V.A.4 Characterization of Fuel Cell Materials

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Objectives

- Develop new, innovative microanalysis and imaging techniques to characterize fuel cell 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 fuel cell component developers and manufacturers, university researchers, and other national laboratories, to evaluate materials using electron microscopy and complimentary microstructural/compositional analysis techniques; provide feedback for 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
(G) Start-up/Shut-down Time and Energy/Transient Operation

Technical Targets

This project is focused on conducting fundamental characterization studies on the stability of individual constituents comprising fuel cell 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, proton exchange (or polymer electrolyte) membrane fuel cell (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 PEM fuel cells. Insights gained will be applied toward the design and manufacture of fuel cell materials that meet the following DOE 2015 MEA targets:

- Cost: ≤$5/kW
- Durability with cycling: ≤80°C – 5,000 h; >80°C – 5,000 h
- Operating temperatures: ≤120°C
- Total catalyst loading (for both electrodes): 0.2 g/kW (rated)
- Extent of performance degradation over lifetime: 5%

Accomplishments

- Investigated microstructural and compositional contributions to cathode carbon-support corrosion mechanisms in electrochemically-aged MEAs.
- Conducted detailed microstructural studies of Pt migration as a function of changing aging protocols.
- Applied advanced statistical analysis techniques to evaluate Å-scale elemental and compositional analyses and segregation within catalyst nanoparticles (multivariate statistical analysis – principal component analysis).
- Continued 'proof-of-principle' testing of ORNL's 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).
- Established several new research collaborations in FY 2010 with industry (3M, UTC Power), other laboratories (Naval Research Laboratory, Jet Propulsion Laboratory) and universities (University of Texas at Austin, Brown University).
- Supported a full-time graduate student from Rensselaer Polytechnic Institute working on microstructural characterization of PA-PBI

membranes (Kelly Perry received her Ph.D. from Rensselaer Polytechnic Institute in December 2009 and now works at ORNL on fuel cell characterization).

- Continued extensive alloy catalyst nanoparticle characterization studies using sub-Å resolution high angle annular dark field scanning transmission electron microscopy (HAADF-STEM).

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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 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.

The techniques developed as part of this "baseline" research project are also being applied to other fuel cell systems.

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 mm-Å-scale characterization of the material constituents of fuel cells (electrocatalyst,

support, membrane, etc.). ORNL applies these advanced analytical and imaging techniques for the evaluation of the microstructural and microchemical changes of each material constituent and correlating these observations with fuel cell performance (aging studies are conducted at collaborators 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 (Shared Research Equipment, Center for Nanophase Materials Science, and High Temperature Materials Laboratory), and (3) collaborative non-proprietary research via the Microstructural Characterization Project that is in line with ORNL's "baseline" research activities.

The research effort in FY 2010 was focused on establishing two primary characterization focus areas for the evaluation of the degradation of fuel cell materials as a function of aging protocol; (1) understanding the mechanisms of cathode carbon support corrosion and (2) performing the in-depth characterization of Pt migration and re-precipitation during PEMFC aging. In addition, the application of statistical data analysis techniques, in particular multivariate statistical analysis and principal component analysis to the compositional analysis (energy dispersive spectroscopy and electron energy loss spectroscopy spectrum imaging) of nanoparticles (bi- and ternary-alloy catalysts) has been optimized (not discussed). Significant progress has been made in each of these focus areas.

Results

Carbon Corrosion

Carbon support corrosion is a well-recognized degradation problem during the operation of PEM fuel cells, and is particularly problematic at the cathode. While the rate of carbon corrosion is relatively low during "normal" fuel cell operation, the oxidation of the carbon support is severe during fuel (H_2) starvation and under open circuit voltage conditions experienced during start-up/shut-down cycling (cathode potentials >1.2 V). There are several recent studies that have focused on the kinetics of carbon support corrosion under adverse fuel cell operating conditions [1-5] and several mechanisms for electrochemical carbon oxidation have been postulated. At the center of these mechanisms is the permanent *loss* of carbon in the cathode layers due to oxidation via the reaction:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

This mechanism has been confirmed (at least to some degree) by the direct observation of collapsed cathode layers and the measurement of the CO_2 (and

CO) evolution during operation. Carbon *loss* at the cathode has been associated with decreased catalyst utilization in the cathode due to Pt agglomeration and Pt detachment from the carbon support, thereby decreasing the electrochemically active surface area (EASA). While it is clear that there is increased carbon corrosion during fuel cell operation under high potential-cycling conditions, the actual structural reasons for, and mechanism of, carbon corrosion have yet to be unambiguously identified.

Recently, several electrochemically-aged MEAs that have experienced significant cathode corrosion (most of these MEAs are at end-of-life, EOL), have been evaluated using high-resolution electron microscopy imaging and analysis techniques to elucidate the microstructural and compositional factors that play a role in (1) the observed structural collapse/compression of the cathode layer(s) and (2) changes/growth of Pt

cathode catalyst nanoparticles contributing to loss of EASA. For example, a "typical" thinned/compressed cathode (composed of Pt-supported on Vulcan XC72) observed after 1,500 0.1-1.2 V (10 mV/sec) cycles is shown in Figure 1. The high-resolution (HR)-TEM images shown in Figure 2 compare the structure of the as-processed (Pt loaded) Vulcan XC72 carbon support (2a) and the same material after potential cycling (2b) in an MEA. There was a significant amount of carbon remaining in the cathode structure after aging, however, the crystalline structure of the Vulcan changed dramatically during potential cycling. The graphitic nature of the starting Vulcan support (2a) was completely amorphous after aging (2b) and these amorphous (glassy) carbon particles were tightly bound (sintered) and densified together, resulting in extensive densification (compression) of the cathode. This graphitic-to-amorphous transformation was confirmed by electron energy loss spectroscopy, as shown in
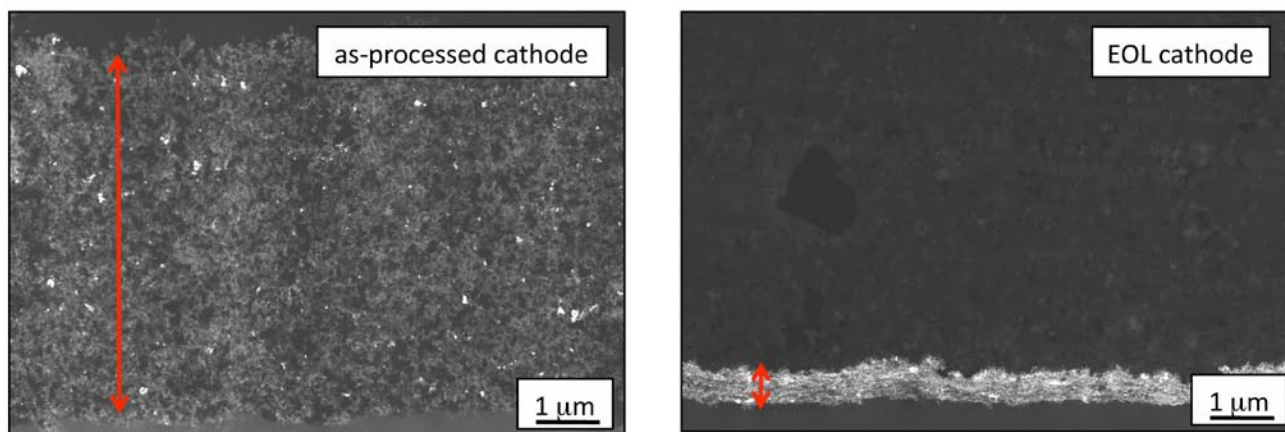

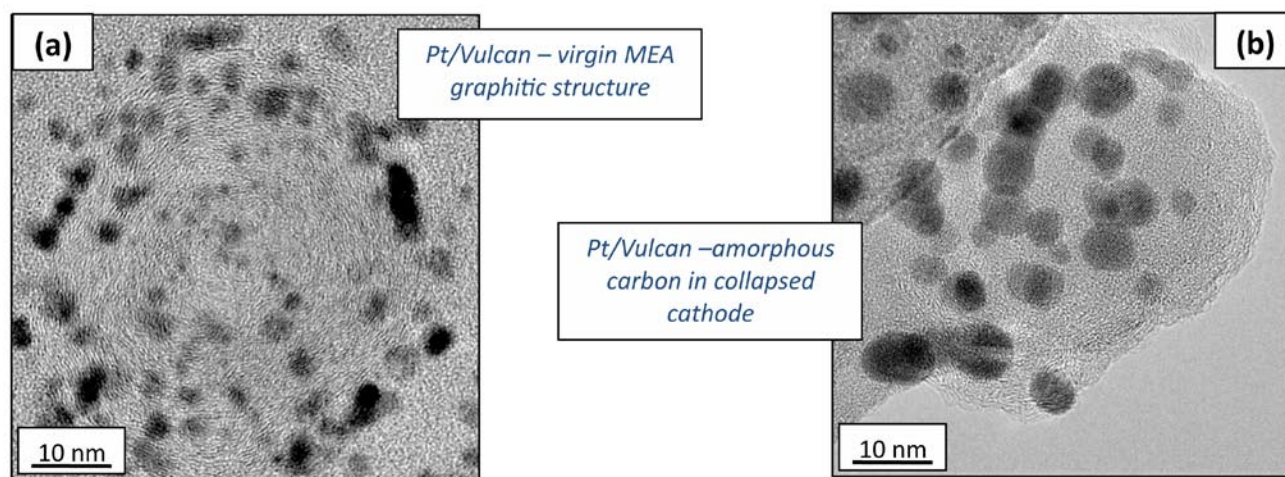**FIGURE 1.** Typical Cross-Section of a "Collapsed" EOL Cathode

FIGURE 2. TEM images of (a) Pt nanoparticles on Vulcan XC72 carbon particle and (b) Pt nanoparticles on Vulcan carbon particle after aging.
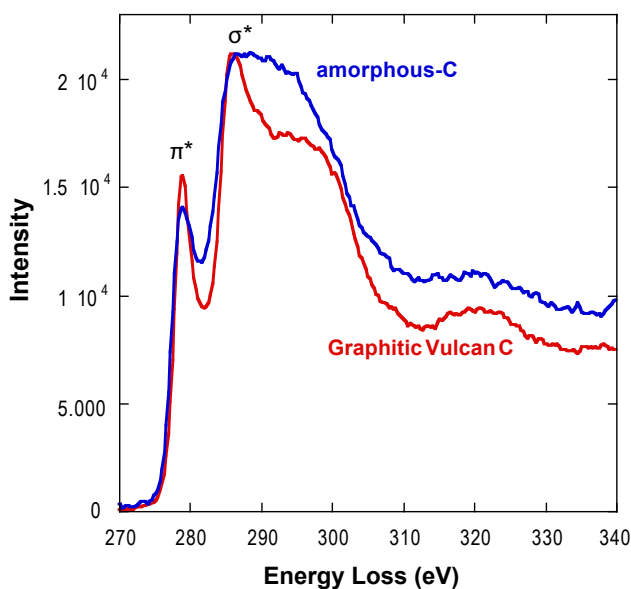
FIGURE 3. EEL spectra comparing the nature of Vulcan before (exhibiting turbostratic/graphitic structure) and after (exhibiting amorphous/glassy structure) aging.

Figure 3, which also indicated relatively high oxygen contents within the amorphous carbon regions. The Pt particles clearly coalesce during potential cycling, but this phenomenon is exacerbated by the enhanced carbon oxidation due to the presence of Pt and the sintering together of the carbon particles. The Pt particles do not become detached from the carbon support (as previously reported by other research groups), but experience significant growth and remain attached to a non-conductive, amorphous, O-enriched carbon support structure. The combination of these major degradation events will have a detrimental impact on fuel cell life.

These results are typical of the types of structures found in compressed/collapsed cathodes after electrochemical aging – in FY 2011, additional (and systematically aged using different aging protocols) examples will be analyzed to establish carbon-corrosion mechanisms and to directly correlate microstrucural degradation with durability (extent of performance loss).

Pt Migration

The migration of Pt^{2+} from the cathode layer into the membrane during fuel cell operation, and the consequent re-precipitation as Pt nanoparticles at different locations in the membrane (related directly to H_2 and O_2 gas cross-over) has been documented in the literature [6-8]. This Pt re-precipitation phenomenon is commonly referred to as "Pt-band" formation, since the larger Pt crystallites (or the highest number density) tend to precipitate at a discrete location in the membrane (distance from cathode/membrane interface where H_2

and O_2 cross-over), which is relatively easy to observe/ image in a microscope (optical of scanning electron microscope, SEM) at low magnifications. However, extensive evaluation of aged MEAs during the past year has shown that the re-precipitation of Pt at the cathode/ membrane interface AND within the membrane is significantly more complicated than the formation of a simple Pt-band.

To understand the Pt migration as a function of aging protocol, numerous aged cross-sectioned (intact) MEAs have been characterized via TEM/STEM in terms of size, crystalline nature, and distribution (distance from cathode layer) within the membrane (from cathode/membrane interface to anode/membrane interface), the results of which will be directly correlated with performance loss. In addition, the amount of Pt loss from the cathode layer will be quantified. These analyses will be extended to include Pt-alloy catalysts to determine leaching effects and the stability of alloy catalysts during aging.

Figure 4 shows an example of the measurements being made via TEM/STEM, where the MEAs evaluated (Pt loaded on both cathode and anode layers) were subjected to a low number (4-5) of freeze-thaw cycles. In this case, the only differences between the cells evaluated (cell #1 and cell #2) were the type of membrane used (Nafion® 111 vs. 211) and the type of gas diffusion layer (GDL) used (paper vs. cloth). Figure 4(a) shows a cross-section SEM image of a typical Pt-band. Figure 4(b) shows the typical size and morphology of the Pt-nanoparticles from two separate areas of the membrane; within the Pt-band (single-crystal cubeoctohedron-shaped Pt particles ranging in size from ~30-70 nm) and away from the Pt-band (closer to the anode, single-crystal Pt particles ranging in size from ~3-10 nm). The Pt particle distribution profiles were completely different, as shown in Figure 4(c), where cell #2 (Nafion® 211 membrane and cloth GDL) exhibited significantly larger (and fewer) Pt particles distributed across the entire membrane and a well-defined Pt-band at a distance between 15-30 μm from the cathode, and cell #1 (Nafion® 111 membrane and paper GDL) exhibited a linear decrease in Pt nanoparticle size from the cathode side (from 15 nm to 5 nm, cathode to anode) and a less distinct Pt-band at a distance between 30-40 μm from the cathode layer. The reasons for such dramatic differences in Pt migration are not fully understood, but additional data from other aged MEAs will permit the correlation of such behavior with performance. This work will continue in FY 2011.

Conclusions and Future Directions

- Several new collaborations have been established during the past year that have accessed the unique imaging (microscopy) capabilities at ORNL via:
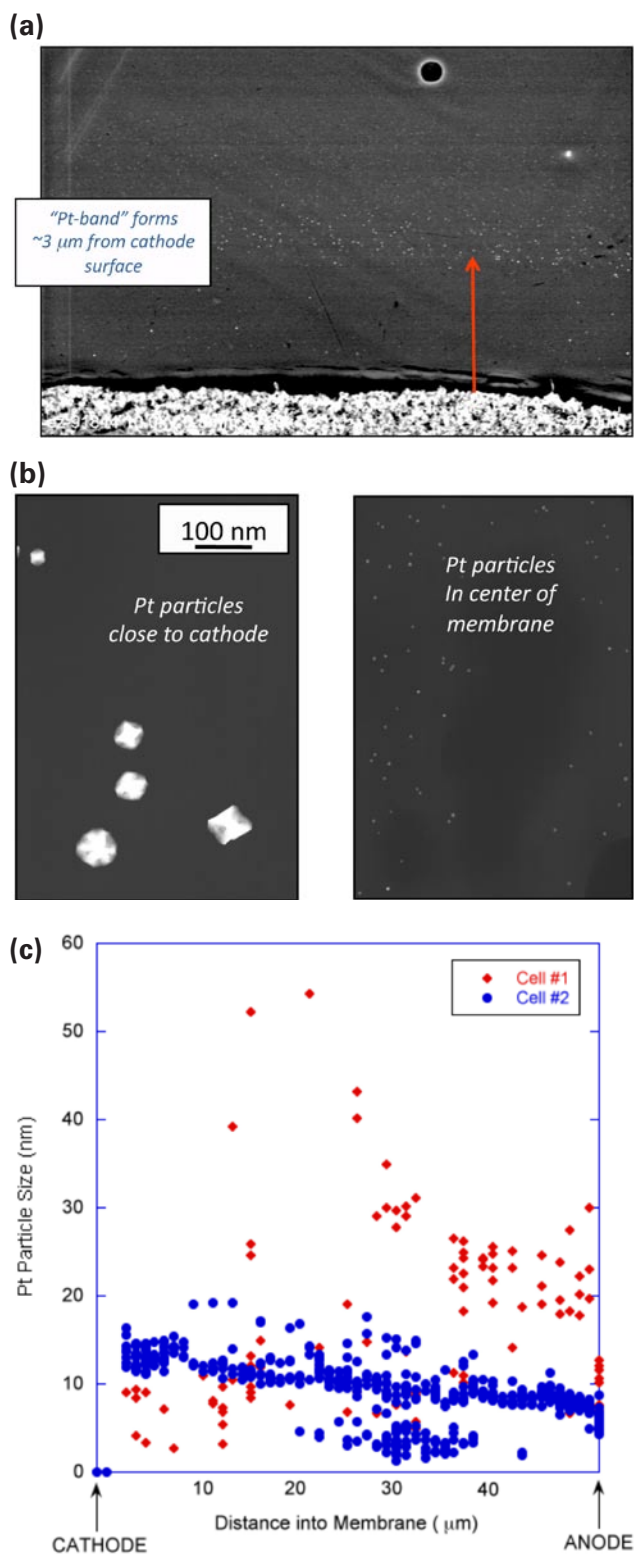 – Work for others (proprietary research).

(a)

"Pt-band" forms
~3 µm from cathode
surface

(b)

100 nm

Pt particles
close to cathode

Pt particles
In center of
membrane

(c)

FIGURE 4. (a) SEM cross-section image of Pt-band within membrane, (b) comparison of re-precipitated Pt single-crystal nanoparticles within Pt-band and away from Pt-band, and (c) size distribution of Pt nanoparticles across the membrane comparing two MEAs subjected to similar freeze-thaw cycles.

– Shared Research Equipment User Program (non-proprietary research) - University of Houston, University of Texas, Brown University, Rensselaer Polytechnic Institute.

– ORNL's "baseline" Microstructural Characterization Program (non-proprietary).

We will continue to establish new collaborations with industries, universities, and national laboratories (including access via ORNL User Facilities) to facilitate "transfer" of unique capabilities. We will also continue to support new DOE fuel cell projects with microstructural characterization and advanced characterization techniques.

• Progress to date to develop in situ liquid TEM/STEM as a viable technique to monitor the degradation of fuel cell materials has been hampered in FY 2010 for one primary reason – while we have been able to meet all program milestones for FY 2010 regarding optimizing the holder design and windows/chips, we are still delayed because of unreliable delivery of "working" windows/chips for the cell. Addressing this issue will be a priority in FY 2011.

• Initiated microstructural and microchemical characterization of EOL PEMFC MEAs to assess cathode carbon-support degradation mechanisms. Several collaborations have recently been pursued (General Motors and UTC Power) to systematically evaluate the progression of carbon corrosion as a function of aging conditions (via durability studies) rather than using EOL MEAs, which will be a primary focus of research in FY 2011.

• The migration and re-precipitation of Pt into and within has been studied in greater detail. Detailed studies to evaluate the amount, particle shape, size distributions, etc. of Pt from the cathode and into the membrane are being correlated with EASA losses and extent of carbon corrosion to fully interpret degradation behavior as a specific function of aging protocol. These correlative studies will be continued in FY 2011.

FY 2010 Publications/Presentations

1. K.L. More, K.S. Reeves, and R.L. Borup, "Pt-Co Bimetallic Catalysts for PEM Fuel Cell Cathodes," invited presentation at *Microscopy & Microanalysis 2009*, Richmond, VA, July 26–30, 2009.

2. K.L. More, L.F. Allard, and K.S. Reeves, "Electron Microscopy of Fuel Cell Catalyst and Catalyst Support Degradation," invited presentation at the Fall Meeting of the Materials Research Society, Boston, MA, November 30 – December 4, 2009.

3. K.L. More, "Analysis of Nanomaterials for PEM Fuel Cells," invited tutorial at the Fall Meeting of the Materials

Research Society, Boston, MA, November 30 – December 4, 2009.

4. K.L. More, K.S. Reeves, and R.L. Borup, "Pt-Co Bimetallic Catalysts for PEM Fuel Cell Cathodes," Microscopy and Microanalysis 15[Suppl. 2] (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," to be published in *Nature Chemistry*.

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," Chemistry of Materials 21[19] 4515-4526 (2009).

7. L.F. Xiong, K.L. More, and T. He, "Synthesis, Characterization, and Catalytic Oxygen Electroreduction Activities of C-Supported PtW Nanoparticle Catalysts," *Journal of Power Sources* 195[9] 2570-2578 (2010).

8. Z.Y. Liu, J.L. Zhang, P.T. Yu, J.X. Zhang, R. Makharia, K.L. More, and E.A. Stach, "TEM Observation of Corrosion Behaviors of Platinized Carbon Blacks under Thermal and Electrochemical Conditions," *Journal of The Electrochemical Society* 157[6] B906-B913 (2010).

References

1. K.H. Kangasniemi, D.A. Condit, and T.D. Jarvi, *J. Electrochem. Soc.* **151**[4] E125 (2004).

2. A.B. Ofstad, J.R. Davey, S. Sunde, and R.L. Borup, ECS Trans. **16**[2] 1301 (2008).

3. K.H. Lim, H.-S. Oh, S.-E. Jang, Y.-J. Ko, H.-J. Kim, and H. Kim, *J. Power Sources* **193** 575 (2009).

4. W. Li and A.M. Lane, *Electrochem. Comm.* **11** 1187 (2009).

5. J. Hu, P.C. Sui, S. Kumar, and N. Dijilali, *Electrochim Acta* **54** 5583 (2009).