V.I.2 Microstructural Characterization of PEM Fuel Cell Membrane Electrode Assemblies

Karren L. More
Oak Ridge National Laboratory
1 Bethel Valley Rd.
Oak Ridge, TN 37831-6064
Phone: (865) 574-7788; Fax: (865) 576-5413; E-mail: morekl1@ornl.gov

DOE Technology Development Manager: Nancy Garland
Phone: (202) 586-5673; Fax: (202) 586-9811; E-mail: Nancy.Garland@ee.doe.gov

Objectives

- Elucidate membrane electrode assembly (MEA) degradation and/or failure mechanisms by conducting extensive microstructural characterization of both fresh and aged (under load) MEAs.
- Correlate differences between as-processed MEA microstructures and performance.
- Collaborate with polymer electrolyte membrane (PEM) fuel cell developers/manufacturers to evaluate their MEAs using advanced electron microscopy techniques and 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:

- O. Stack Materials and Manufacturing Cost
- P. Durability
- Q. Electrode Performance

Approach

- Through established collaborative R&D programs (non-proprietary and proprietary collaborations), prepare thin cross-section specimens from fresh and aged (under load) MEAs using the ultramicrotomy technique developed at Oak Ridge National Laboratory (ORNL).
- Use high-resolution scanning, transmission, and analytical electron microscopy (SEM, TEM, and AEM) techniques to evaluate nm-scale microstructural features/changes within MEA layers (including membrane, electrocatalyst layers, and gas diffusion layers).
- Establish correlations between microstructure, performance, and MEA durability.

Accomplishments

- Collaboration with Los Alamos National Laboratory (LANL) was initiated to evaluate electrode processing effects on microstructural development and the subsequent effect on MEA performance. The MEAs used in this study were fabricated at LANL using the "thin-film decal" method. Processing variables evaluated in this study included:
  - Effect of vol% recast Nafion ionomer in the cathode layer (17%-66%)
  - Effect of type of electrocatalyst (Pt, PtRu, Pt_3Cr, PtCoCr)
  - Effect of catalyst application technique (hand vs. mechanical)
  - Effect of H_2SO_4 boiling step (unboiled vs. boiled)

- The performance of LANL-produced MEAs was directly correlated with the microstructural differences produced by utilizing different vol% recast Nafion ionomer. The cathode layer with 28 vol% ionomer achieved the best performance, and this catalyst layer composition exhibited the optimum distribution of electrocatalyst constituents (Pt/C, recast ionomer, and porosity), which supported percolation theory.
- Microstructural changes occurring in LANL-produced MEAs were evaluated during life-testing of H_2/air PEM fuel cells. Extensive Pt (anode) and Pt_3Cr (cathode) catalyst particle coarsening (loss of surface area) and Pt migration into the Nafion membrane were observed and explained the performance decay observed (loss of 54 mV) during 1000 h cell operation.
- Initiated collaboration with Plug Power to evaluate microstructural changes occurring during PEM fuel cell aging.
- Initiated collaboration with Fuel Cell Energy to evaluate aging effects during durability testing of MEAs.
- Initiated collaboration with Gore Fuel Cell Technologies to use high-resolution microstructural characterization to evaluate fresh MEA structures.

Future Directions

- Complete work currently underway with LANL and initiate additional studies to characterize MEA degradation/aging.
- Improve ultramicrotomy sample preparation technique for studying gas diffusion layers (GDLs).
- Further evaluate the nm-scale chemical/compositional properties of recast Nafion ionomer (within electrocatalyst layers) and Nafion membrane before and after durability testing using electron energy loss spectroscopy.
- Establish new collaborations with industrial partners to conduct relevant MEA evaluation studies.

Introduction

Proton exchange (or polymer electrolyte) membrane fuel cells (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 <100°C) under load. The microstructural characterization project at the Oak Ridge National Laboratory (ORNL) has been designed to work with PEMFC developers/manufacturers to evaluate as-fabricated and electrochemically aged PEMFC MEAs using advanced microstructural characterization techniques in order to establish 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 processing changes required for optimized PEMFC durability and performance.

Approach

In this work, the non-proprietary aspects of MEA evaluation were carried out in collaboration with the Los Alamos National Laboratory (LANL). The MEAs were fabricated at LANL using the "thin decal" process. In this process, catalyst inks (a suspension of XC-72 carbon ink, Nafion ionomer, glycerol, and precious metal catalyst particles) were painted onto Teflon-coated fiberglass substrates (the decal) and heat-treated. Layers of catalyst were sequentially painted and heat-treated until the desired electrode thickness was attained. The decals were then hot-pressed onto both sides of a Nafion 112 membrane for 5 minutes at 205°C. Finally, the decals were peeled off, leaving the MEA, which was boiled for 2 hours in H_2SO_4 to convert the Nafion to its proton-conducting form. Several different processing variables and their effects on resulting MEA microstructure and performance were studied:

(1) amount (%) Nafion ionomer in cathode
(2) type of electrocatalyst(s) used
(3) painting process (hand vs. mechanical)
(4) effect of the H_2SO_4 boiling step on electrode phase (constituent) distribution

The aged MEAs were electrochemically (durability) tested in a LANL single-cell testing system for times up to 2200 hours [1].

Bulk MEA compositional and microstructural changes were evaluated before (fresh) and after (aged) aging using backscatter electron imaging (BSE) and wavelength dispersive spectrometry (WDS) in a JEOL 8200 electron probe microanalyzer (EPMA). Transmission electron microscopy (TEM) using a Philips CM200 FEG-TEM/STEM was also carried out on as-fabricated and aged MEAs. Thin (<75 nm) cross-section MEA specimens were prepared for TEM analysis using room-temperature ultramicrotomy (Leica UCT). Details for preparing TEM specimens from PEMFC MEAs have been described previously [2].

Results

The primary focus areas for the LANL/ORNL collaborative effort during FY 2004 were twofold: (1) establishing the relationship between the amount (vol%) of recast Nafion ionomer within the cathode catalyst layer and the MEA electrochemical performance, and (2) identifying the MEA microstructural changes which resulted in loss of performance during electrochemical aging. In the first study, the amount of recast Nafion ionomer within the cathode catalyst layer was varied from a low ionomer content of ~17% to a high content of ~67%. A total of six MEAs with different ionomer contents were evaluated, and performance measurements showed that the ionomer content had a significant effect on the MEA performance over the entire current range and that the optimum performance was obtained at ~28 vol% ionomer [3]. The constituent networks (carbon/Pt, recast ionomer, and pore sizes and distributions) within the cathode catalyst layers were measured for each of the six MEAs (17%, 20%, 25%, 28%, 40%, and 67% ionomer contents) from representative TEM micrographs, similar to that shown in Figure 1 (for

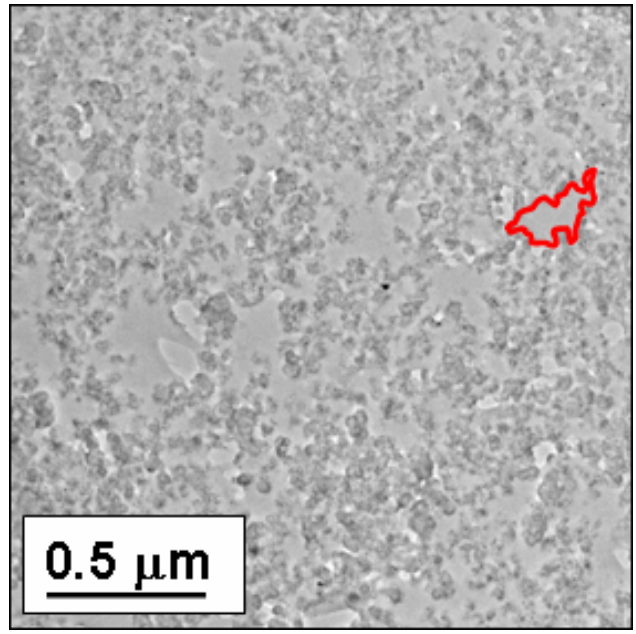

Figure 1. Low-Magnification TEM Image of 28-Vol% Nafion Ionomer Cathode Catalyst Layer Showing Relationship between Different Constituents (carbon/Pt, ionomer, porosity)

28% Nafion). Binary images were then created for each of the different constituents, and these images were superimposed to create a 2-D image of the interpenetrating constituent networks (Figure 2, also for 28% Nafion). In Figure 2, the network shown in black (darkest) is the carbon/Pt, the network shown in red is the recast ionomer, and porosity is shown in green (lightest). These images are useful for comparing the size, distribution, and interconnectivity of the different constituent networks within different catalyst layers in order to optimize the microstructure of the catalyst layer during processing. The cathode with 28% recast ionomer had the best performance because finer-scale percolating networks formed between the three primary catalyst layer constituents, which in turn increased access (proton, electron, gas) to active catalyst sites.

In the second collaborative study with LANL, morphological changes in the catalyst layers in LANL-produced MEAs were monitored via TEM during the course of (interrupted) life-testing. For this work, the microstructure of the fresh (baseline) MEA was compared with the microstructures following a 1000-hour durability test under load.

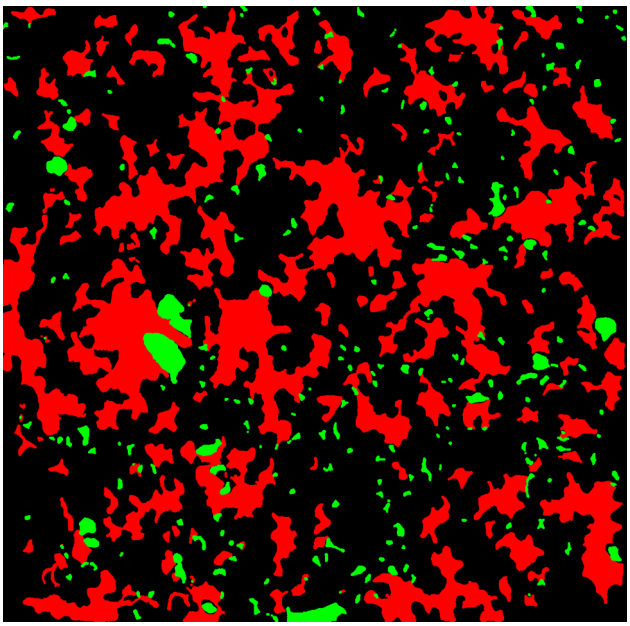

Figure 2. Overlapping Binary Images (from TEM image shown in Figure 1) Clearly Showing 2-D Visualization of Interpenetrating Networks in Cathode Catalyst Layer (In this image, black shows the carbon/Pt network, red shows the recast Nafion ionomer, and green shows the porosity distribution.)

The MEAs consisted of a 0.20±0.01 Pt/cm^2 anode catalyst layer and a 0.20±0.01 Pt_3Cr/cm^2 cathode catalyst layer. The MEA performance decayed at a rate of 54 μV/h during the 1000-h durability test [4]. Coarsening (~2X) and sintering of the Pt_3Cr catalyst particles occurred in the cathode during aging, from ~3-10 nm in the fresh cathode to ~6->20 nm after 500 hours aging, as shown in Figure 3. Additional Pt_3Cr coarsening and sintering was minimal during the full 1000-h test, indicating that most of the catalyst particle coarsening occurred during the first 500 hours of operation. Within the anode catalyst layer, Pt particle coarsening was more severe. During the first 500-h life test, Pt particles were coarsened (~2.5X); the size of the Pt particles changed from ~1-12 nm in the fresh anode layer to ~5-15 nm after 500 hours of testing. After the full 1000-h test, the Pt particles within most of the anode catalyst layer did not coarsen further; however, Pt particles directly at the anode-membrane interface not only coarsened an additional 3-4X (from 5-15 nm to 20-40 nm) but significantly changed shape,

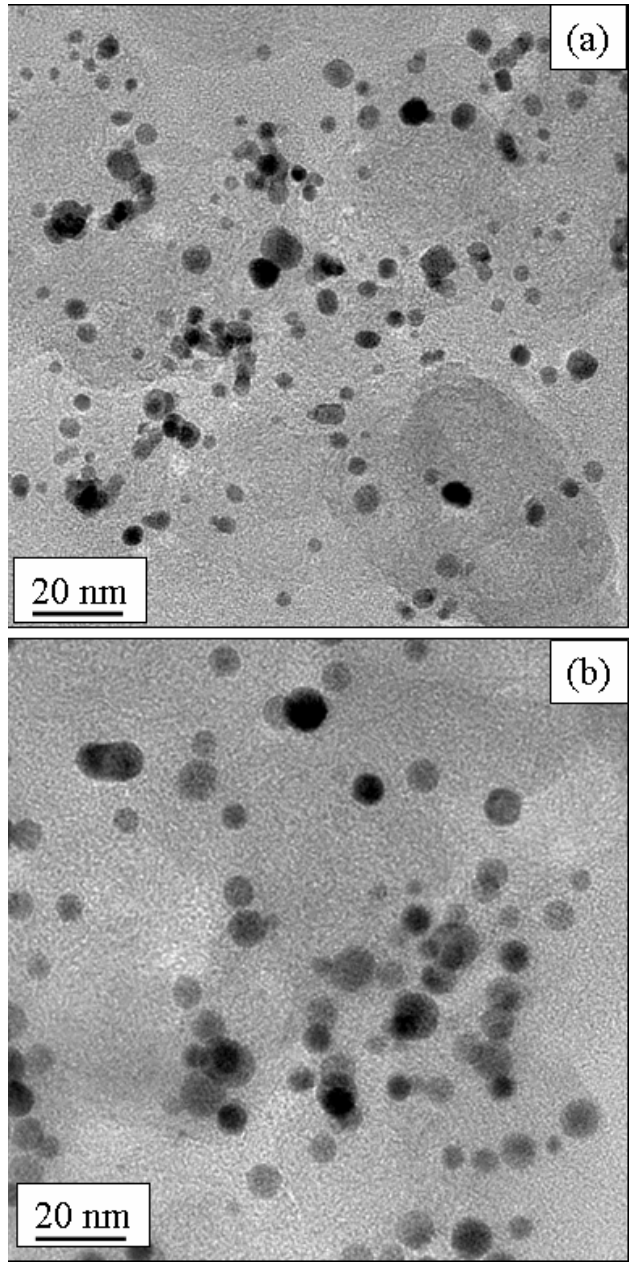

Figure 3. TEM Images of Pt_3Cr Catalyst Particles in (a) Fresh Cathode Catalyst Layer and (b) Cathode Catalyst Layer in MEA Electrochemically Aged for 500 h

becoming cuboidal with faceted sides (Figure 4). This coarsening was accompanied by observable Pt migration from within the anode layer to the anode-membrane interface (Figure 5), as well as migration of Pt into the Nafion membrane. Metallic Pt particles

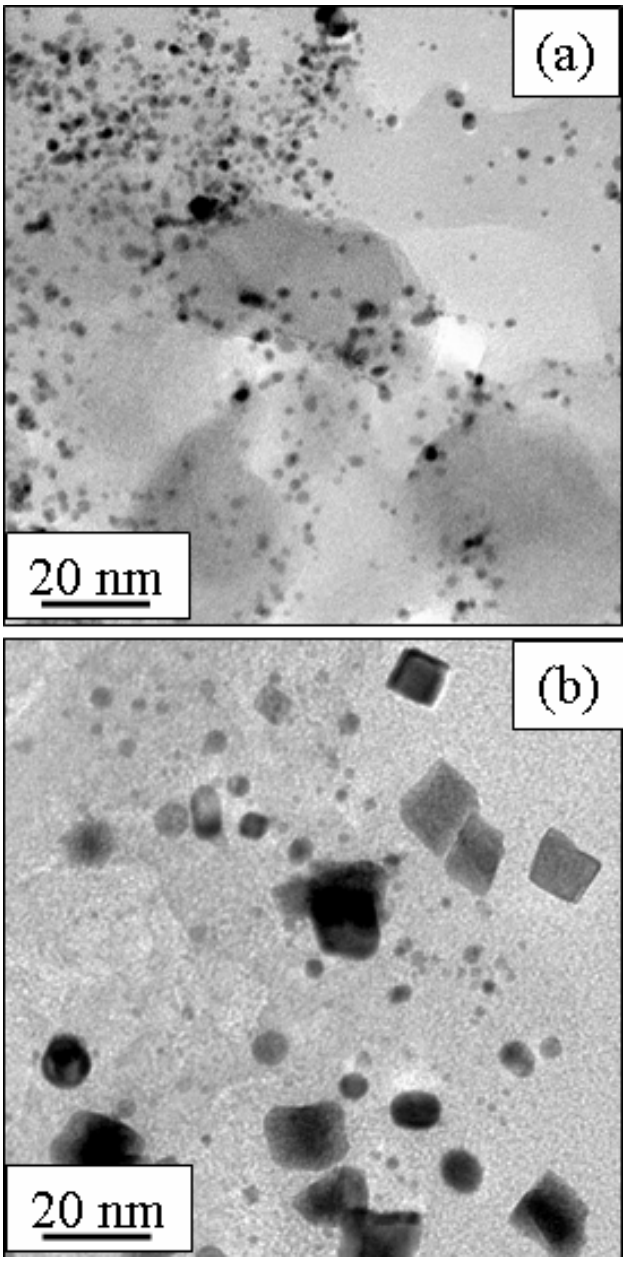

Figure 4. TEM images of Pt Catalyst Particles in (a) Fresh Anode Catalyst Layer and (b) Anode Catalyst Layer at Anode-Membrane Interface in MEA Electrochemically Aged for 1000 h.

were identified within the membrane ~3 μm from the anode-membrane interface (Figure 6). Additional characterization work is necessary to fully understand the mechanism of Pt migration within the anode catalyst layer and into the Nafion membrane and to fully evaluate this effect on MEA durability and fuel cell performance.

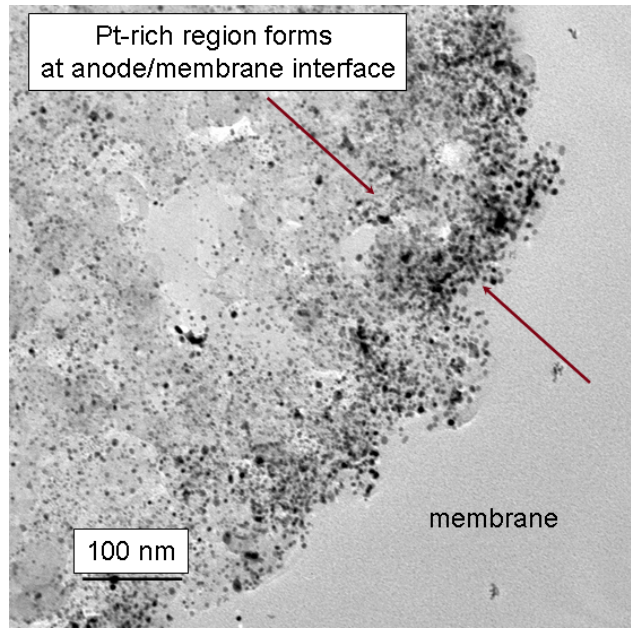

Figure 5. TEM Image Showing Pt Migration Towards the Anode-Membrane Interface after MEA Durability Test for 500 h

Conclusions

- Rapid and reproducible preparation of TEM thin sections by ultramicrotomy has been achieved, allowing for a greater number of MEAs to be evaluated.
- Distinct microstructural differences were observed between cathode catalyst layers containing differing amounts (vol%) of Nafion ionomer, and these microstructural differences were correlated with MEA performance (collaboration with LANL). Results of this work have been submitted to *Journal of The Electrochemical Society.*
- Following 1000 hours of durability testing of a LANL-produced MEA, significant coarsening of Pt_3Cr particles in the cathode catalyst layer was observed. Greater Pt particle coarsening was observed on the anode side, where coarsening was accompanied by migration of Pt to the anode-membrane interface and into the membrane itself. Results of this work have been submitted to *Journal of The Electrochemical Society.*

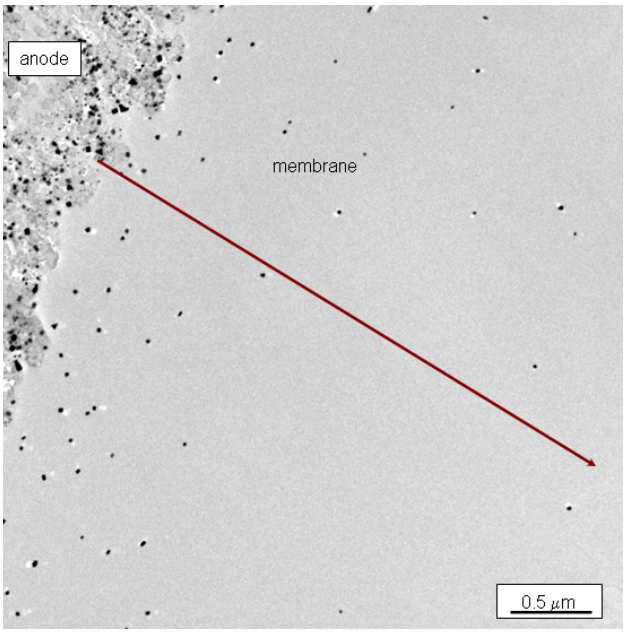

Figure 6. TEM Image Showing Pt Particle Formation Within the Nafion Membrane Due to Pt Migration from Anode Catalyst Layer During Electrochemical Aging for 1000 h

- In addition to the ongoing non-proprietary research with LANL, several new proprietary studies have been started in FY 2004 (with Gore Fuel Cell Technologies, Plug Power, and Fuel Cell Energy).

References

1. T.E. Springer, M.S. Wilson, and S. Gottesfeld, *Journal of The Electrochemical Society* **140** (1993).

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** (2003).

3. J. Xie, K.L. More, T.A. Zawodzinski, and W.H. Smith, "Porosimetric Structure of the Membrane Electrode Assemblies Made by Thin Film Decal Method and Its Effect on the Performance of Polymer Electrolyte Fuel Cells," paper submitted to *Journal of The Electrochemical Society* (2004).

4. J. Xie, D.L. Wood, K.L. More, P. Atanassov, and R.L. Borup, "Microstructural Changes of MEAs During Polymer Electrolyte Fuel Cell Durability Testing at High Humidity Conditions," paper submitted to *Journal of The Electrochemical Society* (2004).

FY 2004 Publications/Presentations

1. K.L. More, K.S. Reeves, J. Bentley, and J. Xie, "Microstructural Characterization of PEMFC MEAs," presented at 2003 Fuel Cell Seminar, Miami Beach, FL, November 3-6, 2003.

2. K.L. More, K.S. Reeves, J. Bentley, and J. Xie, "Evaluation of Processing Parameters on the Microstructure and Performance of PEMFC MEAs," presented at the 106th Annual Meeting of The American Ceramic Society, Indianapolis, IN, April 18-21, 2004.

3. J. Xie, K.L. More, T. Zawodzinski, and W.H. Smith, "Porosimetric Structure of the MEAs Made by the "Thin-Film Decal" Method and Its Effect on the Performance of PEMFCs," publication submitted to *Journal of The Electrochemical Society*, February 2004.

4. J. Xie, D.L. Wood, K.L. More, P. Atanassov, and R.L. Borup, "Microstructural Changes of MEAs During PEMFC Durability Testing at High Humidity Conditions," publication submitted to *Journal of The Electrochemical Society*, May 2004.

5. K.S. Reeves, K.L. More, L.R. Walker, and J. Xie, "TEM Evaluation of Aged PEMFCs," accepted for publication in Proceedings of Microscopy & Microanalysis 2004.