V.H.3 Characterization of Fuel Cell Materials

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

Overall Objectives

- Identify, develop, and optimize high-resolution imaging and microanalysis techniques, and unique specimen preparation methodologies, for the µm- to sub-Å-scale characterization of the material constituents comprising fuel cells (FCs) (e.g., electrocatalyst, catalyst support, ionomer, and membrane).
- Elucidate fundamental relationships between the material constituents within FC membrane electrode assemblies (MEAs) and correlate these data with MEA stability and performance using guidance from the FC community.
- Integrate microstructural characterization as a core resource within other DOE FC projects.
- Evaluate microstructural and microchemical changes contributing to FC performance loss, identify degradation mechanisms, and devise mitigation strategies related directly to material improvements.
- Make capabilities for advanced characterization and expertise available to the FC community outside of ORNL.

Fiscal Year (FY) 2013 Objectives

- Quantify extent of carbon corrosion in MEAs subjected to accelerated stress tests (ASTs) by building on previous observations related to carbon structural changes (e.g., formation of graphite oxide and its dependence on initial graphitic structure/content) using a combination of analytical microscopy techniques and X-ray photoelectron spectroscopy.
- Establish imaging and analysis parameters/conditions that should be used to best characterize and quantify the structure and composition of ionomer thin films (less than 10-nm thick) *within* the MEA electrodes without inducing artifacts/damage.
- Establish imaging and analysis parameters/conditions that should be used to image and quantify the structure and composition of individual electrocatalyst nanoparticles (as-synthesized, incorporated in MEAs, and post-aging) using large solid angle silicon drift detectors to minimize beam damage. These studies should be correlated with electron tomography experiments.
- Correlate µm-scale electrode architecture with processing to optimize microstructure for enhanced performance.
- Develop in situ liquid microscopy capabilities for electrochemistry of FC materials to study electrocatalyst coarsening and carbon corrosion.

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 on the stability of individual material constituents comprising FC MEAs. Of primary importance is relating electrode microstructural/material changes occurring during 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 electrocatalyst targets listed in Table 1.

FY 2013 Accomplishments

- Based on input from the FC Tech Team, ORNL and Los Alamos National Laboratory (LANL) collaborated on a series of ASTs to quantitatively assess the extent of carbon oxidation as a function of carbon-support type used in the cathode. These MEAs were studied to correlate carbon-support oxidation (microstructural observations) with CO_2 evolution to further understand the critical parameters that govern both electrocatalyst and carbon support stability.

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-group metal

- Separate ionomer studies with General Motors (GM) and Ballard were continued during FY 2013, with particular attention paid to ionomer thin films on model substrates and identifying the proper microscopy conditions to reliably analyze thin ionomer films. This is ongoing work with the ultimate goal being the assessment of "real" ionomer films in catalysts layers.
- David Cullen spent one month at Commissariat à l'Energie Atomique (CEA) in Grenoble, France, collaborating on two primary FC studies: 3-dimensional tomography of nanostructured thin-film catalysts before and after aging, and mapping ionomer distributions within catalysts layers. CEA has unique capabilities that complement ORNL techniques, and this valuable visit will help us identify critical operating parameters necessary for our ongoing research.
- ORNL collaborated with Nuvera Fuel Cells on the Sustained Power Intensity with Reduced Electrocatalyst Program to quantify Pt electrocatalyst degradation in terms of Pt coarsening and migration. These data are currently being used as experimental input for models being developed by researchers at Argonne National Laboratory (ANL).

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INTRODUCTION

Polymer electrolyte membrane (PEM) FCs 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 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 the gas diffusion layer/microporous layer. The structural and chemical degradation mechanisms contributing to performance loss have not been fully elucidated and/or quantified. During the past several years, the Microstructural Characterization Project at ORNL has been focused on forming collaborative relationships with numerous MEA and FC developers/manufacturers, universities, and national laboratories, to apply ORNL's advanced electron microscopy capabilities and expertise to characterize as-synthesized (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. These studies are used to establish critical processing-microstructure-performance relationships and to understand 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 FC durability and performance.

APPROACH

The microstructural characterization task utilizes advanced electron microscopy analysis techniques to characterize the individual material components comprising FC MEAs, before and after incorporation into an MEA structure, and after electrochemical aging. ORNL's 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 Å-scale characterization of the material constituents (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 FC performance (aging studies—ASTs and field-aging—are conducted at a variety of collaborator's laboratories). These studies are designed to elucidate the microstructure-related degradation mechanisms contributing to FC performance loss. ORNL makes the techniques and extensive staff expertise and knowledge available to a broad community of

FC researchers outside of ORNL via several collaborative mechanisms: (1) work for others for proprietary research, (2) ORNL User Facilities (e.g., Shared Research Equipment User Facility), and (3) collaborative non-proprietary research projects supported via the Microstructural Characterization Project that are consistent with ORNL's research activities, which has been the primary mechanism for conducting collaborative research—partners have included: LANL, ANL, National Renewable Energy Laboratory, Brookhaven National Laboratory, Lawrence Berkeley National Laboratory, Sandia National Laboratory, GM, 3M, Automotive Fuel Cell Cooperation, Proton OnSite, W.L. Gore, Ballard, Nuvera Fuel Cells, Fuel Cell Energy, UTC-Power (now ClearEdge Power), and numerous universities.

RESULTS

During FY 2013, ORNL continued its efforts related to topics of interest to the FC community through collaborations with numerous partners, which have included research specific to understanding carbon corrosion mechanisms, the characterization of thin ionomer films, catalyst nanoparticle evaluation via electron microscopy, and progress made in the area of in situ liquid-cell electrochemical microscopy (the last two topics are not included in this report). These tasks build upon research conducted during the last several years to establish vital correlations between the structure-chemistry of individual MEA components and their durability and stability during electrochemical aging.

Carbon Corrosion (collaboration with LANL)

To better understand carbon corrosion in FC cathodes, LANL supplied ORNL with a series of MEAs having cathode layers that were prepared using three different carbon black (CB)-supported Pt inks:

- High surface area carbon (HSAC) + 20% Pt
- Vulcan carbon (VC) + 20% Pt
- Low surface area carbon (LSAC) + 20% Pt

These MEAS were subjected to the carbon corrosion AST, 1.2-V hold at 80°C and 100% relative humidity, for time increments ranging from 5 h to 400 h. After each test, MEAs were cut in cross-section by ultramicrotomy for examination by electron microscopy to microstructurally quantify the extent and mechanisms of carbon corrosion as a function of hold time at 1.2 V and type of CB used CO_2 evolution was measured during selected ASTs.

The cathode prepared using HSAC + 20% Pt exhibited the poorest durability and was characterized by extensive performance loss after only 20 h at 1.2 V, as shown in the polarization curves in Figure 1a, which could be directly correlated with severe cathode thinning (greater than 50% thickness loss after 20 h), Figure 1b, and loss of porosity (greater than 50% porosity loss after 20 h), Figure 1c. The MEA prepared with VC, on the other hand, exhibited somewhat enhanced durability compared to HSAC, as shown in Figure 2a, but some performance loss was observed after only 50 h at 1.2 V. Although extensive cathode thinning/compression was characteristic of both HSAC and VC, the extent of losses was significantly greater for the HSAC; after 100 h at 1.2 V, where less than 20% of the cathode thickness and only 2% porosity were retained, whereas after 400 h at 1.2 V, the VC retained 40% cathode thickness accompanied by less than 5% porosity. Examination of the structural components, specifically the structure of the carbon support and the Pt catalysts, showed evidence for carbon corrosion in terms of carbon structural changes, but these changes were non-homogeneous within the catalyst layer (extremely localized) and not as extensive as originally believed. Figure 3a shows that the most degraded regions within the cathode containing HSAC (exhibiting the highest carbon corrosion) were localized within compressed "bands" running parallel

(b) (c)

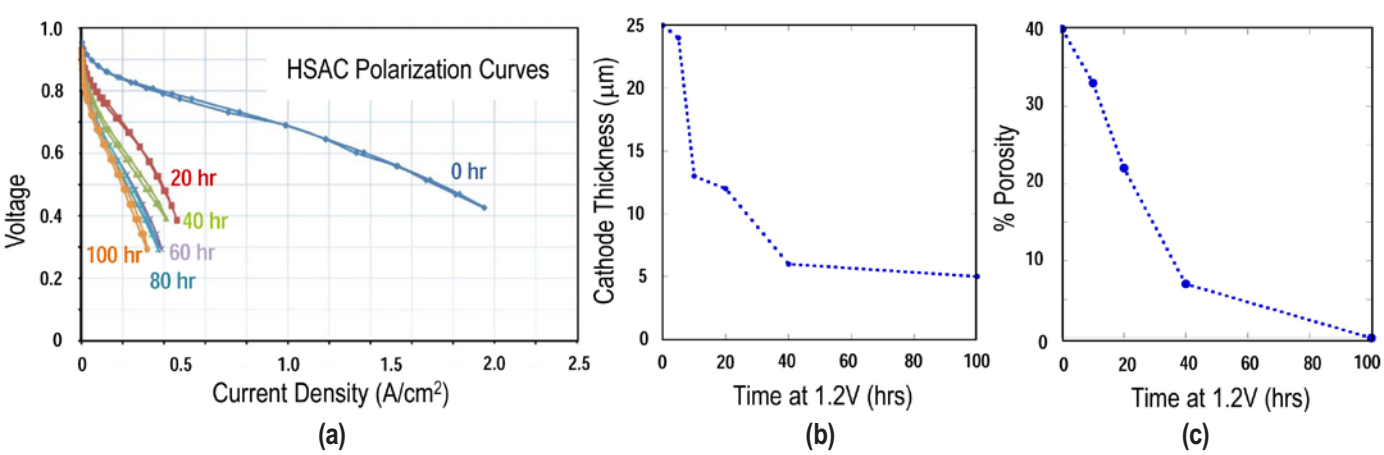

FIGURE 1. (a) Polarization curves for an MEA with HSAC + 20% Pt cathode tested at 1.2 V for 20, 40, 60, 80, and 100 h. (b) HSAC cathode thickness loss as a function of hold time at 1.2 V. (c) HSAC cathode porosity loss as a function of hold time at 1.2 V.

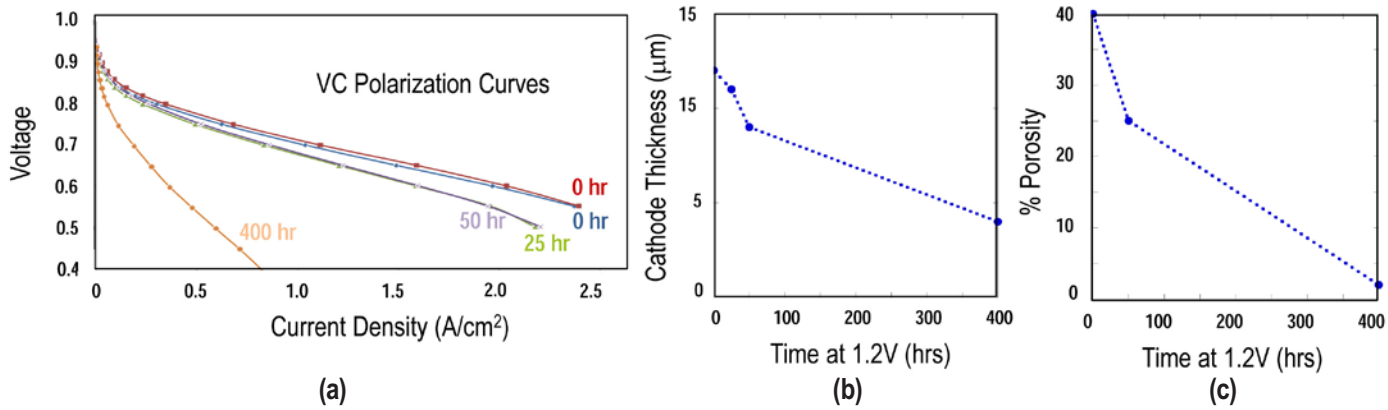

FIGURE 2. Polarization curves for an MEA with VC + 20% Pt cathode tested at 1.2 V for hold times of 25, 50, and 400 h. (b) VC cathode thickness loss as a function of hold time at 1.2 V. (c) VC cathode porosity loss as a function of hold time at 1.2 V.

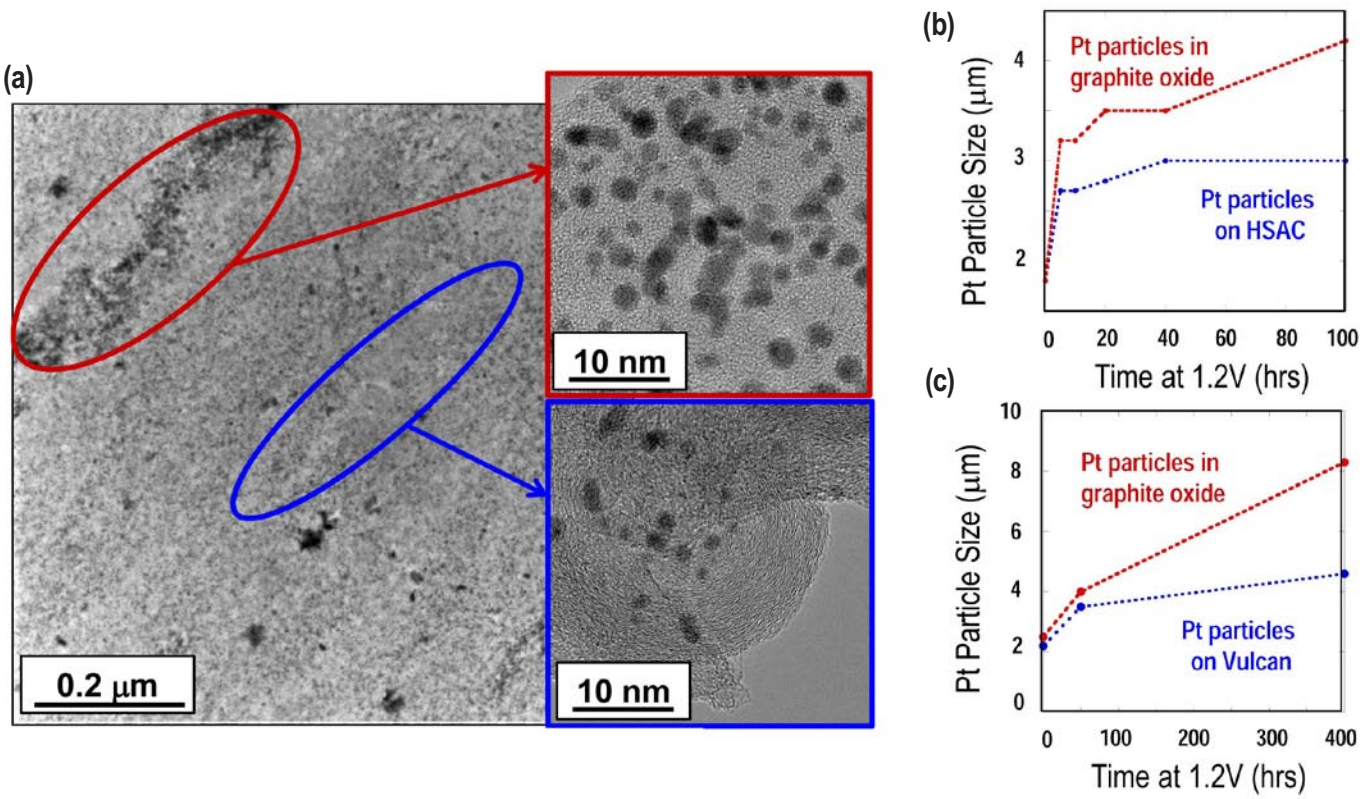

FIGURE 3. (a) HSAC cathode exhibiting formation of dense "bands" of graphite oxide formation embedded in regions showing limited oxidation of the HSAC meso-graphitic structure. (b) Pt particle sizes measured within dense graphite oxide "bands" and less-oxidized HSAC regions. (c) Pt particle sizes measured within dense graphite oxide "clusters" and less-oxidized VC regions.

to the cathode-membrane interface. These bands consisted of dense regions of amorphous, partially oxidized carbon (graphite/carbon oxide) with a significantly larger Pt particle size (Figure 3b). The highly oxidized bands comprised only ~10% of the entire cathode layer, whereas the remainder of the cathode layer exhibited much less carbon corrosion, and in fact, much of the HSAC structure was retained to some extent (much less incorporation of oxygen within the HSAC support). The cathode layer prepared with VC exhibited a similar trend of localized densification and graphite oxide formation, except that these regions appeared as much smaller "clusters" throughout the cathode rather than the densified "bands" observed for HSAC, as shown in Figure 3b, and the extent of corrosion of the VC appeared more

uniform than for the HSAC. Significantly greater Pt particle coalescence was associated with the highly oxidized regions of the VC cathode, similar to observations for the HSAC.

These microstructural observations are consistent with the CO_2 evolution measured during several ASTs; for both the HSAC and VC cathodes the evolved CO_2 was extremely low (less than 400 ppm after 100 h) supporting less carbon corrosion based strictly on correlating performance loss due only to loss of carbon through the

$$C + H_2O \rightarrow CO_2 + 4H^+ + 4e'$$

reaction. Current results clearly demonstrate a structural change to the carbon support particles, which is supported by the observation of a progressive and non-homogeneous formation of localized dense graphite oxide bands/regions within the catalyst layer, as the overriding carbon degradation mechanism. The regions of greatest graphite oxide formation are also associated with the most Pt coarsening; in fact, much of the loss of Pt electrochemically active surface area (ECSA) can be directly attributed to the localized areas exhibiting the most graphite oxide formation, as shown in Figures 3b (HSAC) and 3c (VC). When the localized changes in carbon structure are combined with the progressive loss of porosity and cathode thinning/compression observed after the carbon corrosion ASTs (1.2 V hold), the performance losses can be fully explained in terms of electrode and support structural changes.

The extent of carbon corrosion and Pt coarsening, and therefore overall FC performance, can be directly related to the starting structure of the CB+Pt used in the cathode. The structures of the various CB supports are illustrated for comparison in the schematics and associated high-resolution transmission electron microscopy (TEM) images shown in Figure 4. HSAC is characterized as having an extremely small particle size (typically 10-50 nm diameter) with a highly defective meso-graphitic outer shell and an amorphous core—the Pt particles are primarily within this core. The VC support particles, on the other hand, are denser with a much larger overall particle size (typically 30-100 nm) with a thicker, more graphitized outer shell and a smaller amorphous core—the Pt particles are on the surface of the VC particles. LSAC (results not discussed in this report, but this carbon support exhibits significantly enhanced resistance to carbon corrosion), which is graphitized HSAC, exhibits a graphitic outer shell with a hollow core—the Pt attaches to the surface of the LSAC non-homogeneously at edges/

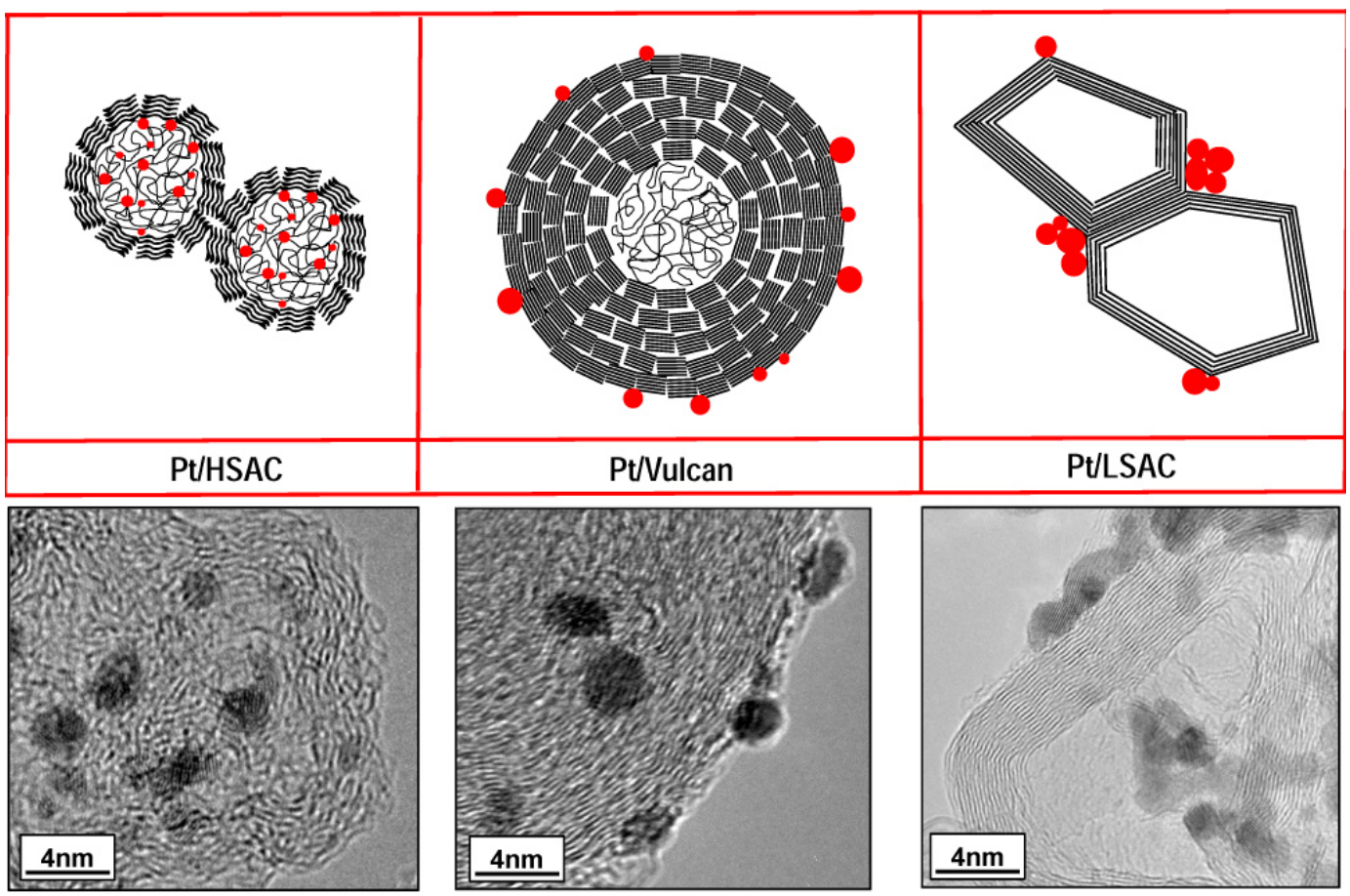

FIGURE 4. Schematics and associated high-resolution TEM images showing structure of HSAC + Pt, VC + Pt, and LSAC + Pt.

corners of the graphite shell. As a result of the number and type of surface defects associated with each of the different CBs, each carbon structure will exhibit a different corrosion behavior. The HSAC has the highest number of defects, which are primarily grain boundaries separating the meso-graphitic domains. These grain boundaries serve as rapid pathways for H_2O to enter the carbon structure and oxidize the amorphous core, and diffuse through the carbon edge planes, rapidly disrupting the meso-graphitic structure and forming graphite oxide. VC is a denser and more graphitic structure than HSAC, but is also characterized by a high number of defects (grain boundaries) between the meso-graphitic domains, making VC susceptible to oxidation, and this results in a slower, but still significant, rate of graphite oxide formation. LSAC is highly graphitized, with a large grain size, and few defects such as grain boundaries. LSAC particles are characterized by large, flat graphite basal plane surfaces, which are inherently oxidation resistant (no dangling edge bonds as associated with the less textured, misfit domain structure of VC) and have defects only associated with corners or edges where the large graphite surface facets adjoin/impinge. Clearly, a highly graphitized structure with a predominance of (002) surfaces and few defects will be more corrosion resistant.

Microscopy of Thin Ionomer Films

ORNL has established collaborations with GM and Ballard to use advanced microscopy techniques to study thin ionomer films, both on model substrates (silicon and Pt, for example) and within cathode layers. This research is focused on identifying the microscopy parameters that should be used to efficiently and non-destructively quantify the composition and structure of thin ionomer films before and after electrochemical aging. Ultimately, these studies are aimed at tracking ionomer stability and dispersions across the entire thickness of a catalyst layer and to determine how ionomer loading, thickness, and composition affect FC performance. Understanding ionomer distributions and changes to its structure and composition require that microscopy imaging and analysis methodologies be optimized to minimize beam damage. To date, many different microscope conditions have been evaluated for ionomer studies (voltage effects, current effects, temperature effects). This work will be continued in FY 2014, with the goal of quantifying the optimum microscope conditions needed to fully assess the nature of the ionomer within the cathode catalyst layer.

CONCLUSIONS AND FUTURE DIRECTIONS

ORNL's microstructural studies continue to provide insight regarding the structural and compositional characteristics of MEA material components that control stability and durability. We have focused primarily on carbon corrosion, electrocatalyst evaluation, and ionomer studies during FY 2013, and will continue to make progress on these issues in FY 2014:

- Carbon corrosion studies will continue in FY 2014, with greater emphasis placed on LSAC and mechanisms by which Pt dispersions may be improved on this corrosion-resistant support.
- Collaborations with GM and Ballard will continue and be expanded to determine the exact microscope conditions for reliably imaging and analyzing changes to ionomer thin films within catalyst layers. The primary goal of this work will be to "map" changes to the ionomer throughout the catalyst layer thickness and correlate these observations with carbon corrosion (graphite oxide formation) and Pt dispersions (especially lower Pt loadings).
- Perform/optimize in-house capabilities for in situ liquid-cell electrochemical microscopy. Several issues have delayed progress being made over the past two years, but ORNL is in a much better position now to perform experiments to study catalyst coarsening and carbon corrosion in real-time under potential hold and cycling conditions.
- Study field-aged PEMFCs to correlate materials degradation observations with results from ASTs.
- ORNL will continue to establish new collaborations with industrial and academic partners to provide characterization support and insight regarding FC materials durability and stability.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Karren L. More received the 2013 DOE Hydrogen and Fuel Cells Program R&D Award in Recognition of Outstanding Achievements in Microstructural Characterization of Fuel Cell Materials (May 2013).

2. K. Shawn Reeves received the 2013 Microscopy Society of America (MSA) Outstanding Technologist Award, Physical Sciences, in Recognition of (in part) her Development of Microtomy Techniques for Preparing Fuel Cell MEAs for Microscopy (August 2013).

FY 2013 PUBLICATIONS/PRESENTATIONS

1. A. Korvina, Y. Garsany, A. Epshteyn, A.P. Purdy, K.L. More, K.E. Swider-Lyons, and D.E. Ramaker, "Understanding Oxygen Reduction on Tantalum Oxyphosphate and Tantalum Oxide Supported Pt by X-Ray Absorbtion Spectroscopy," *Journal of Physical Chemistry C* **116**[34] 18175-18183 (2012).

2. K. Sykes Mason, K.C. Neyerlin, M.-C. Kuo, K.C. Horning, K.L. More, and A.M. Herring, "Investigation of a Silicotungstic Acid Functionalized Carbon on Pt Activity and Durability for the Oxygen Reduction Reaction," *Journal of the Electrochemical Society* **159**[12] F871-F879 (2012).

3. R.T. Atanasoski, L.L. Atanasoska, D.A. Cullen, G.M. Haugen, K.L. More, and G.D. Verstrom, "Fuel Cells Catalyst for Start-Up and Shutdown Conditions: Electrochemical, XPS, and STEM Evaluation of Sputter-Deposited Ru, Ir, and Ti on Pt-Coated NSTF Supports," *Electrocatalysis* **3**[3-4] 284-287 (2012).

4. L. Meng, D.A. Cullen, K. Sasaki, N.S. Marinkovic, K.L. More, and R.R. Adzic, "Ternary Electrocatalysts for Oxidizing Ethanol to Carbon Dioxide: Making Iridium Capable of Splitting C-C Bond," *Journal of the American Chemical Society* **135**[1] 132-141 (2013).

5. B.P. Pearman, N. Mohajeri, R.P. Brooker, M.P. Rodgers, D.K. Slattery, M.D. Hampton, D.A. Cullen, and S. Seal, "The Degradation Mitigation Effect of Cerium Oxide in Polymer Electrolyte Membranes in Extended Fuel Cell Durability Tests," *Journal of Power Sources* **225** 75-83 (2012).

6. G. Wu, K.L. More, P. Xu, H.-L. Wang, M. Ferrandon, A.J. Kropf, D.J. Myers, S. Ma, C.M. Johnston, and P. Zelenay, "A Carbon-Nanotube-Supported Graphene-Rich Non-Precious Metal Oxygen Reduction Catalyst with Enhanced Performance Durability," *Chemical Communications* **49**[32] 3265-3364 (2013).

7. C.-N. Sun, K.L. More, G.M. Veith, and T.A. Zawodzinski, "Composition Dependence of the Pore Structure and Water Transport of Composite Catalyst Layers for Polymer Electrolyte Fuel cells," *Journal of the Electrochemical Society* **160**[9] F1000-F1005 (2013).

8. M.P. Rodgers, B.P. Pearman, L.J. Bonville, D.A. Cullen, N. Mohajeri, and D.K. Slattery, "Evaluation of the Effect of Impregnated Platinum on PFSA Degradation for PEM Fuel Cells," *Journal of the Electrochemical Society* **160**[10] F1123-F1128 (2013).

9. Y. Garsany, A. Epshteyn, K.L. More, and K.E. Swider-Lyons, "Oxygen Electroreduction on Nanoscale Pt/[$TaOPO_4$]/VC] and Pt/[Ta_2O_5/VC] in Alkaline Electrolyte," *ECS Electrochemistry Letters* **2**[10] H46-H50 (2013).

10. S. Pylypenko, A. Borisevich, K.L. More, A.R. Corpuz, T. Holme, A.A. Dameron, T.S. olson, H.N. Dihn, T. Gennett, and R. O'Hayre, "Nitrogen: Unraveling the Secret to Stable Carbon-Supported Pt-Alloy Electrocatalysts," *Energy & Environmental Science* published on line DOI: 10.1039/c3ee40189h (2013).

11. ECS Short Course: K.L. More, "Advanced Microscopy Methods for Studying PEM Fuel Cell Materials" *223rd Meeting of the Electrochemical Society* Toronto, Canada – May 12, 2013.

12. Plenary Lecture: K.L. More, "Application of Advanced Microscopy Methods to Understand PEMFC-MEA Materials Degradation," Workshop on Advanced Characterization of Energy Conversion and Storage Materials, McMaster University, Hamilton, Ontario, Canada – May 17, 2013.

13. Invited Presentation: K.L. More and D.A. Cullen, "Application of Advanced Microscopy to Elucidate Materials Degradation Mechanisms in PEM Fuel Cells," Pacific Rim International Conference on Advanced Materials (PRICM-8), Waikoloa, HI – August 4–9, 2013.

14. Invited Presentation: D.A. Cullen, H.M. Meyer, K.S. Reeves, D.W. Coffey, and K.L. More, "Developing Fuel Cell Technologies Through Electron Microscopy," Microscopy & Microanalysis 2013, Indianapolis, IN – August 4–9, 2013.

15. Invited Presentation: K.L. More, "Characterization and Optimization of Cathode Materials for PEM Fuel Cells," 246th National Meeting of the American Chemical Society, Indianapolis, IN – September 8–12, 2013.