

V.A.5 Characterization of Fuel Cell Materials

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complementary microstructural/compositional analysis techniques, and provide feedback for materials (and MEA) optimization.

Technical Barriers

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

- (A) Durability
- (C) Performance

Technical Targets

This project is focused on conducting fundamental characterization studies on the stability of individual material constituents comprising fuel cell MEAs. Of primary importance is relating MEA microstructural changes during aging to fuel cell durability and performance. Insights gained through these extensive microstructural studies will be applied toward the design and manufacture of MEAs that meet the following DOE 2015 MEA targets:

- Cost: \leq \$5/kW
- Durability with cycling: 5,000 hours
- Operating temperatures: \leq 120°C
- Total catalyst loading (for both electrodes): 0.2 g/kW (rated)
- Extent of performance degradation over lifetime: 5%

Fiscal Year (FY) 2012 Objectives

- Develop and/or apply novel preparation, imaging, and analytical methods to characterize fuel cell materials and architectures in the as-processed (fresh) state, during operation (in situ), and after electrochemical testing (post-mortem). Fuel cell materials of particular interest include novel electrocatalysts (especially related to low catalyst loadings, alloy electrocatalysts, and non-Pt-group metal catalysts), catalyst support structures (carbon and non-carbon supports), ionomer layers, gas diffusion layers (GDLs), and microporous layers (MPLs).
- Elucidate membrane electrode assembly (MEA) degradation and/or failure mechanisms by conducting extensive microstructural characterization using advanced electron microscopy techniques, with a specific focus on distinguishing the structural and chemical contributions from the material constituents contributing to fuel cell performance loss.
- Develop the critical correlations between MEA microstructure, composition, and architecture and MEA durability.
- Compare microstructural changes resulting from accelerated stress testing (AST) with microstructures observed after field aging.
- Collaborate with polymer electrolyte membrane fuel cell (PEMFC) component developers and manufacturers, university researchers, and other national laboratories, to evaluate MEAs using electron microscopy and

FY 2012 Accomplishments

- Continued effort to characterize a series of MEAs subjected to various ASTs at Los Alamos National Laboratory (LANL) designed to accelerate either carbon corrosion or catalyst degradation. These studies focused on evaluating “material-specific” Å-scale structural and compositional changes contributing to measured performance loss.
- Completed study with Nissan Technical Center North America to characterize a series of Pt/C with varying Pt loadings and carbon supports. This study focused on establishing a correlation between Pt nanoparticle morphology, dispersion, and size distribution with carbon support structure. Recently, aged MEAs with the same cathode Pt/C materials were sent to ORNL to quantify the material’s structural degradation.
- Initiated study with General Motors (GM) to characterize ionomer layers deposited on Pt surfaces, which has evolved to include ionomer layers deposited

in several model single-crystal surfaces. The goal of this study is to establish critical bonding characteristics of ionomer layers of varying thickness on relevant surfaces.

- Initiated study with Ballard to study the effect of catalyst and ionomer loading on MEA architecture and correlate structural observations with performance.
- Collaborated with Naval Research Laboratory researchers to characterize the nature of Pt nanoparticle interactions (anchoring) with tantalum phosphate films deposited on Vulcan carbon supports.
- Established method(s) to quantify the amount of Pt loss due to dissolution and migration from cathode – this work was done in collaboration with Nuvera and LANL and focused on establishing differences in Pt migration/loss as a function of Pt loading, carbon support, and AST, and results were correlated with catalyst degradation in cathode due to coalescence.
- Collaborated with Proton OnSite to characterize manufacturing defects in catalyst layers.



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 relative humidity (RH) 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, ionomer, polymer membrane, and GDL/MPL. Unfortunately, the structural and chemical degradation mechanisms contributing to performance loss have not been fully quantified. During the past several years, the Microstructural Characterization Program at ORNL has been focused on forming collaborative relationships with numerous industrial PEMFC developers/manufacturers, universities, and national laboratories, to apply ORNL's advanced electron microscopy techniques and expertise to characterize as-fabricated (fresh) fuel cell materials (individual constituents and/or materials incorporated in fresh MEAs), MEAs subjected to ASTs designed to degrade specific MEA components, and field-aged MEAs. These studies are used to establish critical processing-microstructure-performance correlations and to elucidate the individual materials changes contributing to measured MEA degradation, performance loss, and failure. Understanding the structural and compositional changes of the materials comprising the MEA during electrochemical aging will allow for the implementation of processing changes and critical materials development that are required for optimizing PEMFC durability and performance.

Approach

The microstructural characterization task 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 \AA -scale characterization of the material constituents of fuel cells (electrocatalyst, catalyst support, ionomer, membrane, etc.). ORNL applies these advanced analytical and imaging techniques for the evaluation of the microstructural and microchemical changes of each material constituent and correlates these observations with fuel cell performance (aging studies are conducted at the collaborator's laboratories). These studies are designed to elucidate the microstructure-related degradation mechanisms contributing to fuel cell performance loss. Most importantly, ORNL is making the techniques and expertise available to fuel cell researchers outside of ORNL via several mechanisms – (1) work for others (proprietary) research, (2) ORNL User Facilities (e.g., Shared Research Equipment User Facility), and (3) collaborative non-proprietary research projects via the Microstructural Characterization Project that are consistent with ORNL's "baseline project" research activities.

Results

In addition to extensive microstructural characterization of a wide range of starting/fresh materials used in PEMFC MEAs, previous annual reports have summarized observations for the structural and compositional degradation of MEA constituents, primarily the electrocatalyst and carbon catalyst supports. ORNL's FY 2011 report focused on initial attempts to characterize the structure and chemistry of the ionomer, studies which continued in FY 2012 as part of new collaborations initiated with GM, 3M, and Ballard. These new collaborations are specifically focused on characterizing ionomer films of varying thicknesses (1-10 nm) deposited on specific model surfaces (e.g., Pt on 3M's nanostructured thin films [NSTF] or on low surface area carbon [LSAC] surfaces) and loading variations within electrode structures. These new studies will take advantage of ORNL's new aberration-corrected low-voltage scanning transmission electron microscope (STEM), the Nion UltraSTEM 60-100. These studies are ongoing.

A major research focus in FY 2012, which was initiated as a result of requests from two major partners (3M and Nuvera), has been to *quantify* the amount of catalyst (Pt) loss specifically due to migration out of the cathode into the membrane following various aging protocols. The fact that Pt migrates into the membrane is well known; [1,2]

however, quantifying differences in migration profiles resulting from specific aging conditions or specific materials used in the cathode, have not been conducted successfully. Many techniques have been used to try and fully quantify the Pt loss in the membrane, including scanning electron microscopy (SEM), electron probe microanalysis (EPMA), X-ray photoelectron spectroscopy (XPS), etc., [3] but none have accurately captured the extent of Pt migration out of the cathode. We have focused our effort on using transmission electron microscopy (TEM) imaging to establish particle size distributions across intact MEAs as a viable method for quantifying the amount of Pt loss.

MEAs subjected to different AST protocols were prepared in cross-section via microtomy such that the entire 3-layer MEA could be imaged in the TEM (cathode-membrane-anode). A series of high-magnification images were acquired from the cathode-membrane interface across the entire membrane to the anode-membrane interface. Particle size distributions were measured across the membrane thickness (within sequential areas $\sim 1 \mu\text{m} \times 5 \mu\text{m}$) to compare Pt migration profiles from the different MEAs and ASTs, and to calculate the amount of Pt present within each membrane particle. Examples of MEA cross-sections with different Pt particle distributions in the membrane are shown in Figure 1. The baseline Pt (number of atoms) present in the same cathode area was established for fresh MEA cathodes. For example, the Pt dispersion/morphology in a $1 \mu\text{m} \times 5 \mu\text{m}$ area of a cathode containing 0.2 mg/cm^2 Pt supported on high surface area carbon (HSAC), Figure 2a, is quite different from 0.2 mg/cm^2 Pt supported on LSAC,

Figure 2b. This comparison is especially noteworthy since the resulting cathode thickness ($25 \mu\text{m}$ and $15 \mu\text{m}$) and porosity are significantly different for the Pt/HSAC and Pt/LSAC, respectively, which impacts the Pt morphology and dispersion even for the same Pt loading (0.2 mg/cm^2). The particular MEAs described here were supplied and tested by collaborators at LANL; additional MEAs were provided by Nuvera and 3M. All MEAs characterized thus far were prepared with reinforced (3-layer) membranes.

An example of the Pt migration profiles resulting from an AST for carbon corrosion (1.2 V hold in H_2/N_2) for the Pt/HSAC and Pt/LSAC after 100 h and 400 h, respectively, are compared in Figure 3 (particles present in the cathode side of the 3-layer membrane are shown for simplicity). Most notable is the number of Pt particles observed in the membrane for the Pt/HSAC cathode after only 100 h (144 particles), Figure 3a, compared to the significantly lower number of Pt particles present in the membrane for the Pt/LSAC cathode after a longer hold time of 400 h (23 particles), Figure 3b. The amount of Pt loss from the cathode can be directly related to the starting microstructures of the Pt/HSAC vs. Pt/LSAC (shown in Figure 2) and is calculated as 9.5% and 1.3% Pt loss into the membrane, respectively, from the starting Pt loading in the cathode. Clearly, the Pt/LSAC is significantly more stable than Pt/HSAC and exhibits much less (by $\sim 8\text{X}$) Pt loss (as well as less Pt coalescence and carbon corrosion (not shown)) for 4X longer hold times compared with Pt/LSAC. Similar measurements are being made for other ASTs and cathode materials (alloy electrocatalysts, Pt/NSTF, Pt loadings, etc.).

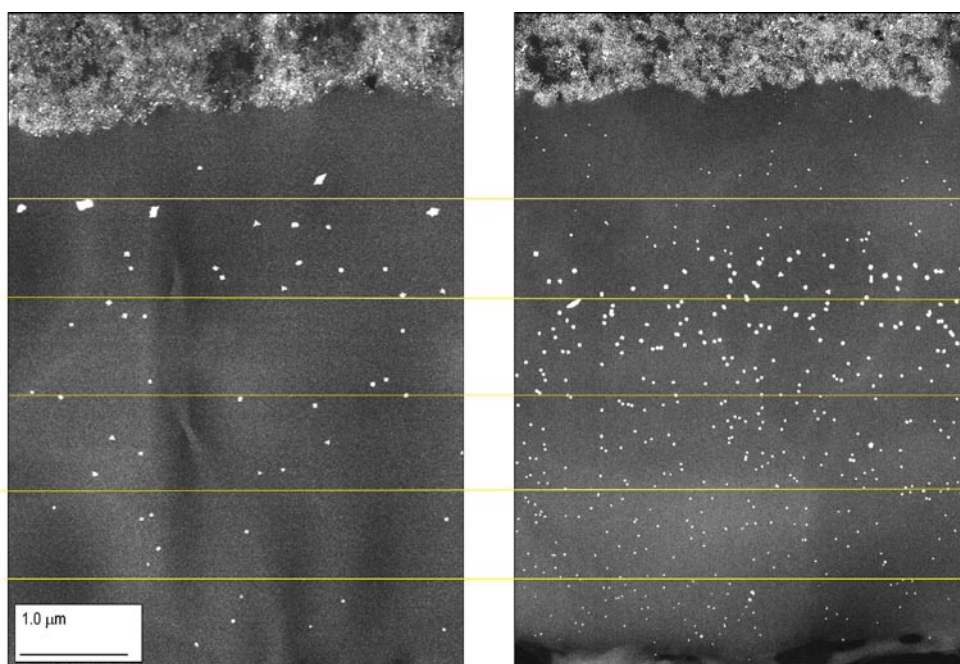


FIGURE 1. Example Pt particle distributions in the membrane (cathode side) following aging under different AST protocols

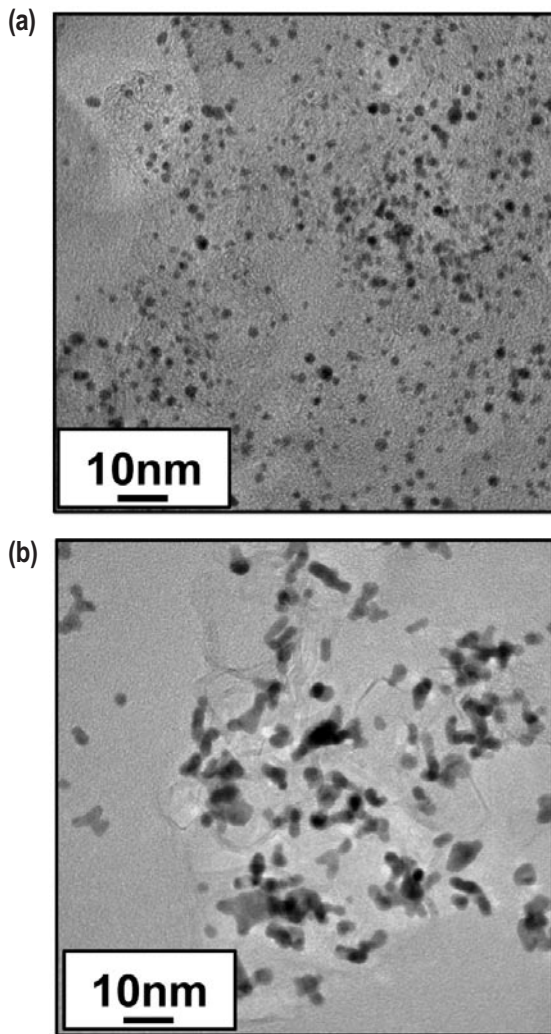


FIGURE 2. TEM images of (a) 0.2 mg/cm² Pt supported on HSAC (25- μ m thick cathode) and (b) 0.2 mg/cm² Pt supported on LSAC (15- μ m thick cathode)

Conclusions and Future Directions

- ORNL continues to focus on relevant materials degradation studies that provide insight regarding fuel cell material’s durability and stability. Specifically, ORNL research has focused on characterizing the microstructural- and microchemical-related mechanisms that contribute to materials degradation and performance loss.
- Correlate microstructural/compositional observations with AST protocols (automotive and stationary), especially related to catalyst dissolution, coarsening, and migration, carbon corrosion, membrane degradation – these studies continue to be a priority of this research program and have been part of ongoing and proposed “future” research each year.
- Expand on ionomer studies with GM to include interactions with carbons(s) using the low-voltage imaging/electron energy loss spectroscopy capabilities of ORNL’s Nion UltraSTEM microscope.
- Develop in situ liquid TEM/STEM as a priority for ORNL’s baseline characterization project – this has emerged as a future work topic because of community-wide interest and the fact that we have successfully demonstrated such capabilities for battery research.
- Continue to establish collaborations with industries, universities, and national laboratories (including access via ORNL User Facilities) to facilitate “transfer” of unique capabilities. This will include supporting new DOE projects with microstructural characterization and developing/applying advanced characterization techniques.

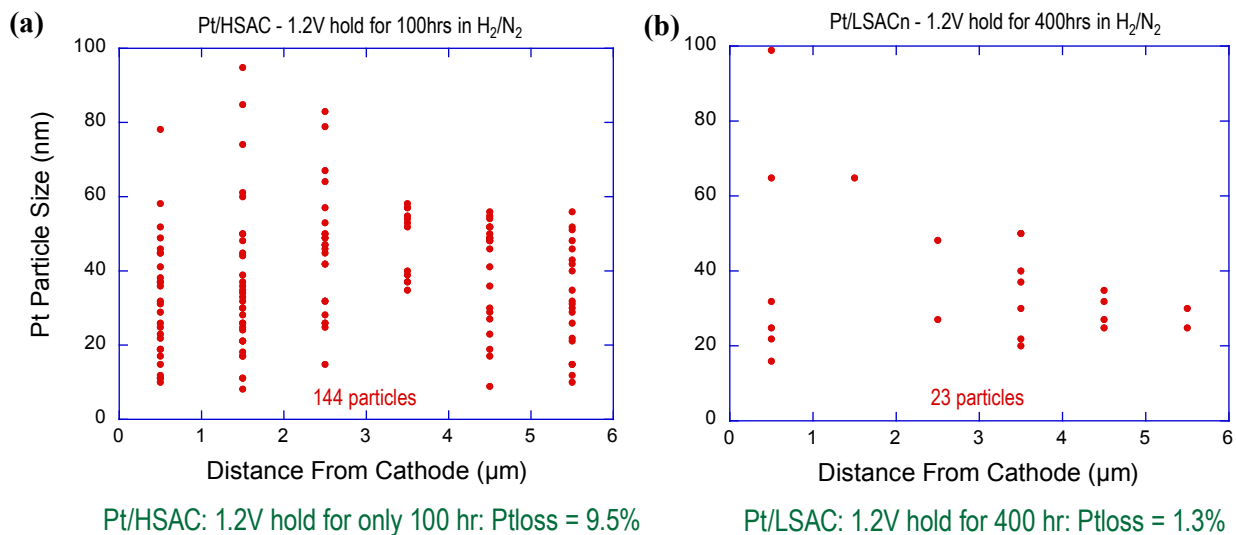


FIGURE 3. Pt particle migration profiles for AST of 1.2 V hold in H₂/N₂ for (a) Pt/HSAC after 100 h and (b) Pt/LSAC after 400 h

FY 2012 Publications/Presentations

1. Y. Liu, M. Chi, V. Mazumder, K.L. More, S. Soled, J.D. Henao, and S.H. Sun, "Composition-controlled Synthesis of Bimetallic PdPt Nanoparticles and Their Electro-oxidation of Methanol," *Chemistry of Materials* 23[18] 4199-4203.
2. C. Wang, M. Chi, D. Li, D. van der Vliet, G. Wang, Q. Lin, J. Mitchell, K.L. More, N.M. Markovic, and V.R. Stamenkovic, "Synthesis of Homogeneous Pt-Bimetallic Nanoparticles as Highly Efficient Electrocatalysts," *ACS Catalysis* 1[10] 1355-1359 (2011).
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5. D.A. Cullen, K.L. More, K.S. Reeves, G.D. Vernstrom, L.L. Atanasoska, G.M. Haugen, and R.T. Atanasoski, "Characterization of Durable Nanostructured Thin Film Catalysts Tested Under Transient Conditions Using Analytical Aberration-corrected Electron Microscopy," *ECS Transactions* 41[1] 1099-1103 (2011).
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7. K.J. Blackmore, L. Elbaz, E. Bauer, E.L. Brosha, K.L. More, T.M. McCleskey, and A.K. Burrell, "High Surface Area Molybdenum Nitride Support for Fuel Cell Electrodes," *Journal of the Electrochemical Society* 158[10] B1255-B1259 (2011).
8. V. Mazumder, M. Chi, M.N. Mankin, Y. Liu, O. Metin, D.H. Sun, K.L. More, and S.H. Sun, "A Facile Synthesis of MPd (M=Co, Cu) Nanoparticles and Their Catalysis for Formic Acid Oxidation," *Nano Letters* 12[2] 1102-1106 (2012).
9. C. Wang, D.G. Li, M. Chi, J. Pearson, R.B. Rankin, J. Greeley, Z.Y. Duan, G.F. Wang, D. van der Vliet, K.L. More, N.M. Markovic, and V.R. Stamenkovic, "Rational Development of Ternary Alloy Electrocatalysts," *Journal of Physical Chemistry Letters* 3[12] 1668-1673 (2012).
10. *Keynote Presentation*: M.P. Brady, K.L. More, T.J. Toops, H.M. Meyer, P.F. Tortorelli, M. Abd Elhamid, G. Dadheech, J. Bradley, H. Wang, and J.A. Turner, "PEM Fuel Cell Metallic Bipolar Plates: Technical Status and Nitridation Surface Modification for Improved Performance," *Technoport 2012*, Trondheim, Norway – April 16, 2012.
11. *Short Course*: K.L. More, "Advanced Microscopy Methods for Studying PEM Fuel Cell Materials" *221st Meeting of the Electrochemical Society*, Seattle, WA – May 6, 2012.
12. *Invited Presentation/Tutorial*: K.L. More, D.A. Cullen, M. Chi, and J.-C. Idrobo, "Advanced Microscopy Methods for Studying PEM Fuel Cell Materials," *221st Meeting of the Electrochemical Society*, Seattle, WA – May 8, 2012.
13. *Keynote Presentation*: K.L. More, "Application of Advanced Microscopy Methods to Understand MEA Materials Degradation," *International Workshop on the Characterization and Quantification of MEA Degradation Processes*, Grenoble, France – September 26, 2012.

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