V.A.4 Microstructural Characterization of PEM Fuel Cell MEAs

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

Objectives

- Elucidate membrane electrode assembly (MEA) degradation and/or failure mechanisms by conducting extensive microstructural characterization using advanced electron microscopy techniques (comparing as-processed and electrochemically-aged MEAs).
- Develop correlations between MEA structure/composition and durability/performance.
- Collaborate with proton exchange membrane fuel cell (PEMFC) component developers and manufacturers, university researchers, and other national laboratories to evaluate MEAs using electron microscopy and complimentary microstructural/compositional analysis techniques; provide feedback for MEA optimization.

Technical Barriers

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

(A) Durability

(B) Cost

(C) Performance

Technical Targets

This project is focused on conducting fundamental characterization studies on the stability of individual constituents comprising PEMFC MEAs. Of primary importance is relating MEA microstructural changes during aging to fuel cell durability and performance. Long-term MEA aging studies are being conducted in collaboration with numerous external partners, including MEA manufacturers, PEMFC stack manufacturers, universities, and national laboratories. Insights gained will be applied toward the design and manufacture of MEAs that meet the following DOE 2010 MEA targets:

- Cost: ≤$10/kW
- Durability with cycling: ≤80°C – 5,000 h; >80°C – 2,000 h
- Operating temperatures: ≤120°C
- Total catalyst loading (for both electrodes): 0.30 g/kW (rated)
- Extent of performance degradation over lifetime: 10%

Accomplishments

- Completed study in collaboration with Los Alamos National Laboratory (LANL) to evaluate the effect of catalysts' ink processing parameters (such as type and length of mixing utilized, catalyst loading, catalyst support, etc.) on stability of catalyst particles on support surfaces using high-resolution transmission electron microscopy (HR-TEM). These results were reported to LANL on February 11, 2008.
- Completed study with Honda Research Institute (HRI) to evaluate three new Pt-W alloy cathode catalysts using HR-TEM. This study was a follow-up to an initial collaboration with HRI to characterize Pt-W and Pt-Ti alloy catalysts. These data were provided to HRI.
- Initiated collaboration with Brookhaven National Laboratory (BNL) to characterize their Pt-ML alloy catalysts using high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM).
- Initiated collaboration with 3M to characterize their NSTF catalyst samples using HAADF-STEM.
- Initiated collaboration with Cabot Superior MicroPowders to conduct a systematic study of Pt-Co alloy catalysts subjected to different heat treatments. These data were discussed with Cabot on May 5, 2008.
- Hosted a graduate student from Rensselaer Polytechnic Institute (RPI) working on microstructural characterization of phosphoric-acid-doped polybenzimidazole membranes.
- Conducted extensive catalyst characterization studies using HAADF-STEM, including initial sub-angstrom resolution in situ microscopy studies

using a specialized heating holder. Additional modifications to microscope holder have been discussed and will be implemented in Fiscal Year 2009 to more realistically simulate an operating PEMFC in situ.

Introduction

PEMFCs are being developed for future use as efficient, zero-emission power sources. However, the performance of PEMFCs degrades rapidly with time at elevated temperature (currently limited to ~80°C) during electrochemical aging. Performance degradation can be attributed to the durability of individual components comprising the MEA, such as the electrocatalyst, catalyst support, and/or the proton-conducting polymer membrane. However, many of the mechanisms contributing to decreased stability within the MEA during long-term electrochemical aging are not fully understood. 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 utilize advanced microscopy techniques to evaluate as-fabricated and electrochemically-aged PEMFC MEAs and to characterize individual PEMFC material components. These studies are used to establish critical processing-microstructure-performance relationships and to elucidate MEA degradation and failure mechanisms. Understanding the structural and compositional changes to the materials comprising the MEA during electrochemical-aging will allow for the implementation of processing changes and critical materials development that are required for optimized PEMFC durability and performance.

Approach

The microstructural characterization task utilizes advanced electron microscopy techniques to characterize the material components comprising PEMFC MEAs. During the past year, there has been an accelerated effort to implement the HAADF-STEM technique to characterize the unique structures of cathode catalyst nanoparticles at extremely high resolution, <0.1 nm. The HAADF-STEM technique, commonly referred to as Z-contrast imaging, allows for imaging the atomic structure of a catalyst particles based on atomic number (Z) differences. Image contrast variations arise because of atomic number differences between the atoms (elements) forming the nanoparticle and the atomic-scale image contrast will vary as Z^2. For example, this technique is particularly useful for imaging high-Z particles (Pt-catalysts) supported on a low-Z substrate (carbon) and alloy catalyst particles that are composed of atoms having a fairly large Z difference (i.e., Pt-Co, Pt-Pd, Pt-Cr, etc.). This effort has focused on applying three separate imaging techniques to the characterization of catalyst particles; (1) imaging surfaces and core-shell morphologies of alloy catalyst systems, (2) in situ microscopy development to image catalyst degradation as *f* (temperature), and (3) depth-sectioning and three-dimensional (3D) reconstruction of individual catalyst particles. Significant progress has been made in each of these focus areas.

Results

Numerous cathode catalyst systems were characterized during the past year with external collaborators using the advanced microscopes available at ORNL. Collaborations were established or were continued with industrial partners (Cabot, 3M, HRI, Arkema), national laboratories (LANL, BNL, Argonne National Laboratory), and universities (RPI), and nearly all involved the use of the HAADF-STEM technique to evaluate the unique sub-angstrom-scale structure of the catalyst nanoparticles produced by the different organizations. Several issues were of primary importance to these collaborators, and defining the atomic structure of the produced catalyst was at the forefront, i.e., Was a core-shell structure formed? Were the particles atomically ordered? What was the nature of the surface? How crystalline were the particles (including size, shape)?

Images were acquired using the JEOL 2200FS aberration-corrected TEM/STEM on carefully prepared specimens. During image collection, 2 images are acquired simultaneously, a HAADF-STEM image and a bright-field (BF) STEM image, as shown in Figure 1. In this way, a pixel-to-pixel correlation can be established between the catalyst nanoparticles (emphasized in HAADF-STEM image in Figure 1a, where the contrast is sensitive to Z) and the carbon support (more evident in Figure 1b, where contrast is not sensitive to Z). The Pt particles shown in Figure 1a are all <2 nm in diameter, exhibit varying degrees of crystallinity (some exhibit a disordered arrangement of atoms), and Pt is also distributed atomically (as adatoms) across the carbon surface. The high-Z atoms/particles are not readily evident in Figure 1b, but their positions can be identified in the image as a result of the pixel-to-pixel correlation between the HAADF and BF images (as shown by the yellow and green areas circled in Figures 1a and 1b). In addition, the crystalline nature of the carbon support is observed clearly in the BF-STEM image (Figure 1b), which will be extremely useful for in situ support degradation studies in the future.

In the 2007 Annual Report, the application of the HAADF-STEM technique for studying atomic-

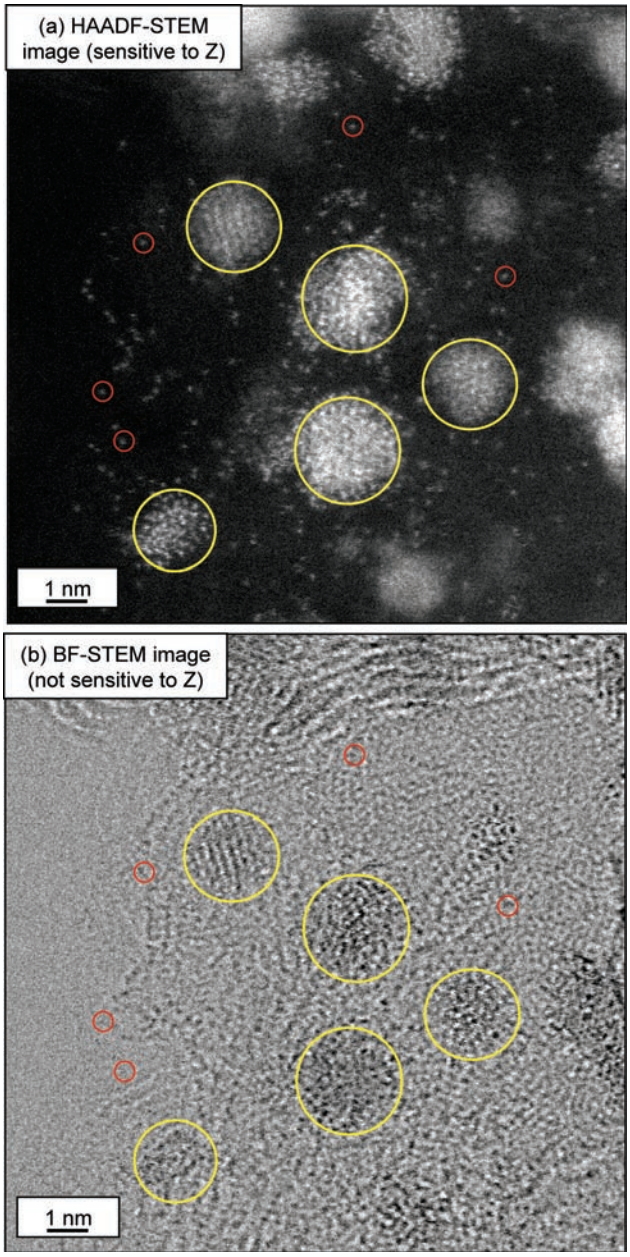

FIGURE 1. STEM images of Pt nanoparticles supported on carbon (a) HAADF-STEM image and (b) simultaneously acquired BF-STEM image. Circled areas correlate observations in HAADF-STEM image with positions in BF-STEM image.

scale ordering in Pt-Co alloy catalysts was presented. During the current year, much effort was devoted to characterizing catalyst core-shell morphologies in order to understand (1) the uniformity of core-shell particles and (2) the atomic-scale nature of the particles (core vs. shell). As an example, Figure 2 shows images the core-shell structure of a two individual nanoparticles of BNL's Pt-monolayer(ML)/Pd catalysts. The catalyst particles ranged from 4-8 nm, and were slightly elongated (a shape that is typical of Pd catalysts). The

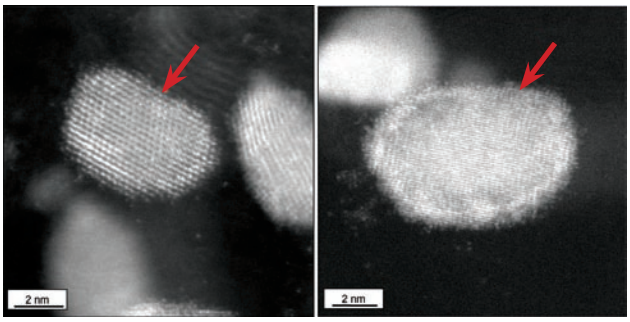

FIGURE 2. HAADF-STEM Images of the Core-Shell Morphology of a Pt(ML)/Pd Catalyst

HAADF STEM images clearly show a "brightly" imaging Pt-shell that is 2-3 ML thick (as opposed to a single ML) surrounding the "darker" imaging Pd core. Note also that the flat surface of the nanoparticle (shown by arrows), where the Pd particle is bonded to the carbon support exhibits little/no Pt on the surface (as would be expected since the surface is not available for Pt deposition). In addition to directly imaging the atomic structure of these core-shell catalysts, 3D depth profiling (through thickness imaging) of individual catalyst nanoparticles is being conducted via the technique described by Borisevich et al. [1]. This technique, which allows for the acquisition of STEM images at different locations through the particle thickness (at depths of 2-4 nm) and subsequent image reconstruction, is an excellent mechanism to evaluate the nature of the core and the shell of individual catalyst particles. Research in this area is ongoing, but initial results were presented at the 2008 Annual Merit Review.

A significant effort during the past FY was invested in the development of in situ methods by which to expose catalyst nanoparticles to relevant fuel cell operating conditions inside the column of the electron microscope. A step-by-step approach is being used to implement the necessary exposure conditions, and low-temperature in situ heating was the initial focus. A heating holder was developed for the JEOL 2200FS this past year [2], which allowed for short-time temperature cycling and the acquisition of high-resolution HAADF-STEM images following each temperature cycle. Nanoparticle coalescence was observed and recorded. The holder is extremely stable – individual catalyst particles, and their changes during heating, are monitored as a function of exposure time. Care is taken to minimize beam damage by closing the gun valve (limiting beam exposure) between cycles. In this way, the particle(s) are imaged, the beam valve is closed, temperature is applied, the beam valve is opened, an image is acquired, and the beam valve is closed. This procedure is iterated many times and the images acquired are then reconstructed (usually as a movie) to monitor changes to the individual particles

in the field-of-view. A sequence of images acquired following heating of Pt/C nanoparticles is shown in Figure 3, where the Pt/C was heated for 8 cycles for 1.5 minute increments at 150°C, followed by 3 cycles for 12 minutes each at 150°C, and finally a hold for 24 minutes at 150°C, for a total exposure time of 48 minutes at 150°C. Significant coalescence of the nanoparticles occurred during this time at temperature; it was observed that the <2 nm Pt particles (within a 6-8 nm diameter) actually moved across the carbon support surface (rather than breaking up and moving atomically) towards the nearest Pt particle. Once in contact, the Pt particles coalesced into a single particle, and rather than forming a polycrystalline "agglomerate" of nanoparticles (as might be expected due to secondary nucleation), the Pt particles formed a larger, single crystal particle, by orienting itself with respect to the original particle. The Pt adatoms on the carbon surfaces also migrated towards the nearest Pt particle, and attached to the Pt, minimizing the number of adatoms.

While this initial experiment was conducted on a "fresh" Pt/C powder (no ionomer), it provides some insight into the mechanism of particle coalescence. It also leads to several important experiments that will be conducted in the near future. Of primary concern is the role of the ionomer, which surrounds the Pt/C in an electrode, and how it contributes to catalyst degradation; i.e., does the ionomer enhance or preclude the movement/migration of individual particles or does the ionomer enhance the likelihood of Pt dissolution? In addition, the effect of particle size and inter-particle spacing on particle coalescence must be investigated.

The development of in situ microscopy to study nanoparticle and support degradation must also include additional (and relevant) fuel cell operating parameters, such as water-vapor (even liquid) exposure and voltage cycling. The development of a holder to conduct exposures of fuel cell materials in-operandi will be actively pursued in FY 2009. Several ideas for this specialized holder, including a "flow-cell" between electron-transparent windows or an environmental cell without windows, are being investigated.

Conclusions and Future Directions

- Many new collaborations have been established during the past year that have "taken advantage of" the unique imaging (microscopy) capabilities at ORNL via different access paths:
  - Work-for-Others (proprietary research)
  - Shared Research Equipment (SHaRE) User Program (non-proprietary research)
  - Baseline DOE PEMFC-MEA Characterization Program (non-proprietary)
- Significant progress is being made in developing in situ STEM as a viable technique to follow degradation of PEMFC materials by implementing a step-by-step approach.
- 3D STEM and image reconstruction is an extremely useful technique to look at the tomography of bulk agglomerates as well as individual nanoparticles and has been used to characterize PEMFC catalyst morphologies.

Future Directions:

- Continue to take necessary steps to design, develop, and implement an in situ holder for near live-time, nm-scale microscopy of PEM fuel cell material constituents under relevant operating conditions - temperature, potential cycling, humidity.
- Statistical analysis of catalyst nanoparticle coalescence (with and without ionomer) as a function of temperature, relative humidity and volume.
- Design in situ experiments to understand mechanisms of carbon support degradation.
- Further develop the 3D STEM technique for catalyst nanoparticles.

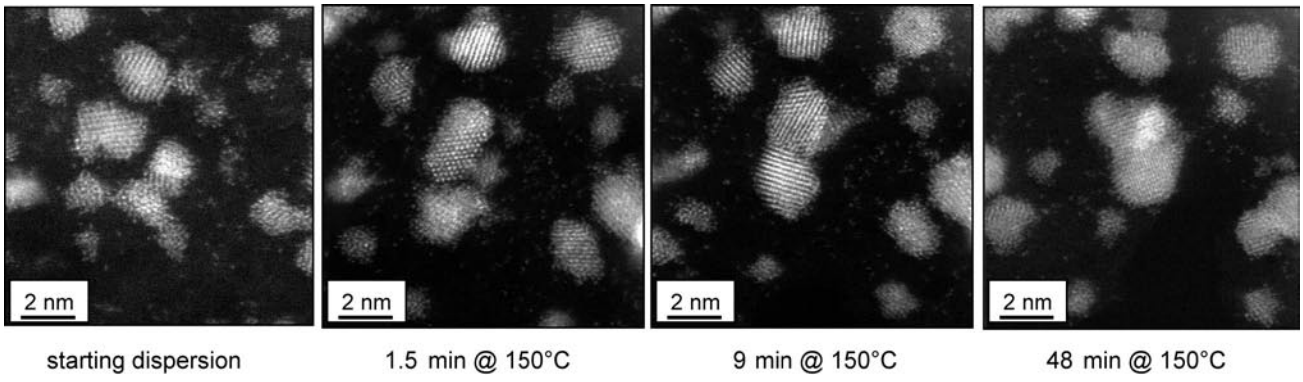

FIGURE 3. Sequence of HAADF-STEM Images of Pt/C Showing Pt Nanoparticle Coalescence during Heating for 48 Minutes at 150°C

- Continue to establish collaborations with industries, universities, and national laboratories (including access to ORNL User Facilities) to facilitate "transfer" of unique capabilities.
- Support new DOE projects with microstructural characterization and technique development.

Special Recognitions & Awards/Patents Issued

1. K.L. More was recognized as a Society Fellow by The American Ceramic Society in September 2007.

2. Research Project was selected as one of the top three FreedomCAR Tech Team DOE Highlights/ Accomplishments for FY 2007.

FY 2008 Publications/Presentations

1. K.L. More, K.S. Reeves, and D.A. Blom, "Atomic-Scale Characterization of Bimetallic Catalyst Particles for PEM Fuel Cell Cathodes," *invited presentation* at the Fuel Cells Durability & Performance Workshop, Miami, FL, November 14-16, 2007.

2. K.L. More, K.S. Reeves, and D.A. Blom, "Atomic-scale Imaging of Bimetallic Catalyst Particles for PEM Fuel Cell Cathodes," poster presentation at the Fuel Cell Seminar, San Antonio, TX, October 15-18, 2007.

3. R. Borup, et al, "Scientific Aspects of PEM Fuel Cell Durability and Degradation," *Chemical Reviews* 3904 (2007).

4. E. Ding, K.L. More, and T. He, "Preparation and Characterization of Carbon-Supported PtTi Alloy Electrocatalysts," *Journal of Power Sources*) 794 (2008).

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1. A.Y. Borisevich, A.R. Lupini, and S.J. Pennycook, "Depth Sectioning with the Aberration-Corrected Scanning Transmission Electron Microscope," *Proceedings of the National Academy of Science* **103**[9] 3044-3048 (2006).

2. L.F. Allard, W.C. Bigelow, D. Nackashi, J. Damiano, and S.E. Mick, "A New Paradigm for Ultra-High-Resolution Imaging at Elevated Temperatures," to be published in Microscopy & Microanalysis **14**[Suppl.2] (2008).