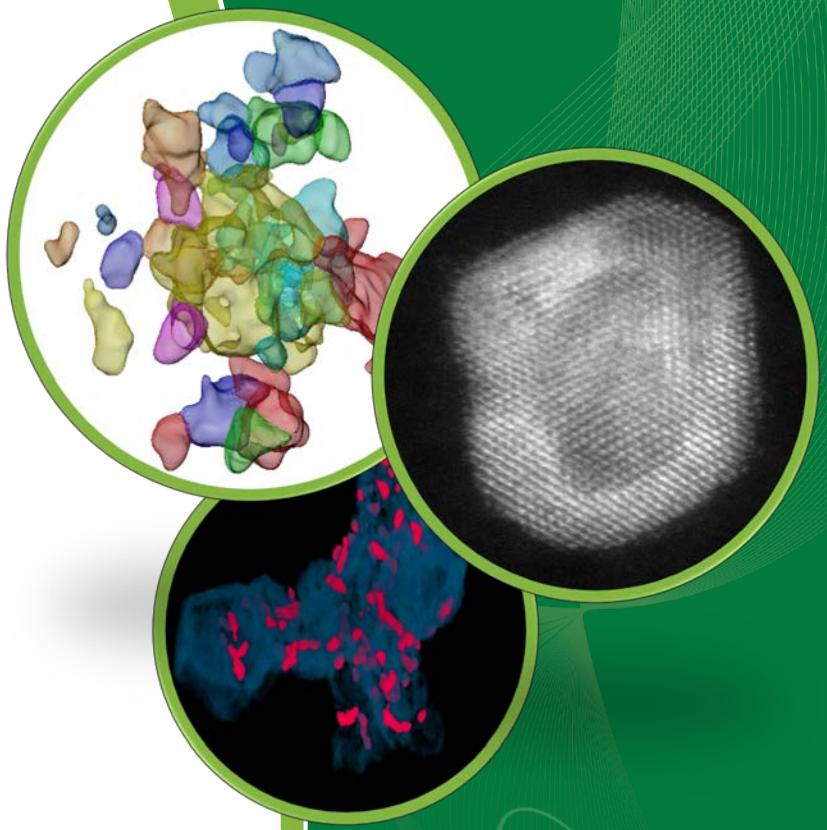
New Fuel Cell Materials: Characterization and Method Development

Project ID FC020



PI: Karren L. More

David A. Cullen, Brian T. Sneed, and K.S. Reeves

Oak Ridge National Laboratory

Oak Ridge, TN 37831-6064

2016 DOE Hydrogen and Fuel Cells Annual Merit Review Meeting

June 8, 2016

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Project Overview

Timeline and Budget

- *Present project initiated in FY2016:* Previous project funding redirected into two separate projects:
  - Characterization of New Fuel Cell Materials (FC020)
  - FC-PAD (FC135)
- FY15 DOE Funding: $600k
- FY16 DOE Funding: $300k
- Total DOE Funds Received to Date: $

Barriers

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

Partners

- Los Alamos National Laboratory
- Argonne National Laboratory
- Lawrence Berkeley National Laboratory
- National Renewable Energy Laboratory
- University of Tennessee
- Proton OnSite
- Giner inc.
- Ion Power
- 3M Co.

Relevance – ORNL's Research Objectives

- Identify and develop novel high-resolution imaging and compositional/chemical analysis techniques, and unique specimen preparation methodologies, for the μm-to-Å-scale characterization of individual fuel cell materials (catalysts, support, ionomer, membrane) and new materials incorporated in membrane electrode assemblies (MEAs)
- Optimize imaging/spectroscopy methodologies towards specific fuel cell materials:
  - Electrocatalyst atomic-scale structure and chemistry
  - Ionomer mapping in catalyst layers
  - 3D electron tomography
- MAKE UNIQUE CAPABILITIES AND EXPERTISE AVAILABLE TO FUEL CELL RESEARCHERS OUTSIDE OF ORNL

Approach: Use Facilities in ORNL's Materials Characterization Center (MCC) to Investigate Structure of Fuel Cell Materials

Microscopy-Based Technique Development/Optimization

Use advanced electron microscopy techniques to characterize fuel cell materials and MEAs → μm-to-sub-Å-scale:

- Catalyst nanoparticles – composition, structure, chemistry, size, morphology
- Ionomer dispersions within catalyst layers
- Support materials

Use information to optimize materials through iterative synthesis/fabrication and characterization

Correlate with durability, stability, and performance measurements

Establish New Partnerships

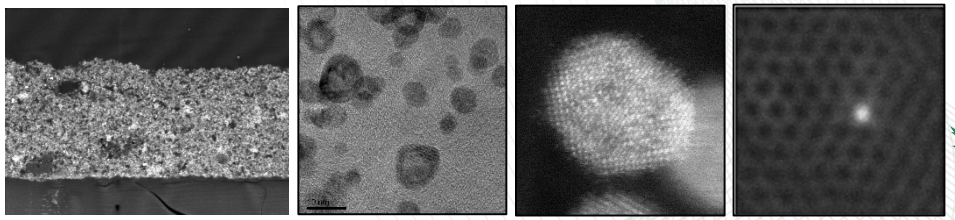
DOE's FCTO will provide a 50% cost share to collaborate with ORNL – opportunity to support projects with total values up to $50k including partner contribution

↓

ORNL staff scientists collaborate directly with partners on DOE-FCTO mission-aligned projects

↓

Partnerships implemented via a streamlined short-form CRADA



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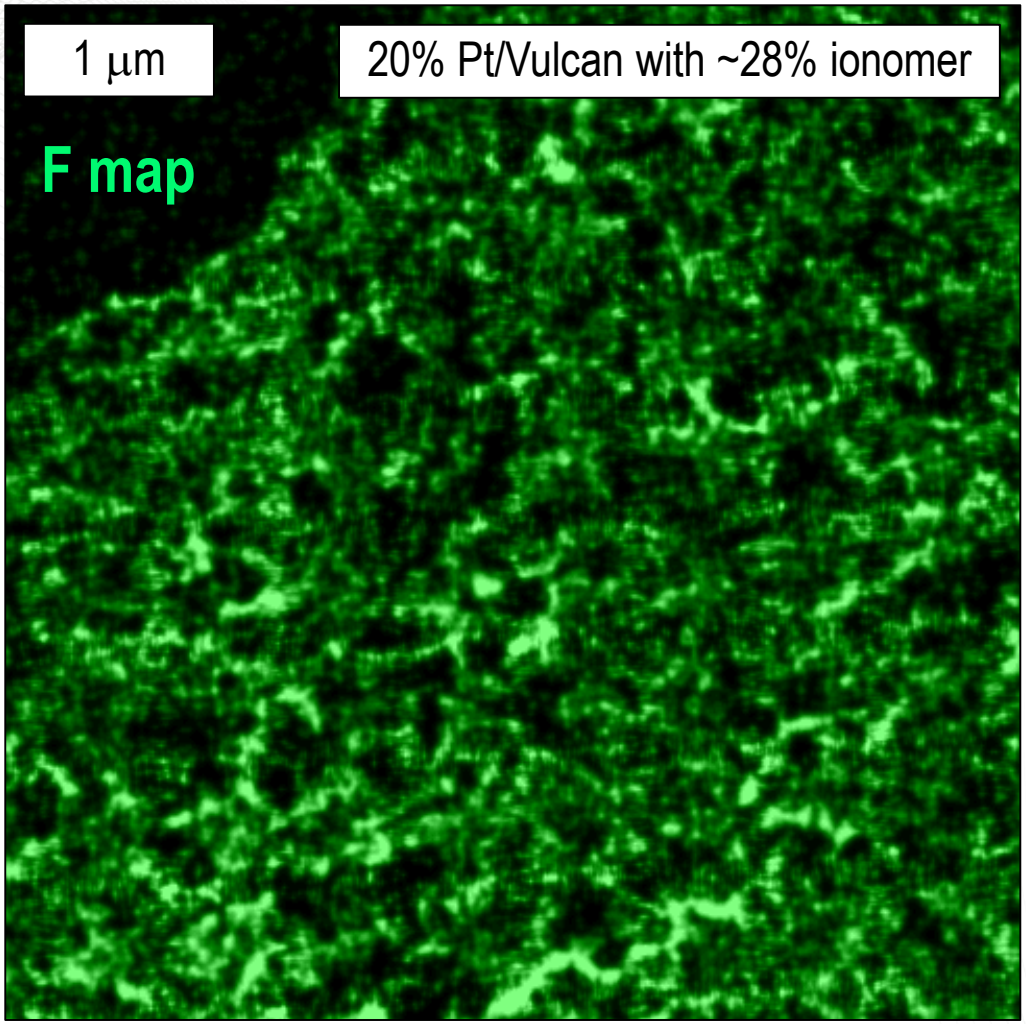
Approach – Project Milestones FY15 and FY16

- **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. *Completed*
  - ✧ 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. *Ongoing*
  - ✧ Initiate at least two new collaborations with industry during FY15 to characterize fuel cell catalyst layer material components (electrocatalyst, support, ionomer). *Completed*

- **FY16 Milestones:**
  - ✧ Identify industrial collaborator and initiate systematic study of ionomer distribution comparison between ink and cathode layers (CLs) prepared using various solvents, supports, Pt loadings, and CL preparation method. *Underway*
  - ✧ Report preliminary results of 4D tomography study of ionomer distribution in "real" MEA (4D tomography combines imaging and spectroscopic data sets). *Completed*
  - ✧ Complete publication of study focused on Pt-dispersion effects as a function of hetero-atom doping of graphitized carbon. *Ongoing*
  - ✧ Complete summary report for full characterization of a new materials before and after incorporation in a CL/MEA system comprised of novel electrocatalyst or new support material, with a specific focus on full characterization of different stages of development (as-synthesized components, inks, and architectures of MEAs) to identify optimum processing conditions. *On Track*

Technical Accomplishments and Progress: Imaging Ionomer Dispersions in Catalyst Layers



Fluorine map (green) shows dispersion of ionomer
Black areas are predominantly pores

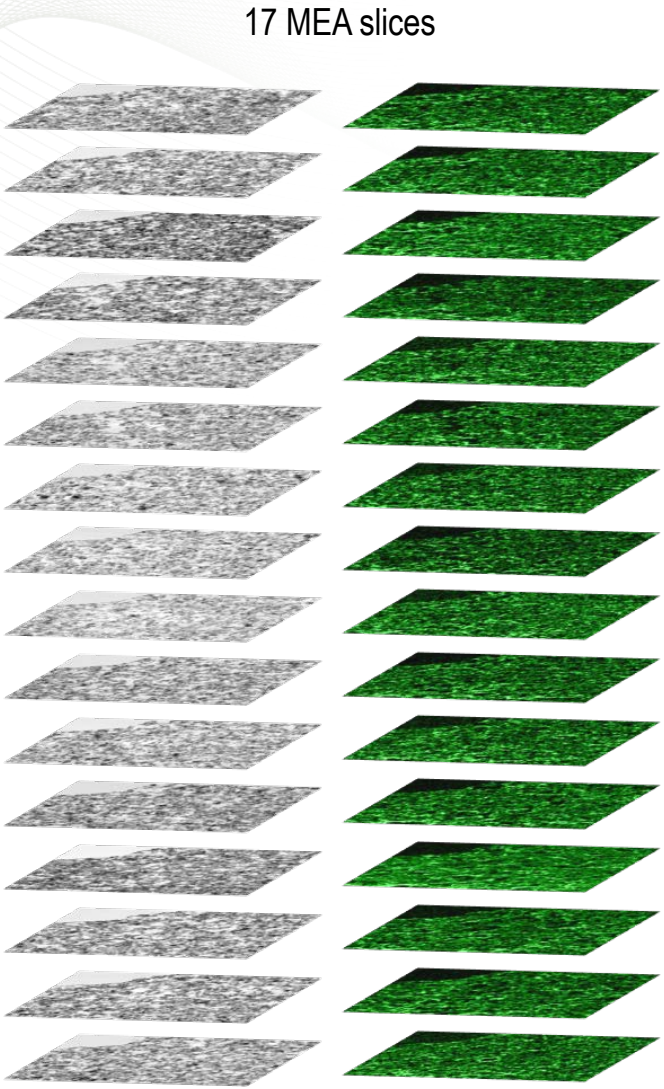
Highlight from 2015 AMR:

- Mapping ionomer dispersions (F maps) within catalyst layer (CL) cross-sections in ***2D***

- Correlated STEM mapping/imaging results typically showed:
  - a non-homogeneous ionomer distribution within CL
  - ionomer aggregates ranging in size from <10nm to >>100nm
  - most ionomer aggregates associated with secondary pores

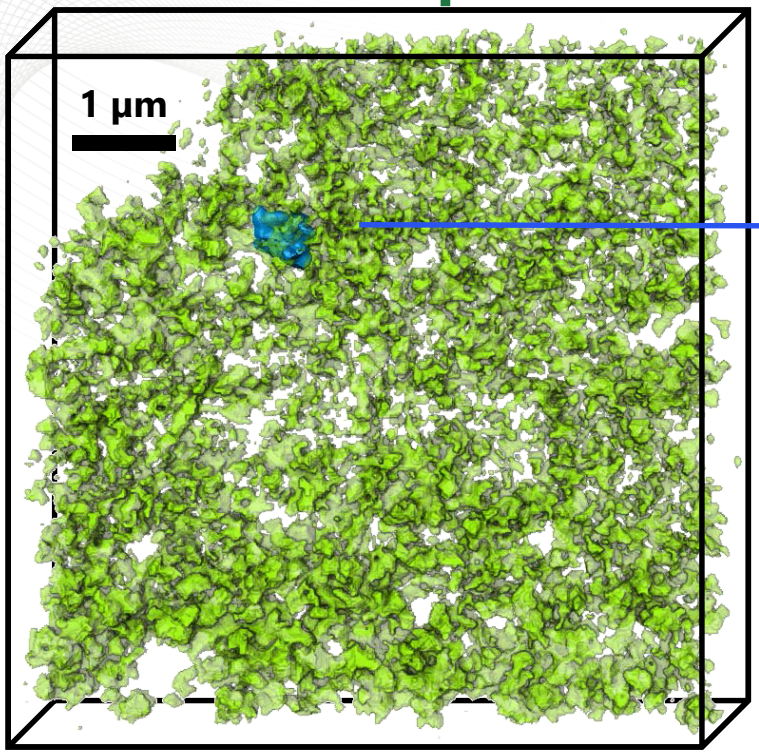
*Can we improve our understanding of ionomer dispersions through **3D** STEM mapping/imaging?*

Technical Accomplishments and Progress: Imaging Ionomer Dispersions in Catalyst Layers in *3D*

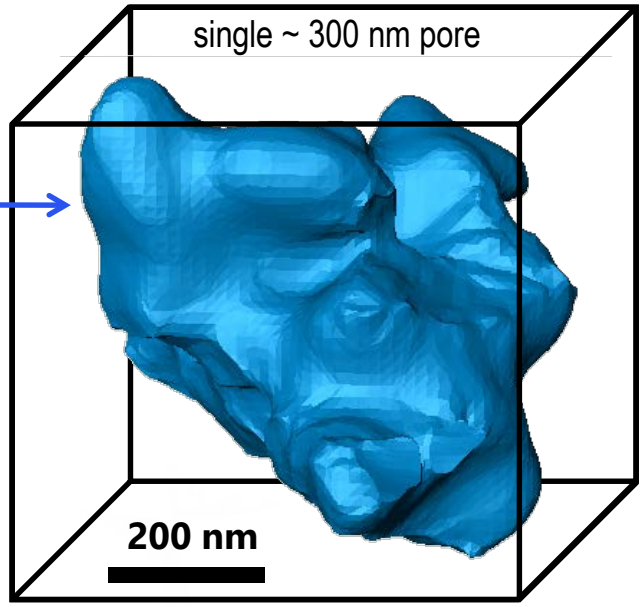


Individual F maps acquired from "slices" are stacked to create a ***3D rendering/reconstruction*** of the ionomer distribution within a given volume of the CL

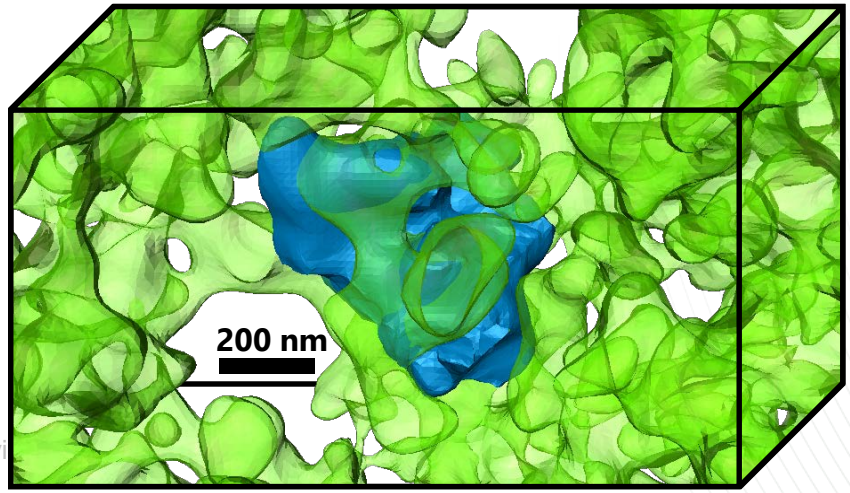
Technical Accomplishments and Progress: Imaging Ionomer Dispersions in Catalyst Layers in *3D*

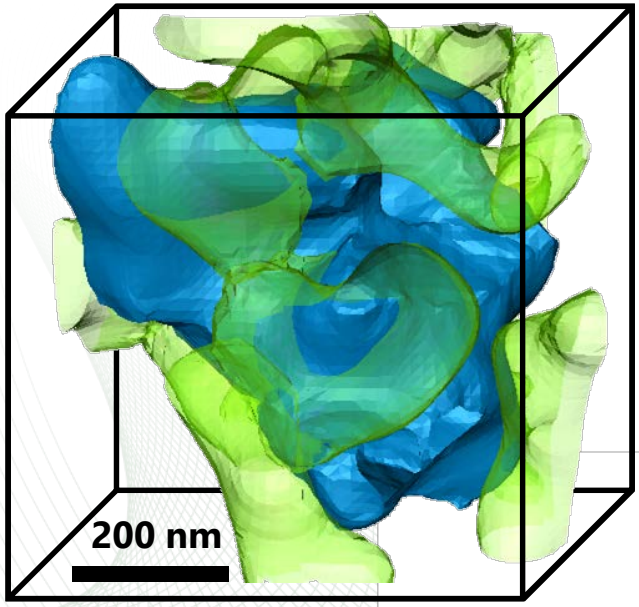


To correlate ionomer with porosity (and simplify visualization), a single secondary pore is selected from CL volume using corresponding STEM images



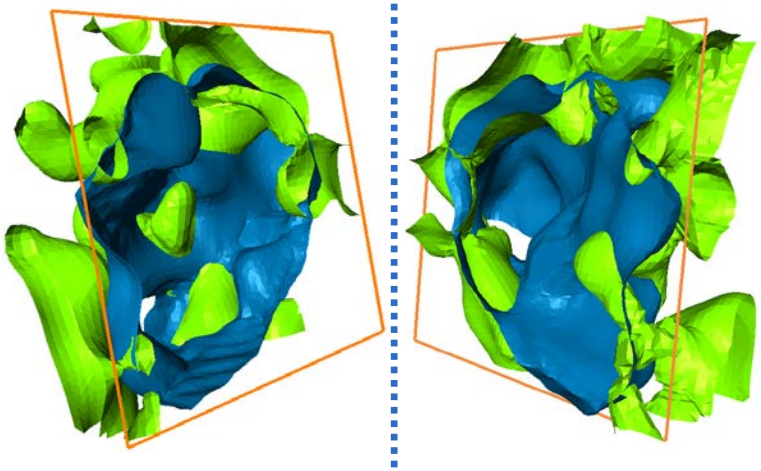
Same pore with ionomer



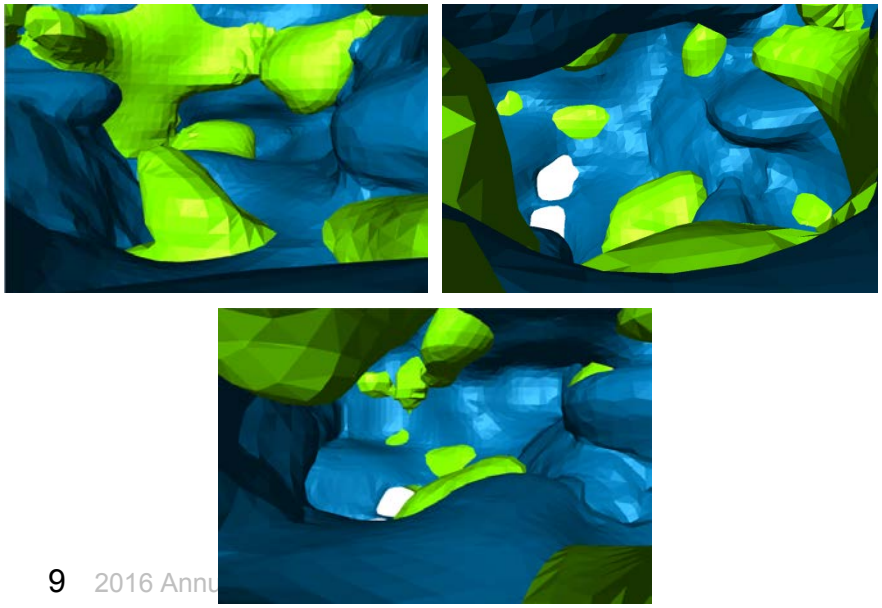


Technical Accomplishments and Progress: Imaging Ionomer Dispersions in Catalyst Layers in *3D*

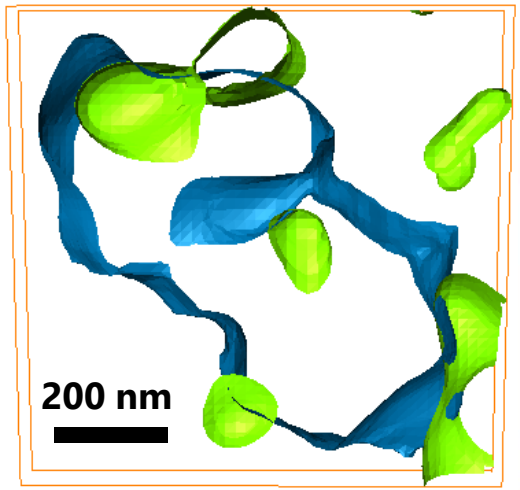
pore "halved"

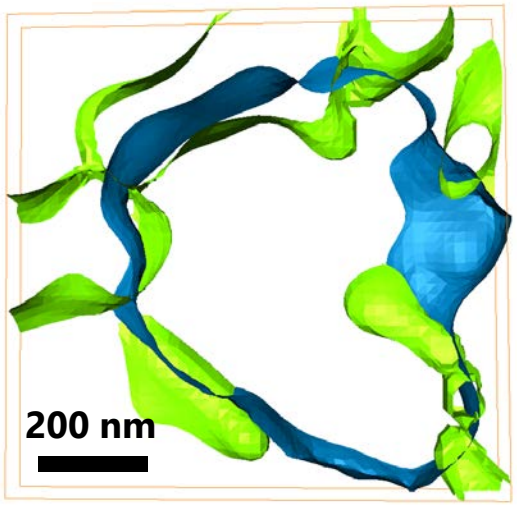


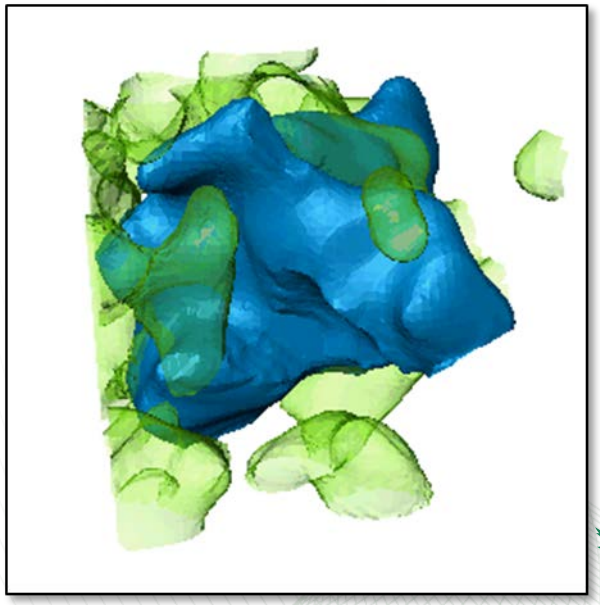
views from inside the pore



~50 nm cross-sections







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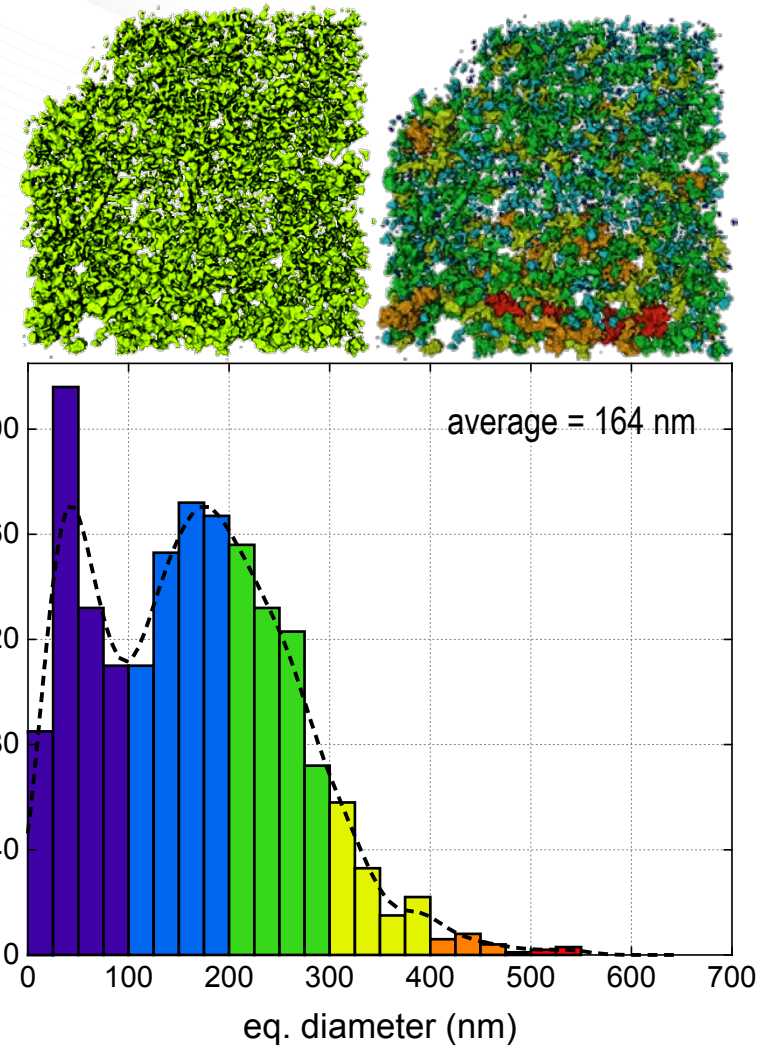
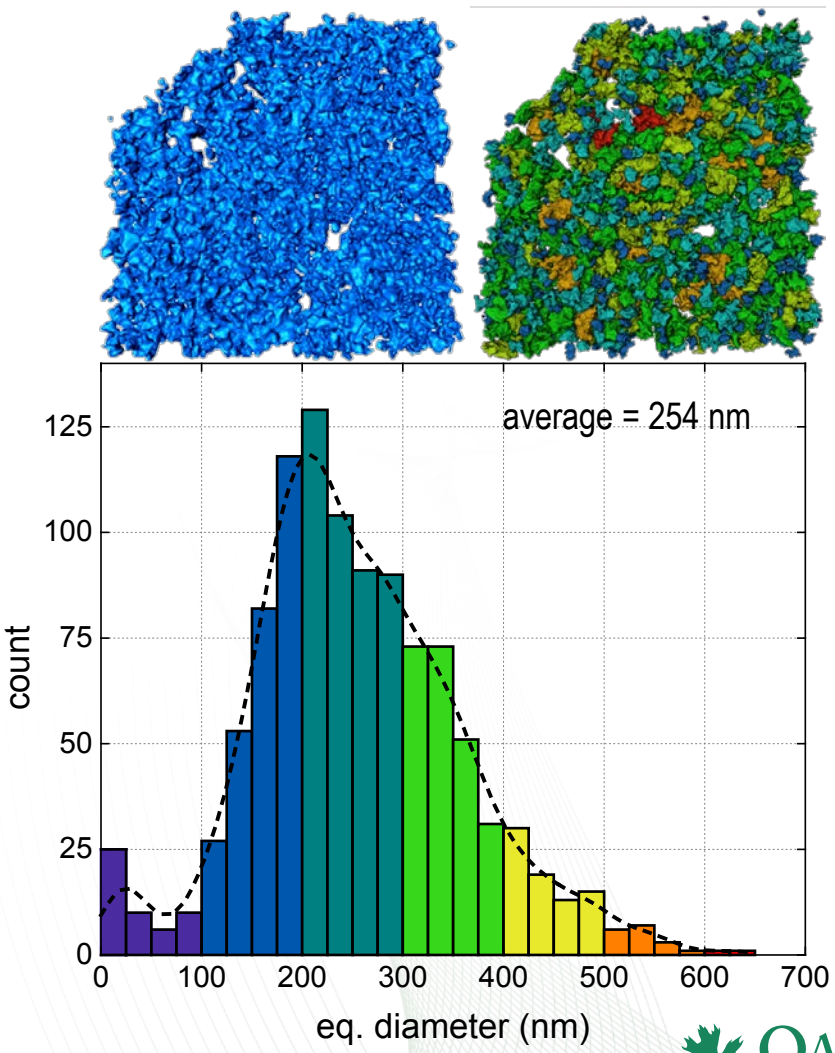
Technical Accomplishments and Progress: Imaging Ionomer Dispersions in Catalyst Layers in *3D*

Ionomer aggregation in CL



Porosity size distributions in CL



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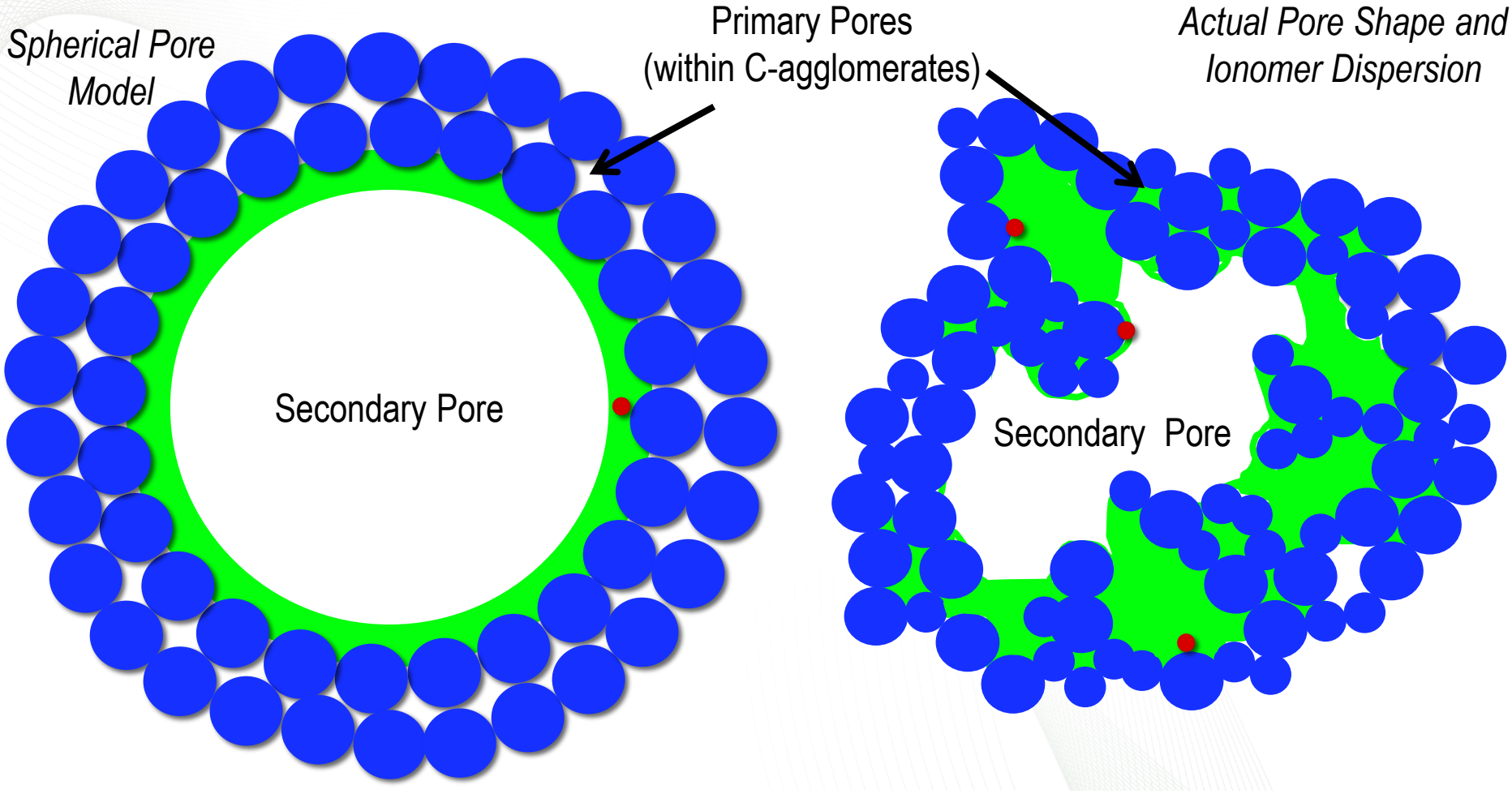
Technical Accomplishments and Progress: Modeling Ionomer Dispersions in Catalyst Layers



- We need to rethink our ideas of how ionomer is distributed within the catalyst layer:
  from uniform *ionomer thin films* to *ionomer pockets that fill pore space*
- How does ionomer aggregation affect Pt utilization in both primary and secondary pores?

Technical Accomplishments and Progress: Imaging Ionomer Dispersions in Catalyst Layers in *3D*

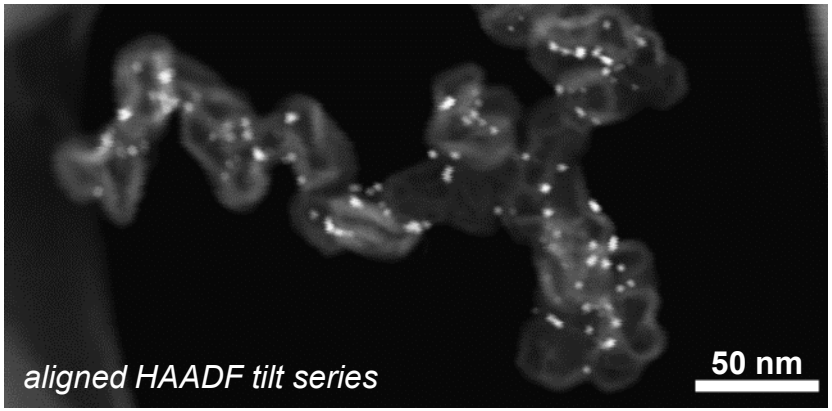
Many questions still need to be addressed:

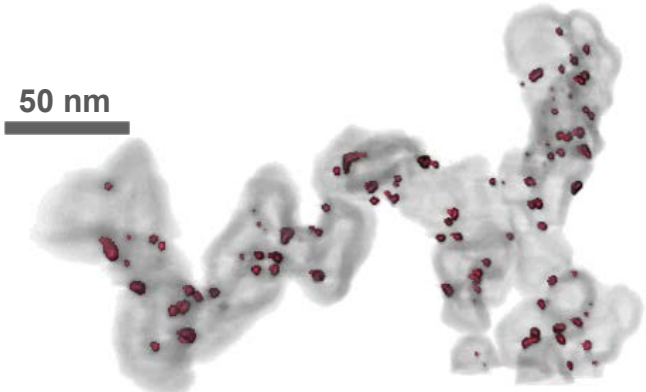
- How does ionomer aggregation affect Pt utilization?
- Ionomer thickness – how thick is "too thick" for efficient oxygen transport?
- Ionomer thickness – how thick is "too thin" for efficient proton transport?
- Exactly what is the role of non-homogeneous ionomer dispersion on surfaces of Pt/C on water transport in CL?
- *How can ionomer distribution be optimized in the CL via ink processing?*

Will require systematically processed SOA inks and MEAs coupled with extensive characterization

Technical Accomplishments and Progress: Imaging Electrocatalyst Distributions in *3D*

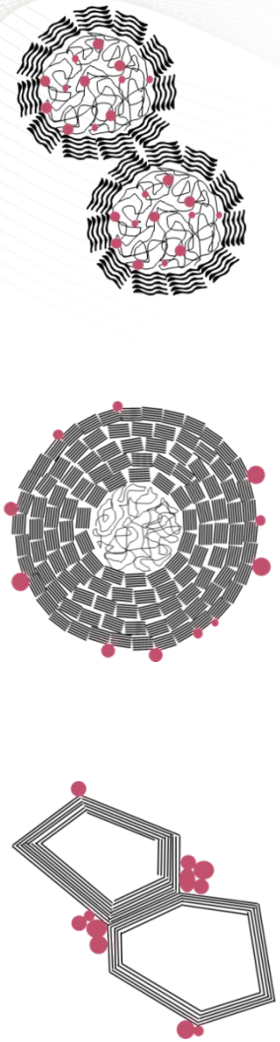
- quantifying differences in the dispersion of catalyst/support and ionomer within membrane electrode assemblies (MEAs)
- development of alternative catalyst/carbon support systems with higher oxidation tolerance
- elucidation of degradation mechanisms (Pt agglomeration, coarsening, dissolution, detachment, and C corrosion)



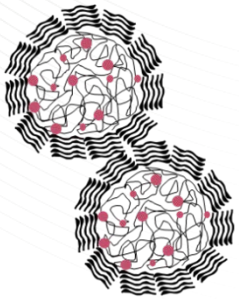


segmentation, visualization, and quantitative analysis

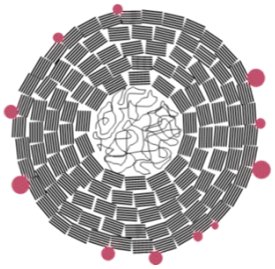
Technical Accomplishments and Progress: Imaging Electrocatalyst Distributions in *3D*



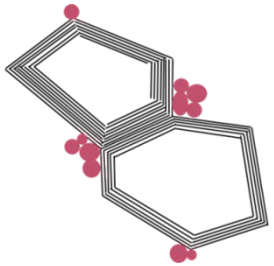
Technical Accomplishments and Progress: Imaging Electrocatalyst Distributions in *3D*



Pt/HSAC

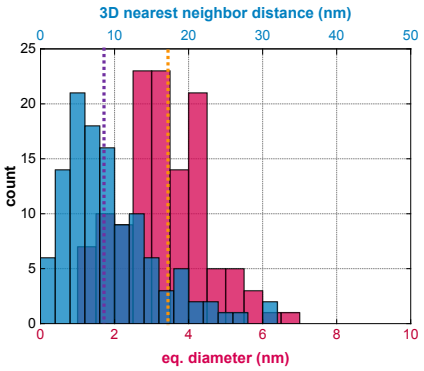


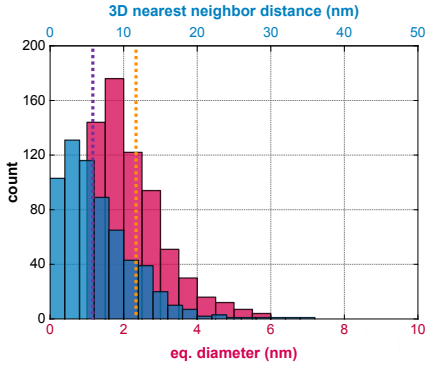
Pt/Vulcan

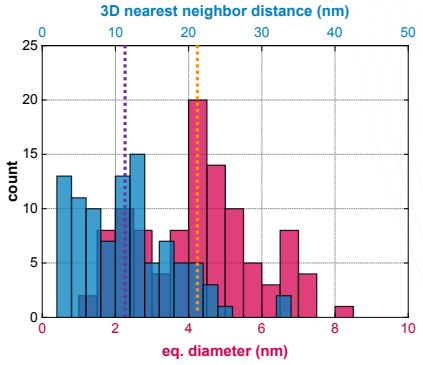


Pt/LSAC

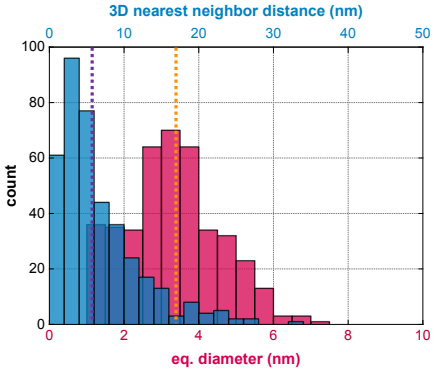
5 wt.% Pt

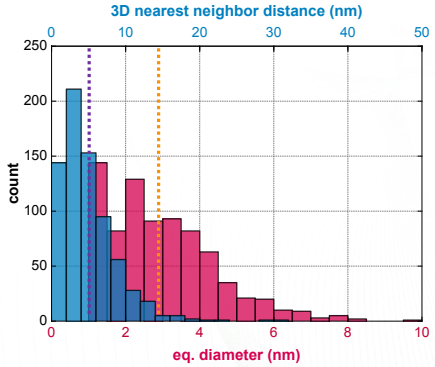


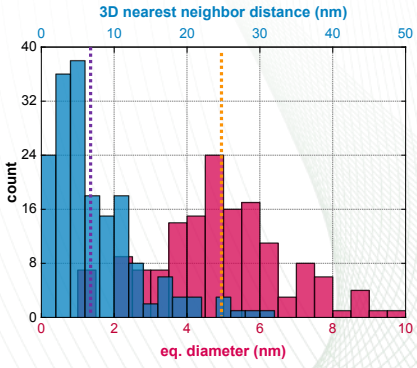




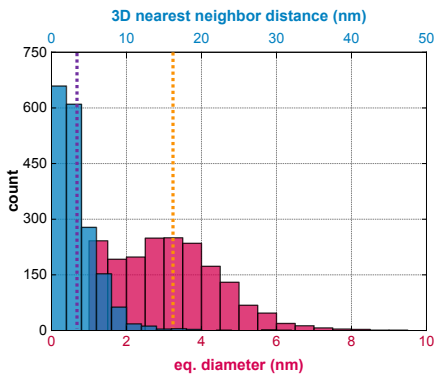
20 wt.% Pt

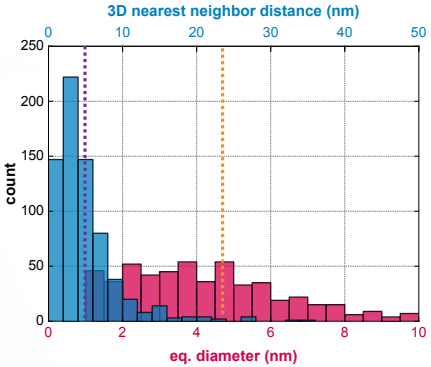


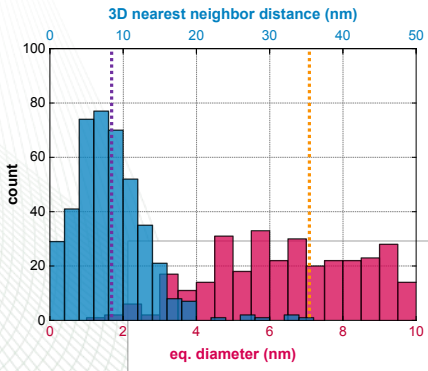




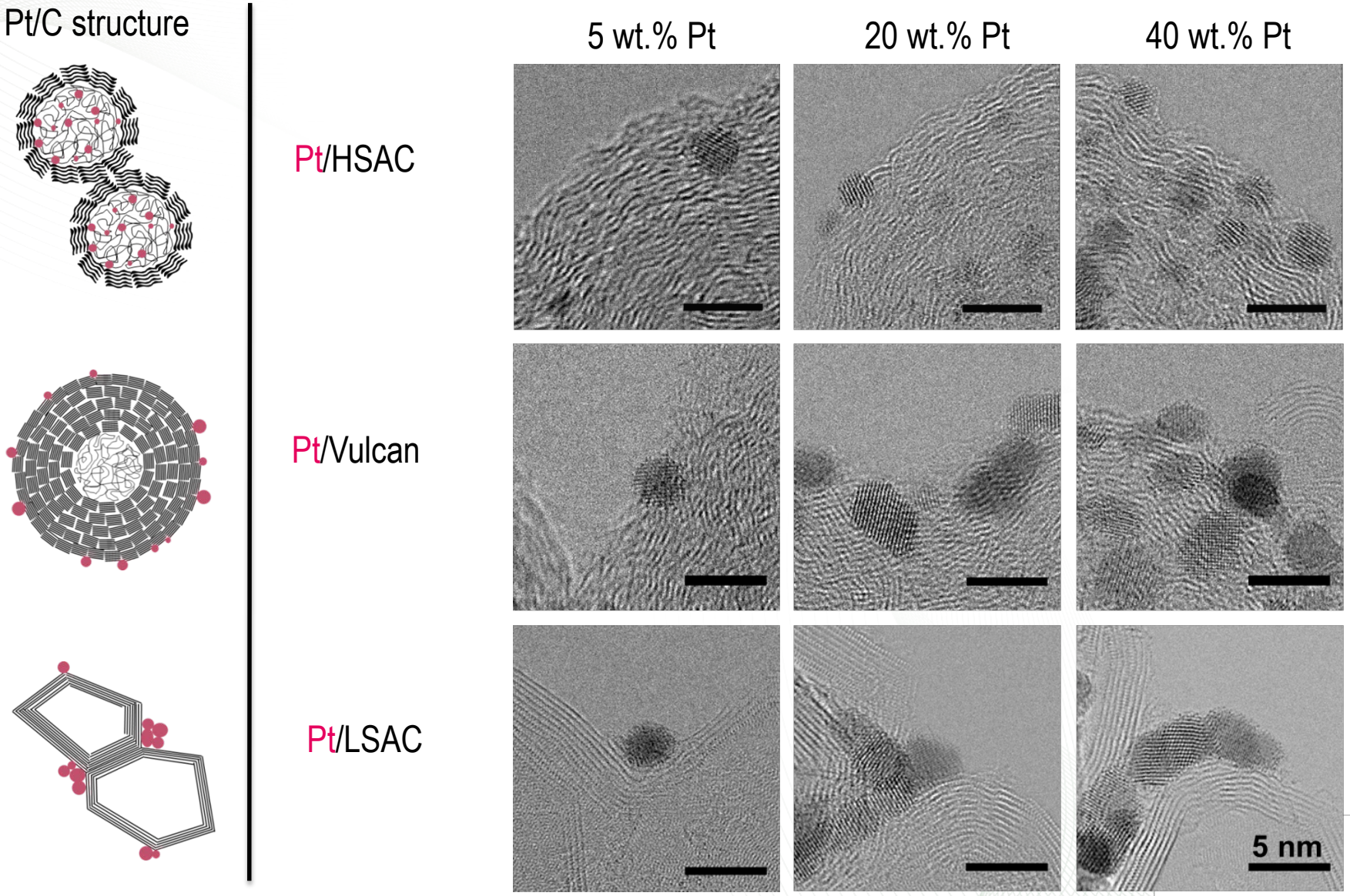
40 wt.% Pt



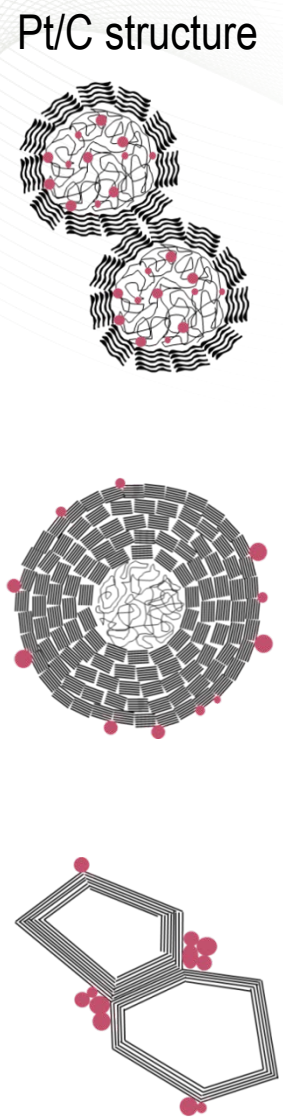




Technical Accomplishments and Progress: Imaging Electrocatalyst Distributions in *2D*



Technical Accomplishments and Progress: Imaging Electrocatalyst Distributions in *3D*



majority of Pt in pores beneath surface, good dispersion

Pt on carbon surface, good dispersion

Pt on carbon surface, not in hollow cavities, poor dispersion from agglomeration near graphitized edge planes

Technical Accomplishments and Progress: Response to Previous Year Reviewers' Comments

Reviewer comments from FY2015 AMR were extremely positive and supportive of ORNL's highly collaborative approach towards evaluating fuel cell materials

Reviewer Comment	Response
There should be more tie-in to more sample-averaged techniques, such as XRD for particle sizes, porosimetry for pore sizes, and NMR or others for Nafion particle sizes. Perhaps a set of "representative" MEA samples can be analyzed to address MEA manufacturer comments on the structure of the MEA used in Nafion analysis.	We always try to coordinate microscopy results with other measurements, such as XRD/SAXS, XPS, Nano-CT, porosimetry, etc., that are performed at partner labs on the same materials. Once analytical techniques are developed and validated at ORNL, we acquire the necessary "representative" MEAs for characterization, but we are limited to materials that manufacturers are "willing" to provide knowing that materials will be interrogated fully and results will be made available to the community (not always possible!)
A user-accessible database for distributing the data would be helpful.	Characterization data (acquired in past, present, and future experiments) will be made available via publicly accessible consortia websites (e.g.,FC-PAD)

Summary

- 3D electron tomography is providing unprecedented insight into material constituents comprising MEAs
  - Visualization and quantification of ionomer dispersions in “real” catalyst layers and correlation with porosity
  - Quantitative differences between catalyst loadings, catalyst dispersions, nearest neighbor distances, and how these change with use
- Techniques are being applied to new materials (bimetallic catalysts, for example) towards understanding durability and stability

Collaborations

- *Established partnerships to acquire new and baseline materials for technique development effort:*
  - Ion Power
  - IRD Fuel Cells
  - Los Alamos National Laboratory
  - University of Tennessee
  - Argonne National Laboratory
  - National Renewable Energy Laboratory

- *Identify new industry/academic to partner with ORNL's MCC:*
  - CRADAs initiated in FY16
    - One CRADA fully executed in early 2016
    - Two CRADAs currently under negotiation
  - ORNL staff will continue to encourage new CRADA partnership opportunities

Remaining Challenges and Barriers

- Achieving DOE's goal of engaging industry/academia in cost-shared CRADA opportunity
  - DOE's goal is 10 partners in FY16
- Receiving SOA materials for characterization
  - Industry is hesitant to supply new materials that would be more relevant for characterization experiments (IP, commercial materials)

Proposed Future Work

- Expand 3D electron tomography to characterize tested MEAs to more fully understand stability issues for SOA materials under development
- Exploit opportunities with industry/academia to optimize CL structure –support structures, Pt-based catalyst distributions, and ionomer dispersions – to achieve enhanced Pt utilization; develop a more complete "database" of processing/microstructure correlations
- Apply high-resolution imaging and spectroscopy towards better understanding of bimetallic catalyst stability
- Encourage new partnerships through DOE's stream-lined, cost-shared CRADA opportunity

Project Summary

Relevance:	ORNL's microscopy expertise and state-of-the-art capabilities are integral to understanding the interplay between structure and composition of individual materials and how these materials are integrated into MEAs
Approach:	Our approach is "unique" in that it is fully collaborative in nature and benefits the entire FC community – developing and applying advanced microscopy methods to understand fuel cell materials and correlating observations with performance
Technical Accomplishments and Progress:	We continue to listen to our partners and address important issues that are relevant to the FC community – we support the FC community with unique capabilities for the microscopic evaluation of FC materials. To this end, we will encourage new partnerships with industry to elucidate materials degradation phenomena that limit fuel cell materials durability and performance.
Collaborations:	ORNL will continue to establish new collaborations to provide access to unique imaging/analysis (microscopy) capabilities and expertise, especially via new CRADAs.
Proposed Future Research:	Our primary goal for the coming year will be to use tomography methods for catalyst layers to better understand and model the interactions between ionomer films and support and/or nanoparticle surfaces and to apply these data towards optimized processing of new materials and durable MEAs.

Technical Back-up Slides

Extra Slide – Electron Tomography Procedure

Electron tomography process (Fiji/Imagej and FEI Aviso):

1) manual image/stack alignment (shift and rotation about common image feature)
2) calibrate z-thickness and interpolate slices (volume reconstructor)
3) median filter for removal of noise (median of every 3 pixels)
4) segmentation (binarization by high-end threshold filter)
5) for pore statistics/viewing (threshold @ 45% Pt/C volume percent):
    a) take the 'not' (inverse) of Pt/C segment from BF stack (55% pore space)
    b) separate objects (watershed)
    c) label objects
    d) kill border (removes partial pores on edges of volume)
    e) label analysis (computes statistics)
6) for ionomer statistics/viewing (threshold @ 30% ionomer volume percent):
    a) separate objects (watershed)
    b) label objects
    c) kill border (removes partial ionomer pockets on edges of volume)
    d) label analysis (computes statistics)
7) visualizations (single component or overlayed components)
    a) volume rendering (opaque/transparent)
    b) isosurface rendering (opaque/transparent)
    c) ortho slice (cross-section/z-slice through volume, like a clipping plane)
    d) generate surface (smooths/resamples labels)
        i. surface view (allows selection of individual label/single pore/ionomer pocket)
        ii. clipping planes (cuts to allow viewing of inner surfaces/inside pores)