
V.F.1 New Fuel Cell Materials: Characterization and Method Development

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Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Identify and/or develop novel high-resolution imaging and compositional/chemical analysis techniques, and unique specimen preparation methodologies, for the μm -to sub- \AA scale characterization of material constituents comprising fuel cell (FC) catalyst layers (electrocatalysts, catalyst supports, ionomer films).
- Optimize imaging and spectroscopy methodologies towards characterizing specific fuel cell materials; electrocatalyst atomic-scale structure and chemistry, ionomer mapping in catalyst layers, and three-dimensional (3D) electron tomography.
- Integrate microstructural characterization within other DOE projects and establish collaborations with industrial partners.
- Make capabilities and expertise available to broad fuel cell research community.

Fiscal Year (FY) 2016 Objectives

- Establish microscopy expertise for conducting high-resolution 3D electron tomography and apply to electrocatalyst, support, and ionomer studies.
- Use structural and spectroscopy data derived from extensive microscopy analyses to optimize materials through iterative synthesis/fabrication and characterization. Correlate materials structure and chemistry with durability, stability, and performance measurements when applicable.
- A goal of this new project is to establish new collaborations with industry and university partners via

a Fuel Cell Technologies Office (FCTO) opportunity to support collaborative projects with a 50% cost share through a streamlined, short-form cooperative research and development agreement (CRADA). ORNL staff scientists can collaborate directly with partners on DOE FCTO mission-aligned projects.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the FCTO Multi-Year Research, Development, and Demonstration Plan.

- (A) Durability
- (C) Performance

Technical Targets

This project is focused on conducting fundamental characterization studies on individual material constituents comprising FCs, with an emphasis on new materials including electrocatalysts, supports, and ionomer before and after incorporation into membrane electrode assemblies (MEAs), and identification and optimization of methods directed specifically towards characterization of FC materials and MEAs. Insights gained through extensive microstructural studies will be applied toward the design and manufacture of catalysts and catalyst supports that meet the DOE 2017 and 2020 targets for integrated polymer electrolyte membrane fuel cell (PEMFC) power systems and FC stacks operating on direct hydrogen for transportation applications (listed in Table 1).

FY 2016 Accomplishments

- Imaged ionomer dispersions in catalyst layers in 3D for the first time using novel ultramicrotomy method combined with high-resolution compositional mapping via electron microscopy. The 3D renderings were used not only to visualize the ionomer, but allowed for quantification of ionomer dispersions in real catalyst layers (CLs) and to develop a correlation with porosity.
- Initiated a significant effort in performing 3D electron tomography of a variety of catalyst nanostructures and supports, including Pt and Pt-alloy catalysts, and PGM-free catalysts, and developed methodology for conducting 3D electron tomography of intact CLs. These data allowed the quantification of differences between catalyst loadings, catalyst dispersions, and catalyst agglomeration and nearest neighbor distances.

TABLE 1. Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2011 Status	2017 Target	2020 Target
PGM total content (both electrodes)	g/kW (rated)	0.19	0.125	0.125
PGM total loading	mg PGM/cm ² electrode area	0.15	0.125	0.125
Loss in initial catalytic activity	% mass activity loss	48	<40	<40
Electrocatalyst support stability	% mass activity loss	<10	<10	<10
Mass activity	A/mg Pt @ 900 mV	0.24	0.44	0.44
Non-Pt catalyst activity per volume of supported catalyst	A/cm ² @ 800 mV	60 (at 0.8 V) 165 (extrapolated from > 0.85 V)	300	300

PGM – Platinum (Pt) group metal

- Further optimized the use of low-voltage, sub-Å-scale imaging and spectroscopy of PGM-free catalysts.
- Established new industrial collaboration through streamlined CRADA process, with several additional industrial partnerships being considered and/or negotiated.



INTRODUCTION

PEMFCs are being developed for future use as efficient, zero-emission power sources. However, the performance of PEMFCs degrades with time during electrochemical aging in automotive and stationary applications. Performance degradation can be directly attributed to the durability of individual material constituents comprising the MEA, including the electrocatalyst, catalyst support, recast ionomer, and polymer membrane. In order to enhance the stability of PEMFCs, the structural and chemical characteristics of the materials used must be understood and optimized. The “New Fuel Cell Materials: Characterization and Method Development” project at ORNL is focused on several primary objectives: (i) characterizing the microstructural and microchemical nature of new materials developed for PEMFCs using state-of-the-art imaging and spectroscopy techniques, (ii) identifying, developing, and/or optimizing methodologies specifically aimed at materials for FCs, and (iii) forming collaborative relationships with industrial PEMFC developers/manufacturers, universities, and national laboratories, to apply ORNL’s advanced electron microscopy techniques and expertise (available through ORNL’s Materials Characterization Center via a streamlined CRADA process) to conduct relevant studies towards understanding materials stability and durability issues and to develop materials-based strategies required for optimizing PEMFC durability and performance.

APPROACH

ORNL’s microstructural characterization and method development project utilizes advanced electron microscopy analysis techniques to characterize the individual material components comprising PEMFCs, before and after incorporation into an MEA, and after electrochemical aging. Our approach is focused on identifying and optimizing novel high-resolution imaging and compositional/chemical analysis techniques, and developing unique specimen preparation methodologies, for the μm-to-sub-Å-scale characterization of the material constituents of fuel cells (electrocatalysts, catalyst supports, recast ionomer films, membranes, etc.). ORNL applies these advanced analytical and imaging techniques for the evaluation of the microstructural and microchemical characteristics of each material constituent and correlates these observations with FC performance. Most importantly, ORNL is making the techniques and expertise available to FC researchers outside of ORNL via several mechanisms: (1) strategic partnership projects for proprietary research, (2) a new streamlined short-form CRADA process whereby DOE’s FCTO provides a 50% cost share to collaborate with ORNL’s Materials Characterization Center on DOE FCTO mission-aligned projects, and (3) access via ORNL user facilities (e.g., Center for Nanophase Materials Sciences).

RESULTS

Electron tomography research was initiated in collaboration with Laure Guatez at CEA-Grenoble, France several years ago to study the morphological changes in PtNi nanostructured thin film catalysts during aging [3]. Electron tomography was a concerted effort at ORNL during FY 2016, which was specifically aimed at optimizing the technique towards conducting “four-dimensional (4D) electron tomography” studies on fully intact MEAs to combine high-resolution scanning transmission electron microscopy (STEM) imaging and chemical/compositional spectroscopy such that materials inter-relationships within CLs can be further understood at the nm-scale. Recent improvements

in the application of advanced/enhanced energy dispersive spectroscopy techniques to quantify ionomer layer/film dispersions within catalyst layers complement existing capabilities to image the carbon support and nanoparticle catalyst structures; these datasets can be combined to produce 3D renderings towards fully interrogating the various material components and interfaces comprising the CLs, and to understand the role of constituent dispersions and interfaces within the architectures of catalyst inks and electrodes.

STEM-based tomography was performed on a 200 kV FEI Talos F200X using a Gatan high-tilt tomography holder. Bright field and high-angle annular dark field STEM images were acquired in 2° increments over a 140° tilt range ($\pm 70^\circ$ for a total of 71 image pairs). Tilt series alignment and tilt-axis corrections were performed manually for each image in the sequence using Gatan software and adjusted iteratively prior to reconstruction to ensure convergence. 3D reconstructions were performed using a model-based iterative reconstruction algorithm [1,2]. Visualizations were rendered using FEI Aviso and Fiji/ImageJ software. High- and low-pass filter thresholding was applied to the reconstructed volumes for 3D segmenting and rendering of both Pt and C, with statistics computed using Aviso.

To demonstrate STEM tomography, Pt/C catalysts were compared with different Pt loadings (5%, 20%, 50%) and three different carbon supports (Vulcan XC-72 [V], high surface area carbon [HSAC], and low surface area graphitized carbon black [LSAC]) for a total of six Pt/C samples. These samples were chosen to compare the differences associated with Pt nanoparticle dispersion as a function of carbon support structure and Pt loading. A comparison of 3D tomography results for the lowest Pt loading (5%) on HSAC, V, and LSAC supports are shown in Figure 1. For the same carbon support area, there are significantly more Pt nanoparticles on HSAC compared with Vulcan and LSAC, and the average diameter of the Pt nanoparticles on HSAC (2.0 nm) and Vulcan (~ 2.75 nm) were much smaller than Pt deposited on LSAC (4.25 nm).

To visualize ionomer distributions within CLs, a different sample preparation was employed. MEAs (in this example, a 40% Pt/V CL was used) were embedded using standard procedures for ultramicrotomy after a Au fiducial layer/marker was sputter coated on the catalyst layer surface (used to locate same area for imaging and elemental mapping). The Leica ultramicrotome was used to carefully slice individual MEA cross-sections, one slice at a time, to “depth-profile” through the catalyst layer cross-section. Each catalyst layer slice was approximately 100 nm thick and we were able to cut 17 sections to use for reconstruction of the catalyst layer. 3D reconstructions were performed using FEI’s Aviso software package.

A 3D reconstruction of the stacked images from the 17 microtome slices showing the ionomer distribution



FIGURE 1. STEM electron tomography reconstructions demonstrating the location and size differences of Pt nanoparticles (loading of 5%) supported on HSAC (top image), V (middle image), and LSAC (bottom image)

(green fluorine energy dispersive spectroscopy maps acquired for each microtome slice reconstructed into the volumetric rendering) within a volume of the catalyst layer ($7 \mu\text{m} \times 7 \mu\text{m} \times 1.5 \mu\text{m}$) is shown in Figure 2. In addition to visualization of ionomer features within a specific volume, the strength of acquiring electron tomography data, especially within a fully intact CL, is the ability to quantify size characteristics of the individual constituents as opposed to extracting data from traditional two-dimensional (2D)

images. This becomes especially relevant for quantifying the ionomer dispersions and porosity, where the sizes of specific features are larger than the thickness of the microtomed cross-section (50–100 nm). Figure 3 shows the results of quantifying the ionomer aggregate size and porosity size distributions for the 3D tomography data shown in Figure 2. The color-coding shown in both the 3D rendering and size distribution plots are directly correlated with specific feature

size ranges. For this particular CL, the average ionomer aggregate size is ~164 nm and the pore size is ~254 nm. The ionomer aggregate size is much larger than expected, and indicates severe ionomer aggregation associated with regions of the electrode with no ionomer; the aggregates are characterized as having an aspect ratio of 2:1, as shown in Figure 4, and are associated directly with “filling in” asperities in the large scale secondary pores as well as filling smaller pores within the CL.

CONCLUSIONS AND FUTURE DIRECTIONS

Microstructural and microchemical studies continue to provide insight regarding the structural and compositional characteristics of PEMFC constituents that ultimately dictate the specific material’s stability and durability during operation. In FY 2016, studies were primarily focused on 3D electron tomography of electrocatalysts, supports, and fully intact CLs. We will continue to support these studies in FY 2017 through collaborations with industrial and academic partners, which will be a significant focus of the project, while emphasizing studies focused on new materials for PEMFCs and using the knowledge gained towards materials optimization and improving electrocatalyst and ionomer interactions and dispersions.

- Continue to establish new collaborations with FC manufacturers and researchers to identify and

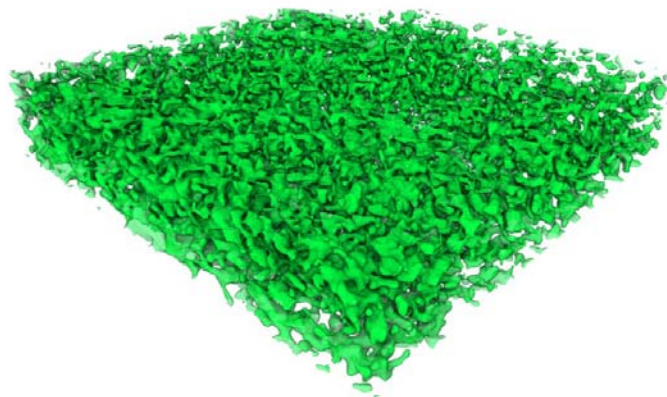


FIGURE 2. 3D electron tomography reconstruction of the ionomer dispersion within a 40% Pt/V CL containing ~30 vol% Nafion®. Green represents fluorine signal (energy dispersive spectroscopy) from each slice reconstructed into 3D volume

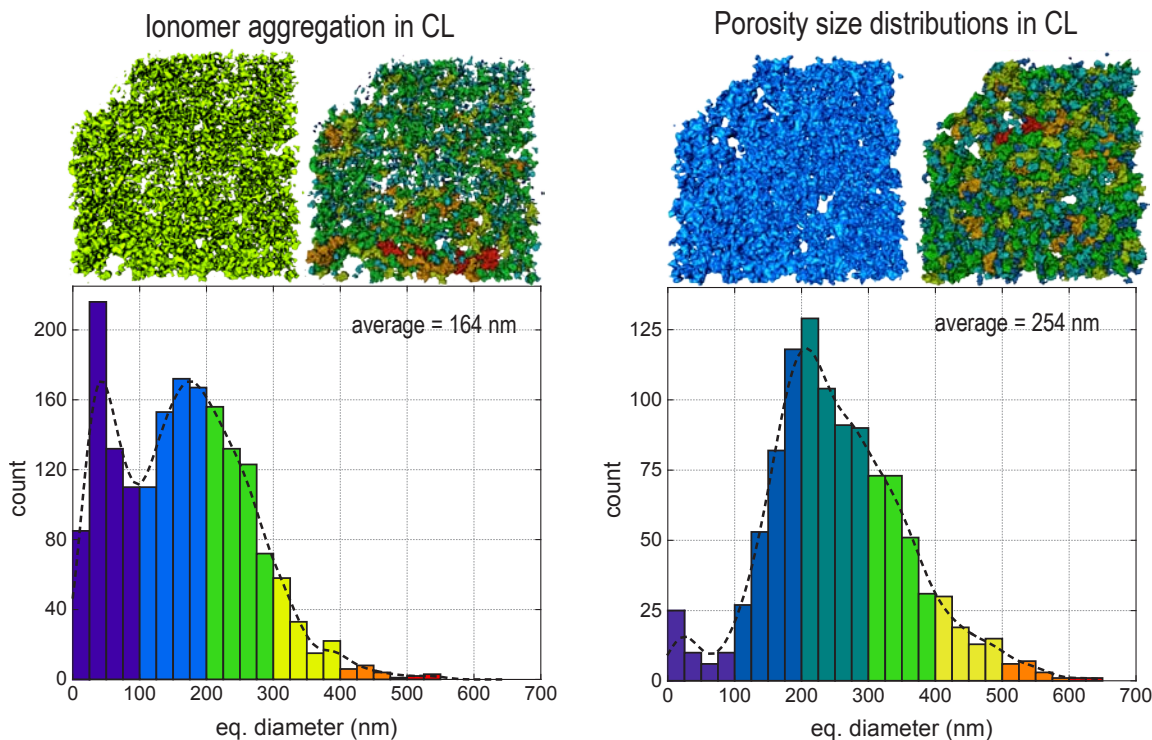


FIGURE 3. Ionomer aggregate size distribution and associated 3D renderings of ionomer (left) and pore size distribution and associated 3D renderings of pores (right) acquired from the same CL shown in Figure 2

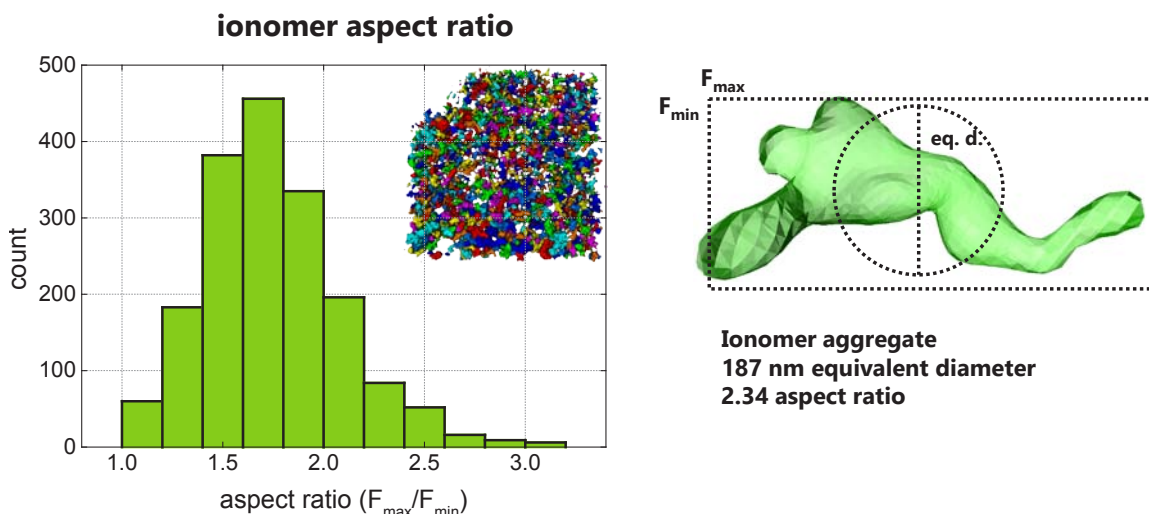


FIGURE 4. Plot of ionomer aspect ratios determined for 3D ionomer map (left) and rendering of a typical ionomer aggregate (right) extracted from ionomer map shown in Figure 2

characterize new FC materials to improve stability and durability. Input from the Fuel Cell Tech Team, reviewer comments from the Annual Merit Review, and establishing new collaborations are key to the success of this Characterization and Method Development project and to identify relevant and critical research directions.

- Refine 3D electron tomography methods to correlate and quantify interactions between ionomer layers, Pt-based catalysts and their distributions within CLs, and new/novel catalyst supports. Establish relationships between ionomer-Pt-support resulting from ink preparation methods.
- Continue to characterize ionomer distributions in “real” CLs through the use of high-resolution 3D electron tomography studies (combine structural and compositional tomography).

FY 2016 PUBLICATIONS/PRESENTATIONS

1. U. Martinez, J.H. Dumont, E.F. Holby, K. Artyushkova, G.M. Purdy, A. Singh, N.H. Mack, P. Atanassov, D.A. Cullen, K.L. More, M. Chhowalla, P. Zelenay, A.M. Dattelbaum, A.D. Mohite, and G. Gupta, “Critical Role of Intercalated Water for Electrocatalytically Active Nitrogen-doped Graphitic Systems,” *Science Advances* **2**[3] e1501178 (2016).
2. D. Raciti, J. Kubal, C. Ma, M. Barclay, M. Gonzalez, M. Chi, J. Greeley, K.L. More, and C. Wang, “Pt₃Re Alloy Nanoparticles as Electrocatalysts for the Oxygen Reduction Reaction,” *Nano Energy* **20** 202–211 (2016).
3. F.H. Garzon, M.S. Wilson, D. Banham, S.Y. Ye, and K.L. More, “Carbonaceous Nanowire Supports for Polymer Electrolyte Membrane Fuel Cells,” *Journal of the Electrochemical Society* **163**[2] F115–F121 (2016).
4. M. Chi, C. Wang, Y.K. Lei, G.F. Wang, D.G. Li, K.L. More, A. Lupini, L.F. Allard, N.M. Markovic, and V.R. Stamenkovic, “Surface Faceting and Elemental Diffusion Behavior at Atomic Scale for Alloy Nanoparticles During *in situ* Annealing,” *Nature Communications* **6** Article 8925 (2015).
5. L. Elbaz, J. Phillips, K. Artyushkova, K.L. More, and E.L. Brosha, “Evidence of High Electrocatalytic Activity of Molybdenum Carbide Supported Platinum Nanorrafts,” *Journal of The Electrochemical Society* **162**[9] H681–H685 (2015).
6. Invited Presentation: K.L. More, D.A. Cullen, B. Sneed, and K.S. Reeves, “Materials/Interfacial Homogeneity within PEM Fuel Cell Electrode Structures: The Interplay between Electrocatalyst, Catalyst-Support, and Ionomer Films and Effect on Durability and Performance,” 3rd International Workshop on Degradation Issues of Fuel Cells and Electrolyzers, Santorini, Greece, September 29–October 1, 2015.
7. Contributed Presentation: K.L. More, “Assessment of Nanofiber Electrode MEA Durability through Advanced Microscopy,” 228th Electrochemical Society Fall Meeting, Phoenix, AZ, October 12–16, 2015.
8. Contributed Presentation: B.T. Sneed, D.A. Cullen, and K.L. More, “Characterization of Catalytic Materials for PEM Fuel Cells by STEM Tomography,” MRS Fall Meeting, Boston, MA, November 29–December 3, 2015.
9. Contributed Presentation: D.A. Cullen, K.L. More, H.M. Meyer III, H.T. Chung, and P. Zelenay, “Analytical Characterization of Non-PGM Catalysts for PEM Fuel Cells,” MRS Fall Meeting, Boston, MA, November 29–December 3, 2015.
10. Invited Presentation: K.L. More, D.A. Cullen, and B.T. Sneed, “New Fuel Cell Materials: Characterization and Technique Development,” USCAR Fuel Cell Tech Team, Detroit, MI, February 17, 2016.
11. Contributed Presentation: K.L. More, D.A. Cullen, and B.T. Sneed, “Understanding Ionomer Dispersions in PEM Fuel Cell

Catalyst Layers,” MRS Spring Meeting, Phoenix, AZ, March 28–April 1, 2016.

12. Contributed Presentation: B.T. Sneed, D.A. Cullen, and K.L. More, “Towards 4D STEM Imaging of PEM Fuel Cell Catalyst Dispersions,” MRS Spring Meeting, Phoenix, AZ, March 28–April 1, 2016.

13. Invited Presentation: D.A. Cullen, “Advancing Fuel Cell Materials through Electron Microscopy,” Tech Connect, Washington DC, May 14–17, 2016.

14. Contributed Presentation: D.A. Cullen, B.T. Sneed, and K.L. More, “Impact of Evolving Electrode Morphology on Fuel Cell Performance: From the Nano to Mesoscale,” 229th Electrochemical Society Meeting, San Diego, CA, May 29–June 3, 2016.

15. Contributed Presentation: K.L. More, B.T. Sneed, and D.A. Cullen, “Understanding Electrocatalyst Morphology, Dispersion, and Stability in Catalyst Layers of PEM Fuel Cells Via 3D Electron Tomography,” 229th Electrochemical Society Meeting, San Diego, CA, May 29–June 3, 2016.

16. Invited Presentation: D.A. Cullen, B.T. Sneed, and K.L. More, “Fuel Cell Electrode Optimization through Multi-scale Analytical Microscopy,” Microscopy & Microanalysis 2016, Columbus, OH, July 24–28, 2016.

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3. D.A. Cullen, M. Lopez-Haro, P. Bayle-Guillemaud, L. Guetaz, M.K. Debe, and A.J. Steinbach, “Linking Morphology with Activity through the Lifetime of Pretreated PtNi Nanostructure Thin Film Catalysts,” *Journal of Materials Chemistry A* 3[21] 11660-11667 (2015).