

Microstructural Characterization of PEM Fuel Cells

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Objectives

- Use transmission electron microscopy (TEM) characterization techniques to observe the distribution of precious metal catalyst, pore space and ionomer in proton exchange membrane (PEM) electrodes
- Understand the processing/structure/property relationship for membrane electrode assembly (MEA) electrodes to allow for optimization of the electrode structure for higher performance
- Characterize/quantify microstructural changes and their relation to the performance loss in PEM MEAs upon use in a fuel cell system to understand issues relating to durability and lifetime

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 R,D&D Plan:

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

Approach

- Prepare thin cross-sections of PEM MEAs via diamond knife ultramicrotomy
- Using TEM techniques, characterize the structure of the electrodes (e.g. size of catalyst particles, amount and location of ionomer, spatial distribution of supported catalyst) and relate to performance and/or processing
- Investigate the electrode/membrane interfaces for evidence of microchemical degradation of the ionomeric membrane after extended use in a fuel cell

Accomplishments

- Successfully prepared cross-sections of MEAs provided by Los Alamos National Laboratory (LANL)
- Improved the sectioning technique to routinely achieve 100 nm thick sections (vs. former 300 nm thicknesses) for greatly improved electron transparency and structural detail
- Characterized the electrode structure effect of boiling the MEA in sulfuric acid
- Characterized the as-prepared catalyst distribution for an advanced MEA design

Future Directions

- Investigate the effects of ionomer content on the structure of the electrodes
 - Characterize the microstructural changes which occur between standard decal painting of the electrodes and tape casting
 - Study the role the catalyst composition plays in the development of the overall electrode structure
 - Suggest modifications to the electrode forming process to optimize the use of the precious metal catalyst
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Introduction

Proton exchange membrane (PEM) fuel cells hold great promise for use as an environmentally friendly power source for automobiles. One of the key requirements in making PEMs commercially viable is to reduce the cost by reducing the amount of precious metal catalyst necessary to provide high power density operation at low temperature. In order for efficient catalysis to occur, gas molecules must be able to easily interact with the surface of the catalyst particles. A pathway for diffusion of protons must exist in close proximity to the active sites on the catalyst, and an electrically conductive pathway from the catalyst to the electrodes is required for electron transport. Finally, water (the by-product of the fuel cell reaction) has to be transported away from the catalyst for continuing reaction to occur. These requirements show the complexity of building an efficient PEM fuel cell and clearly indicate the opportunity for atomic-scale microstructural and chemical characterization to provide feedback on the geometry and distribution of the various components for optimum performance.

PEM fuel cells are well known to "age" upon application as a power source. Over time, the performance of both individual cells and the overall system degrades. By examining the structure and composition of the MEAs before and after use in a fuel cell environment, the changes which may have occurred can provide valuable information on the mechanism(s) of performance loss. Understanding the primary degradation mechanisms is the first step to successfully engineering an improved MEA with less performance loss.

Approach

Cross-sections of PEM MEAs were prepared for transmission electron microscopy (TEM) by techniques of ultramicrotomy. Small sections from the MEAs, approximately 3 mm by 8 mm, were selected for sample preparation. The samples were placed into silicone embedding molds, and an Araldite epoxy resin was added to the molds to embed the sample. The resin was polymerized at least 16 hours at 60°C in order to produce a solid epoxy piece with the MEA sample embedded. The epoxy embedded sample was trimmed initially using a Leica EM Trim tungsten carbide trimming tool. A tungsten carbide tip was used to rapidly remove excess epoxy from around the MEA sample to produce a small, flat area suitable for ultramicrotomy. The nature of the MEAs dictated a narrow (0.25 to 0.5 mm), long (1-2 mm) area for ultramicrotomy. The epoxy-embedded MEA was then secured into the cutting arm of a Leica Ultracut UCT Ultramicrotome. A 45° diamond knife was used to slice several sections of various thicknesses from each sample. The goal is always to produce the thinnest possible slice for TEM examination. Slice thicknesses were typically 100 nm or less under room temperature microtomy conditions, facilitated by proper development of the appropriate resin mixture. The thin slices were floated off the diamond knife edge onto distilled water and then collected onto copper mesh grids.

The thin samples were observed in either a Hitachi HF-2000 field-emission transmission electron microscope (FE-TEM) or in a Hitachi HD-2000 dedicated scanning transmission electron microscope

(STEM, also a field emission instrument). Both high resolution TEM imaging of individual catalyst particles and their carbon support and atomic number (or “Z-contrast”) STEM imaging of the electrode structure were performed. The structure of the electrodes is key for good performance. The “three phase boundary” where porosity, ionomer and catalyst particles come together is where effective catalysis occurs. Both imaging and chemical composition analysis are provided by TEM at the length scale which is appropriate for understanding the details of the electrode structure. Additionally, the boundary between the electrode and the membrane is of great interest to the fuel cell community. A number of indirect electrochemical measurements suggest that the interface between the electrode and the membrane is a weak point in the durability of the overall system. Analysis of the structure and composition of this area for both freshly prepared MEAs and MEAs which have been used in a fuel cell for a number of hours provides a first step towards reducing the degradation of PEM fuel cells over time.

Results

Advances in room temperature ultramicrotomy this fiscal year have allowed us to prepare MEA cross-sections which are below 100 nm in thickness. Figures 1 and 2 are Z-contrast micrographs of sections from the same MEA electrode illustrating the benefits of the thinner section. Z-contrast imaging is a technique in the STEM which forms an

image from the electrons, which are scattered to large angles by the atoms of the sample (1). Atoms with a larger atomic number (Z) scatter electrons to high angles more strongly than atoms with lower atomic number. In the case of PEM fuel cell electrodes, the high atomic number catalyst particles (typically Pt) scatter electrons to a much greater degree than the surrounding ionomeric material and therefore appear as bright specks in the image. The sample shown in Figure 1 is 300 nm thick, which is sufficiently thin for successful imaging and microanalysis of the electrode. Transmission electron microscopy always involves the projection of a three-dimensional microstructure onto a two-dimensional image. In this case, significant overlap of the catalyst particles is observed with a thickness of 300 nm. Significant data can be extracted from images such as Figure 1, including the size distribution of the catalyst particles and the gross electrode structure. However, details of the spatial distribution of the ionomer and the porosity are obscured by the thickness of the section shown in Figure 1. Figure 2 is a Z-contrast micrograph from a 100 nm thick section of the same MEA. The individual catalyst particles are more easily seen in Figure 2 versus Figure 1. Additionally, the porosity of the electrode is seen in the dark area in the lower section of the micrograph. Evidence of the carbon black support of the catalyst particles is seen in the grayscale difference between the background of the image and the brighter areas around the catalyst particles. The catalyst particles are seen to coat the surface of the carbon black

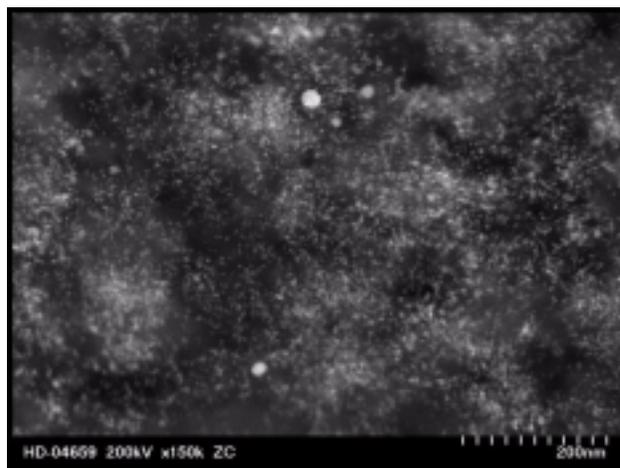


Figure 1. Z-contrast Micrograph of a 300 nm Thick Section of an MEA Electrode

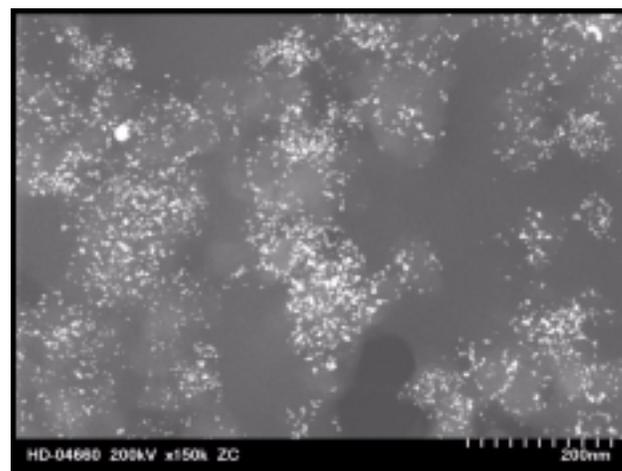


Figure 2. Z-contrast Micrograph of a 100 nm Thick Section of an MEA Electrode

support. A much more thorough understanding of the detailed structure of the electrode is possible from the image in Figure 2 as compared to the image in Figure 1. The thicker specimen allows for the characterization of the catalyst particles and the gross spatial distribution of the catalyst, while the thinner specimen allows, for the first time, a direct observation of the spatial distribution of all three phases of an MEA electrode: catalyst and support, ionomer and porosity.

The effect of boiling the MEA in sulphuric acid on the initial microstructure of the electrode was also investigated this fiscal year. Figures 3 and 4 are TEM micrographs of electrode for sections ~100 nm thick. Bright-field TEM images are formed from unscattered and low-angle scattered electrons. At low resolution, the bright areas of the image correspond to porosity and/or low scattering parts of the sample. The MEA shown in Figure 3 did not undergo the boiling step during the preparation process for the MEA. The section was sufficiently thin that the porosity, catalyst and support and ionomer are clearly distinguishable. The small black specks are the individual catalyst particles, while the larger circular features are the carbon black support. The ionomer is the overall light grey background, while the porosity is visible as the white areas in the

micrograph. The catalyst clusters are very close together in Figure 3, with very little ionomer-only area visible. Figure 4 illustrates the electrode structure on an MEA which was boiled in sulphuric acid as part of the fabrication process. The section thickness and micrograph magnification are the same as in Figure 3. The catalyst clusters are better separated, with obvious areas of ionomer visible in the image. Catalyst particles in PEM fuel cell MEAs have previously been shown to coarsen with time during fuel cell use. The microstructure in Figure 3, where the catalyst particles start off much closer together than the corresponding structure in Figure 4, is much more susceptible to catalyst coarsening and the subsequent performance loss.

Conclusions

- Room temperature ultramicrotomy is capable of producing MEA cross-sections 100 nm thick.
- Sections that are 100 nm thick allow for the characterization/analysis of **all** the components of a PEM fuel cell electrode, while thicker sections do not.
- Boiling in sulphuric acid has a great effect on the initial microstructure of the electrode in a PEM fuel cell MEA.

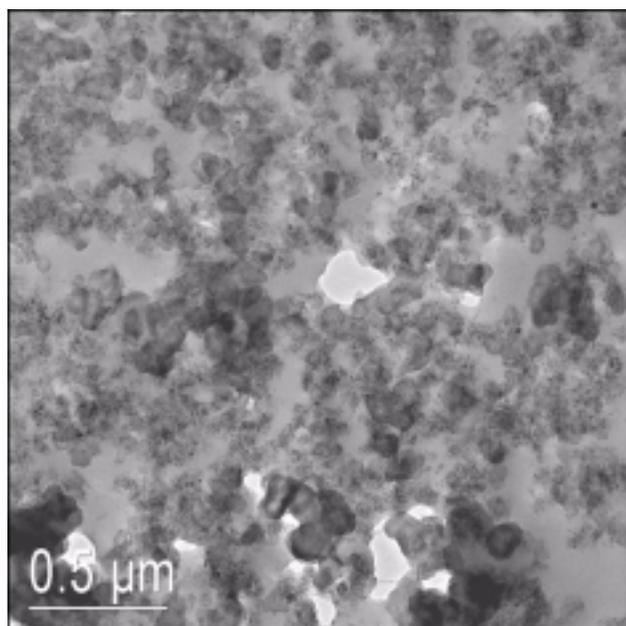


Figure 3. TEM Micrograph of an MEA Electrode not Boiled in Sulphuric Acid

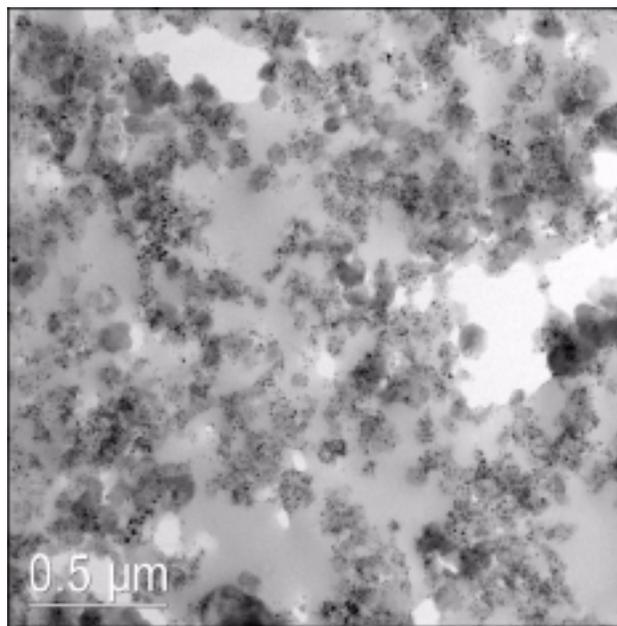


Figure 4. TEM Micrograph of an MEA Electrode which was Boiled in Sulphuric Acid

- The boiling process is expected to improve the durability of the electrode by increasing the distance between catalyst particle regions.

References

1. S. J. Pennycook and D. E. Jesson, "High-Resolution Incoherent Imaging of Crystals", *Phys. Rev. Lett.*, 64 (8), 938.

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