

## V.A.7 Microstructural Characterization of PEM Fuel Cell MEAs

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direction determined annually by DOE

### Objectives

- Develop new, innovative microanalysis and imaging techniques to characterize polymer electrolyte membrane fuel cell (PEMFC) material constituents before, during, and after electrochemical aging.
- 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 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 (HFCIT) 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. ORNL research is focused not only on the pre- and post-mortem analysis of powders, membranes, and MEAs, but also on the development and application of in situ microscopy techniques to elucidate degradation mechanisms that contribute to limiting the life of PEMFCs. Insights gained will be applied toward the design and manufacture of MEAs that meet the following DOE 2010 MEA targets:

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

### Accomplishments

- Acquired and evaluated a Si-drift detector (SDD) for energy dispersive spectroscopy (EDS) on the JEOL 2200 aberration-corrected scanning transmission electron microscopy (STEM) for Å-scale compositional analysis and elemental mapping – this new technology results in a 5-10 fold increase in the spatial resolution for EDS.
- Acquired and conducted initial ‘proof-of-principle’ testing of a new specialized liquid cell holder for in situ electrochemical testing of fuel cell materials in the Hitachi HF-3300 transmission and scanning transmission electron microscopy (TEM-STEM).
- Acquired and utilized a new  $360^\circ$  rotation-tomography holder to study catalyst distributions on different support materials.
- Developed ultra-low-angle microtomy (ULAM) technique to evaluate the through-thickness compositional/chemical nature of polymer membranes and electrodes within an MEA.
- Continued collaboration with Brookhaven National Laboratory (BNL) to characterize their Pt-ML alloy catalysts using high-angle annular dark field (HAADF)-STEM.

- Continued collaboration with 3M to characterize nano-structured thin film catalyst samples using HAADF-STEM.
- Supported a full-time graduate student from Rensselaer Polytechnic Institute working on microstructural characterization of phosphoric acid-doped polybenzimidazole membranes.
- Conducted extensive alloy catalyst nanoparticle characterization studies using sub-Å resolution HAADF-STEM, including in situ microscopy studies using a specialized heating holder to observe catalyst coalescence.



## 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 individual material components comprising PEMFCs, before and after incorporation into an MEA. Traditionally, fuel cell degradation has been studied by evaluating MEAs before and after electrochemical testing. While a significant portion of the ORNL research still focuses on characterizing fuel cell materials this way (established collaborations with

Los Alamos National Laboratory, for instance), there has been a recent shift in the ORNL research to focus on the development and implementation of in situ microscopy techniques, i.e., using a specialized liquid cell holder, to study fuel cell materials degradation at high spatial and temporal resolution. Proof-testing of a recently designed liquid holder has been conducted using a fuel cell catalyst.

The HAADF-STEM technique, commonly referred to as Z-contrast imaging, allows for Å-scale imaging of the atomic structure of a catalyst particles based on atomic number (Z) differences, has been used to characterize many different alloy catalyst compositions, and has recently been complimented by the addition of an SDD for the simultaneous acquisition of compositional data (line scans, elemental maps, etc.) from nanoparticles. The combination of in situ microscopy and the ability to image and analyze materials at the sub-nm scale using an aberration-corrected electron microscope, will enable the direct interpretation of the critical phenomena contributing to fuel cell degradation during electrochemical aging.

The research effort in FY 2009 was focused on the initial stages of development, optimization, and application of three primary characterization techniques for the evaluation of fuel cell materials; (1) imaging surfaces and core-shell morphologies of alloy catalyst systems using HAADF-STEM coupled with compositional analysis of the nanoparticle using the new SDD on the aberration-corrected STEM, (2) the development of an in situ electrochemical cell for high spatial and temporal resolution in an electron microscope, and (3) development of a new technique for sectioning MEAs for analysis by X-ray photoelectron spectroscopy (XPS). Significant progress has been made in each of these focus areas.

## Results

### In Situ Microscopy of Fuel Cell Materials

During FY 2009, initial testing of the liquid flow cell holder (made for the Hitachi HF3300 TEM/STEM) was conducted. For these initial assessments, the liquid cell was filled with a dilute saline solution + 20% Pt<sub>3</sub>Cr on Vulcan fuel cell catalyst. These ‘proof-of-principle’ tests were designed to evaluate two primary features of the liquid cell: (1) the thickness of the liquid gap as well as the ability of the cell to hold a flowing and a non-flowing liquid and (2) the image resolution in STEM mode.

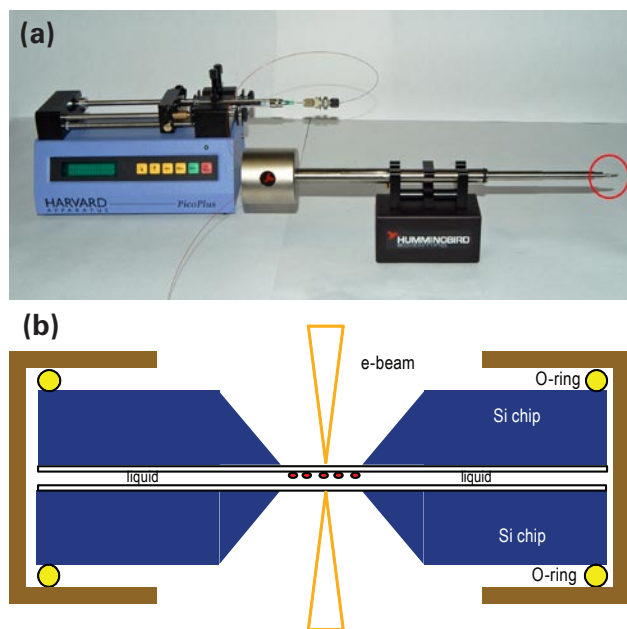
A picture of the specimen holder and a schematic of the flow cell are shown in Figures 1(a) and 1(b), respectively. The holder design is based on an initial liquid cell design by de Jonge, et al. [1]. The cell is composed of two small (2 mm by 3 mm) Si chips with a thin layer of (electron-transparent) silicon nitride

(~50 nm) on the opposing surfaces. A small region on the back side of the Si chips is etched away to the silicon nitride layer, forming an electron transparent “window” for transmission of the electron beam and imaging of the solid material(s) held within the liquid-filled gap.

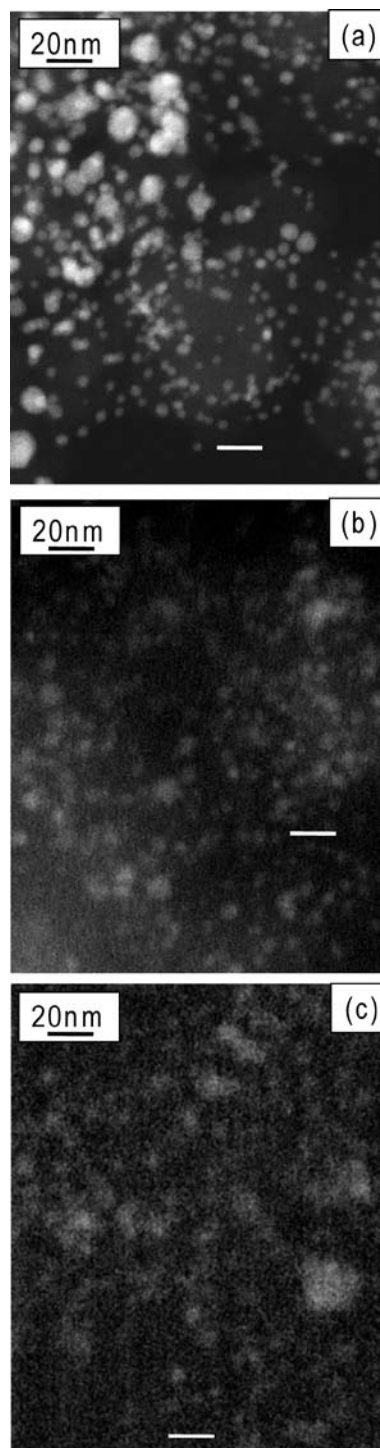
A 20% Pt<sub>3</sub>Cr supported on Vulcan carbon black (Pt/C) was dispersed in a dilute saline solution (provides a conductive liquid). A 2 mL droplet was applied to the “top” silicon nitride surface (across window) and the “bottom” chip was placed on the surface. To create a somewhat reliable gap thickness and to protect the windows from any sharp edges of the solid material that could cause the windows to break, small latex spheres (~5 μm diameter) were applied to the edges of the silicon nitride surface of the top window. Once the liquid-filled cell was secured in place at the tip of the holder (see Figure 1(a)), the holder was inserted into the column of the Hitachi HF3300 TEM/STEM.

Figure 2 demonstrates the image quality (and resolution) for this initial test; Figure 2(a) shows an image of the Pt<sub>3</sub>Cr/C not held within the cell (normal image in vacuum), Figure 2(b) shows an image of the Pt<sub>3</sub>Cr/C imaged through the two silicon nitride windows (no liquid in the cell), and Figure 2(c) is an image of the Pt<sub>3</sub>Cr/C imaged through a 7 mm thick liquid layer (the gap thickness measured for this test). The images are HAADF STEM images, where the Pt<sub>3</sub>Cr particles image

“brightly” as a result of their high atomic number. In this initial test, a <3 nm resolution was demonstrated for the Pt<sub>3</sub>Cr particles (Figure 2(c)).



**FIGURE 1.** (a) New liquid-cell holder (developed in collaboration with Hummingbird Scientific) for the Hitachi HF3300 TEM/STEM. Red circle designates “tip” where liquid cell is held. (b) Schematic of liquid cell used for evaluating catalysts immersed in a liquid layer.



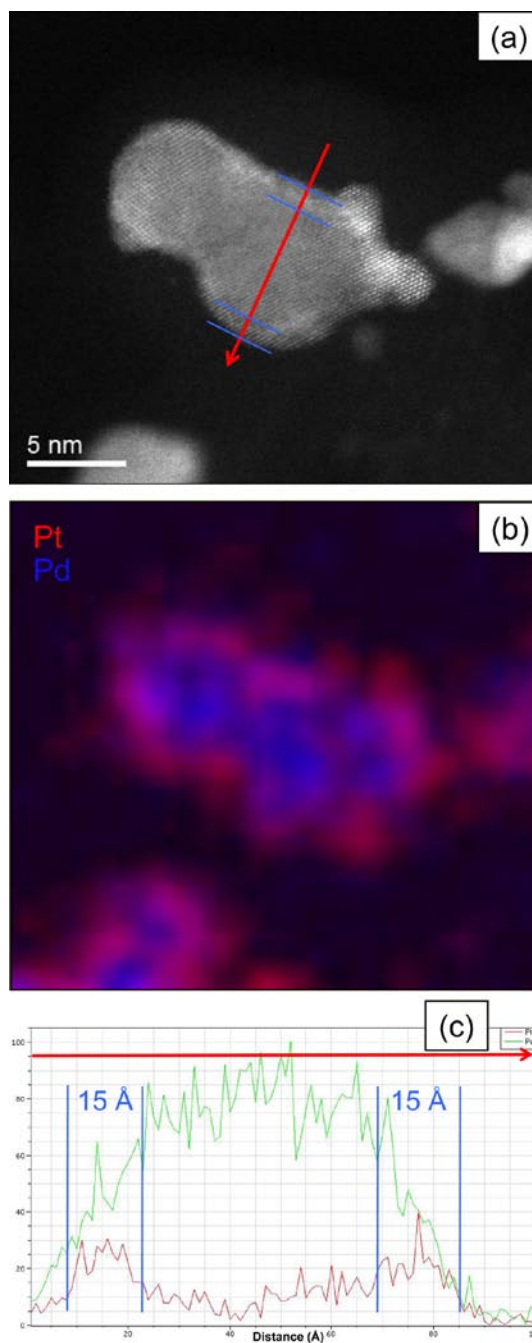
**FIGURE 2.** (a) Conventional HAADF-STEM of Pt<sub>3</sub>Cr/C (no liquid), (b) HAADF-STEM image of Pt<sub>3</sub>Cr/C imaged through two silicon nitride windows (no liquid), and (c) Pt<sub>3</sub>Cr/C imaged through a 7 μm thick saline solution layer demonstrating ~3 nm resolution.

## High Spatial Resolution EDS of Nanoparticles

Research in FY 2009 has also focused on the evaluation of an EDS system recently installed on ORNL's aberration-corrected STEM, the JEOL 2200FS. The manufacturer of the EDS system being evaluated is Bruker and the major improved component of this system is the incorporation of an SDD. There are numerous advantages to SDD technology, including fast EDS spectrum imaging and data acquisition, as well as high geometric collection efficiency which can be extremely important for beam-sensitive materials. In addition modern SDDs are actually providing better spectral resolution (<125 eV) than traditional Si-Li detectors. The Peltier cooling completely eliminates the need for a large liquid nitrogen dewar hanging off the column, removing concerns about image degradation from either liquid nitrogen boiling or enhanced acoustic coupling with background noise in the instrument environment. Though SDDs are primarily available for SEMs, the technology is slowly becoming available for TEM/STEM instruments. Though the high count rate (e.g., <100 kcps) capability of an SDD is not the critical specification for most TEM/STEM instruments (especially aberration-corrected instruments), the large geometric collection efficiency and operation of SDDs will be very important. Thus, we are comparing this technology with data collected on our non-aberration-corrected STEM instruments using conventional Si-Li EDS detectors and its applicability to the compositional characterization of nanoparticles (catalysts).

The major limitation for characterizing small particles by EDS in a STEM is the probe diameter and the low count rate – since many catalyst particles are <3 nm in diameter, there are clear limitations regarding data collected from different areas of individual particles. Data acquired on very small particles has been limited to “bulk” or average particle compositions. It has been virtually impossible to identify core-shell, surface-enrichment, etc. from data for extremely small particles and reliable data interpretation must be limited to the larger particles in the distribution regarding elemental segregation. The advantage for adding EDS data acquisition capabilities to an aberration-corrected instrument is clearly the reduced probe size to <1 Å and increased beam current. The probe can be scanned across much smaller areas/particles to evaluate compositional segregation effects.

The improvement in the spatial resolution of data acquired using the SDD on the aberration-corrected STEM is increased by a factor of 5-10X and is illustrated by the line scan and elemental maps collected from Pt-ML/Pd/C catalysts produced by BNL shown in Figure 3(a) and 3(b), respectively. The ~1.5 nm Pt-enriched shell surrounding the Pd-core is clearly evident in both the map and the line scan in Figure 3, confirming the initial observations of a core-shell structure by HAADF-STEM imaging, as shown in Figure 3(c).

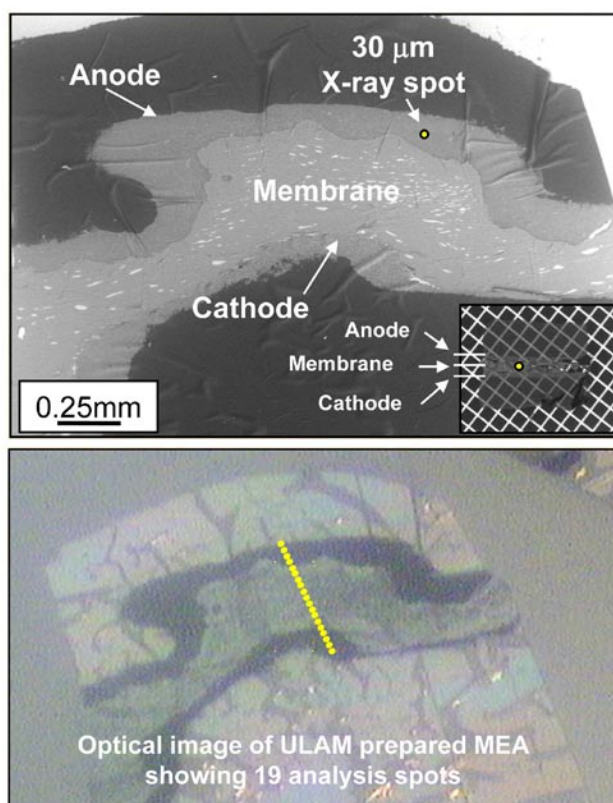


**FIGURE 3.** (a) Line scan and (b) elemental maps collected from Pt-ML/Pd/C catalysts produced by BNL. The ~1.5 nm Pt-enriched shell surrounding the Pd-core is clearly evident in both the map and the line scan confirming the initial observations of a core-shell structure by (c) the corresponding HAADF-STEM image.

## ULAM of Fuel Cell MEAs and Polymer Membranes for XPS

In order to conduct chemical/compositional analyses of membranes and MEAs via XPS, i.e., cross-sectional XPS profiles through the “bulk” membrane, a novel technique for preparing angle-cut microtome

sections has been developed at ORNL. XPS analyses of polymer membranes can be quite challenging for several reasons; (1) the typical thickness of polymer membranes is 10-20  $\mu\text{m}$  and the minimum X-ray spot-size for XPS is  $\sim 30 \mu\text{m}$ , thus analyses have been limited to the air and film (substrate) surfaces only, which do not provide information regarding the bulk (or through-thickness) composition of the membranes and if an electrode is on the surface (as for an MEA), the membrane surfaces can not be analyzed, (2) depth-profiling from the surface into the membrane by sputtering is not a viable option since the membranes are easily damaged by the sputtered ions, and (3) the polymer membranes are easily damaged by the X-ray beam and data must be accumulated relatively rapidly (within several minutes). To this end, polymer membranes and MEAs are being prepared by significantly elongating the cross-sections using ULAM. The membranes are positioned in an epoxy block such that the diamond knife sections through the membrane at a fairly shallow angle, creating an elongated section through the thickness. This is illustrated in Figure 4 – MEA and membrane cross-sections having widths of 100-400  $\mu\text{m}$  have been prepared using this technique.



**FIGURE 4.** Image comparing ULAM-prepared MEA and conventional MEA - MEA and membrane cross-sections having widths of 100-400  $\mu\text{m}$  have been prepared using the ULAM technique.

## Conclusions and Future Directions

### Conclusions

- Several new collaborations have been established during the past year that have accessed the unique imaging (microscopy) capabilities at ORNL via:
  - Work-for-Others (proprietary research).
  - Shared Research Equipment (SHaRE) User Program (non-proprietary research) - University of Houston, University of Texas, University of Connecticut, Rensselaer Polytechnic Institute.
  - Baseline HFCIT-sponsored PEM-MEA Characterization Program (non-proprietary).
- Progress to date to develop in situ liquid STEM as a viable technique to monitor the degradation of PEMFC materials has been slower than expected in FY 2009 – several critical issues have yet to be resolved, but initial ‘proof-of-principle’ tests have been conducted to demonstrate a  $<3 \text{ nm}$  resolution in a 7-9  $\mu\text{m}$  thick layer of water.
- The addition of SDD technology to the aberration-corrected high spatial resolution STEM will enable  $<2 \text{ \AA}$  compositional analysis – optimization of data collection parameters will be ongoing.
- ULAM has been established as a unique and reproducible technique to prepare membranes and MEAs for cross-sectional XPS analysis.

### Future Directions

- Continue to evaluate and add capabilities to the in situ liquid microscopy holder for high spatial and temporal resolution microscopy of PEMFC material constituents operated under relevant operating conditions – liquid electrolytes, temperature, potential cycling, etc. This will be a significant research effort in FY 2010.
- Further develop 3-dimensional tomography methods for characterizing fuel cell materials (catalyst particle coalescence, carbon support degradation, etc.).
- Continue to establish new collaborations with industries, universities, and national laboratories (including access via ORNL User Facilities) to facilitate “transfer” of unique capabilities.
- Support new DOE projects with microstructural characterization and advanced characterization techniques.

### Special Recognitions & Awards/Patents Issued

1. Research selected as one of the top three FreedomCAR Fuel Cell Tech Team – DOE Highlights/Accomplishments for 2008.

## FY 2009 Publications/Presentations

1. K.L. More, L.F. Allard, and K.S. Reeves, “Atomic-Scale Characterization of the Stability of PEM Fuel Cell Cathodes,” invited presentation at the Gordon Research Conference on Aqueous Corrosion, July 21, 2008.
2. K.L. More, L.F. Allard, and K.S. Reeves, “In-situ Microscopy Characterization of Catalyst Degradation,” invited presentation at CARISMA-Progress MEA, September 24, 2008.
3. K.L. More, L.F. Allard, and K.S. Reeves, “Atomic-Scale Imaging of Pt-Based Catalyst Particle Coalescence During Low-Temperature In-situ Heating,” presentation at 214<sup>th</sup> Meeting of The Electrochemical Society, October 14, 2008.
4. K.L. More, L.F. Allard, and K.S. Reeves, “Atomic-Scale Characterization of Catalyst Particles for PEM Fuel Cell Cathodes,” invited presentation at TMS 2009 – 138<sup>th</sup> Annual Meeting, February 18, 2009.
5. P. Strasser, S. Koh, T. Anniye, J. Greeley, K.L. More, S. Kaya, H. Ogasawara, M.F. Toney, and A. Nilsson, “Lattice-Strain Controls Unique Catalytic Activity in Dealloyed Core-Shell Pt Bimetallic Nanoparticles,” submitted to *Nature Materials*.
6. G. Gupta, D. Slanac, P. Kumar, J. Wiggins, X. Wang, S. Swimmer, K.L. More, S. Dai, K. Stevenson, and K. Johnston, “Highly Active and Exceptionally Stable Pt-Cu Oxygen Reduction Electrocatalysts Supported on Mesoporous Graphitic Carbon,” submitted to *Journal of The American Chemical Society*.

## References

1. de Jonge, et. al., *PNAS* **106**[7] 2159-2164 (2009).