

V.G.3 Microstructural Characterization of PEM Fuel Cell MEAs

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Start Date: FY 1999

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

Long-term MEA aging studies are being conducted in collaboration with numerous external partners, including MEA manufacturers, PEM fuel cell (PEMFC) stack manufacturers, and national laboratories.

Insights gained will be applied toward the design and manufacture of MEAs that meet the following DOE 2010 MEA targets:

- Cost: \leq \$15/kW
- Durability with cycling: \leq 80°C – 5,000 h; $>$ 80°C – 2,000 h
- 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 PEM fuel cell 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 (3.4.4.2) of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Electrode Performance
- (D) Thermal, Air, and Water Management

Technical Targets

This project is focused on conducting fundamental studies on the stability of individual constituents comprising proton exchange membrane (PEM) fuel cell MEAs. Of primary importance is relating MEA microstructure to fuel cell durability and performance.

Accomplishments

- Continued study with Los Alamos National Laboratory (LANL) to conduct catalyst particle coarsening measurements on electrochemically-aged MEAs using high resolution transmission electron microscopy (TEM) for comparison with x-ray diffraction studies (conducted at LANL). The effects of potential cycling, operating temperature, and percent relative humidity (%RH) on cathode Pt catalyst and Nafion[®] membrane durability were evaluated. Several techniques for using TEM imaging to quantify catalyst particle size distributions were evaluated and used.
- Continued Phase II of collaborative research with Arkema to evaluate polyvinylidene fluoride (PVDF)-based membranes for PEMFCs. The high-resolution analytical microscopy techniques for studying the fine-scale microstructural/compositional variability in stand-alone membranes were developed as part of this research.
- Several alternative bi- and tri-metallic catalysts were characterized before and after aging to elucidate observed instabilities resulting in performance degradation.
- Completed collaborative study with Plug Power to quantitatively evaluate Pt and Pt-Ru catalyst coarsening and migration when using different catalyst supports during electrochemical aging. Reported results to Plug Power.
- Continued collaboration with Gore Fuel Cell Technologies to use high-resolution microstructural characterization to evaluate fresh MEA structures for comparison with electrochemically aged MEAs.

- Initiated collaborative characterization research project with Argonne National Laboratory (ANL) to study Pt catalyst stability.

Introduction

Proton exchange (or polymer electrolyte) membrane fuel cells 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 $\sim 80^{\circ}\text{C}$) during electrochemical aging. Performance degradation can be attributed to the durability of individual components comprising the membrane electrode assembly (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 Oak Ridge National Laboratory (ORNL) has been focused on forming collaborative relationships with numerous National Laboratories and PEMFC developers/manufacturers to evaluate as-fabricated and electrochemically aged PEMFC membrane electrode assemblies (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 are conducted in collaboration with Los Alamos National Laboratory. Most of the MEAs used for the ORNL research are fabricated at LANL 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 transmission electron microscopy (A/TEM) and scanning electron microscopy (SEM) techniques to characterize the atomic-scale microstructure and composition of fully-intact layered MEAs. These high-resolution analyses are conducted on both fresh (baseline) MEAs and in many cases, the same MEAs following aging under load.

ORNL has developed the appropriate A/TEM sample preparation methodologies for evaluating the 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 ($<75\ \mu\text{m}$), uniform TEM specimens from 3-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.

Results

The non-proprietary research conducted in collaboration with LANL during FY 2006 was focused in three primary areas: (1) quantifying the effects of potential cycling, temperature, and %RH on Pt stability in the cathode, (2) evaluating additional microstructural changes within 3-layer MEAs during electrochemical aging, and (3) instabilities associated with alternative bi- and tri-metallic electrocatalysts. Results/highlights from these different areas will be discussed.

Pt stability during MEA cycling

To provide insight regarding loss of Pt surface area during electrochemical aging, LANL provided a series of tested 3-layer MEAs to ORNL for microstructural characterization. Each of these MEAs was prepared using Pt on Vulcan XC-72 C support (both anode and cathode) and a Nafion[®] 112 membrane. For this study, particular attention was focused on the cathode Pt, since this electrode is where the maximum degradation occurs. The following 5 cm² tested 3-layer MEAs were analyzed via transmission electron microscopy at ORNL for comparison with x-ray diffraction data acquired at LANL:

1. US06 drive cycle test @ 50% RH, 80°C, 2,350 h
2. US06 drive cycle test @ 100% RH, 80°C, 1,200 h and 2,000 h
3. CV cycled @ 100% RH, 80°C, 0.1-0.96 V, 20,200 cycles
4. CV cycled @ 100% RH, 80°C, 0.1-0.7 V, 1,500 cycles
5. CV cycled @ 50% RH, 120°C, 0.1-0.96 V, 1,500 cycles
6. CV cycled @ 50% RH, 80°C, 0.1-1.2 V, 1,500 cycles

The TEM data from these potential cycling tests were compared to TEM data acquired from MEAs that were aged at LANL under steady-state conditions (0.6 V, 80°C, 100% RH for 900 h and 3,500 h).

Figure 1 shows TEM images comparing the Pt sizes and distributions for the (a) fresh cathode, (b) steady-state aged for 900 h, (c) steady-state aged for 3,500 h, and (d) US06 drive cycle tested for 1,200 h (all of these samples were tested at 80°C and 100% RH). Many

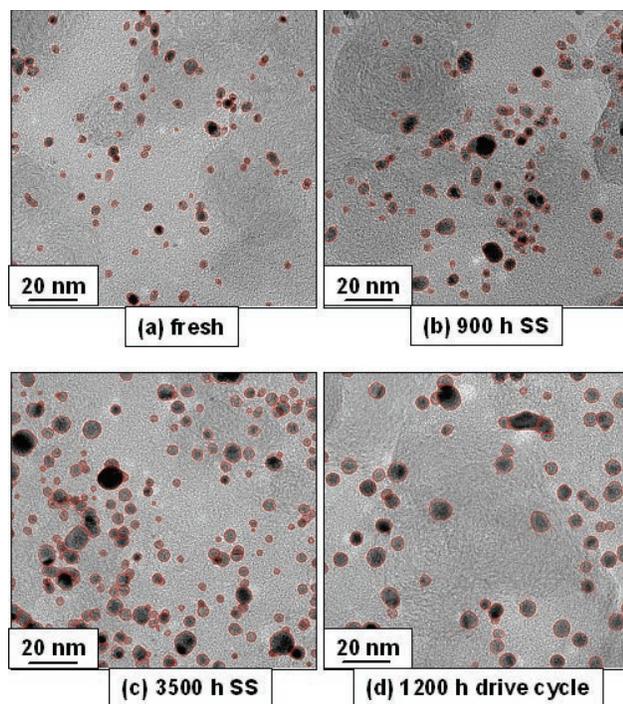


FIGURE 1. TEM images of Pt catalyst particles in cathode of (a) fresh MEA, (b) MEA steady-state aged for 900 h, (c) MEA steady-state aged for 3,500 h, and (d) MEA tested using US06 drive cycle.

similar TEM images were used to measure the Pt sizes and distributions for each of the aged samples such that thousands of particles were counted from different areas within the cathode (from cathode/membrane interface to surface of porous cathode layer) for statistically valid comparisons between the samples. For the cathode Pt particles shown in Figure 1 (i.e., same MEAs), the Pt size distributions are compared in Figure 2. The TEM data clearly show that potential cycling (US06 drive cycle) has a much greater effect on cathode Pt particle coarsening (loss of electrochemically active surface area, EASA) than steady-state fuel cell operation, even at significantly shorter aging times (3,500 h steady-state vs. 1,200 h drive cycle in Figure 2).

The effects of relative humidity on cathode Pt size distributions are illustrated in Figure 3(a), where two MEAs were subjected to the same US06 drive cycle tests at either 50% or 100% RH. Under similar drive cycle test conditions, the MEA cathode subjected to 100% RH showed increased loss of EASA compared with the MEA cathode tested at 50% RH, even for shorter aging times (2,000 h and 100% RH vs. 2,350 and 50% RH). A higher humidity results in a greater average Pt size, a broader Pt size distribution, and a tendency towards a more “bimodal” distribution of particles. This last observation is illustrated in the low magnification TEM image and insets from the cathode of the MEA US06 drive cycle tested at 100% RH shown in Figure 3(b). These TEM images show two different

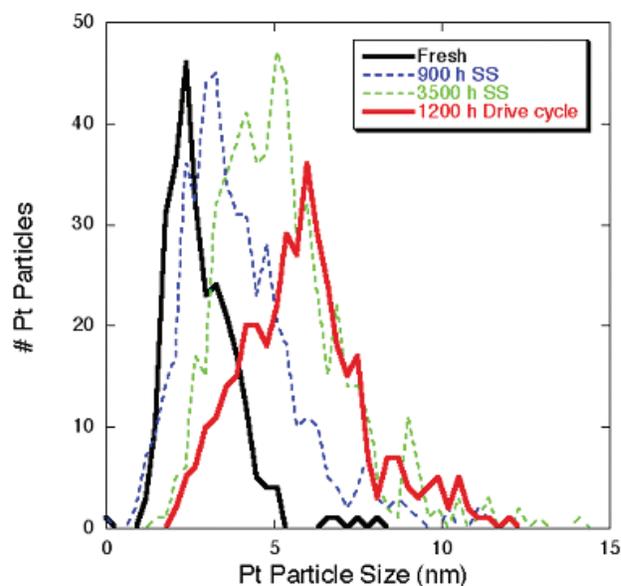


FIGURE 2. Cathode Pt size distributions determined from TEM images comparing samples shown in Figure 1.

types of regions within the cathode where the Pt sizes were very different; most regions of the cathode show a uniform dispersion of relatively small Pt particles (average Pt particle size ~6 nm), but localized regions (circled in Figure 3(b) and inset) showed much larger Pt particles (>8 nm) that were in close proximity to each other. These localized regions of larger Pt particles sizes result from the initial inhomogeneous dispersion of Pt in the fresh catalyst layer, where Pt particles are not dispersed “evenly” throughout the cathode during porous layer fabrication, but have a tendency to locally group close together on and/or between the carbon support, as illustrated in the schematic in Figure 4. In addition to increased localized Pt particle coarsening, this inhomogeneous initial Pt dispersion also leads to enhanced carbon corrosion within the higher Pt areas due to Pt-catalyzed carbon combustion [4].

Characterization of PtRu and Pt₃Cr Electrocatalysts

Fresh MEAs having porous catalyst layers containing either PtRu (anode) or Pt₃Cr (cathode) alloyed electrocatalysts are being characterized using TEM. PEM fuel cell MEA porous catalyst layers containing these types of electrocatalysts have demonstrated performance losses during electrochemical aging [5] some of which can be attributed to inhomogeneities present in the composition of the starting catalyst/support materials. For example, many PtRu/C used in anode catalyst layers are comprised of catalyst particles having a wide range of particle sizes and compositions. This is illustrated for a commercial PtRu/C alloy catalyst shown in Figure 5. The wide distribution of PtRu particle sizes is clear in the TEM

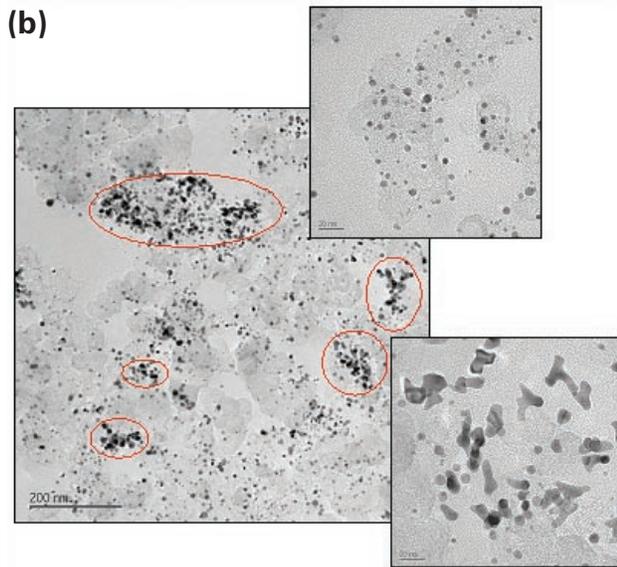
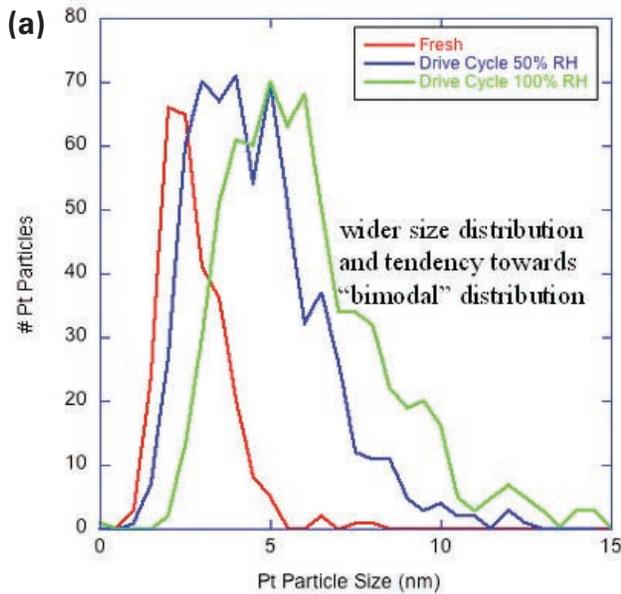


FIGURE 3. Effect of % RH used for US06 drive cycle aging on Pt coarsening, (a) cathode Pt size distributions and (b) TEM images showing localized regions of larger Pt particles within cathode.

image and the associated particle size distribution plot, which compares the PtRu alloy particles to Pt particles (Figure 5(a)). Rather than a distribution of fully-alloyed, compositionally similar (~50:50 Pt:Ru) catalyst particles having the preferred (for catalyst activity) face-centered cubic (fcc) crystal structure, the actual composition and crystal structure of the individual Pt-Ru particles was found to vary with particle size, as shown in Figure 5(b). Particle sizes <6 nm had a very high Ru content (≥ 70 atomic %) and an hexagonal close-packed (hcp) crystal structure (the same as pure Ru metal), whereas the larger particles ($\gg 10$ nm) were nearly pure Pt. From the particle size distribution (Figure 5(a)), most

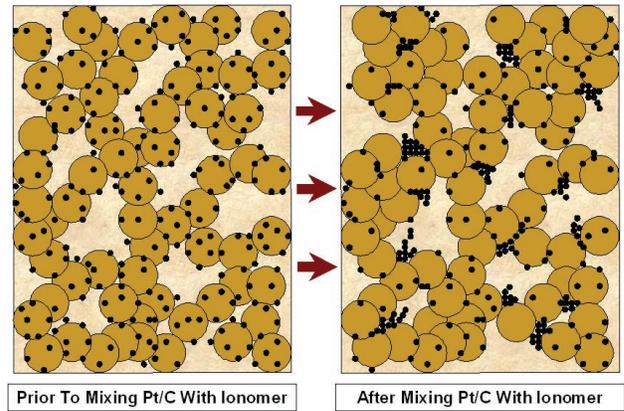


FIGURE 4. Schematic illustrating origin of localized, accelerated Pt coarsening due to initial non-homogeneous Pt dispersion.

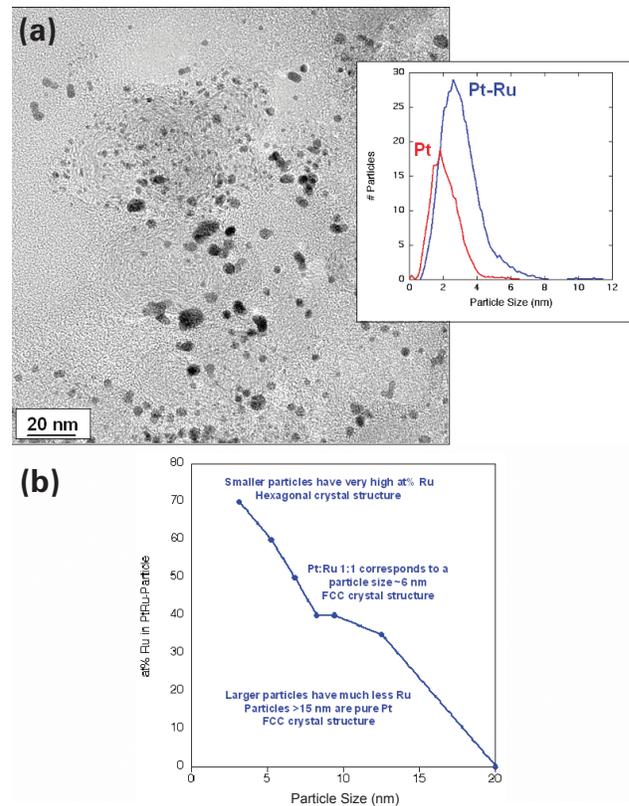


FIGURE 5. Pt-Ru particle distribution in MEA anode (commercial Pt-Ru) (a) TEM image of particles and associated Pt-Ru particle size distribution plot (compared to Pt) and (b) composition of Pt-Ru particles as a function of particle size.

of the Pt-Ru particles are <6 nm, which indicates that the majority of the particles in the anode are hcp Ru, not fcc PtRu alloy particles. Thus, although the “bulk” composition of this particular Pt-Ru powder was close to a 50:50 Pt:Ru ratio, the compositional variation measured between the Pt-Ru anode catalyst particles

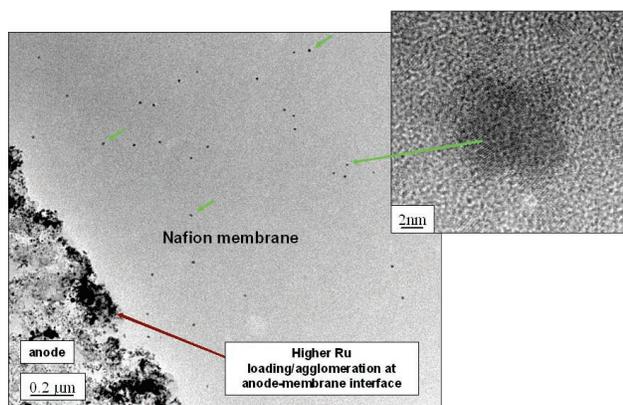


FIGURE 6. TEM image of the anode/membrane interface in a stack-aged MEA showing Ru build-up at anode/membrane interface and Ru particles in membrane due to migration of Ru from within anode to cathode side (through proton-conducting membrane).

demonstrates that the small particles comprising the anode were primarily Ru or were Ru-rich. Ru, if not properly alloyed with Pt, has been shown to migrate, or leach out, of the anode catalyst layer and move into and across the proton-conducting membrane to the cathode in direct methanol fuel cells [6]. This process is referred to as Ruthenium crossover, and a similar effect was observed during electrochemical aging (in a stack) of an MEA containing the same Pt-Ru/C powder described here. As shown in Figure 6, the Ru from the anode migrated to (and agglomerated at) the anode/membrane interface. Large crystalline (12-15 nm) Ru metal particles were identified within the Nafion[®] membrane (shown by green arrows) indicating the migration of Ru ions from the anode into the membrane during fuel cell operation. The Pt concentration within the anode did not change, only the “free” Ru migrated from anode to cathode.

Conclusions and Future Directions

- TEM imaging combined with extensive particle size measurements have been used to correlate microstructural observations of cathode Pt coarsening; TEM data shows Pt coarsening is accelerated during potential cycling and at high relative humidities.
- TEM data also show that the non-homogeneous dispersion of Pt on the carbon support and within the catalyst layer can lead to localized, accelerated Pt coarsening and carbon corrosion due to Pt-catalyzed carbon combustion.
- Migration of Pt from cathode to anode occurs during potential cycling; Pt loss due to migration is

especially evident when MEA is cycled to 1.2 V. Pt migrates well into the Nafion membrane at these high potentials and simultaneous crystallization of the Nafion[®] membrane occurs.

- The instabilities of bi-metallic catalyst particles during electrochemical aging can, in many circumstances, be directly related to compositional and structural inhomogeneities present in the fresh catalyst powders. This has been demonstrated for commercial Pt-Ru/C and Pt₃Cr/C.
- Additional commercial and non-commercial powders of alternative bi- and tri-metallic catalysts on carbon supports will be characterized in terms of structural and compositional homogeneity (FY 2007).
- Fundamentals of carbon corrosion will be studied in terms of support structure and type and loading of electrocatalyst (FY 2007).
- Non-proprietary work with both LANL and ANL will continue (FY 2007).

Special Recognitions & Awards/Patents Issued

1. K.L. More received the 2006 DOE Hydrogen Program Research & Development Award at the 2006 DOE Hydrogen Program Annual Merit Review Meeting, Washington, DC, May 16-19, 2006.

FY 2006 Publications/Presentations

1. J. Xie, D.L. Wood, K.L. More, P. Atanassov, and R.L. Borup, “Microstructural Changes of MEAs During PEFC Durability Testing at High Humidity Conditions,” *Journal of The Electrochemical Society*, **152**(5) A1011-20 (2005).
2. K.L. More and K.S. Reeves, “Understanding MEA Structure from Evaluations Using Electron Microscopy,” Abstract #316, 2005 Fuel Cell Seminar, Palm Springs, CA, November 14-18, 2005.
3. K.L. More, J. Bentley, and K.S. Reeves, “Microstructural Characterization of PEM Fuel Cell MEAs,” presented to the Fuel Cell Tech Team, USCAR, Southfield, MI, January 18, 2006.
4. J.T. Goldback, K.L. More, and A.L. Manheim, “Nano-Scale Investigation of Morphologies in Polymer Electrolyte / PVDF Blend Membranes,” presented at the 2006 AIChE Spring National Meeting, Orlando, FL, April 24-28, 2006.
5. 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, Smithfield, RI, July 23-28, 2006.

References

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2. D.A. Blom, J. Dunlap, L.F. Allard, and T.A. Nolan, "Ultramicrotomy Sample Preparation of PEMFC Cross Sections," *Journal of The Electrochemical Society* **150**[4] 414-A418 (2003).
3. K.L. More and K.S. Reeves, "Partial embedding of 3-Layer MEAs for Ultramicrotomy," in *Microscopy & Microanalysis* **11**[2] 2104-2105 (2005).
4. D.A. Stevens and J.R. Dahn, "Thermal Degradation of the Support in Carbon-supported Pt Electrocatalysts for PEM Fuel Cells," *Carbon* **43** 179-188 (2005).
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6. P. Piela, C. Eickes, E. Broscha, F. Garzon, and P. Zelenay, "Ru Crossover in DMFC with Pt-Ru Anode Black," *Journal of the Electrochemical Society* **151**[12] A2053-A2059 (2004).