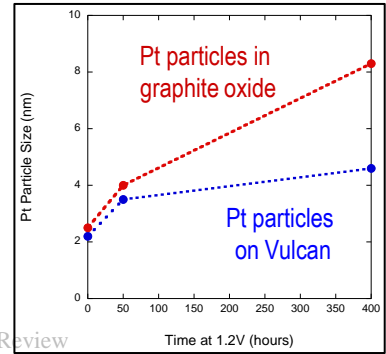
Technical Accomplishments and Progress: Mechanisms Contributing to Collapse of Cathode Layers
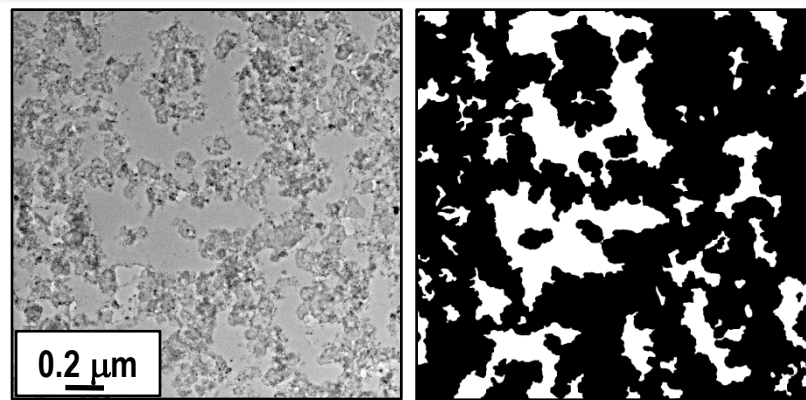
*2D image analysis to visualize and estimate pore volume*

0.2 μm

The same technique can be applied to capture localized regions of high Pt loading that act as "sites" for accelerated carbon corrosion

fresh

100nm

Localized accelerated carbon corrosion (and electrode collapse) can be attributed to initial Pt DISPERSION…

… loss of graphitic structure, support densification, and larger Pt sizes occur in regions of initially closely packed Pt.

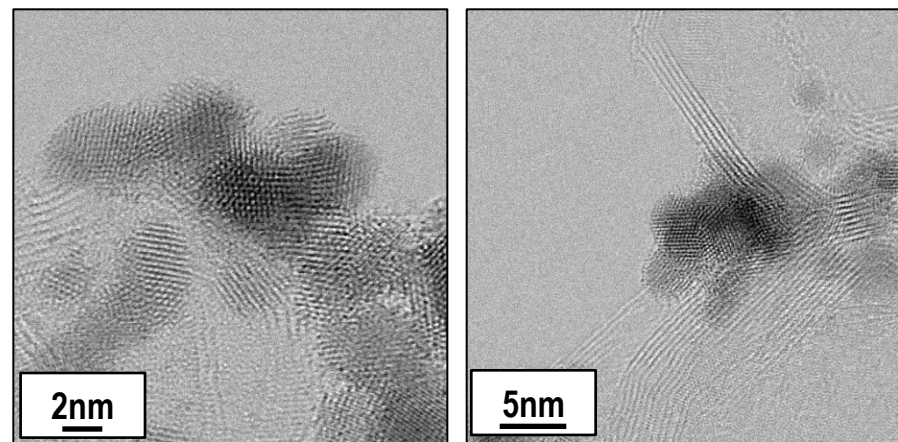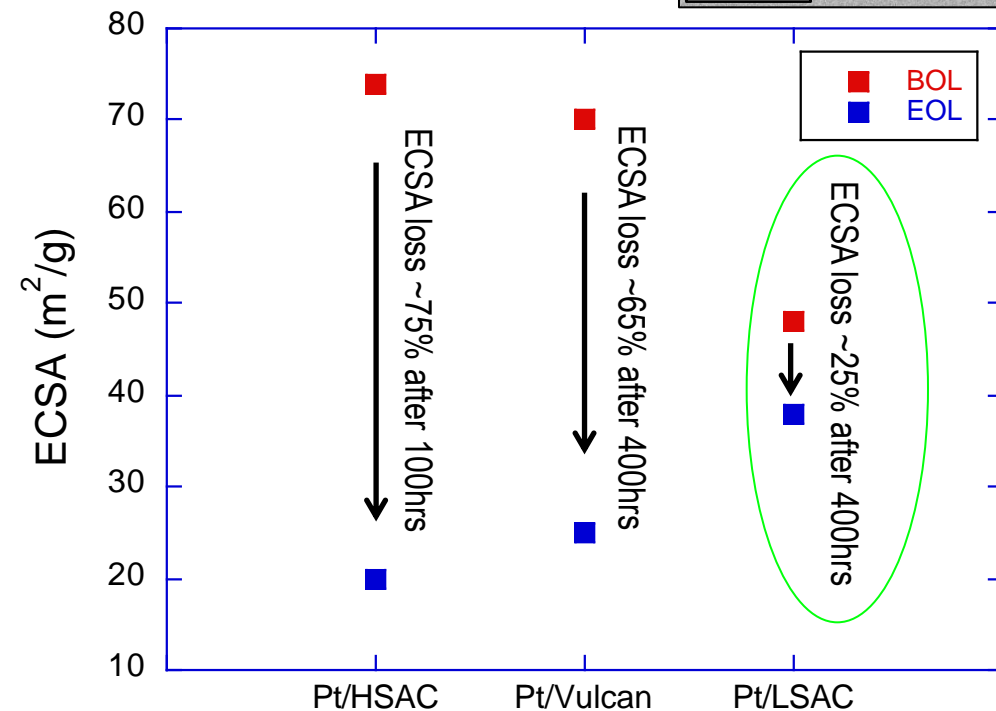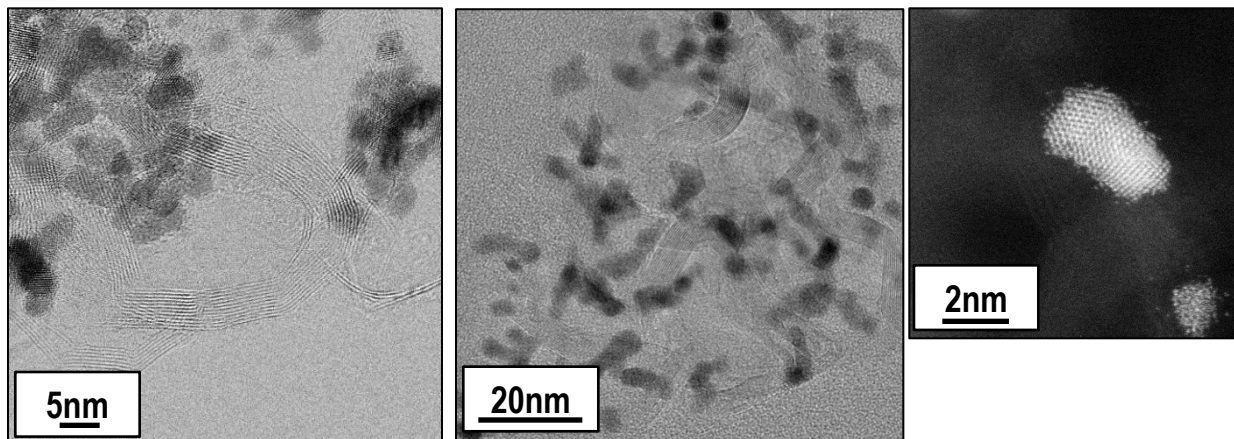10nm

5nm

400h @ 1.2V

100nm
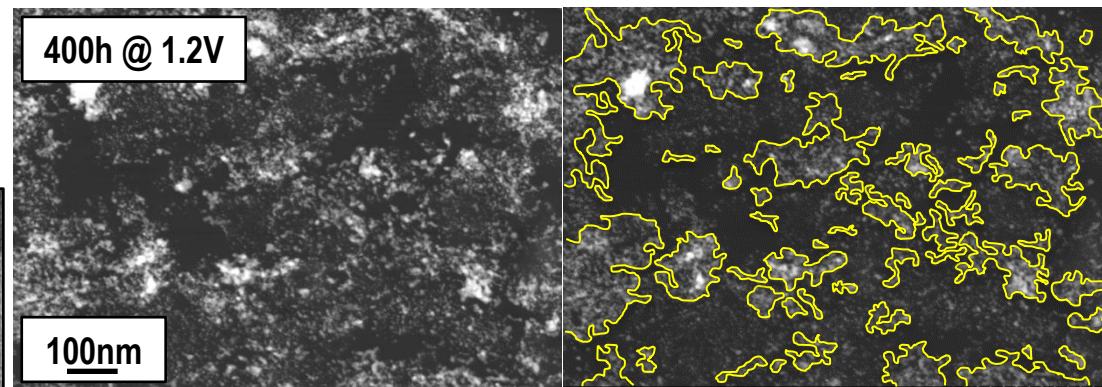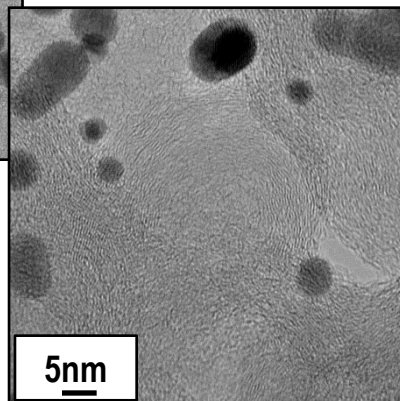
Pt/Vulcan – localized regions of high Pt loading corrode/densify faster than surrounding regions – associated with larger (encapsulated) Pt particle sizes, dense graphite oxide, loss of porosity, and embedded ionomer

Collapse/thinning/compression of cathode catalyst layer occurs via concurrent loss of ionomer network, localized densification and structural/chemical transformation of Vulcan support, and change in pore structure.

Technical Accomplishments and Progress: Pt Dispersion Effects

The primary reasons for the low initial ECSA of Pt/LSAC:

1. **poor Pt dispersion - Pt particles are "stacked-agglomerated" within corners and edges of the LSAC**
2. **Pt particle shape (2nm X 5nm)**

5nm

20nm

2nm

BOL
EOL

ECSA loss ~75% after 100hrs

ECSA loss ~65% after 400hrs

ECSA loss ~25% after 400hrs

ECSA (m²/g)

Pt/HSAC   Pt/Vulcan   Pt/LSAC

2nm

5nm

Poor Pt dispersion results in multiple Pt-Pt particle contacts and non-uniform interparticle spacings

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Technical Accomplishments and Progress: Pt Dispersion Effects
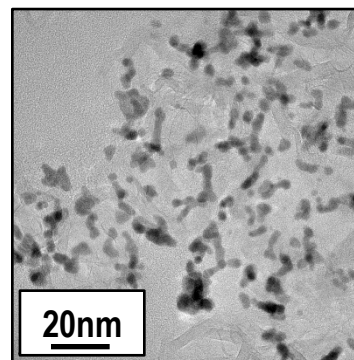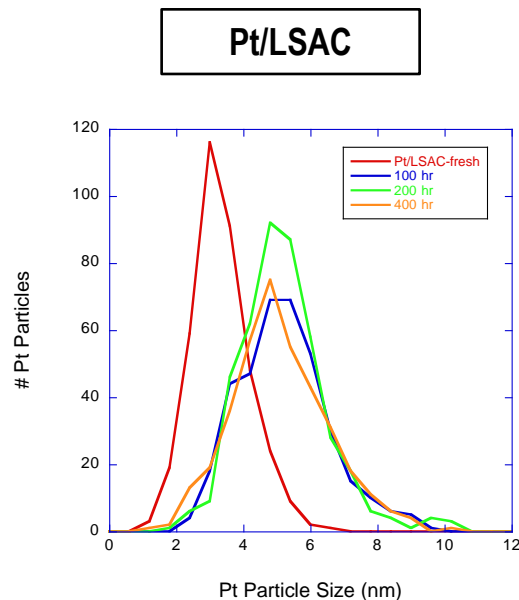
Pt coarsening during ASTs :

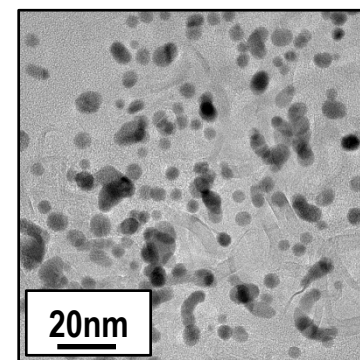1. **Carbon corrosion AST 400 hour hold @ 1.2V**

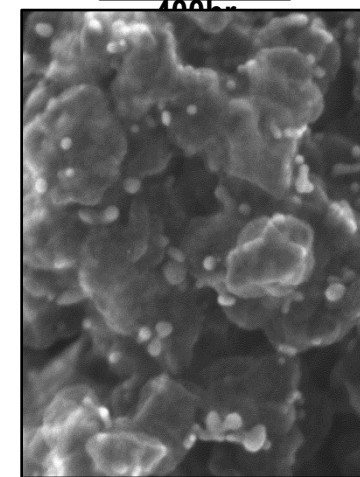   *3.0-to-5.2nm within first 100hrs with no further change*
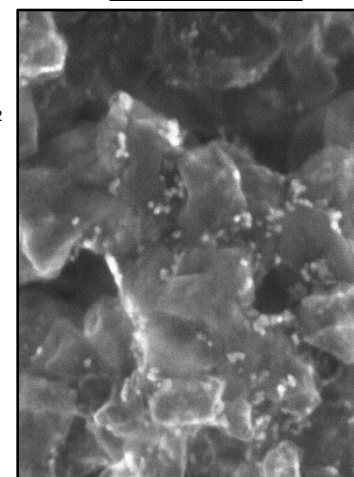
2. **Catalyst degradation AST 30,000 (0.6-1.0V) cycles**
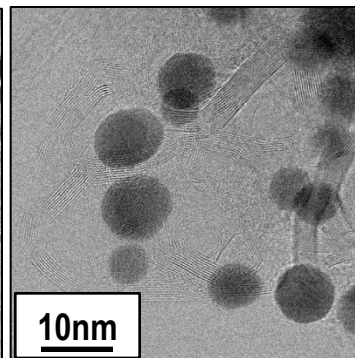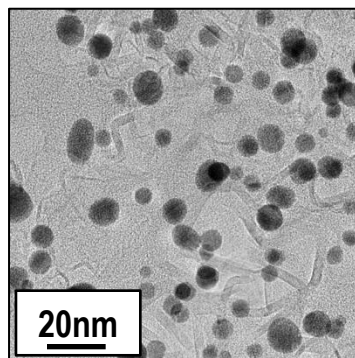
   3.0-to-7.0nm after 30,000 cycles
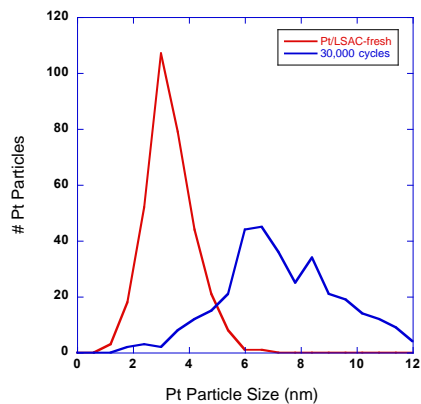

Pt/LSAC

20nm — BOL fresh

20nm — 1.2V-400hr

20nm

10nm

30,000 cycles

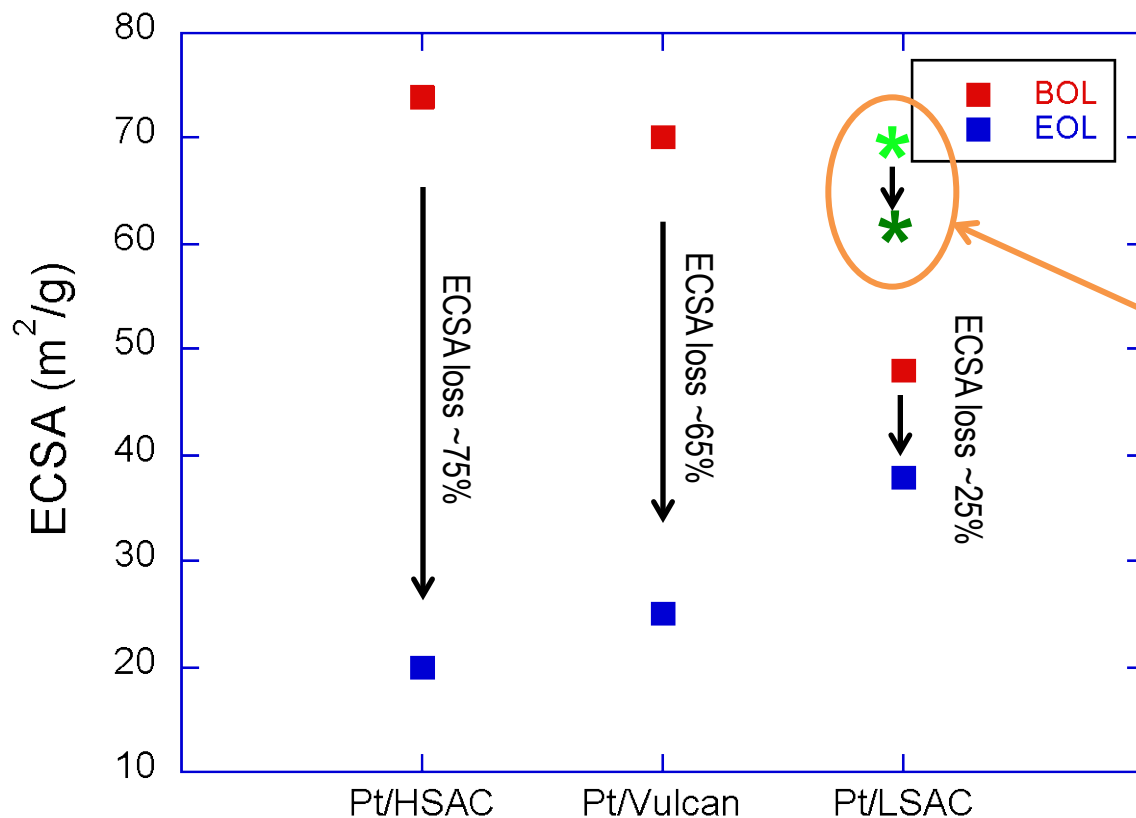*During both carbon and catalyst ASTs, Pt growth due to coalescence of closely spaced nanoparticles on LSAC*

Technical Accomplishments and Progress:
Pt Dispersion to Optimize Stability

Optimized Pt nanoparticle DISPERSION on LSAC combined with its enhanced corrosion resistance:


- *increase BOL-ECSA by uniformly dispersing Pt across ALL surfaces of LSAC support.*

- *more uniform Pt-Pt interparticle spacing will decrease Pt coalescence.*

- *additionally decrease ECSA loss through improved Pt anchoring on graphitized LSAC surfaces.*
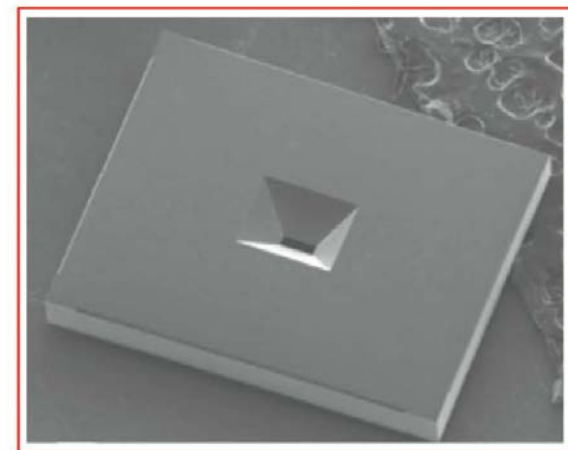
- *retain inherent corrosion resistance of graphitic carbon*

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Technical Accomplishments and Progress:
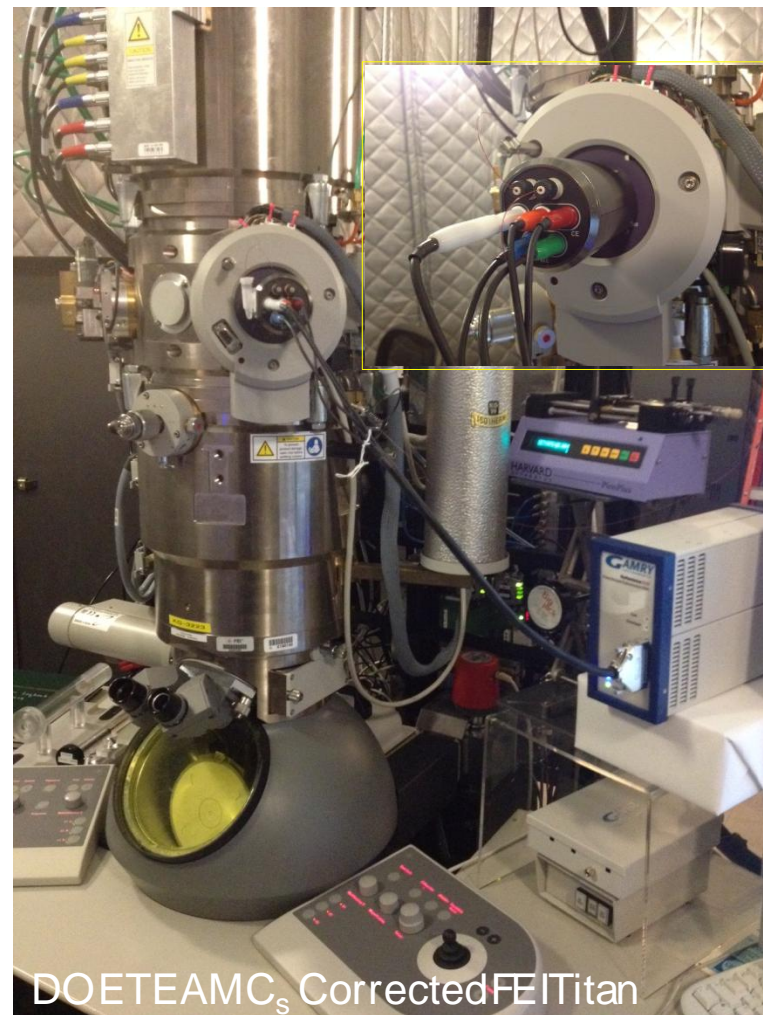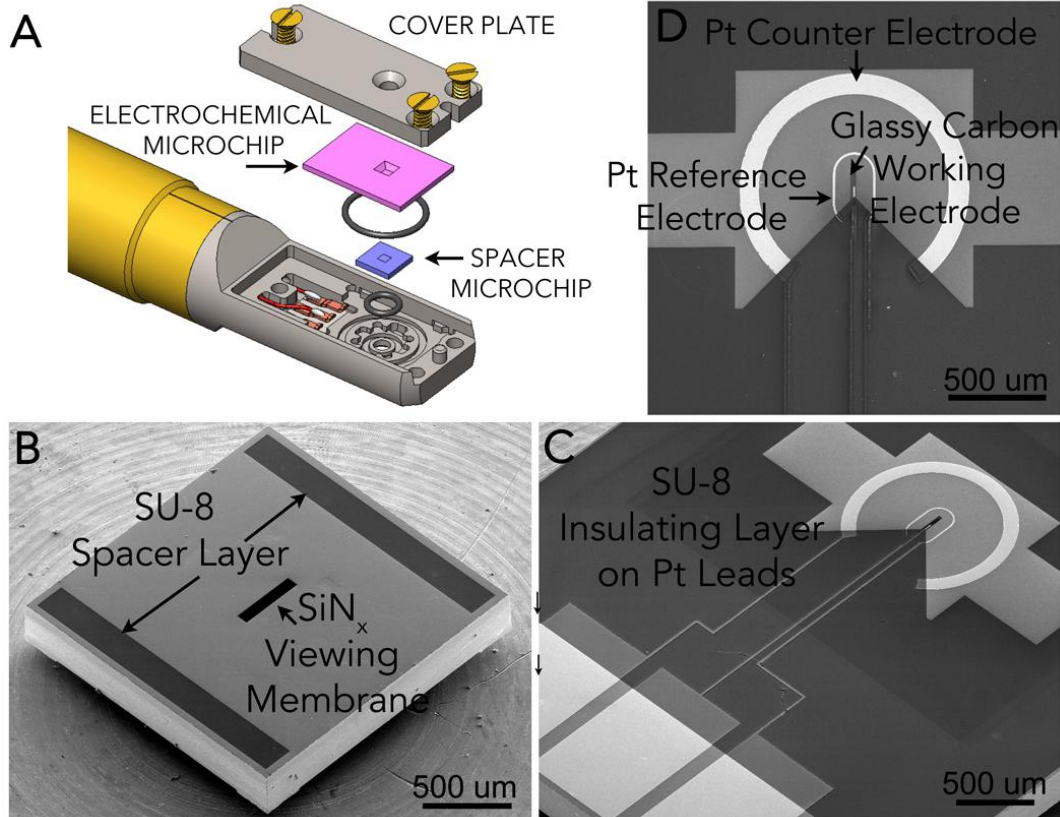# *In Situ* Electrochemical Microscopy (ec:S/TEM)
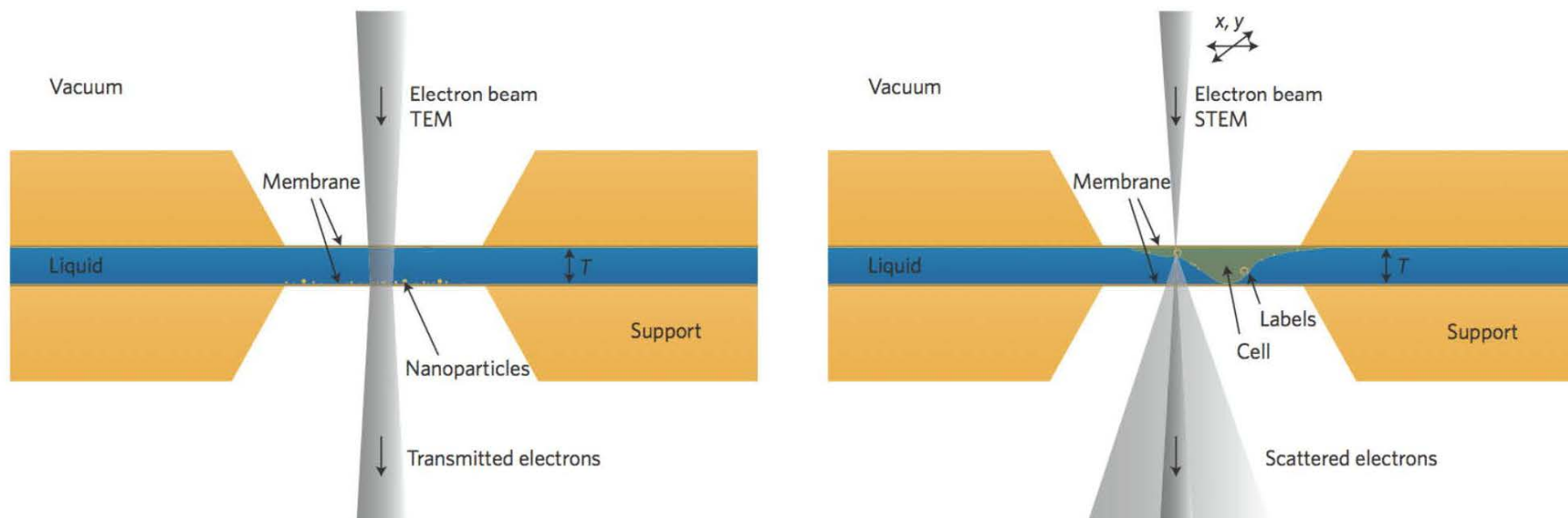
Biological materials (cells), nanocrystal nucleation & growth, particle interactions, fluid-solid interfaces, etc.
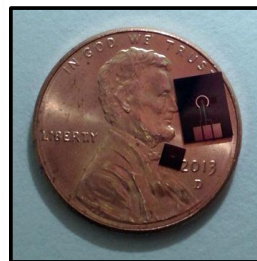
- H. Zheng, et al., *Science* **324** (2009)

- J.E. Evans et al., Nano Letters 11 (2011)

- N. De Jonge and F. Ross *Nature Nanotechnology* **6** (2012)

- H.-G. Liao and H. Zheng *JACS* **135** (2013)

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A COVER PLATE

ELECTROCHEMICAL MICROCHIP

SPACER MICROCHIP

D Pt Counter Electrode

Glassy Carbon Working Electrode

Pt Reference Electrode

500 um

B SU-8 Spacer Layer

SiN$_x$ Viewing Membrane

500 um

C SU-8 Insulating Layer on Pt Leads

500 um

DOE TEAM C$_s$ Corrected FEI Titan

Microfluidic electrochemical cell is sealed within the tip of a TEM holder and interfaced with an external potentiostat and fluid delivery system

Electrochemical characterization of baseline system: ferricyanide/ferrocyanide redox couple
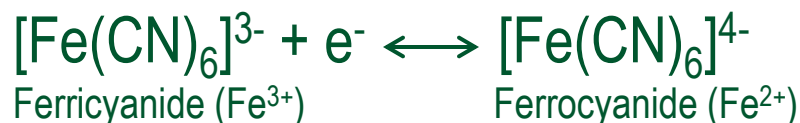
Aqueous Electrolyte Ingredients:
1M KCl – Supporting electrolyte
10mM NaCN – Inhibits analyte decomposition
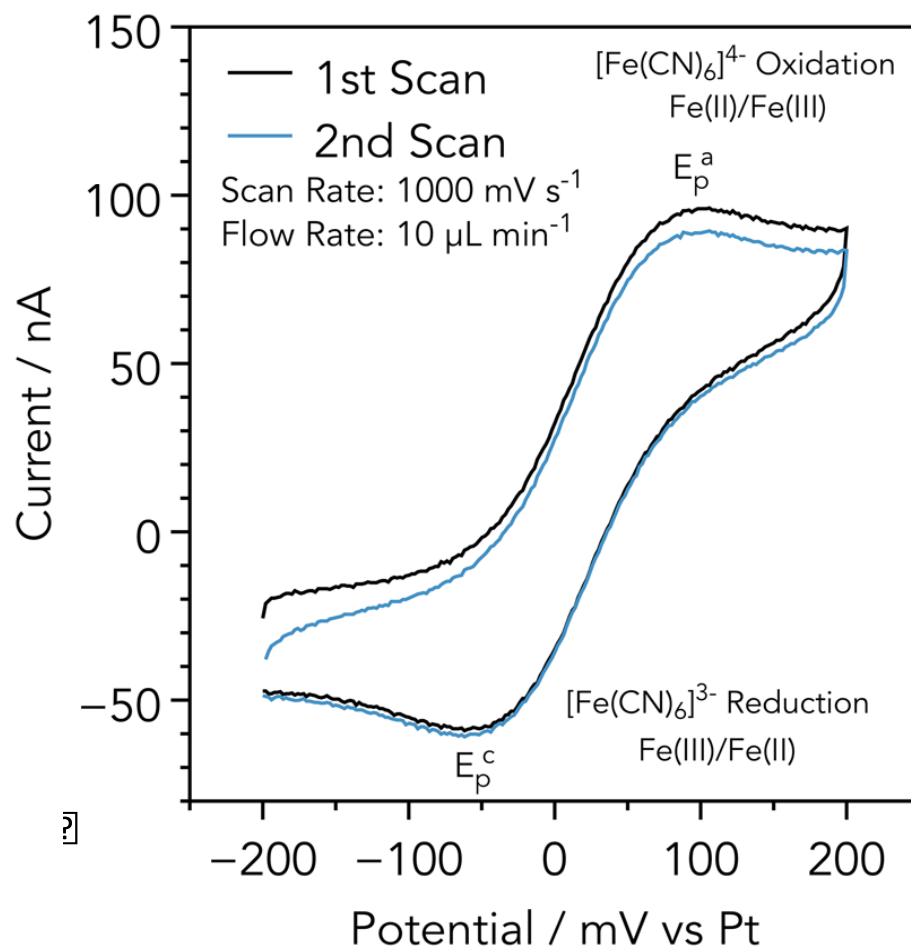and limits formation of Prussian Blue
2 mM $K_3Fe(CN)_6$
2 mM $K_4Fe(CN)_6$

$$[Fe(CN)_6]^{3-} + e^- \longleftrightarrow [Fe(CN)_6]^{4-}$$
Ferricyanide (Fe^{3+})   Ferrocyanide (Fe^{2+})

Cathodic and Anodic Peaks:
Increase in Faradaic current due to redox of
Ferri-Ferro cyanide and changes of the analyte
concentration at the electrode/electrolyte interface

R. Unocic et al., *Microscopy & Microanalysis*, in press (2014)

Technical Accomplishments and Progress:
In Situ Electrochemical Microscopy (ec:S/TEM)

0.5 μm

50 nm

20 nm

Pt/C –Glassy Carbon WE

SiN viewing window
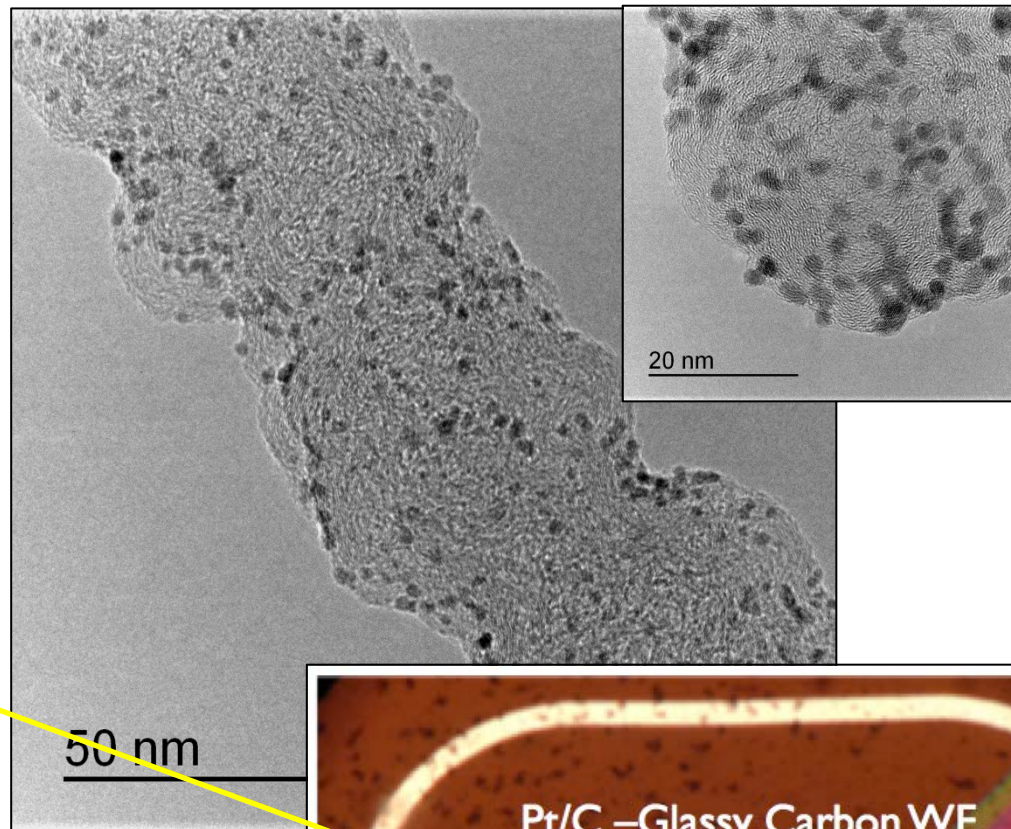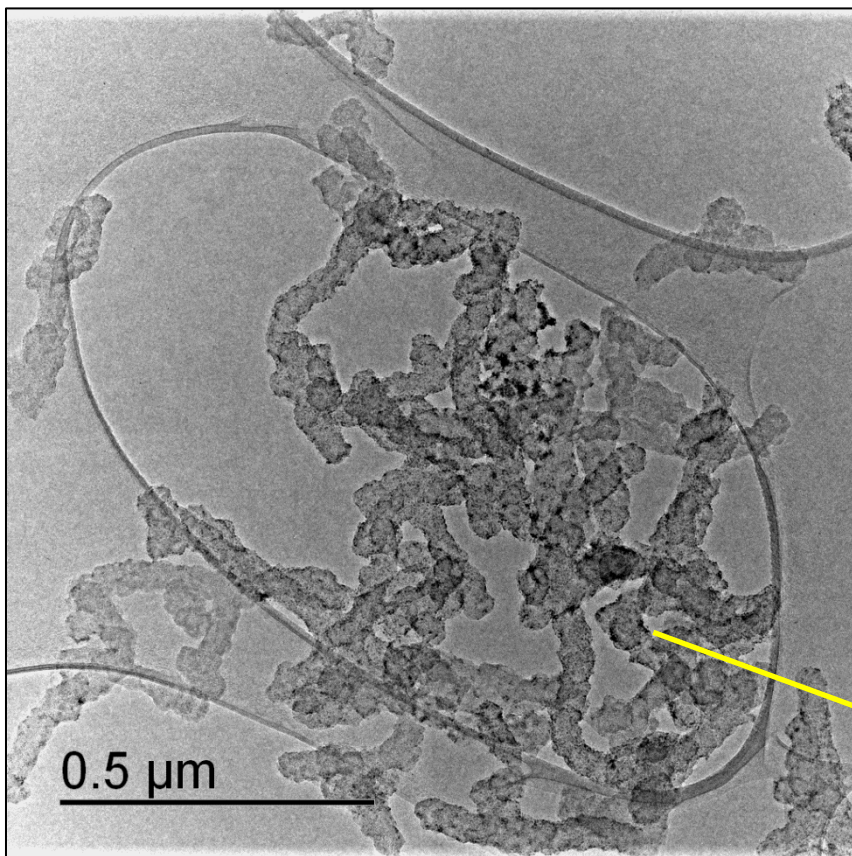
Pt supported on Pyrolyzed Polypyrrole (PPPy) nanowires (~13% Pt) used for catalyst coalescence study (materials prepared at LANL
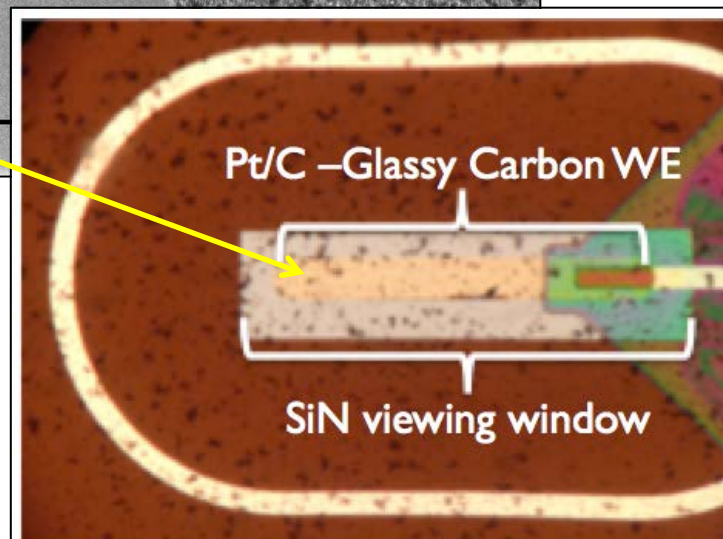
0.2 V
19 nA

0.2 µm

1.2 V
145 nA

0.2 µm
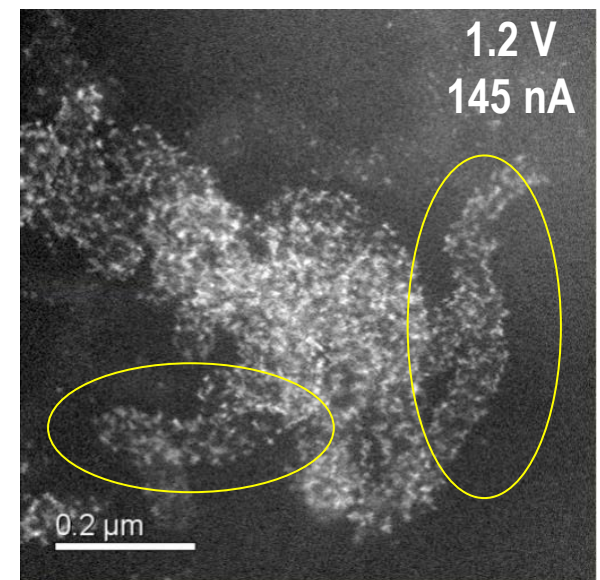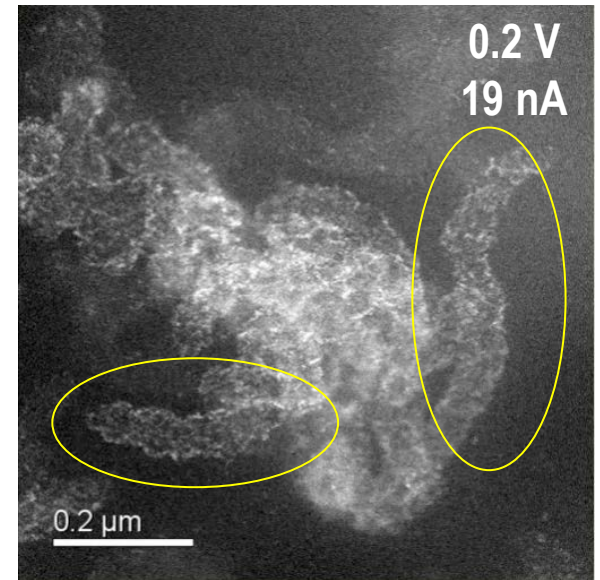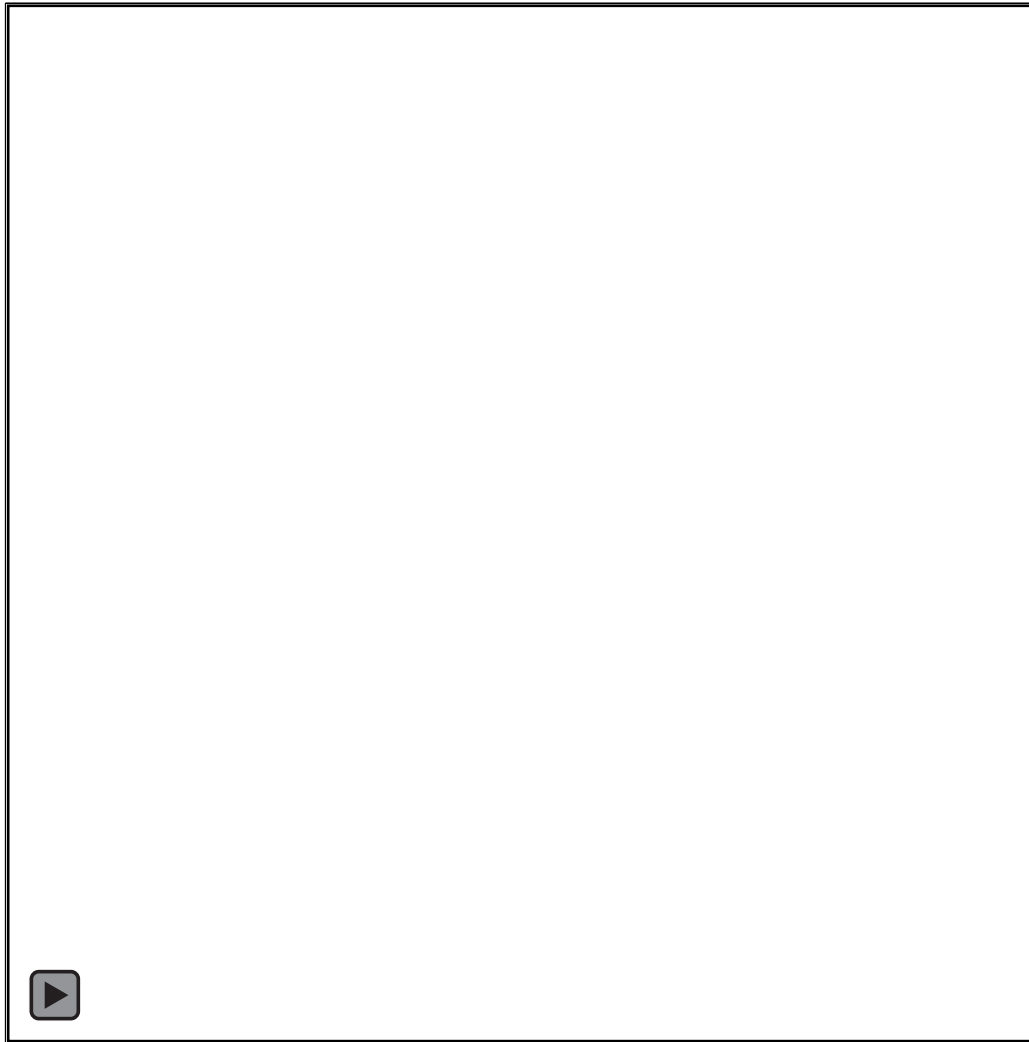
Dynamics of Pt Coalescence-CV

Future Work

- Combine ionomer imaging and microanalysis with modeling efforts to identify ionomer interactions with different carbon surfaces (this task has already been initiated).

- Now that proper imaging and analysis conditions for studying ionomer layers have been established, expand ionomer studies to specifically focus on aging effects as well as electrode/membrane interfaces.

- Perform dispersion optimization studies for Pt on LSAC

- Continue the development, optimization, and application of in-situ electrochemical TEM/STEM - correlate with bench-scale (RDE) catalyst testing and apply to other fuel cell material components (e.g., Pt on other supports, nucleation & growth studies, include ionomer layers etc.)

- Continue to establish collaborations with industry, academia, and national laboratories (including access via ORNL User Facilities) to facilitate "transfer" of unique capabilities.

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Project Summary

Relevance: ORNL's microscopy expertise and state-of-the-art capabilities are integral to identifying materials degradation mechanisms, which are critical for improving materials structure for 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 optimizing imaging and analysis parameters for characterizing ionomer thin films, worked with many partners to characterize new fuel cell materials, and continued the development of in-situ capabilities. We continue to support the FC community with unique capabilities for microscopic 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, and to combine microanalysis and theory to determine the atomic-scale interactions between ionomer films and support and/or nanoparticle surfaces.

2014 DOE Annual Merit Review

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Technical Back-up Slides
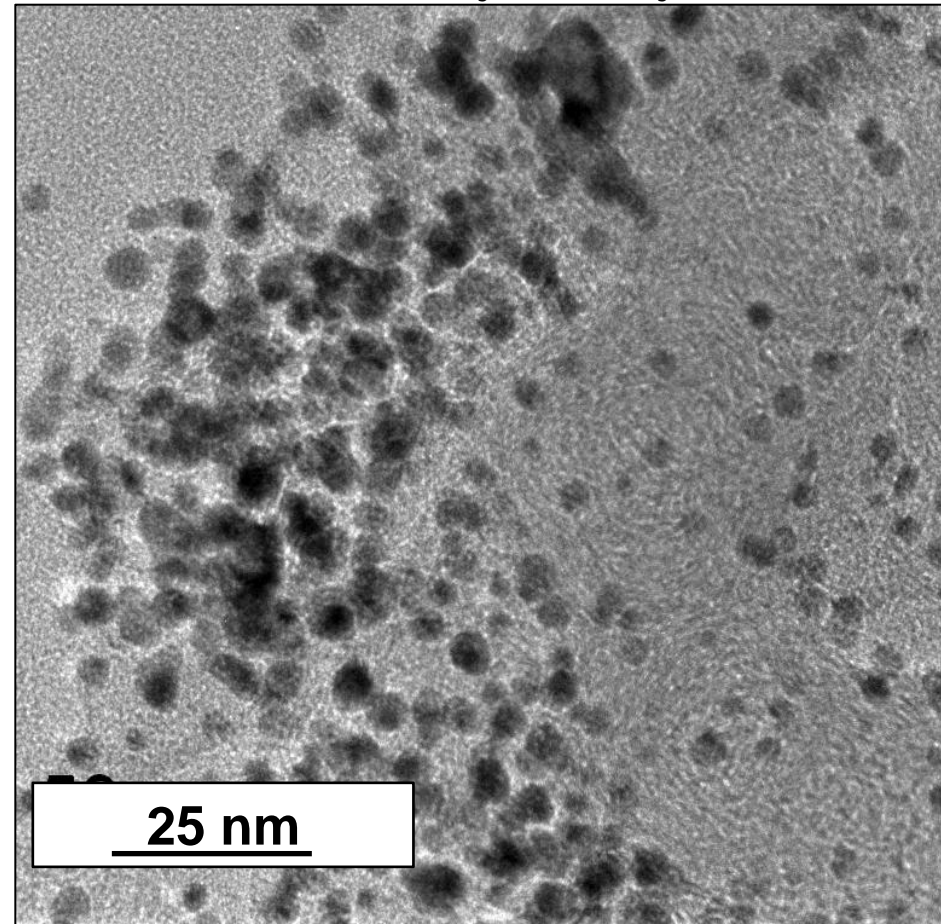
2014 DOE Annual Merit Review

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
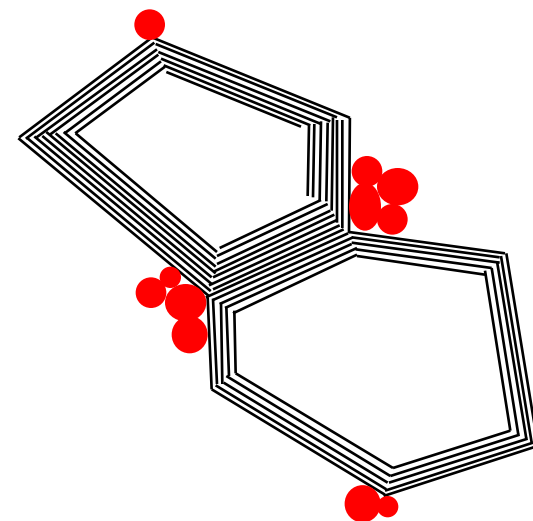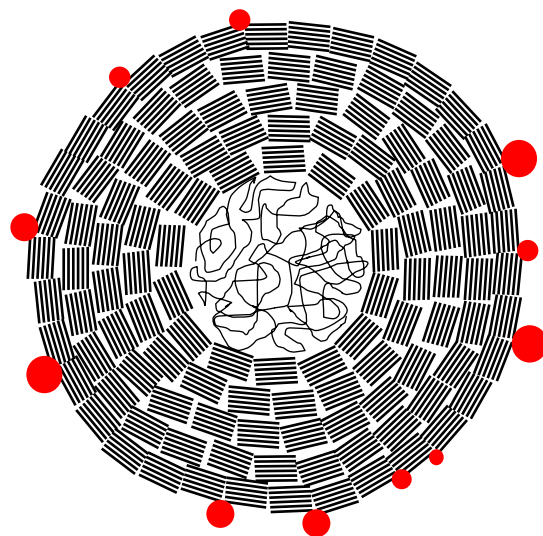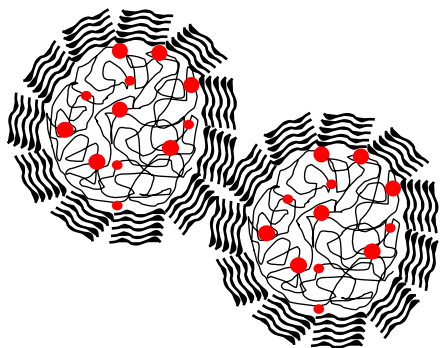
1224 hr "wet" drive cycle
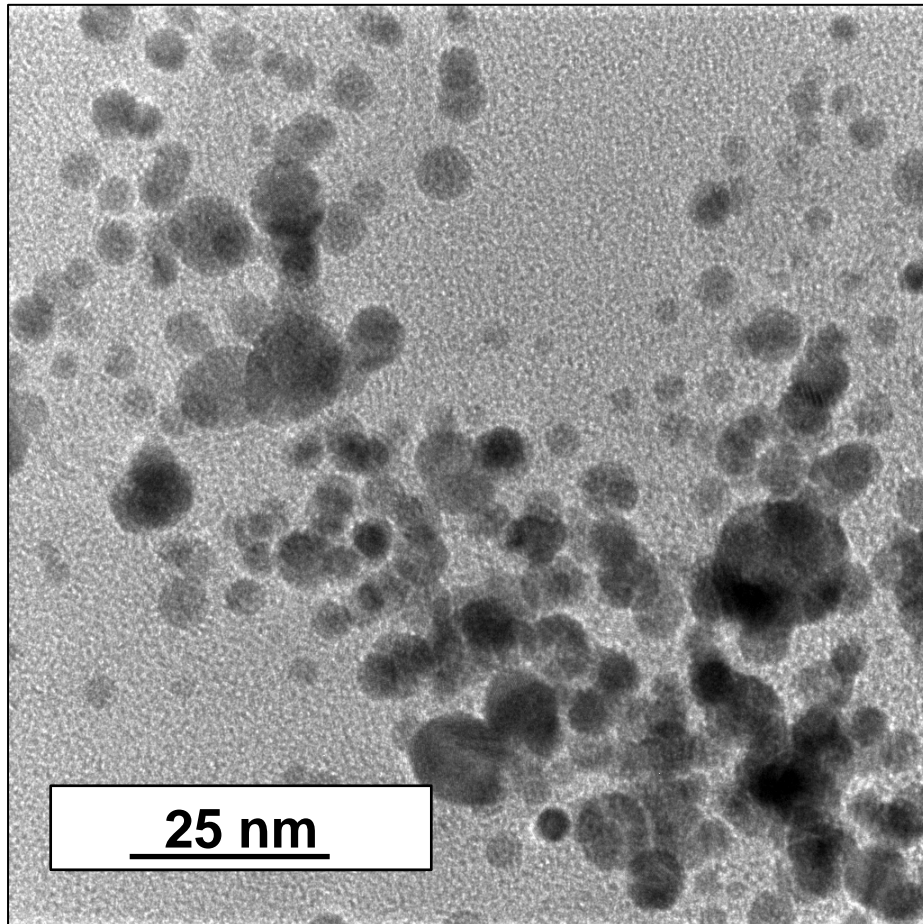
389 hr "wet/dry" drive cycle

25 nm

25 nm

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

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