

## V.A.3 Microstructural Characterization of PEM Fuel Cell MEAs

Karren L. More

Oak Ridge National Laboratory (ORNL)  
1 Bethel Valley Rd., P.O. Box 2008  
Oak Ridge, TN 37831-6064  
Phone: (865) 574-7788; Fax: (865) 576-5413  
Email: morekl1@ornl.gov

DOE Technology Development Manager:

Ingrid M. Milton

Phone: (202) 586-9583; Fax: (202) 586-9811  
E-mail: Ingrid.Milton@ee.doe.gov

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aging studies are being conducted in collaboration with numerous external partners, including MEA manufacturers, PEMFC stack manufacturers, and national laboratories. In addition to aged MEAs, external collaborators are supplying baseline materials for microstructural, chemical, and compositional characterization. Insights gained will be applied toward the design and manufacture of materials and MEAs that meet the following DOE 2010 MEA targets:

- Cost:  $\leq$ \$15/kW
- Durability with cycling:  $\leq$ 80°C – 5,000 hours;  $>$ 80°C – 2,000 hours
- Operating temperatures:  $\leq$ 120°C
- Total catalyst loading (for both electrodes): 0.33 g/kW (rated)
- Extent of performance degradation over lifetime: 10%

### Objectives

- Elucidate membrane electrode assembly (MEA) degradation and/or failure mechanisms by conducting extensive microstructural characterization using advanced electron microscopy techniques (comparing fresh and electrochemically aged MEAs).
- Develop correlations between MEA structure/composition and durability/performance.
- Collaborate with polymer electrolyte membrane fuel cell (PEMFC) developers and manufacturers 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 (3.4) 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 studies on the stability of individual constituents comprising PEMFC MEAs. Of primary importance is relating the microstructure of these MEA materials to fuel cell durability and performance. Long-term MEA

### Accomplishments

- Collaboration with Los Alamos National Laboratory (LANL) to evaluate Pt-Co cathode catalyst MEAs after electrochemical aging using high-resolution transmission electron microscopy/scanning transmission electron microscopy (TEM/STEM) for comparison with similar studies on Pt-only catalyst MEAs. The effects of potential cycling, operating temperature, and percent relative humidity on cathode Pt and Pt-Co catalyst and Nafion® membrane durability were evaluated.
- Applied the high-resolution, high angle annular dark-field (HAADF) STEM technique for the atomic-scale imaging of individual bimetallic catalyst particles supported on carbon. This advanced microscopy technique, commonly known as Z-contrast imaging since the image contrast scales with  $Z^2$ , allows for directly imaging the placement of high-Z atoms (and therefore, distinguishing between the individual atoms) within the catalyst particles supported on a low-Z support (carbon). In this way, the particle structure (morphology, shape), ordering (atomic alloying vs. long-range atomic ordering), surface structure (faceting, surface ordering), and composition, can be characterized and quantified in relation to performance.
- Several alternative bi-metallic catalysts have been evaluated in terms of particle size, composition, and atomic structure. These new catalyst compositions include Pt-Co, Pt-Cr, Pt-Ti-, and Pt-W. These studies were conducted in collaboration with LANL, Argonne National Laboratory (ANL), Honda Research Institute and E-TEK.

- Completed collaborative study with ANL to evaluate Pt stability (dissolution and re-precipitation) during short-term potential cycling in  $H_2PO_4$ .
- Completed collaborative study with Arkema to evaluate polyvinylidene fluoride (PVDF)-blended PEMFC membranes. This initial characterization study/collaboration has resulted in ORNL's inclusion on Arkema's new 4-year DOE research project to further develop these membranes.
- Worked with PlugPower to characterize Pt catalyst particle dispersion/sizes on different carbon support structures.
- Initiated support of a student from Rensselaer Polytechnic Institute (RPI) to develop appropriate techniques to study the microstructure of polybenzimidazole (PBI)-phosphoric acid (PA) membranes for PEMFC applications.



## Introduction

PEMFCs are being developed for future use as efficient, zero-emission power sources. However, the performance of PEMFCs degrades rapidly with time at temperature (currently limited to  $\sim 80^\circ C$ ) during electrochemical aging. Performance degradation can be attributed to the durability of individual components comprising the MEA, such as the electro catalyst, 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 national laboratories and PEMFC developers/manufacturers to evaluate as-fabricated and electrochemically aged PEMFC MEAs using advanced microstructural characterization techniques. 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 that occur during long-term MEA aging will allow for the processing changes and critical materials development required for optimized PEMFC durability and performance.

## Approach

The non-proprietary aspects of MEA characterization have traditionally been conducted in collaboration with LANL, where many of the MEAs used for the ORNL research are fabricated using the "thin decal" process [1] and electrochemically aged at LANL in single-cell test stands under varying steady

state and cyclic conditions. ORNL utilizes advanced analytical and TEM and scanning electron microscopy (SEM) techniques to characterize the atomic-scale microstructure and composition of fully intact, three-layer MEAs. These high-resolution analyses are conducted on both fresh (baseline) MEAs and in many cases, the same MEAs following aging under load. Most recently, we have used an advanced electron microscope, the JEOL 2200FS aberration-corrected STEM and Z-contrast imaging, to characterize, at the sub-angstrom scale, the dispersion of Pt-based catalysts on carbon supports. The use of this technique has provided insight into many aspects of the structure and composition of potential PEMFC electro catalysts that have not been observed previously.

In order to conduct the high-resolution analyses of MEA materials using electron microscopy, ORNL has developed the appropriate TEM sample preparation methodologies for evaluating individual constituents comprising the layered MEAs, such as (i) carbon support, (ii) electrocatalysts, (iii) polymer membrane, and (iv) web-like recast ionomer within the porous catalyst layers. Details for preparing reproducibly thin ( $<75 \mu m$ ), uniform TEM specimens from three-layer PEMFC MEAs have been described previously [2,3]. These unique preparation techniques and the subsequent electron microscopy analyses are then applied to fully evaluate changes to the individual MEA constituents, and the MEA as a whole, as a function of electrochemical aging conditions. In particular, a significant effort during the past year has been focused on (i) preparing, dispersing, and characterizing new electro catalyst compositions supported on carbon and (ii) cryo-techniques for preparing and evaluating "unique" PEMFC membranes using TEM (i.e., PBI/PA, PVDF-blended membranes).

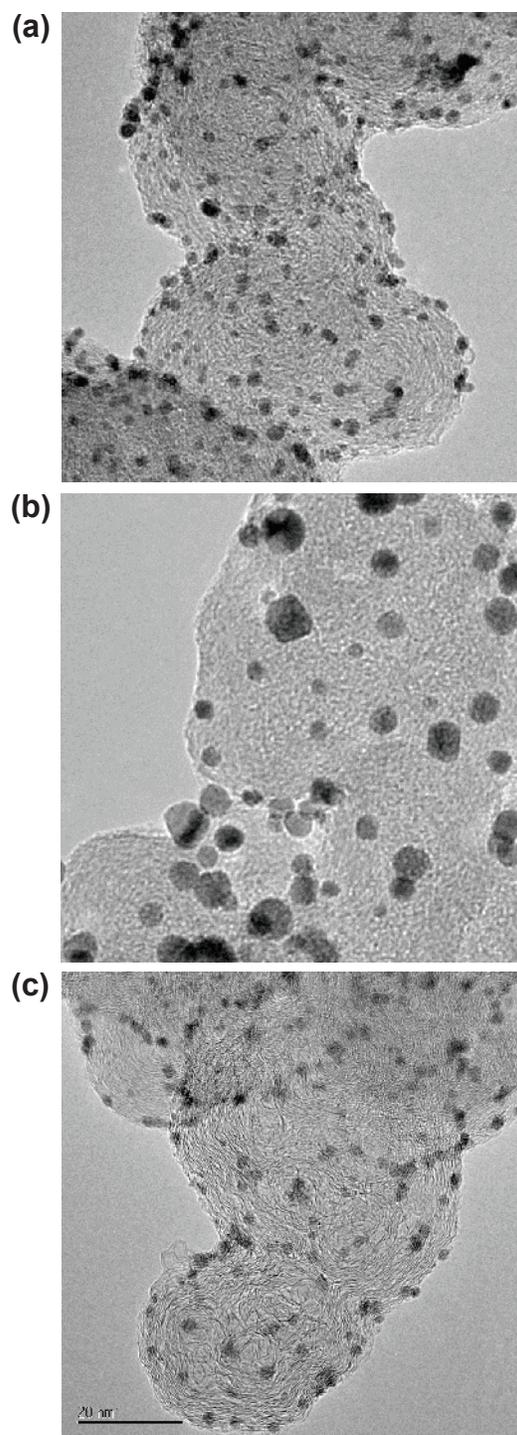
## Results

During this fiscal year, a primary highlight has been the significant progress made in utilizing high-resolution aberration-corrected electron microscopy (ACEM) to characterize the atomic (sub-Angstrom) structure of catalyst nano-particles. At ORNL, the JEOL 2200FS ACEM has been used to directly image the atoms comprising the nano-particles, and is an especially relevant technique for characterizing bi-metallic catalyst structures. The technique used by the JEOL 2200FS is HAADF-STEM imaging, commonly known as Z-contrast imaging since the contrast produced in the STEM image is extremely sensitive to atomic number (Z) and varies with  $Z^2$  [4,5]. For example, for the bi-metallic catalyst Pt-Co, Pt will image significantly brighter in the STEM image than Co, making identification of the single atoms comprising the particle relatively straightforward. Carbon supports typically used for PEMFC catalysts (Vulcan XC-72 or Ketjen black, for example) are ideal

supports for Z-contrast STEM since carbon has a low Z and hence will produce essentially no contrast in the image. Z-contrast STEM imaging has been applied to many different catalyst formulations supported on carbon: Pt-Co, Pt-Cr, Pt-W, Pt-Ti, and Pd-Cu.

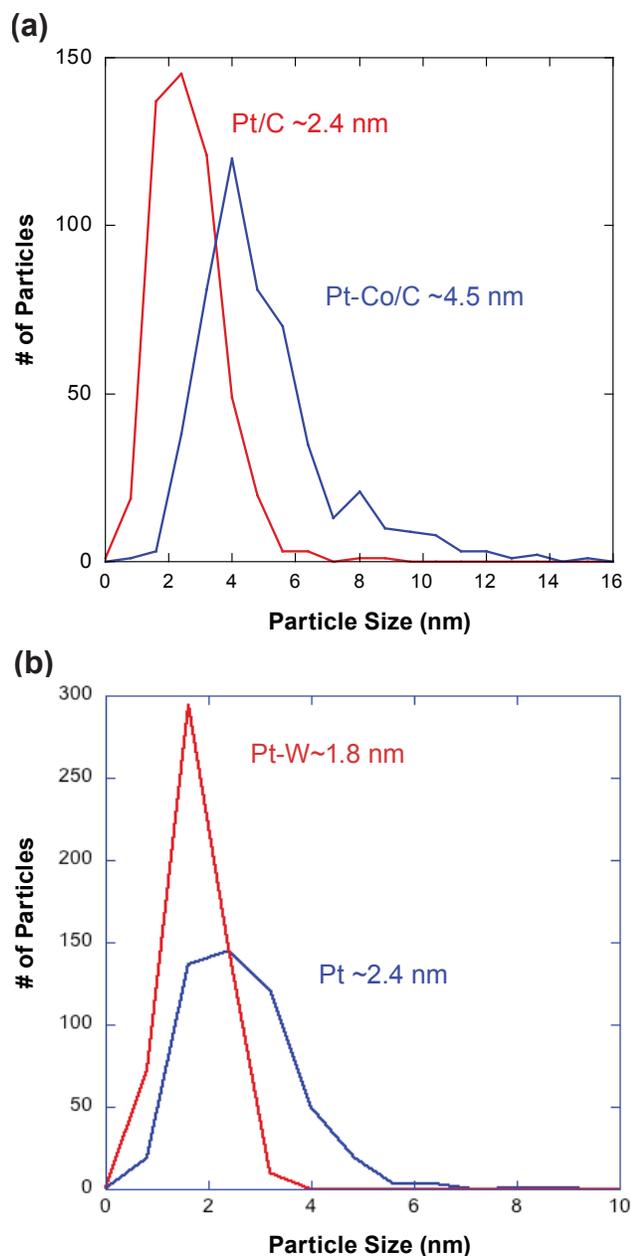
The use of bi-metallic catalysts particles to replace Pt has been a very relevant area of study during the past several years, especially for use in the cathode where the catalysts are subjected to extremely harsh oxidative conditions. There are many reasons to replace Pt for catalysts used in the cathode, most importantly being Pt is expensive and its supply is limited, but improved activity for the oxygen reduction reaction (ORR) and enhanced durability are also required. Pt alloyed with transition metals ( $M=Co, Cr, Ni, W, \text{etc.}$ ) have shown enhanced activity compared with Pt-only catalysts, which may be attributed to several changes in the atomic nature of the nano-particles, including Pt-Pt and Pt-M bond lengths, the atomic coordination and/or nearest neighbors, a change in the electron density of states in the Pt  $5d$  orbital, the nature of the particle morphology and surface, and ordering of the atoms within the particle [6-10]. It becomes increasingly important to fully understand the nature of the atomic-level structure of the individual catalyst nano-particles in order to determine the effects of catalyst microstructure and micro-compositional on the performance of the particular electro catalyst. While much of the electrochemical aging of the catalysts studied thus far have yet to be performed, significant information regarding the structure of the catalysts have been gained thus far by studying the initial, or “fresh” catalysts prior to incorporation into an MEA.

The applicability of high-resolution Z-contrast STEM to the characterization of Pt-based bimetallic catalysts can best be illustrated by comparing the different types of bi-metallic catalyst structures studied to date. Standard (relatively low magnification) TEM images of several different cathode catalyst nano-particles dispersed on carbon supports are shown in Figure 1; 1a shows Pt-only, 1b shows Pt-Co (Pt:Co  $\sim 3:1$ ), and 1c shows Pt-W (Pt:W  $\sim 1:1$ ), and all clearly exhibit different particle sizes (Pt-only  $\sim 2.4$  nm, Pt-Co  $\sim 4.5$  nm, Pt-W  $\sim 1.8$  nm), see Figure 2. The face-centered cubic (fcc) crystal structure and cubo-octohedral morphology of Pt nano-particles has been well characterized by TEM, however, changes to the crystal structure upon addition of alloying elements has not been fully evaluated. For example, X-ray diffraction (XRD) data from the Pt-Co particles shows a larger particle size and a shift to higher 2-theta values indicating a lattice contraction due to incorporation of Co on Pt lattice, but the intensity of the (110) superlattice reflection is very low indicating limited ordering. While this data is certainly informative, little information is gained about the exact nature of the ordering of Pt and Co within individual particles and morphology of the particles themselves. When the Pt-Co



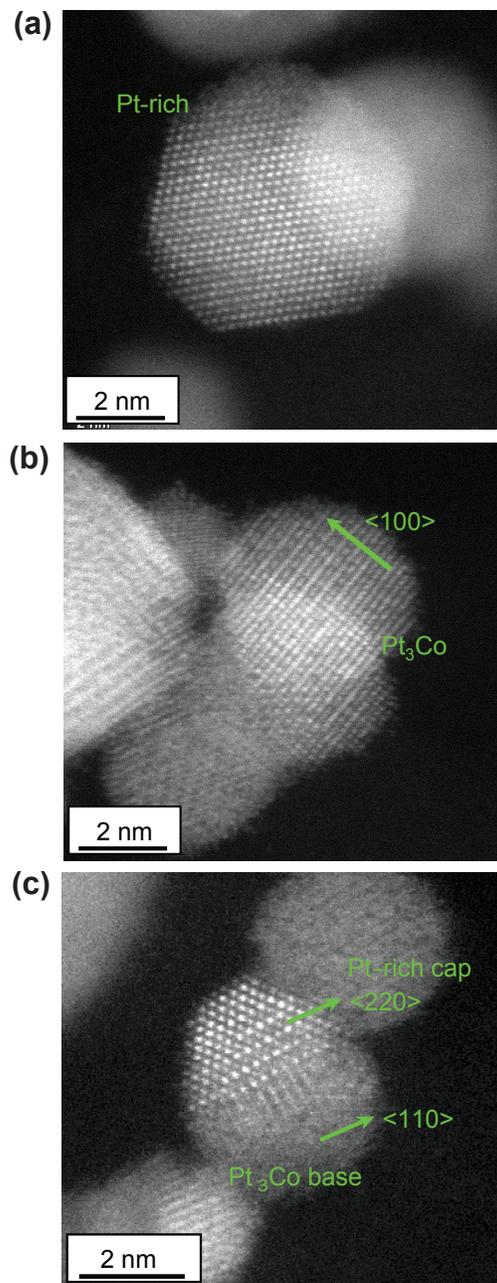
**FIGURE 1.** TEM Images of Pt and Pt-Based Bi-Metallic Cathode Catalyst Particles Supported on Carbon (a) Pt-Only Particles (b) Pt-Co Particles, and (c) Pt-W Particles

nano-particles are imaged using aberration-corrected Z-contrast STEM, the nature of ordering within individual Pt-Co particles can be extracted from the images. Typical STEM images of individual Pt-Co particles are shown in Figure 3. Most of the particles were



**FIGURE 2.** Particle Size Distributions Comparing Pt-Only Catalyst with (a) Pt-Co Catalysts and (b) Pt-W Catalysts

identified as disordered Pt-Co (Figure 3a), where Co randomly substitutes for Pt on the fcc crystallographic lattice creating a solid solution (or alloy) of Pt-Co. A much smaller number of fully ordered  $Pt_3Co$  particles were identified having the  $L1_2$  fcc structure, where Co substitutes for Pt atoms only at the cube corners (Figure 3b). This confirms the reason that the (110) superlattice reflection appeared so low in the XRD data, since only about one in every 20 or so particles in the distribution exhibited a fully ordered  $L1_2$   $Pt_3Co$  structure. Another type of Pt-Co nano-particle structure was also identified



**FIGURE 3.** Individual Pt-Co particles identified in E-TEK Pt-Co (Pt:Co 3:1) fresh powder. (a) Random Pt-Co solid solution disordered particles, (b) fully ordered  $Pt_3Co$  having  $L1_2$  fcc structure, and (c) dual particle with Pt-Co alloy cap and  $Pt_3Co$  base.

in fairly high numbers, a Pt-Co alloy “cap” on an ordered  $Pt_3Co$  “base”, which were easily identified by the interface formed between the cap/base (Figure 3c). In general, the larger particles ( $>5$  nm) having distinct crystallographic facets were ordered, and the smaller particles ( $<5$  nm) were disordered (alloyed).

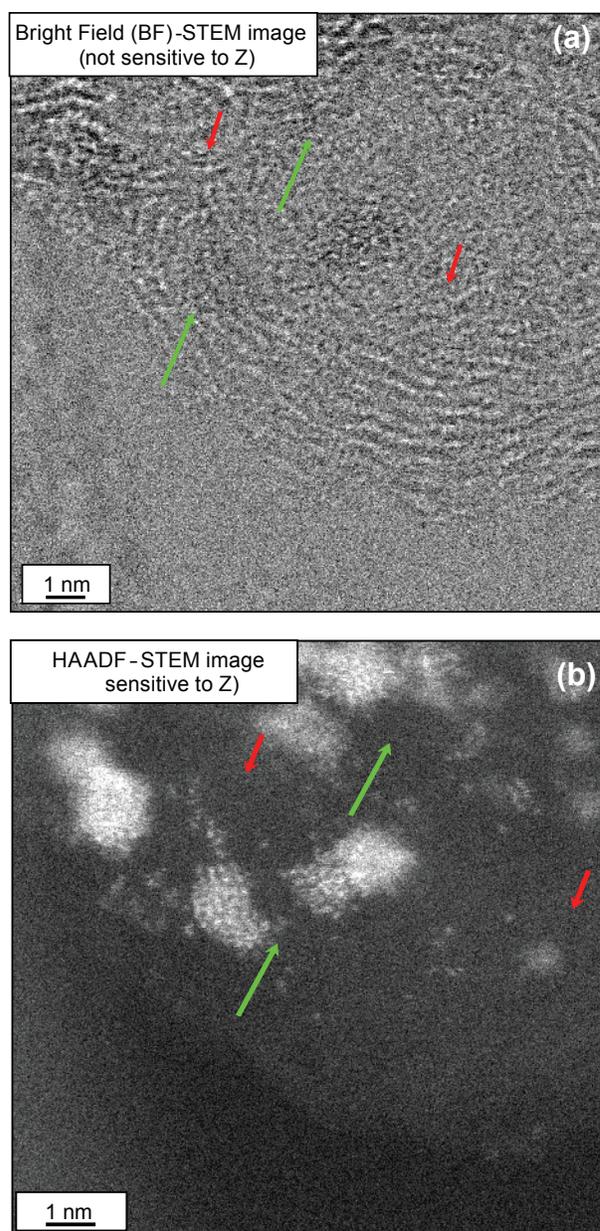
There are many situations where the nature (structure/composition) of the catalyst particles cannot

be identified without directly imaging the particles using a technique such as aberration-corrected Z-contrast (dark field) STEM. The Pt-W catalysts characterized at ORNL fall into this category. XRD data from this catalyst powder shows only wide diffraction peaks, indicating a very small particle size (confirmed by TEM to be  $\sim 1.8$  nm), but little additional information about the structure of the particles. When this catalyst powder is imaged in the ACEM, two important facts become apparent about the catalyst particles and the nature of the dispersion (see Figure 4); (i) very little “assembly” of the Pt-W into distinct crystallographic particles has occurred during preparation of this catalyst (note the lack of lattice organization within the larger clusters designated by green arrows) and (ii) a significant number of single atoms (Pt and W) remain dispersed on the carbon surface (designated by red arrows). The single atom dispersion on the carbon surface can only be imaged in HAADF-STEM mode due to the large difference in atomic number; also shown in Figure 4 is the corresponding bright-field (BF) STEM image that clearly shows the 0.33 nm c-axis spacing of the carbon support; no single atoms are observed in the BF STEM image and the smaller range of non-assembled Pt-W particles are not distinct.

Thus, high-resolution Z-contrast STEM imaging has demonstrated that single atoms can be distinguished (imaged) for these catalysts and important data pertaining to crystallographic structure, surface structure, and particle morphology can be achieved by utilizing this technique. HAADF STEM imaging will be applied to additional catalyst nano-particle compositions and processes in the coming fiscal year to identify the crystallographic features that can be correlated with performance and durability.

### Conclusions and Future Directions

- Z-contrast STEM imaging combined with extensive particle size measurements and particle-to-particle compositional analyses have been used to fully characterize the atomic structure and composition of numerous catalyst compositions at the sub-Angstrom scale. Catalyst compositions studied to date include Pt, Pt-Co, Pt-Cr, Pt-Ti, Pt-W, Pt-Ru, and Pd-Cu.
- TEM/STEM imaging coupled with XRD data also show a wide variety of catalyst particle structures on carbon supports ranging from non-ordered “alloyed” particles (prevalent in Pt-Co, Pt-W, Pt-Ti catalyst particles) to fully ordered (complete ordering in Pt<sub>3</sub>Cr and partial ordering in Pt<sub>3</sub>Co). Atomically dispersed catalysts on carbon supports were also identified (Pt-W and Pt-Ti).
- The stability of a Pt-Co cathode catalyst (20 wt% Pt-Co/C E-TEK) during MEA electrochemical aging was compared with similar experiments conducted



**FIGURE 4.** (a) BF STEM and (b) HAADF (Z-contrast) STEM images of the Pt-W catalyst powder showing the presence of single atoms of both Pt and W dispersed on the carbon surface and poor assembly of Pt-W into particles with a high degree of crystallinity. Single atom resolution is only achievable in HAADF STEM imaging mode as a result of the large difference in atomic number between Pt+W and carbon support.

on a Pt-only catalyst MEA. The Pt-Co catalyst showed a larger initial particle size than Pt and was more stable during long-term aging, i.e., exhibited a lower loss of surface area. Higher percent relative humidity (100% vs. 50%) enhanced particle growth in a similar manner to that observed for Pt, but to a significantly lesser degree.

- A cryo-transfer TEM holder and supplies for cryo-microtomy were purchased towards the

close of the reporting period for the preparation and examination of “beam-sensitive” PEMFC membranes (in particular, PBI/PA and PVDF-blended membranes). Some initial studies have been conducted, but much of this work will be pursued in FY 2008.

- An *in situ* microscopy exposure system (a specialized holder with “flow cell” capabilities) will be developed for the simulated fuel cell (FC) exposure and near-real-time image acquisition during aging of PEMFC materials. These experiments will be extremely useful for monitoring the degradation of the different MEA materials during exposure to relevant FC operating conditions; gas flow, H<sub>2</sub>O, potential cycling, humidity, temperature, etc.
- Additional commercial and non-commercial powders of alternative/new bi-metallic catalysts on carbon supports will be solicited from external researchers and characterized in terms of structural and compositional homogeneity using advanced microscopy techniques, especially aberration-corrected STEM for sub-angstrom Z-contrast imaging (FY 2008).
- Fundamentals of carbon corrosion will be studied in terms of support structure and type and loading of electro catalyst (FY 2008). This work was initiated in FY 2007, but difficulties in imaging due to ionomer films present in the electrodes made this difficult. A more fundamental approach for this study will be pursued in FY 2008.
- Additional non-proprietary work with external collaborators will be pursued in FY 2008, especially related to the preparation of MEAs using well-characterized bi-metallic catalysts and the subsequent aging and post-test characterization of the catalysts.

### Special Recognitions & Awards/Patents Issued

1. K.L. More was named 2007 Fellow of The American Ceramic Society.

### FY 2007 Publications/Presentations

1. K.L. More, “Microstructural Evaluation of MEA Material Constituents to Elucidate PEMFC Degradation Mechanisms,” invited presentation at the 2006 Gordon Research Conference on Fuel Cells, Bryant University, Smithfield, RI, July 23-28, 2006.
2. K.L. More, “Degradation of PEM Fuel Cell MEAs,” invited presentation at the Peer Review for SHaRE User Facility, Oak Ridge, TN, May 2006.

3. K.L. More, “Degradation Mechanisms of PEM Fuel Cell MEAs,” invited presentation/participation at the LANL/NEDO/AIST Workshop on Fuel Cell Degradation & Hydrogen Storage, Santa Fe, NM, August 28-30, 2006. Participants of this workshop contributed to an article submitted to *Chemical Reviews* titled “Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation.”
4. K.L. More, R. Borup, K.S. Reeves, “Identifying Contributing Degradation Phenomena in PEM Fuel Cell MEAs Via Electron Microscopy,” invited presentation at Proton Exchange Membrane Fuel Cells 6, a symposium at The 210<sup>th</sup> Meeting of the Electrochemical Society, Cancun, Mexico, October 30-November 3, 2006. Published in Proton Exchange Membrane Fuel Cells 6, *ECS Transactions* 3[1] (2006) p. 717-725.
5. R.L. Borup, J.R. Davey, F.H. Garzon, D.L. Wood, P.M. Welch, and K.L. More, “PEM Fuel Cell Durability with Transportation Transient Operation,” presentation at Proton Exchange Membrane Fuel Cells 6, a symposium at The 210<sup>th</sup> Meeting of the Electrochemical Society, Cancun, Mexico, October 30-November 3, 2006. Published in Proton Exchange Membrane Fuel Cells 6, *ECS Transactions* 3[1] (2006) p. 879-886.
6. K.L. More, R. Borup and K.S. Reeves, “Microstructural Observations for Carbon Corrosion in PEM Fuel Cell Cathodes,” poster presentation at the Fuel Cell Seminar, Honolulu, HI, November 13–16, 2006.
7. K.L. More, “Degradation Mechanisms in PEM Fuel Cell MEAs,” invited presentation at the 2<sup>nd</sup> FC-Cubic Workshop, Tokyo, Japan, February 6, 2007.
8. K.L. More and K.S. Reeves, “Microstructural Characterization of Life-Limiting MEA Materials Degradation,” invited presentation at the 2007 Meeting of the American Institute of Chemical Engineers, Houston, TX, April 26–27, 2007.

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