

V.F.4 Characterization of Fuel Cell Materials

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Project End Date: Project continuation and direction
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Overall Objectives

- Identify, develop, and optimize novel high-resolution imaging and spectroscopy techniques as well as unique specimen preparation methodologies to characterize the material constituents comprising fuel cells (FCs) at the micrometer to sub-angstrom scale (electrocatalysts, catalyst supports, ionomer)
- Understand fundamental relationships between the material constituents within FC membrane electrode assemblies (MEAs), particularly cathode catalyst layers (CCLs), and correlate structural and chemical data with stability, durability, and performance characteristics (with guidance/input from the FC community); apply knowledge gained towards material and CCL optimization
- Integrate microstructural characterization within other DOE projects and establish collaborations with industrial partners
- Apply advanced analytical and imaging techniques for the evaluation of microstructural and microchemical changes resulting from FC testing, including accelerated stress tests (ASTs), to elucidate microstructure-related degradation mechanisms contributing to FC performance loss
- Make capabilities and expertise broadly available to other FC researchers

Fiscal Year (FY) 2015 Objectives

- Establish several new collaborations with FC manufacturers and researchers to identify and quantify

FC material degradation mechanisms and characterize new FC materials

- Image (map) and quantify the through-thickness distribution of ionomer dispersions within CCLs; correlate ionomer dispersions with materials constituents within CCLs
- Pursue the development of in situ electrochemical transmission electron microscopy methods to study the degradation of catalyst and support materials
- Interrogate material and MEA structures using three-dimensional (3D) electron tomography and optimize this technique for FC materials analysis

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (A) Durability
- (C) Performance

Technical Targets

This project is focused on conducting fundamental characterization studies to assess the stability and durability of the individual material constituents comprising polymer electrolyte membrane fuel cell (PEMFC) MEAs. These studies include the characterization of newly developed materials (electrocatalysts and catalyst supports), the incorporation of these materials in MEAs, and the correlation of electrode microstructural/material changes that occur during electrochemical aging with measured FC durability and performance. 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 PEMFC power systems and FC stacks operating on direct hydrogen for transportation applications (listed in Table 1).

FY 2015 Accomplishments

- Published results from a parametric study with General Motors (GM) to quantify ionomer distributions at multiple length scales within MEAs, e.g., through-thickness distributions within CCLs (100 nm level) and surrounding individual pores within CCLs (<10 nm level) in the *Journal of The Electrochemical Society*, which represent a successful collaboration between ORNL, GM, and Clarkson University

TABLE 1. Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Unit	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 ³ 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 at 900 mV	0.24	0.44	0.44
Non-PGM Catalyst Activity per Volume of Supported Catalyst	A/cm ² at 800 mV	60 (at 0.8 V) 165 (extrapolated from >0.85 V)	300	300

PGM – platinum group metal

- Collaboration continued with Ford Motor Co., to study catalyst dispersions on various catalyst support structures using X-ray photoelectron spectroscopy, high-resolution scanning transmission electron microscopy (STEM), and electron energy loss spectroscopy
- Fully established the capability for mapping ionomer film distributions across CCLs in MEAs using large solid-angle, high collection efficiency STEM-based energy dispersive X-ray spectroscopy (EDS) methods to understand and quantify ionomer aggregation as a function of specific materials components used in CCLs
- Compared results directly with scanning transmission X-ray microscopy data acquired from the same MEAs at McMaster University
- Initiated collaboration with Giner Inc. to study novel oxygen evolution reaction catalysts and support structures (Ir/W_xTi_{1-x}O₂) before and after aging
- Performed extensive low-voltage STEM imaging and spectroscopy on C-based materials comprising non-Pt group metal catalysts to identify potential active sites



INTRODUCTION

PEMFCs are being developed for future use as efficient, zero-emission power sources. However, the performance of PEMFCs degrades with time at elevated temperature and high relative humidity during electrochemical aging in automotive and stationary applications. Performance degradation can be directly attributed to the durability of the individual material constituents comprising the MEA; e.g., the electrocatalyst, the catalyst support, and the ionomer in the CCL. The structural and chemical degradation mechanisms contributing to performance loss have not been fully quantified. The Microstructural Characterization Program at ORNL has focused on forming collaborative relationships with multiple industrial PEMFC developers/

manufacturers, universities, and national laboratories to apply ORNL's advanced electron microscopy techniques and expertise to characterize as-fabricated (fresh) FC materials (individual constituents and/or materials incorporated in fresh MEAs), MEAs subjected to ASTs designed to degrade specific MEA components, and field-aged MEAs, with the ultimate goal of establishing critical processing-microstructure-performance correlations and elucidate the individual materials changes contributing to measured MEA degradation, performance loss, and failure. Understanding the structural and compositional changes of the materials comprising MEAs during electrochemical aging will allow for the implementation of materials-based mitigation strategies required for optimizing PEMFC durability and performance.

APPROACH

The task of microstructural characterization requires utilizing advanced electron microscopy imaging and spectroscopy techniques to characterize the individual material components comprising PEMFCs before and after incorporation into MEAs and after electrochemical aging. These studies also include novel materials (primarily electrocatalysts) developed by partner laboratories. Our approach is focused on identifying and optimizing novel high-resolution imaging and compositional/chemical analysis techniques as well as on developing unique specimen preparation methodologies specifically aimed at micrometer- to angstrom-scale characterization of the material constituents within FC CCLs (electrocatalysts, catalyst supports, and ionomer). These advanced analytical and imaging techniques are applied to evaluate the microstructural and microchemical characteristics of each material constituent, and to allow for correlation of these observations with FC performance (aging studies are conducted at the collaborator's laboratories). These studies are designed to elucidate the microstructure-related material degradation mechanisms that contribute to FC performance loss. Most importantly, ORNL is making available the techniques and expertise it has accrued to FC researchers outside of ORNL via several mechanisms: (1) strategic

partnership projects for proprietary research, (2) through the use of ORNL user facilities (e.g., Center for Nanophase Materials Sciences), and (3) by engaging in collaborative non-proprietary research projects via the Microstructural Characterization Project that are consistent with ORNL's research activities.

RESULTS

The ionomer distribution within the CCL plays a critical role in ionic and mass transport, and therefore, controls electrochemical kinetics. In a recent review article by Holdcroft [1], several unresolved challenges regarding the CCL ionomer distribution were identified. One of these challenges was elucidating the ionomer aggregation phenomenon in CCLs and the correlation between catalyst ink processing and solidification on the resultant CCL morphology. Thus, the primary goal of ORNL's research in FY 2015 was to “visualize” the ionomer distributions within PEMFC CCLs using high spatial resolution spectroscopy methods to understand and quantify ionomer film thickness and dispersion as a function of (1) the material constituents comprising the CCL, (2) ionomer loading, (3) the ink preparation method used, and (4) stability during electrochemical aging. An understanding of these relationships will enable optimization of the ionomer distributions within CCLs. In FY 2014, electron microscopy parameters (accelerating voltage, temperature, and electron dose) were optimized as part of a collaboration with GM to minimize damage to the ionomer during imaging analysis [2], and these established “best practices” were applied towards the study of CCL ionomer distributions. These studies also exploited the recent (over the previous two years) development of high-collection-efficiency, large solid-angle silicon drift detectors for EDS. These detectors were integrated within the column of the STEM to map the elemental distribution, specifically of fluorine, across the full

thickness of cross-sectioned CCLs (micrometer scale) and at higher resolutions surrounding pores and Pt/C agglomerates (nanometer scale) in very short times (typically <10 minutes).

To demonstrate this ionomer visualization technique, Figure 1 shows a representative high-spatial-resolution STEM-EDS fluorine map, acquired from a CCL with Pt catalyst supported on high surface area carbon (HSAC) and 28% Nafion[®] ionomer (with corresponding high-angle annular dark field [HAADF] STEM image). The cross-section HAADF-STEM image of the CCL (Figure 1a) shows several levels of contrast that correspond with specific features in the CCL – pores exhibit the darkest contrast (primary and secondary pores are evident), the HSAC support is characterized by medium (grey) contrast, and the Pt nanoparticles exhibit the brightest contrast. The non-homogeneous distribution of fluorine (Figure 1b, shown in green) is clear and is evidence for significant ionomer aggregation within the CCL. There is evidence for the presence of ionomer thin films within the CCL, as well; however, most of the ionomer is concentrated within ionomer aggregates having an average size of ~70 nm (circled in red in Figure 1b). These aggregates are present *between* the Pt/HSAC agglomerates and *within* the Pt/HSAC agglomerates. Additionally, a large fraction of the Pt/HSAC comprising the secondary pore surfaces (pores between Pt/HSAC agglomerates) has no ionomer layers on its surface, which is consistent with the ionomer filling the irregular regions (or pockets) where Pt/HASC agglomerates meet and also filling primary and secondary pores inside the Pt/HSAC agglomerates. The observation of ionomer aggregation is also evident on a CL containing Pt supported on graphitized carbon (low surface area carbon [LSAC]), as shown in Figure 2, except in this case the ionomer aggregation associated with Pt/LSAC is slightly different because the Pt/LSAC agglomerate density is higher (fewer large-sized pores compared to Pt/HSAC agglomerates). In this case,

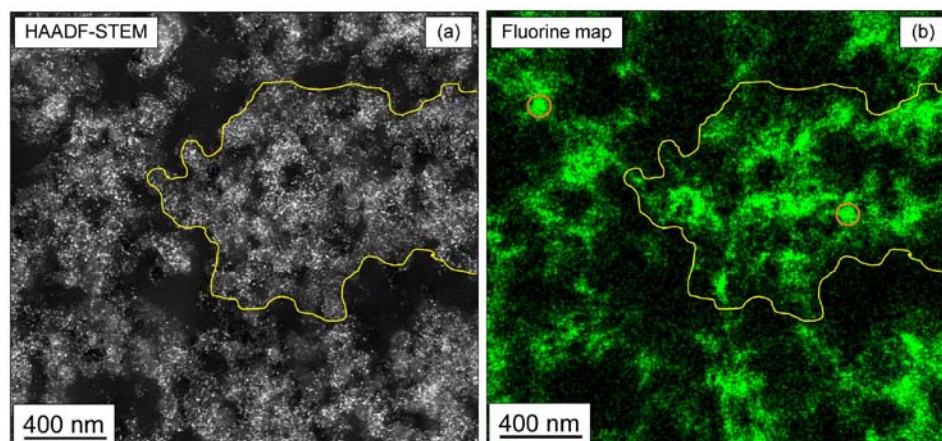


FIGURE 1. (a) HAADF-STEM image and (b) corresponding fluorine map acquired from CCL with Pt/HSAC and 28% Nafion[®] ionomer

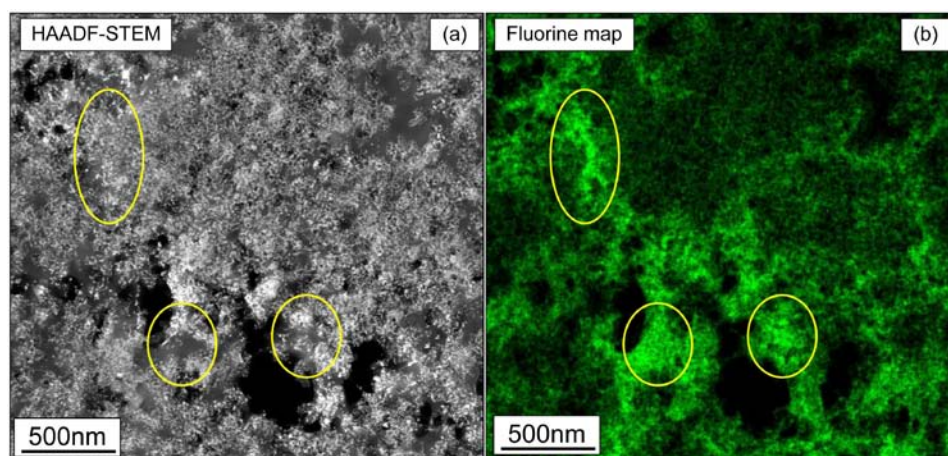


FIGURE 2. (a) HAADF-STEM image and (b) corresponding fluorine map acquired from CCL with Pt/LSAC and 38% Nafion® ionomer

a majority of the large ionomer aggregates were located between Pt/LSAC (circled in yellow in Figure 2), with thinner ionomer films present within the Pt/LSAC agglomerates.

Work is ongoing to establish direct correlations between the observed character of ionomer aggregation and the different types of materials used in CCLs and ink processing methods, with the ultimate goal of preparing CCLs with more uniform ionomer distributions/dispersions.

CONCLUSIONS AND FUTURE DIRECTIONS

ORNL's microstructural studies continue to provide insight regarding the structural and compositional factors of MEA material components that ultimately contribute to the stability and durability of FCs. In FY 2015, studies primarily focused on quantifying ionomer distributions within CCLs and new electrocatalysts. We will continue to support these studies in FY 2016 through collaborations with industrial and academic partners while emphasizing new studies focused on optimizing the interactions and dispersions of the electrocatalyst and ionomer, and on exploiting corrosion-resistant highly graphitized carbon supports by improving catalyst dispersions through surface modification. Specifically, we will:

- Continue to establish new collaborations with FC manufacturers and researchers to identify and quantify FC materials degradation mechanisms and to characterize new FC materials. Input from the Fuel Cell Tech Team, reviewer comments from the Annual Merit Review, and collaborations are key to the success of this microstructural characterization project and identify critical research directions.
- Correlate and quantify interactions between ionomer layers, Pt-based catalysts and their distributions within CCLs, and new/novel catalyst supports; establish

relationships between ionomer-Pt-support resulting from various ink preparation methods.

- Characterize ionomer distributions in “real” CCLs through the use of high-resolution 3D electron tomography studies, combining structural and compositional tomography.
- Perform dispersion optimization studies for ionomers and Pt on graphitic supports through surface modification.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. D.A. Cullen, K.L. More, L.L. Atanasoska, and R.T. Atanasoski, “Impact of IrRu Oxygen Evolution Reaction Catalysts on Pt Nanostructured Thin Films under Start-up/Shutdown Cycling,” *Journal of Power Sources* 269 671–681 (2014).
2. S.M. Alia, S. Pylypenko, K.C. Neyerlin, D.A. Cullen, S.S. Kocha, and B.S. Pivovar, “Platinum-Coated Cobalt Nanowires as Oxygen Reduction Reaction Electrocatalysts,” *ACS Catalysis* 4[8] 2680–2686 (2014).
3. Q. Li, G. Wu, D.A. Cullen, K.L. More, N.H. Mack, H.T. Chung, and P. Zelenay, “Phosphate-Tolerant Oxygen Reduction Catalyst,” *ACS Catalysis* 4[9] 3193–3200 (2014).
4. Y.J. Kang, J. Snyder, M. Chi, D.G. Li, K.L. More, N.M. Markovic, and V.R. Stamenkovic, “Multimetallic Core/Interlayer/Shell Nanostructures as Advanced Electrocatalysts,” *Nano Letters* 14[11] 6361–6370 (2014).
5. D.A. Cullen, R. Koestner, R.S. Kukreja, Z.Y. Liu, S. Minko, O. Trotsenko, A. Tokarev, L. Guetaz, H.M. Meyer III, C.M. Parish, and K.L. More, “Imaging and Microanalysis of Thin Ionomer Layers by Scanning Transmission Electron Microscopy,” *Journal of The Electrochemical Society* 161[10] F1111–F1117 (2014).
6. 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 Nanostructured Thin Film

Catalysts,” *Journal of Materials Chemistry A* 3[21] 11660–11667 (2015).

7. J. Zheng, D.A. Cullen, R.V. Forest, J.A. Wittkopft, Z.B. Zhuang, W.C. Sheng, J.G.G. Chen, and Y.S. Yan, “Platinum-Rhuthenium Nanotubes and Platinum-Rhuthenium Coated Copper Nanowires as Efficient Catalysts for Electro-Oxidation of Methanol,” *ACS Catalysis* 5[3] 1468–1474 (2015).

8. A. Epshteyn, Y. Garsany, K.L. More, H.M. Meyer III, V. Jain, A.P. Purdy, and K.E. Swider-Lyons, “Effective Strategy for Improving Electrocatalyst Durability by Adhesive Immobilization of Catalyst Nanoparticles on Graphitic Carbon Supports,” *ACS Catalysis* 5[6] 3662–3674 (2015).

9. Invited Presentation: K.L. More, D.A. Cullen, and K.S. Reeves, “Correlating Catalyst Stability with Improved Cathode Materials for PEM Fuel Cells,” Gordon Research Conference on Fuel Cells, Bryant University, Smithfield, RI, August 3–8, 2014.

10. Contributed Presentation: K.L. More, D.A. Cullen, and K.S. Reeves, “The Effect of Carbon Support Structure on Ionomer Distributions in PEM Fuel Cell Catalyst Layers,” 226th ECS Meeting, Cancun, Mexico, October 5–10, 2014.

11. Contributed Presentation: D.A. Cullen, K.L. More, J. Erlebacher, D. van der Vliet, S. Luopa, and A.J. Steinbach, “The Impact of Pretreatments and Conditioning on the Structure and Performance of NSTF ORR Alloy Catalysts,” 226th ECS Meeting, Cancun, Mexico, October 5–10, 2014.

12. Invited Presentation: K.L. More and D.A. Cullen, “Understanding Fuel Cell Materials Degradation via Advanced Electron Microscopy Techniques,” 227th ECS Meeting, Chicago, IL, May 25–29, 2015.

13. Contributed Presentation: K.L. More, D.A. Cullen, and K.S. Reeves, “Characterization of Ionomer Thin Film Distributions in PEM Fuel Cell Catalyst Layers using Analytical Electron Microscopy,” ECS Conference on Electrochemical Energy Conversion & Storage with SOFC-XIV, Glasgow, Scotland, July 26–31, 2015.

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1. S. Holdcroft, “Fuel Cell Catalyst Layers: A Polymer Science Perspective,” *Chemistry of Materials* 26[1] 381–393 (2014).
2. D.A. Cullen, R. Koestner, R.S. Kukreja, Z.Y. Liu, S. Minko, O. Trotsenko, A. Tokarev, L. Guetaz, H.M. Meyer III, C.M. Parish, and K.L. More, “Imaging and Microanalysis of Thin Ionomer Layers by Scanning Transmission Electron Microscopy,” *Journal of The Electrochemical Society* 161[10] F1111–F1117 (2014).