

Characterization of Fuel Cell Materials

Project ID FC020

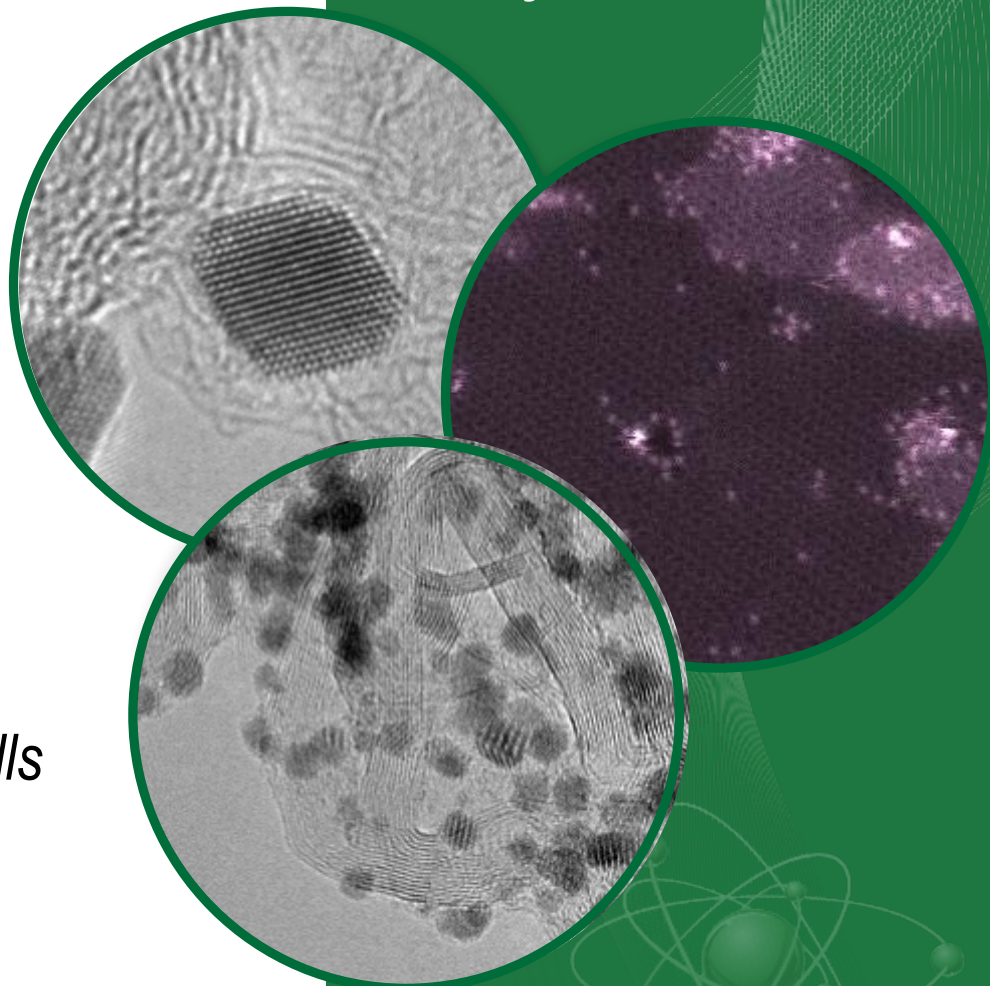
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*2015 DOE Hydrogen and Fuel Cells
Program Annual Merit Review
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Project Overview

Timeline

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

Budget

- Funding in FY14 - \$600k (~1.3 FTE)
- Funding in FY15 - \$600k (~1.3 FTE)

Barriers

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

Partners/Collaborators

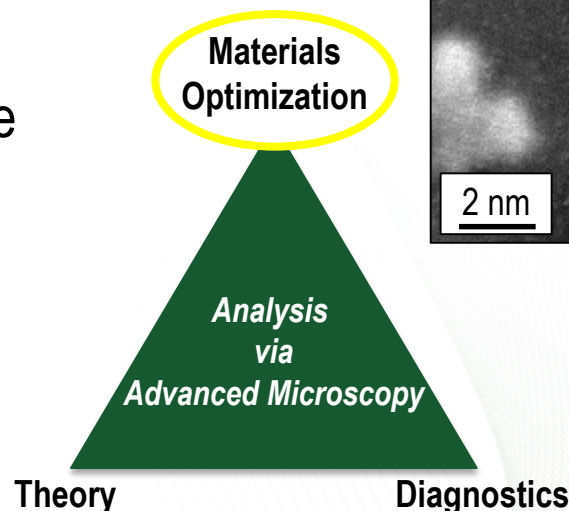
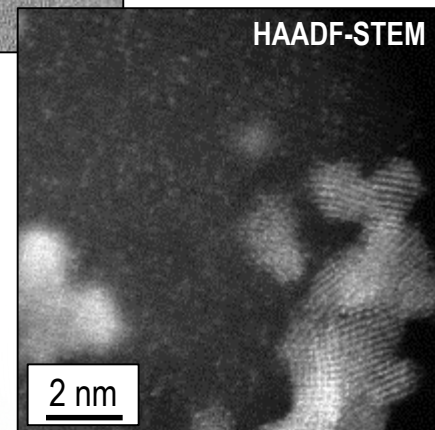
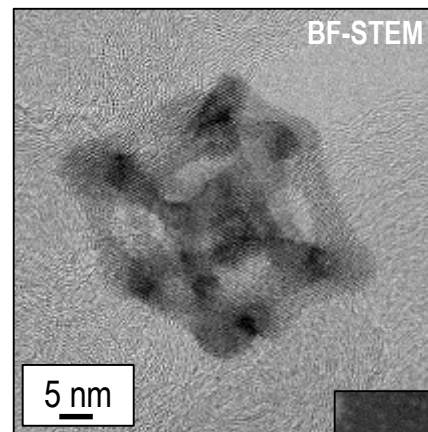
- Los Alamos National Laboratory
- Argonne National Laboratory
- Lawrence Berkeley National Laboratory
- General Motors
- Ford Motor Co.
- Giner Inc.
- Ballard
- Nissan Technical Center North America
- 3M Co.
- Naval Research Laboratory
- Pajarito Powders
- University of Tennessee
- Vanderbilt University
- CEA-Grenoble, France
- University of Connecticut
- McMaster University, Canada
- *Funded DOE collaborations (project extensions) with LANL and ANL - results NOT presented.*

Relevance – ORNL's Research Objectives

- Identify, develop, and optimize novel high-resolution imaging and compositional/chemical analysis techniques, and unique specimen preparation methodologies, for the μm -to- \AA scale characterization of materials comprising fuel cell MEAs (catalyst, support, ionomer, membrane)
- Understand fundamental relationships between MEA material constituents and correlate these data with stability and performance as per guidance/input from the broad 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
- CAPABILITIES AND EXPERTISE ARE AVAILABLE TO FUEL CELL RESEARCHERS OUTSIDE OF ORNL

Approach: Use Advanced Microscopy to Investigate Structure and Composition of Fuel Cell Materials

- Develop and apply state-of-the-art electron microscopy techniques to characterize MEA material constituents → μm - to sub- \AA -scale:
 - Catalyst nanoparticles and NSTF catalysts – composition, chemistry, size, and morphology
 - Re-cast ionomer within catalyst layers
 - Catalyst support materials
- Collaborate with industry, academia, and national laboratories → capabilities and microscopy expertise are available to correlate structure/composition with MEA processing and/or life-testing studies
- Understand materials degradation mechanisms → materials optimization to meet DOE targets



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

component durability

- LANL (sub on extension) – Durability Improvements through Degradation Studies
- LANL – Accelerated Stress Testing (AST) Validation
- Nissan TCNA – Catalyst support durability
- Fuel Cell Energy & University of Connecticut – novel membrane architectures and MEAs
- ANL – MEAs with novel alloy catalysts (e.g., nanoframe catalysts)

novel catalysts and supports

- LANL (sub) – Non-PGM Fuel Cell Cathodes: Catalyst Development and Electrode Structure Design
- 3M – NSTF alloy cathode catalysts
- Vanderbilt University – Pt/carbon-nanofiber supports
- Ford Motor Co. – novel carbon supports and catalyst characterization
- Giner Inc. – characterization of OER catalysts
- Naval Research Laboratory – catalyst support modifications
- Pajarito Powders – Non-PGM catalyst characterization after scale-up
- University of TN – parametric study of Pt/LSAC supports
- ANL (sub on extension) – Nanosegregated Cathode Catalysts with Ultra-low Pt Loadings
- 3M (sub) – High-Performance, Durable, Low Cost MEAs for Transportation Applications

ionomer studies

- GM – quantification of ionomer distribution(s) within electrodes
- Ballard – ionomer distributions as a function of carbon support type and Pt loading
- CEA-Grenoble – tomography studies of ionomer distributions within catalyst layers
- McMaster University – STXM characterization of ionomer distributions in catalyst layers

Approach: Project Milestones – FY14 and FY15

● FY14 Milestones:

- ✧ Initiate new collaboration with an industrial partner to characterize new catalyst and/or catalyst supports. *Completed*
- ✧ Complete parametric study of ionomer thin films with GM and collaboratively publish results. Establish baseline conditions to quantitatively assess ionomer 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. *Completed*
- ✧ Report tomography characterization results to study NSTF catalyst degradation during MEA aging. *Completed*

● FY15 Milestones:

- ✧ Complete study of ionomer dispersions on different carbon surfaces, before and after electrochemical aging – to include molecular dynamics simulations and experimental observations through high-resolution EDS mapping and STXM. Report results. *Completed*
- ✧ Publish results from study of carbon corrosion of supports having varying degrees of graphitization, which will include both experimental and theoretical results. *In Progress*
- ✧ Assess hetero-atom doping of graphitized carbon supports (N and/or B) through extensive characterization via STEM-EELS. Assess effects of doping on catalyst nanoparticle dispersions; incorporate most promising Pt/C into MEA and test in a fuel cell. Report results. *In Progress*
- ✧ Initiate at least two new collaborations with industry during FY15 to characterize fuel cell catalyst layer material components (electrocatalyst, support, ionomer).

Technical Accomplishments and Progress: Responses to 2014 Year Reviewer Comments

- *FY14 Reviewer Comment:* The PI collaborates with key original equipment manufacturers (OEMs) and academia. There is no need for more partners to ensure the quality of work/ progress, etc. *The PI should be open to providing other OEMs with her tools as needed.*
 - *FY15 response:* ALL the OEMs can work with ORNL by contacting the PI or co-PI. As evidenced by the large number of partners, new collaborations are relatively straightforward to establish and encouraged by DOE.
- *FY14 Reviewer Comment:* Because the analysis technique is now mastered, studies on ionomer degradation should go on (e.g., with evolution of ionomer profile and distribution around C). The current studies do not answer the question of how ionomer degrades if it degrades.
 - *FY15 response:* We have made significant progress in characterizing ionomer distributions as a function of aging, which will be presented.
- *FY15 FC Tech Team Recommendation:* Characterize other non-PGM catalysts.
 - *FY15 response:* We are currently working to include new non-PGM partners such that novel ORNL imaging/spectroscopy techniques are available.

Technical Accomplishments and Progress: **Work Focused on Topics Prioritized by FC Community** **(Collaborators, FY15 Tech Team, and FY14 AMR Reviews)**

Past AMR presentations have highlighted ORNL research specific to:

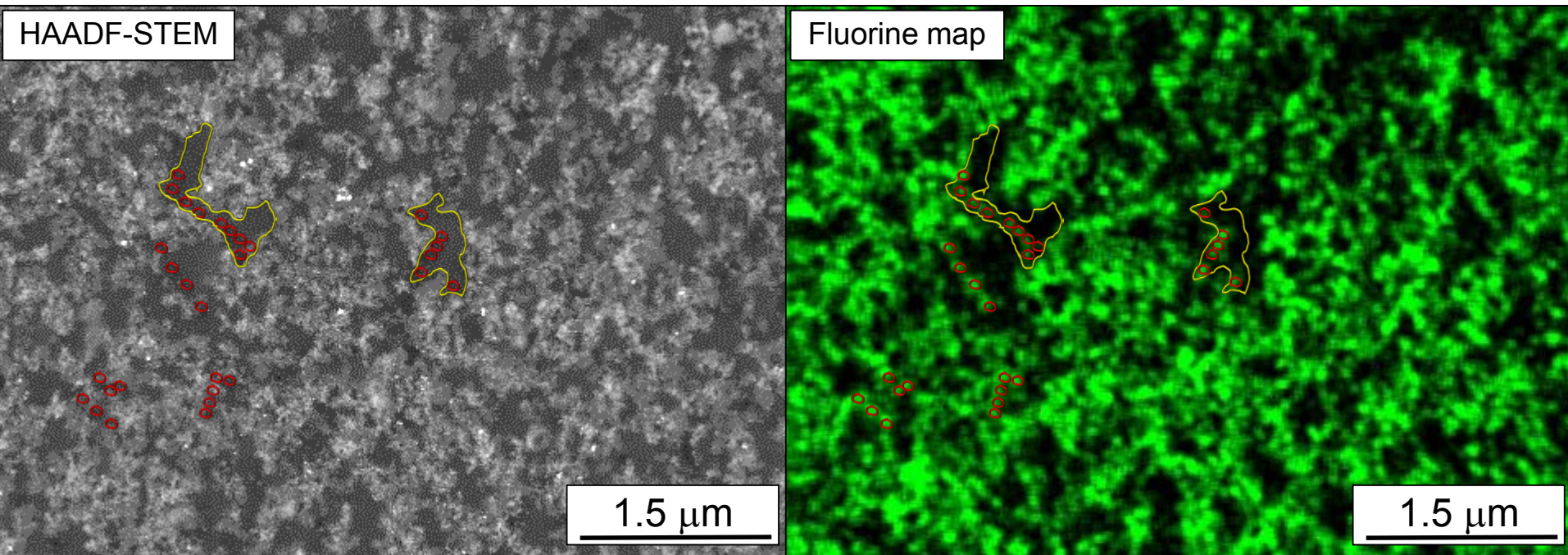
- Sub-Å-scale alloy catalyst nanoparticle characterization
- Established “best practices” for electron microscopy (EM) of ionomer layers in CL
- Elucidating carbon corrosion mechanisms
- Pt dissolution/migration and coarsening studies


Continued to focus resources on these topics, especially with partners, but relevant studies during FY14 have included:

- Quantification of ionomer dispersions for MEAs as a function of materials used and after aging
- Electron tomography

Technical Accomplishments and Progress: Understanding ionomer dispersions in catalyst layers (CLs)

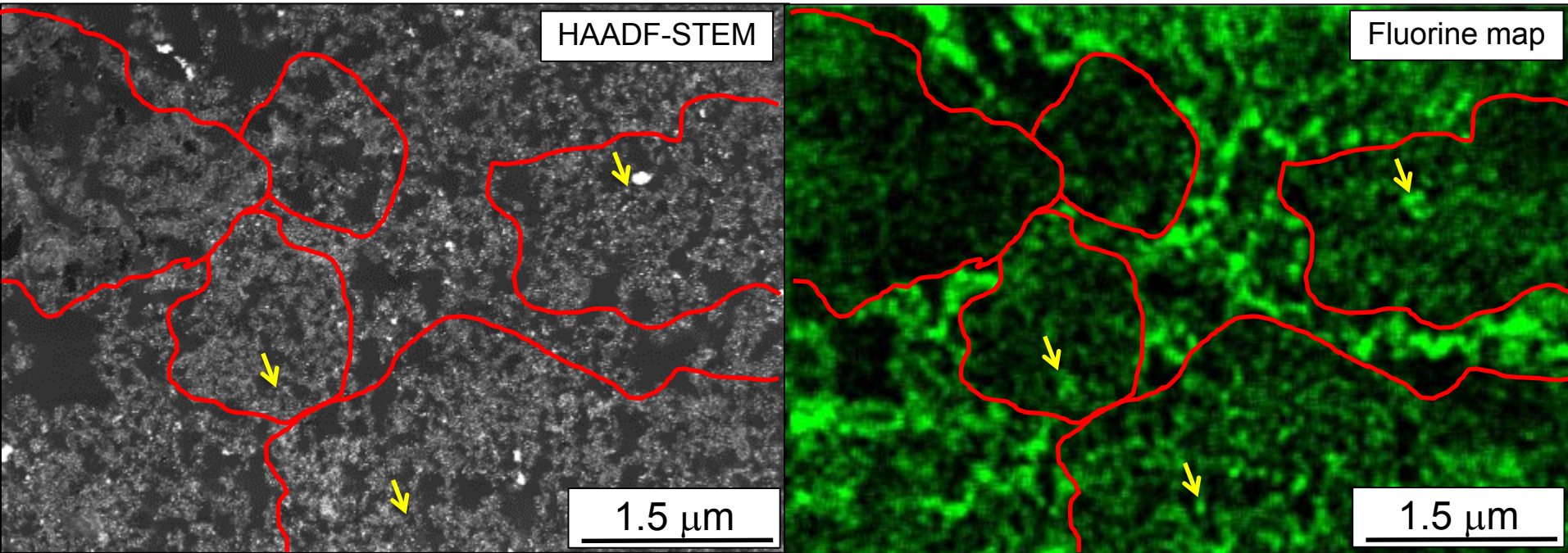
High-spatial-resolution STEM-EDS maps acquired from CL - Pt/HSAC+23% Nafion[®] ionomer



- Ionomer (shown by ) forms a discontinuous “linked chain of aggregates” on surfaces of HSAC particles exposed in secondary pores (several pores are outlined in yellow) - ionomer fills pores <70nm
- Ionomer aggregates are extremely uniform in size ~70nm diameter, which corresponds with the median secondary pore diameter
- Distribution through catalyst layer thickness is very uniform.

Technical Accomplishments and Progress: Understanding ionomer dispersions in catalyst layers (CLs)

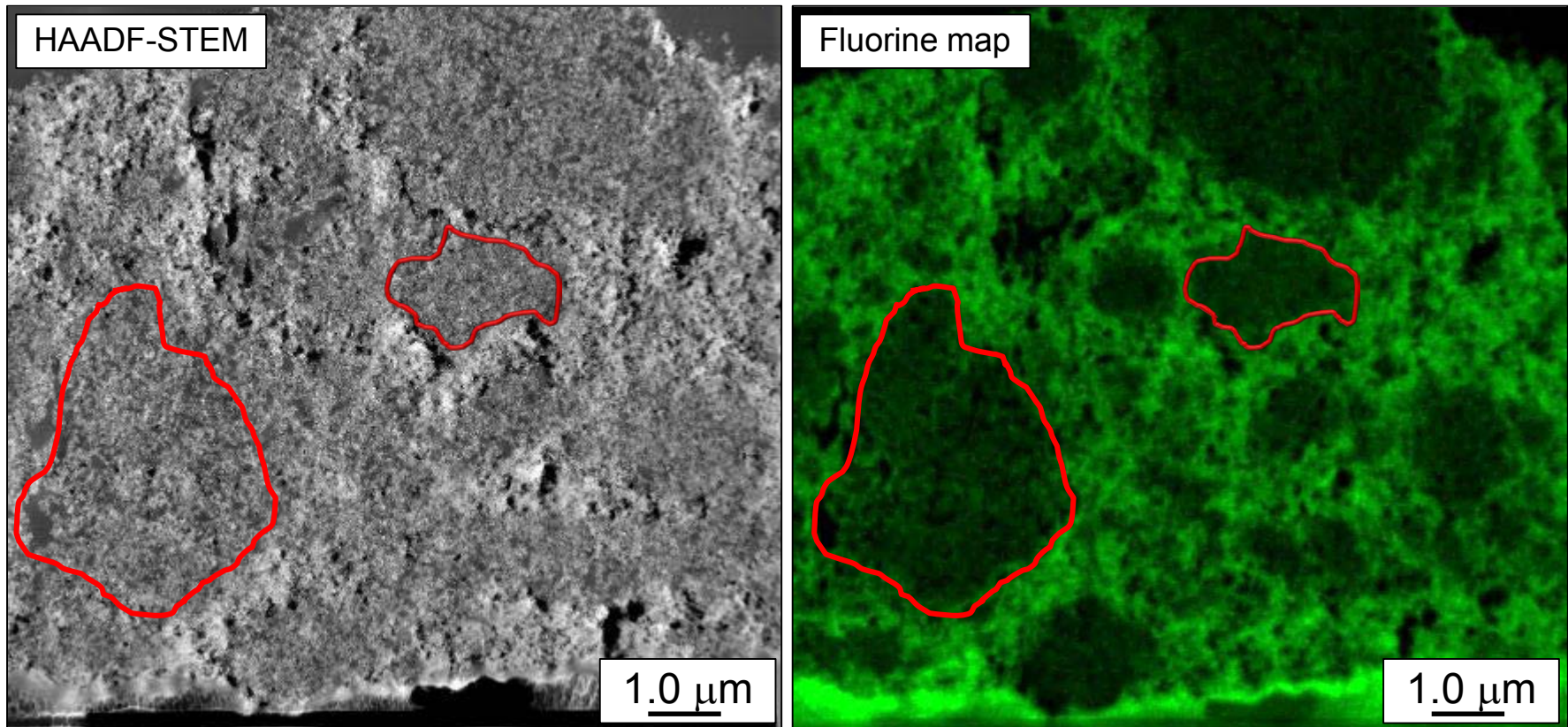
High-spatial-resolution STEM-EDS maps acquired from CLs - Pt/LSAC+23% Nafion® ionomer



- Ionomer disperses as discontinuous, thicker “glue” layers of aggregates between Pt/LSAC agglomerates (outlined in red) and on surfaces of secondary pores
- Ionomer aggregates (~70nm) similar to ionomer + Pt/HSAC, but aggregates are more clustered between Pt/LSAC agglomerates
 - Within Pt/LSAC agglomerates (outlined in red) ionomer is dispersed as smaller aggregates or thinner ionomer layers (10-30nm) surrounding Pt/LSAC particles with ionomer fill-in of some primary pores (sizes <70nm –yellow arrows)
- Ionomer distribution across CL conforms around Pt/LSAC agglomerates.

Technical Accomplishments and Progress: Understanding ionomer dispersions in catalyst layers (CLs)

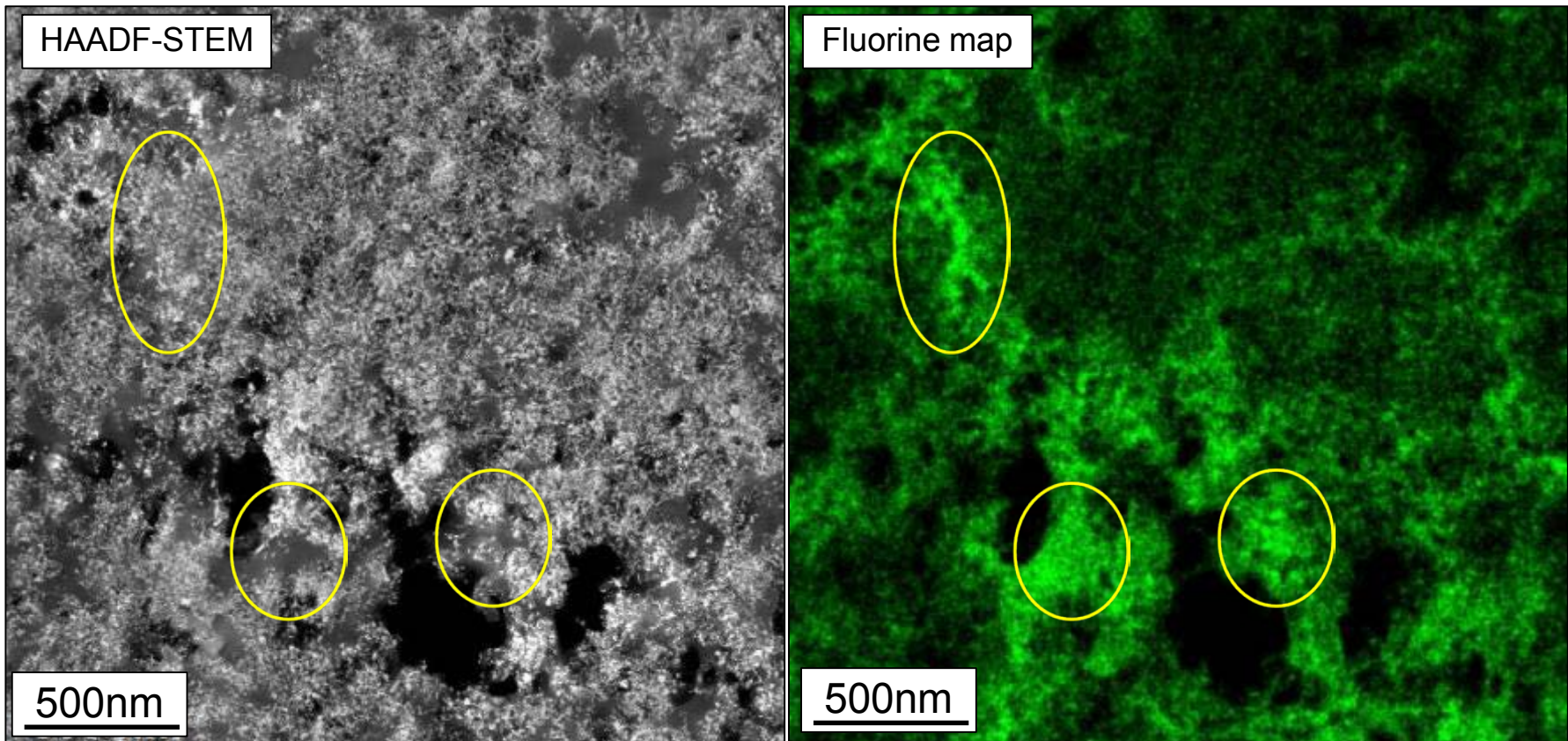
Increasing ionomer content in CL - Pt/LSAC+38% Nafion® ionomer



- The thicker ionomer regions between Pt/LSAC agglomerates becomes more evident as the amount of ionomer is increased in the CL (from ~23% to ~38%) – thickness of ionomer-rich regions clearly increase.
- Ionomer dispersion within Pt/LSAC agglomerates (outlined in red) - thin ionomer films (20-30nm thick) surround individual Pt/LSAC particles
- Distribution through catalyst layer thickness conforms to Pt/LSAC agglomerate size.

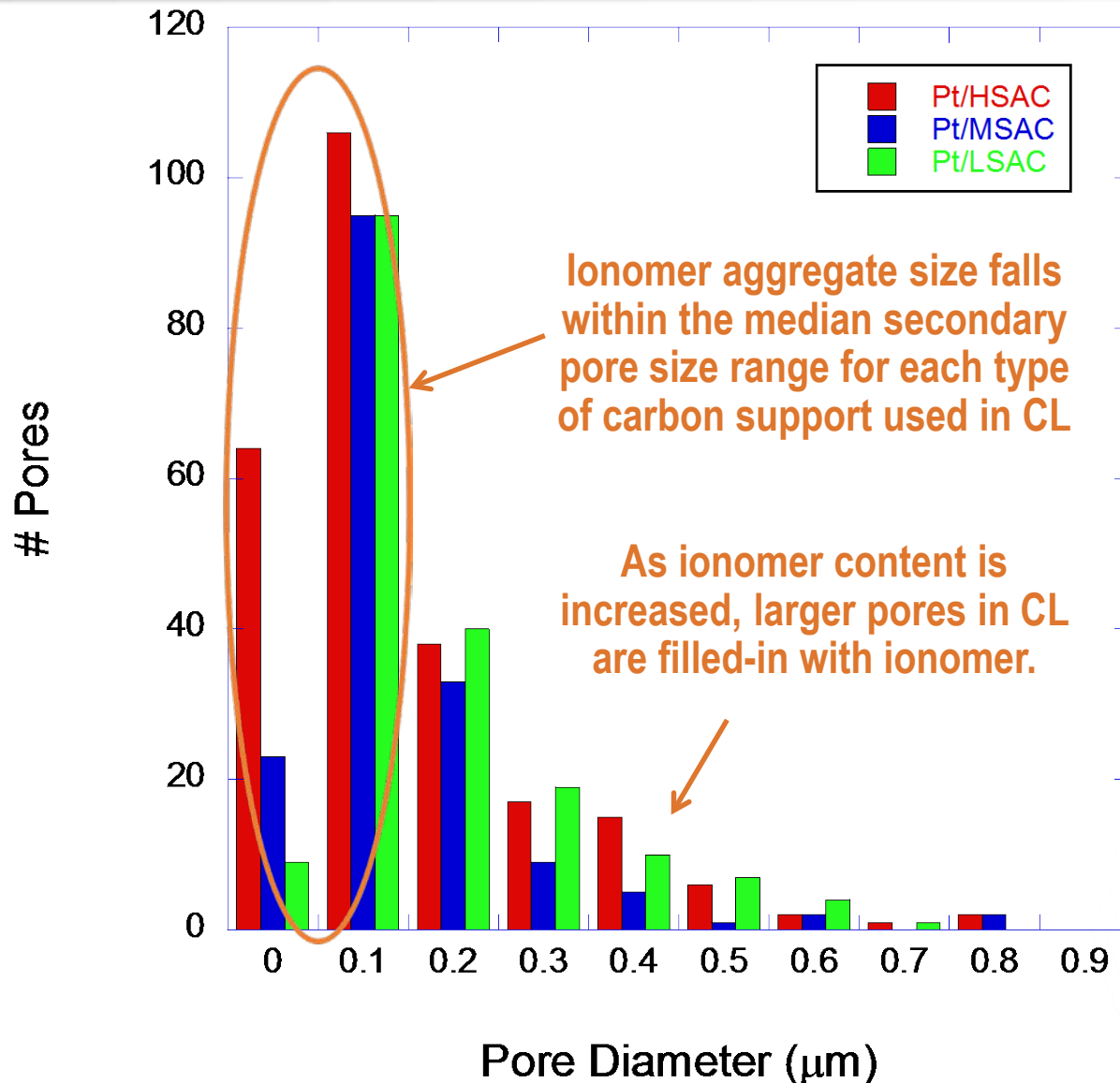
Technical Accomplishments and Progress: Understanding ionomer dispersions in catalyst layers (CLs)

Increasing ionomer content in CL - Pt/LSAC+38% Nafion[®] ionomer

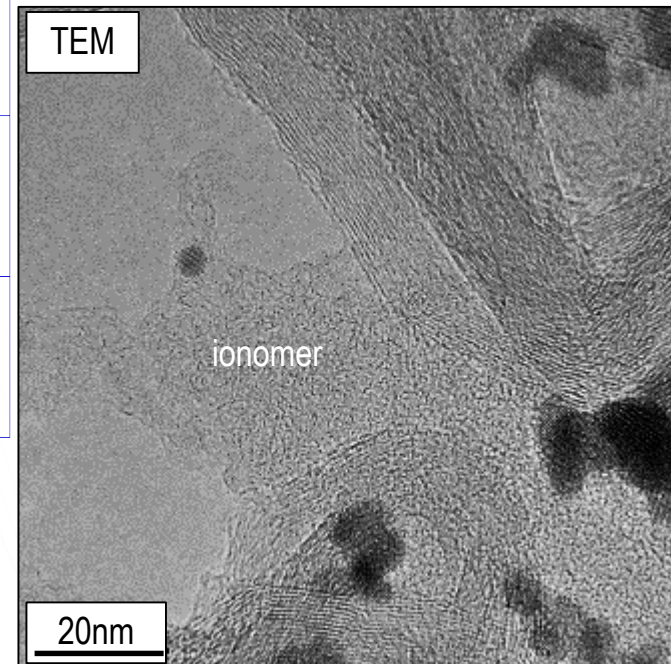
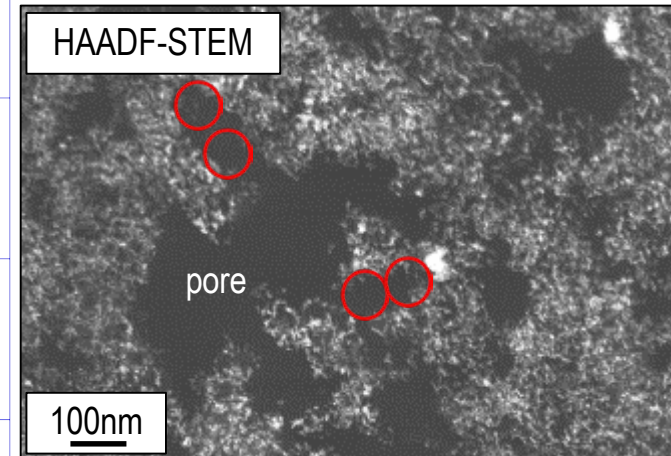


Large ionomer aggregated regions are evident between Pt/LSAC agglomerates as are thinner ionomer layers within Pt/LSAC agglomerates

Technical Accomplishments and Progress: Understanding ionomer dispersions in catalyst layers (CLs)

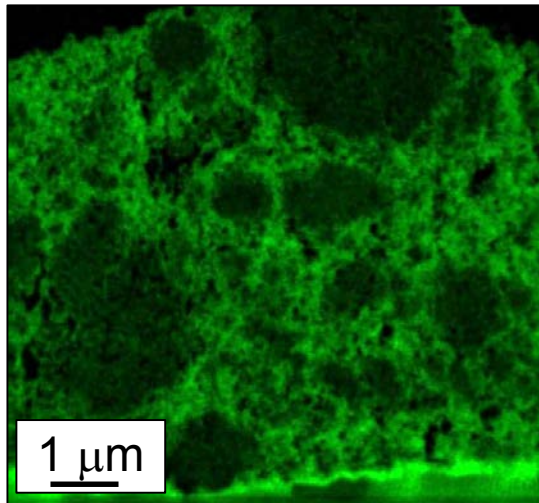
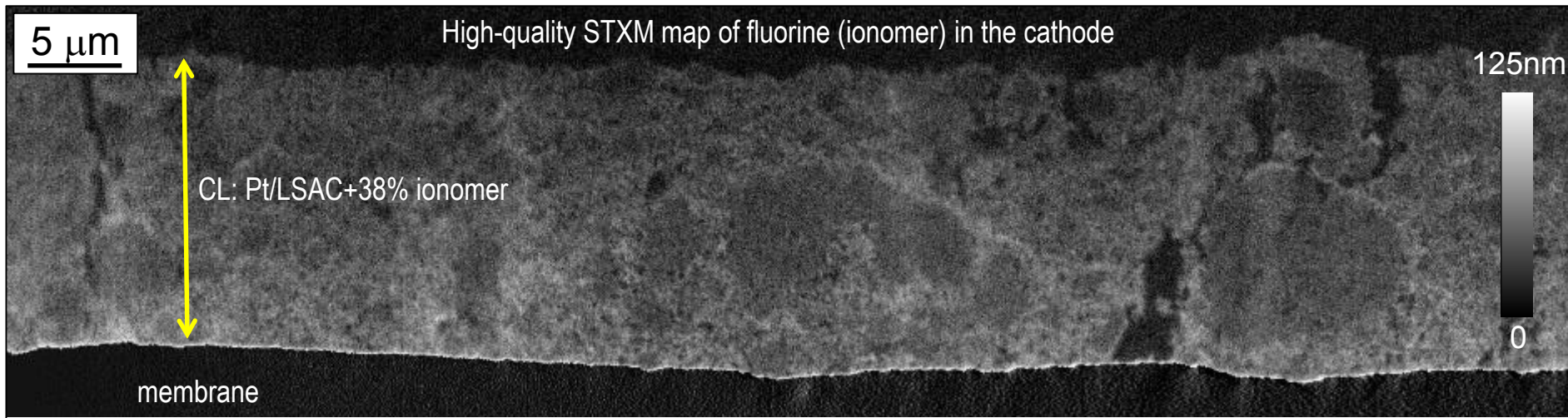


Pore shape plays a critical role in controlling ionomer dispersion



Technical Accomplishments and Progress: Understanding ionomer dispersions in catalyst layers (CLs)

Collaboration with Adam Hitchcock at McMaster University
Correlate observations of ionomer dispersion in CL – STEM-EDS vs. STXM

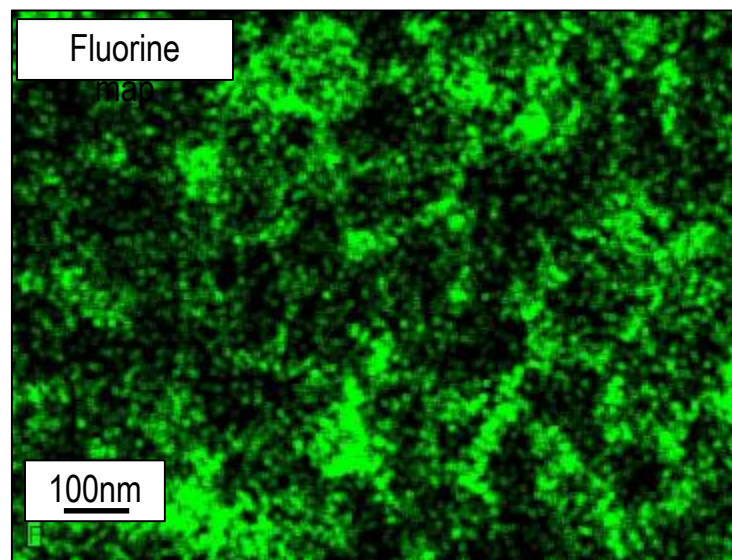
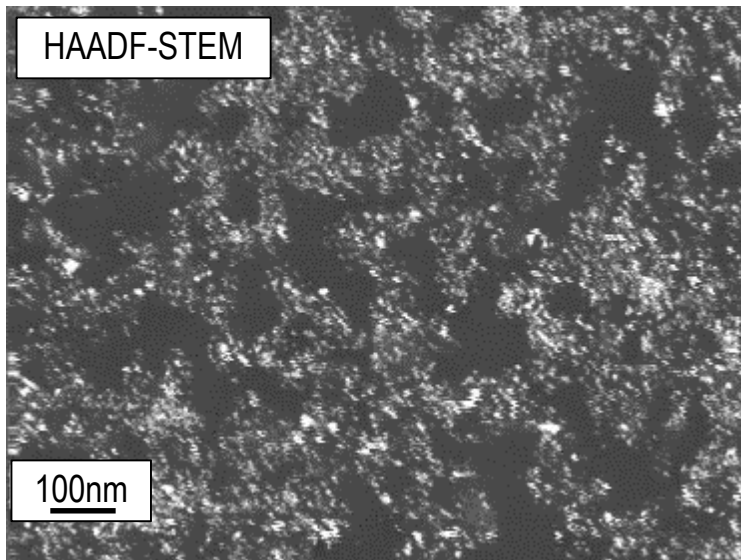


There are advantages to combining imaging techniques:

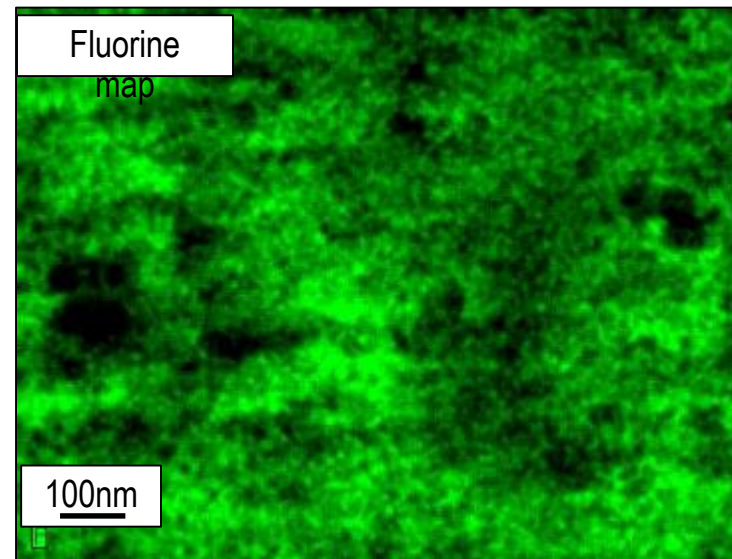
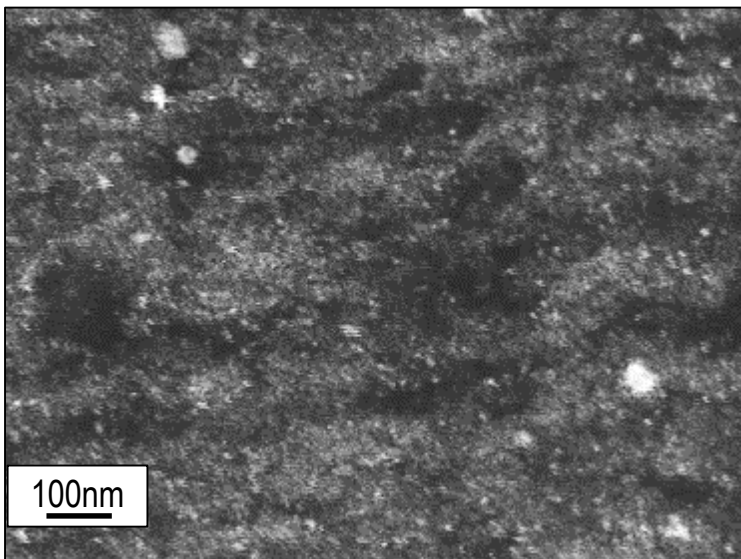
- EDS-STEM provides higher-spatial-resolution images/maps in 2D
- STXM provides large-scale 3D data

Correlative STEM/EDS-STXM from same sample CL areas to better quantify ionomer dispersions

Technical Accomplishments and Progress: Understanding ionomer dispersions in catalyst layers (CLs)

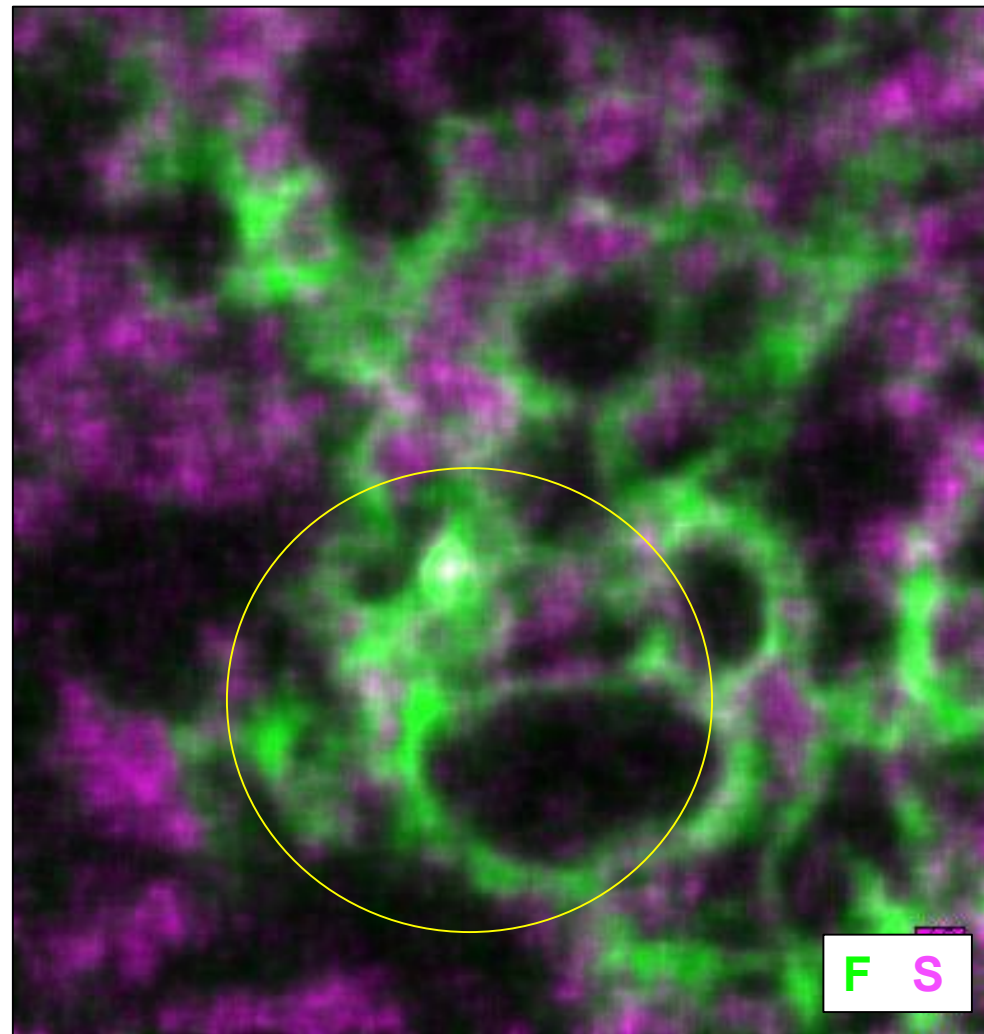
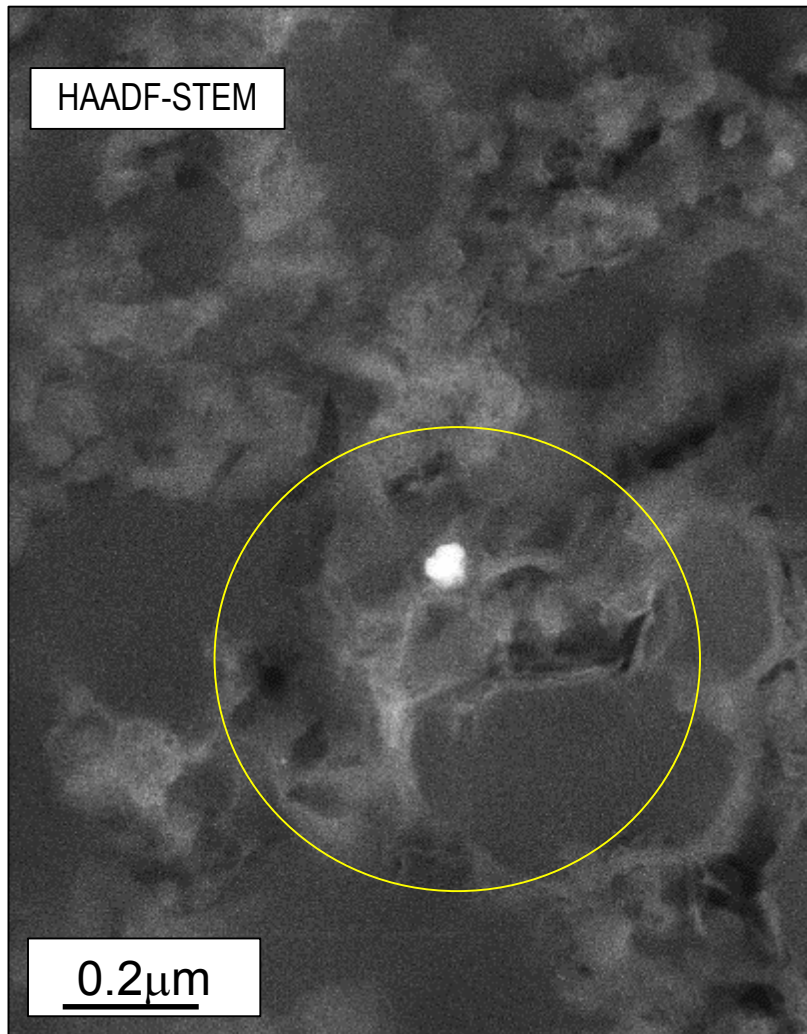


Pt/LSAC CL
400hr @ 1.2V
No carbon corrosion
Ionomer distribution
unchanged



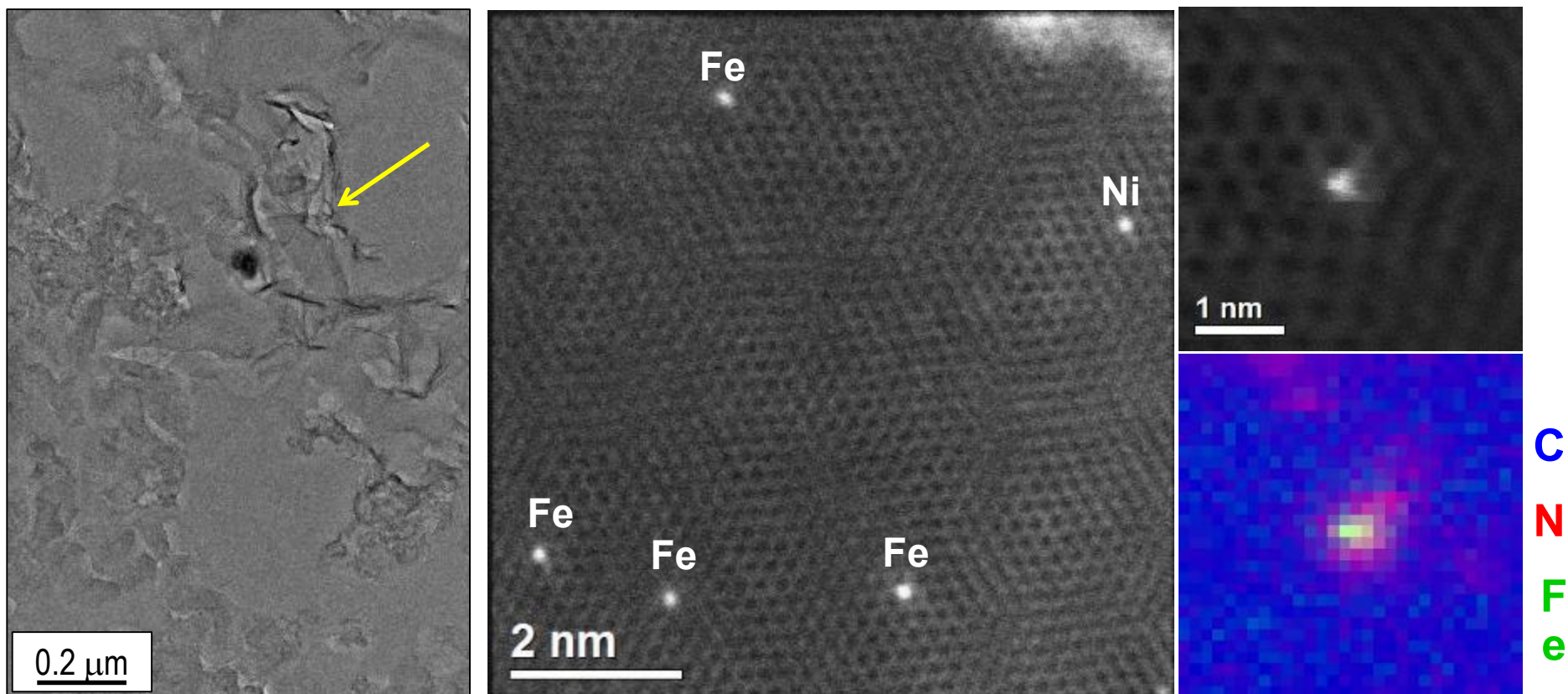
Pt/HSAC CL
100hr @ 1.2V
Extensive carbon
corrosion and CL
thinning
Ionomer distribution
dramatically changes

Technical Accomplishments and Progress: Understanding ionomer dispersions in non-PGM catalyst layers (CLs)



Very thick ionomer layers are observed in non-PGM MEAs - graphene sheets and surfaces of carbonaceous phases in CL are typically embedded in thick ionomer layers

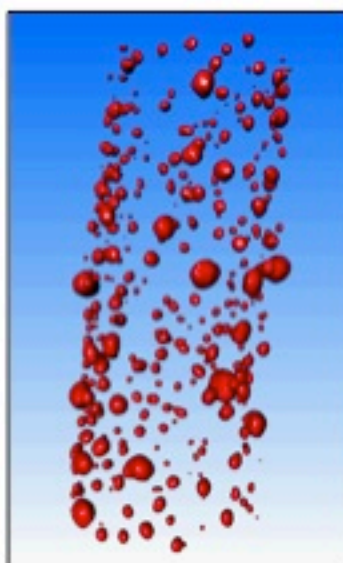
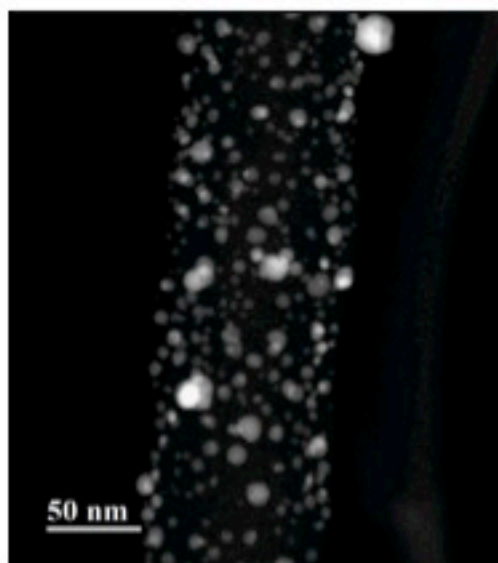
Technical Accomplishments and Progress: Understanding ionomer dispersions in non-PGM catalyst layers (CLs)



Very thick ionomer layers are observed in non-PGM MEAs - graphene sheets and surfaces of carbonaceous phases in CL are typically embedded in thick ionomer layers, which can “bury” the Fe-N catalytic sites

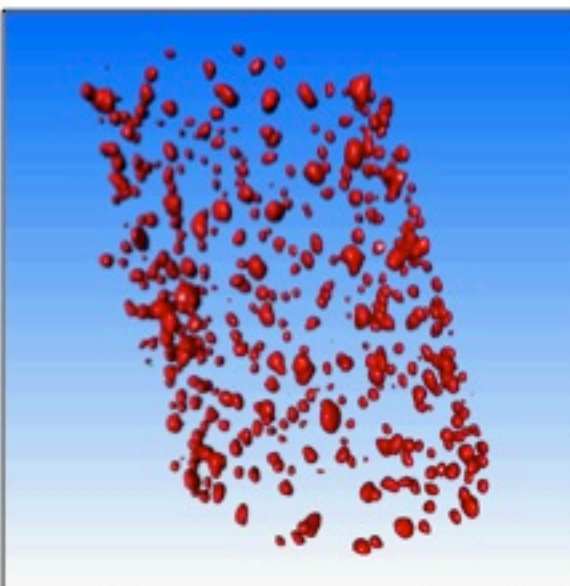
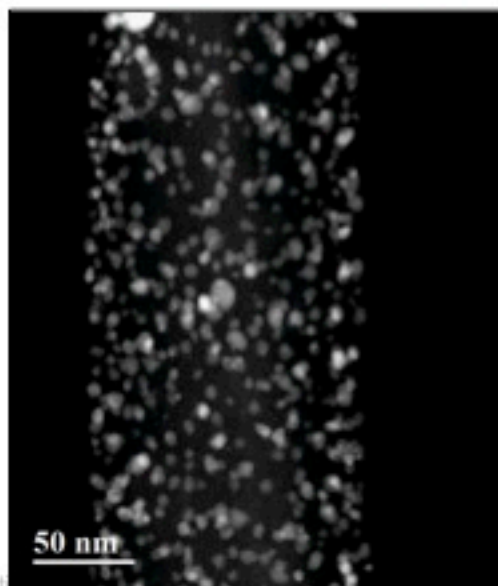
Technical Accomplishments and Progress: Electron tomography of Pt catalysts supported on carbon nanofibers (CNFs)

Pt deposited on surface of CNF



Electron tomography tilt series and image reconstructions used to assess "locations" of Pt nanoparticles supported on CNFs

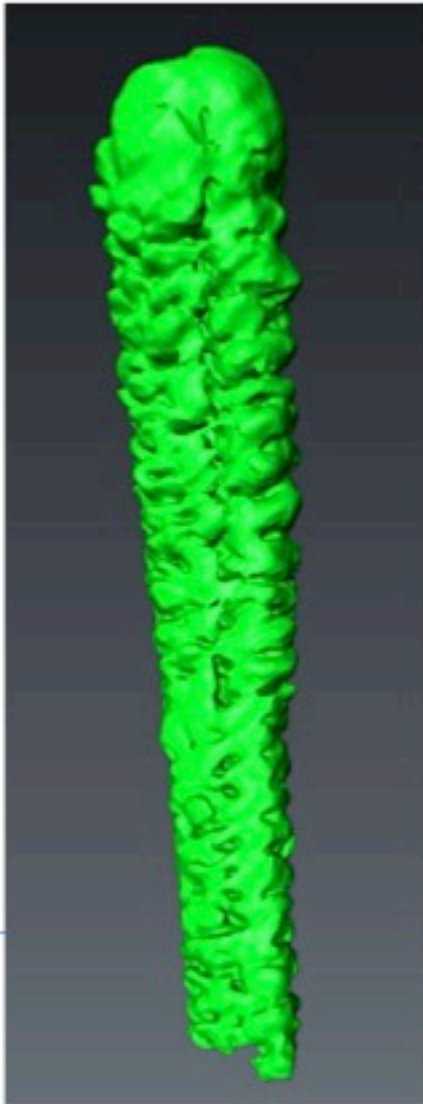
Pt embedded in CNF



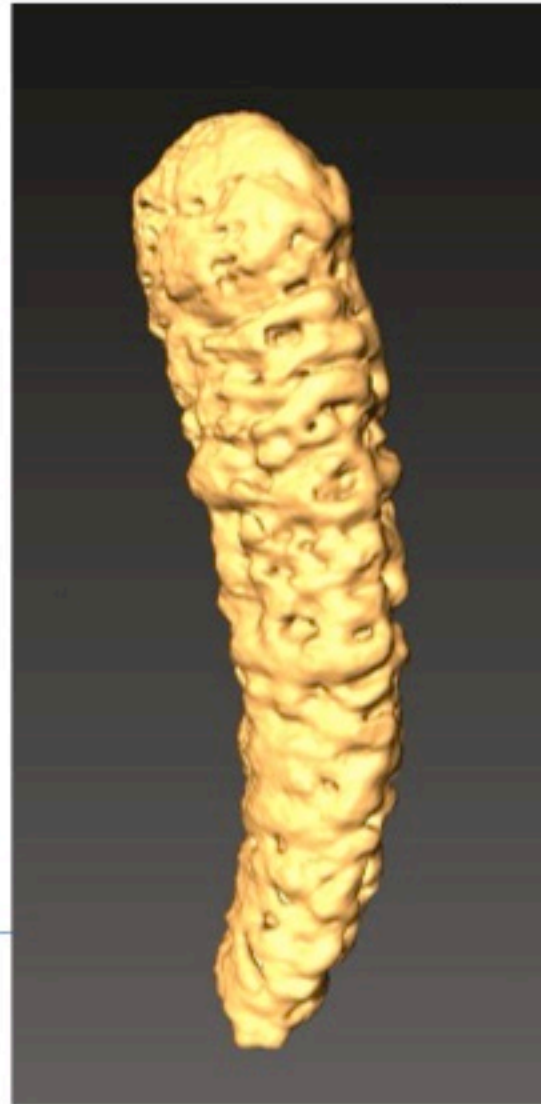
Technical Accomplishments and Progress: Electron tomography of PtNi alloy NSTF

Visualization of NSTF catalyst whisker surfaces and pore structures via 3D tomography

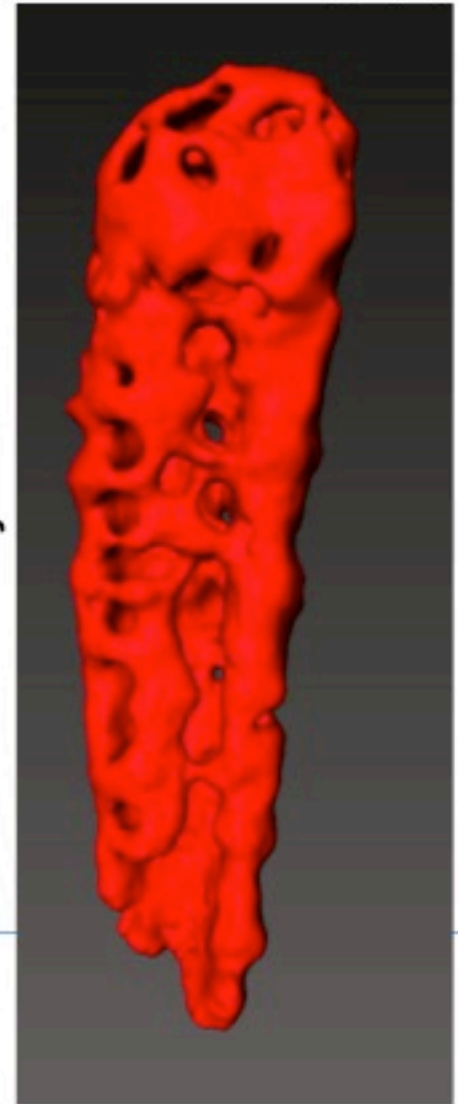
Dealloy+Anneal



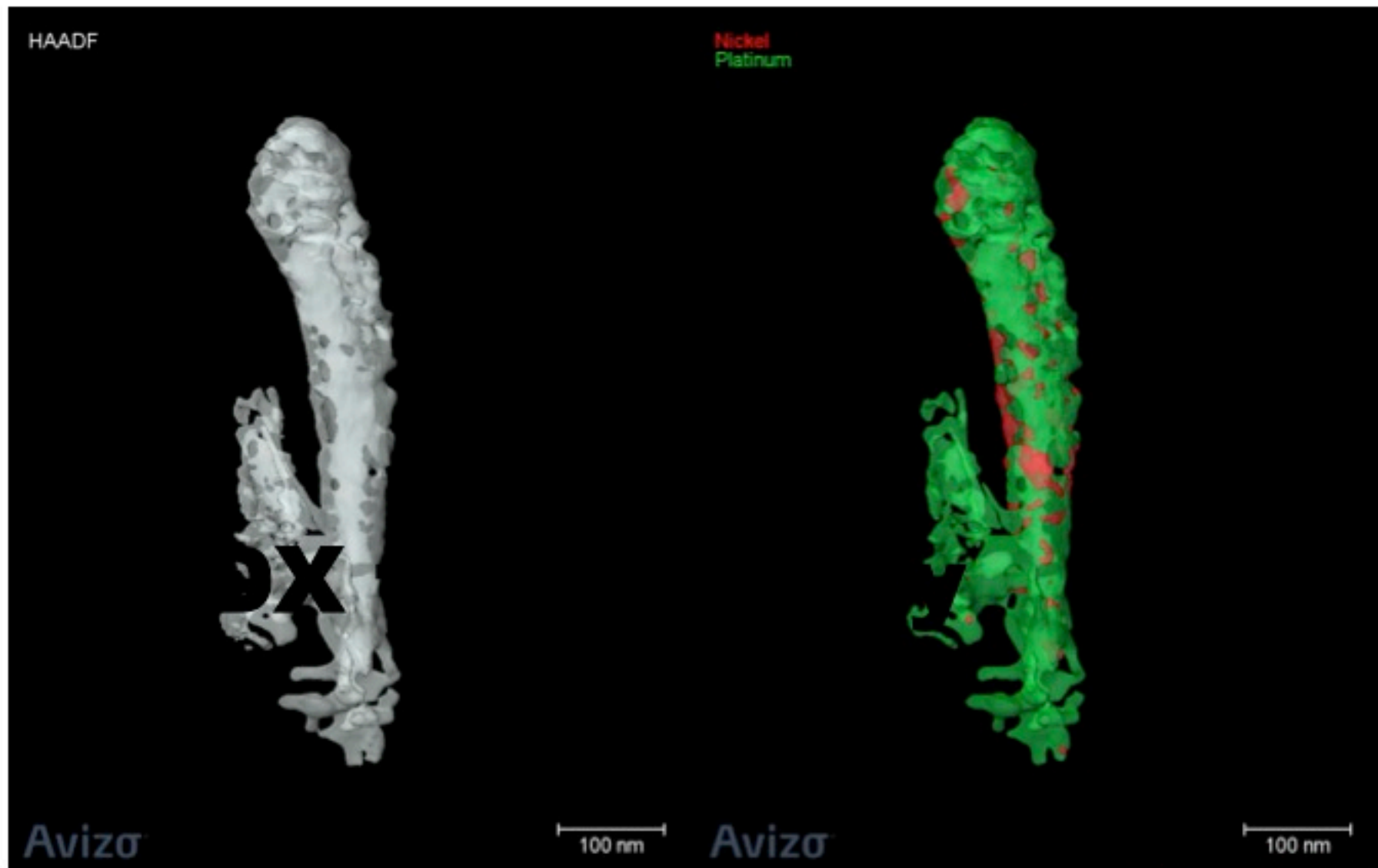
Conditioned



Cycled



Technical Accomplishments and Progress: Correlated 3D imaging and EDS tomography



Future Work

- Further develop electron tomography towards understanding ionomer interactions with surfaces “inside” catalyst layers.
- Work with an OEM to study field-aged MEAs for comparison with numerous studies conducted on AST/durability aged MEAs.
- Continue research into hetero-atom doping of graphitized carbons – this has been an ongoing research effort (results-to-date not reported in AMR presentation) that is focused on improving catalyst dispersions on highly graphitic carbon surfaces.
- Establish a thorough understanding of current state-of-the-art non-PGM catalysts, including basic structural and compositional differences amongst candidate materials. Establish new collaborations in this area and exploit unique capabilities available at ORNL towards these studies.
- Continue to establish key collaborations with industry, academia, and national laboratories (including access via ORNL User Facilities) to facilitate “transfer” of relevant materials information and provide access to unique capabilities and FC expertise available at ORNL.

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 and optimizing materials to enhance 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 that are relevant to the FC community – during FY15 we applied "best practices" established in FY14 towards characterizing ionomer thin films and non-PGM catalysts, and continued our work with many partners to characterize new fuel cell materials. We support the FC community with unique capabilities for the 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 complete our work on hetero-atom doping of graphitic carbon, and to combine microanalysis and modeling to better understand interactions between ionomer films and support and/or nanoparticle surfaces and ionomer aggregation.