

V.H.1 Polymer Electrolyte Fuel Cell Lifetime Limitations: The Role of Electrocatalyst Degradation

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Objectives

- Understand the role of cathode electrocatalyst degradation in the long-term loss of polymer electrolyte membrane fuel cell (PEMFC) performance,
- Establish dominant catalyst and electrode degradation mechanisms,
- Identify key properties of catalysts and catalyst supports that influence and determine their degradation rates,
- Quantify the effect of cell operating conditions, load profiles, and type of electrocatalyst on the performance degradation, and
- Determine operating conditions and catalyst types/structures that will mitigate performance loss and allow PEMFC systems to achieve the DOE lifetime targets.

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
- (B) Cost
- (C) Performance

Technical Targets

This project is conducting fundamental studies of platinum-based PEMFC cathode electrocatalyst degradation mechanisms. Insights gained from these studies can be applied toward the definition of operating conditions to extend PEMFC lifetimes and to the development of cathode electrocatalyst materials that meet the following DOE 2015 electrocatalyst durability targets with voltage cycling:

- 5,000 hours (<80°C) and 2,000 hours (>80°C),
- <40% loss of initial catalytic mass activity, and
- <30 mV loss at 0.8 A/cm²

Accomplishments

- Prepared Ketjen carbon-supported Pt nano-particle electrocatalysts (Pt/C) of varying particle size and incorporated these electrocatalysts into the cathodes of membrane-electrode assemblies (MEAs).
- Quantified Pt/C catalyst oxygen reduction reaction (ORR) activity, electrochemically-active surface area (ECA), and performance losses in a fuel cell as a function of initial Pt particle size and cell parameters (relative humidity, temperature, upper potential limit, and cycling protocol).
- Developed a kinetic Monte Carlo (KMC) code to predict Pt nano-particle evolution under fuel cell conditions.
- Determined Pt particle size and particle size distribution evolution during potential cycling as a function of initial Pt particle size (1.9, 3.2, 5.7, and 9.1 nm) during potential cycling in an aqueous environment, using anomalous small-angle X-ray scattering.



Introduction

One of the primary challenges facing the development of PEMFCs for automotive and stationary power applications is the durability of the fuel cell materials. Though significant progress has been made toward achieving the technical target of 5,000 operating hours, particularly for non-conventional catalyst

architectures, the durability status for conventional stacks is considerably shorter than 5,000 hours [1-3]. Typical degradation rates for constant load conditions are 25-40 $\mu\text{V}/\text{h}$ and can be an order of magnitude higher when operating under non-steady-state conditions prevalent in the automotive application, including load and start-stop cycling and extended time at open circuit [3]. The observed degradation under these conditions has reversible and irreversible components with one of the most dominant contributors to irreversible degradation being loss of cathode oxygen reduction reaction activity. The subjects of this project are the irreversible losses in PEMFC performance, as these are the most challenging in terms of mitigation strategies. Specifically, this project focuses on cathode catalyst degradation, because the degradation of this component has the most profound impact on cell performance. The project's primary focus is elucidation of the effects of catalyst and support physicochemical properties and cell operating conditions on the rates and mechanisms of cathode catalyst degradation, with a secondary focus on the impact of catalyst degradation on the transport properties of the cathode.

Approach

The project approach is to perform systematic cell degradation tests, in situ and ex situ structural characterization of the catalysts, fundamental out-of-cell studies, and theoretical modeling to identify the degradation modes and factors contributing to cathode catalyst degradation. The catalysts to be studied are benchmark Pt on carbon supports with varying properties, Pt alloys with varying oxophilicity, and three classes of Pt catalysts having the highest reported oxygen reduction activity. Specifically, our approach is to utilize accelerated stress tests of MEAs containing various catalysts and supports and in situ and ex situ dissolution, microscopic, structural, and chemical characterization of these catalysts. To elucidate the effect of particle size, we will systematically vary the particle size of Pt and one Pt alloy on a standard support. To elucidate the effect of catalyst type and catalyst oxophilicity, we will study four classes of catalysts: Pt, Pt alloys, acid-leached alloys, and core-shell catalysts with approximately the same particle size and particle size distributions. To elucidate support effects, we will study Pt on carbon supports with systematically varied surface area, pore size, and relative proportions of micro- and mesopores. In addition, to study the role of carbon degradation in ECA loss we will assess the effect of surface area of carbon exposed to the electrolyte and Pt contact area with the carbon using a series of Pt/C catalysts with differing Pt loading. We will also determine the effects of catalyst precursor impurities on degradation rates by post-synthesis doping of a Pt/C catalyst with varying levels of precursor impurities (e.g., Cl, Na, K, and F).

The results of the experimental efforts will feed into coupled models at various levels of complexity from atomic-level, ab initio oxidation and dissolution calculations, to catalyst degradation models, to cell kinetic and transport models. The modeling effort will also define the experiments necessary to complete the cell model. The project can be categorized into three broad and coupled tasks: (1) MEA studies utilizing accelerated stress test protocols, on-line electrochemical diagnostics, and post-test microscopic and X-ray scattering characterization, (2) mechanistic and physicochemical property studies using aqueous electrochemistry, X-ray spectroscopy/scattering, transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and in situ TEM, and quartz crystal microbalance measurements, and (3) model development, verification, and implementation. All of these techniques have been demonstrated to provide important and complementary information regarding catalyst degradation mechanisms.

Results

To establish the background for studies of advanced classes of catalysts, our initial studies have focused on determining the effects of cell operating parameters and initial Pt particle size on cell performance and performance degradation. Catalysts were prepared containing 40 wt% Pt nano-particles with a mean diameter of 1.9 nm on high-surface-area Ketjen black carbon support (Pt/C). This material was heat treated to form catalysts with mean particle sizes of 3.2, 7.1, and 12.7 nm, respectively. These catalysts were studied in an aqueous electrochemical environment (0.1 M HClO_4 electrolyte) using anomalous small angle X-ray scattering, to determine the evolution of Pt particle size and particle size distribution as a function of potential cycling using the DOE cycling protocol (0.6 V to 1.0 V triangle wave; 50 mV/s). These catalysts were also incorporated into the cathodes of MEAs and subjected to the DOE cycling protocol in the fuel cell environment. Cell diagnostics of cathode catalyst ECA, ORR mass activity, and air and oxygen polarization curves were performed after 1,000, 3,000, 5,000, and 10,000 voltage cycles. Studies were also performed on the effect of various fuel cell operating parameters (relative humidity [RH], temperature, cycling profile, and upper potential limit) on the degradation of the cathode electrocatalyst performance on membrane-electrode assemblies containing the 3.2 nm Pt/C as the cathode catalyst. The results of these initial studies are summarized below.

Summary of MEA and aqueous cell particle size study results:

- Cycling to 1.0 V has minimal impact on ECA and oxygen reduction reaction mass activity of catalysts

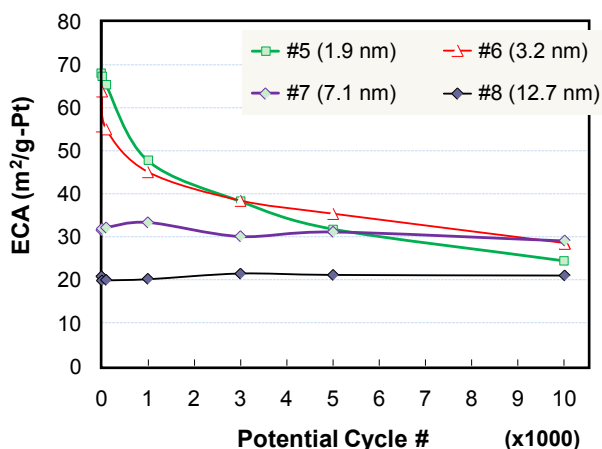


FIGURE 1. Electrochemically-active surface area as a function of cycle number (50 mV/s triangle wave between 0.4 and 1.0 V) for Pt/C cathode electrocatalysts in a membrane-electrode assembly with initial mean Pt particle sizes of 1.9 nm (■), 3.2 nm (▲), 7.1 nm (◇), and 12.7 nm (◆).

- with large initial particle size (7.1 and 12.7 nm; see Figure 1).
- Cycling to 1.0 V degrades the ORR mass activity of catalysts with small initial particle size (1.9 and 3.2 nm) toward that of larger particles (7.1 and 12.7 nm).
- Beginning of life fuel cell performance of MEAs with smaller cathode catalyst particle size (1.9 nm and 3.2 nm) is highest, but voltage cycling degrades performance to below that of MEAs with larger initial particle size (7.1 nm and 12.7 nm).
- MEAs with larger cathode catalyst particles (7.1 nm and 12.7 nm) show minimal performance degradation over 10,000 voltage cycles.
- MEAs with larger cathode catalyst particles (7.1 nm and 12.7 nm) show minimal performance degradation over 10,000 voltage cycles.
- Particles of ~3 nm show growth and narrowing of distribution over 1,750 potential cycles in aqueous electrolyte (Figure 2-top).
- Particles of ~12 nm show no growth or change in distribution over 1,750 potential cycles in aqueous environment (Figure 2-bottom).
- Anomalous small angle X-ray scattering shows that the mean particle diameter of ~3 nm catalyst grows by ~0.1 nm over 1,750 cycles, with the majority of particle growth occurring during the first 900 cycles in aqueous environment
- Potential cycling causes Pt catalysts of 2.4 to 3.7 nm initial size to evolve to identical specific surface areas, independent of initial particle size.

Summary of MEA parametric study results (Figure 3):

- Increasing the upper limit of voltage cycling from 0.95 V to 1.05 V increases cathode catalyst ECA loss and ORR mass activity loss.

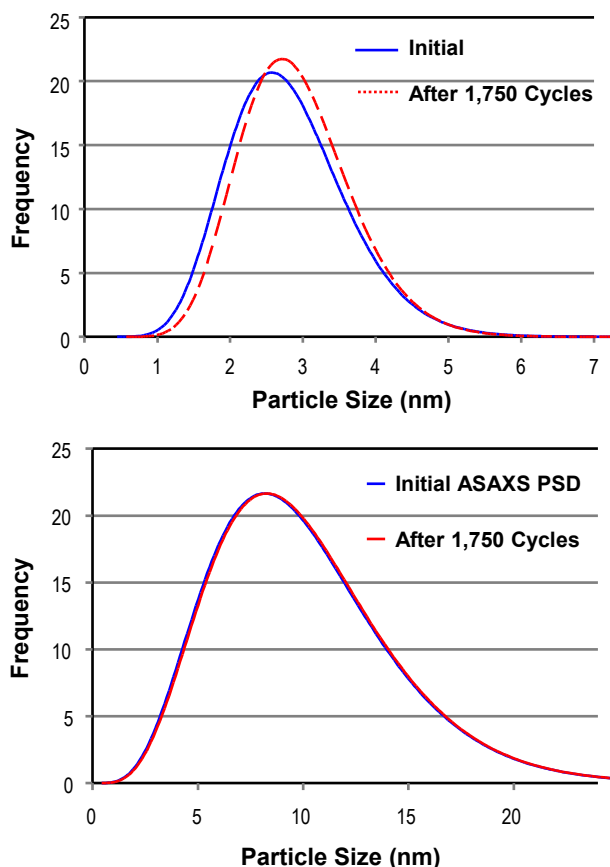


FIGURE 2. Pt particle size distributions for Pt/C catalysts with mean initial particle sizes of ~3 nm (top) and ~7 nm (bottom) before and after 1,750 cycles between 0.4 and 1.0 V at 50 mV/s in aqueous 0.1 M HClO₄ electrolyte.

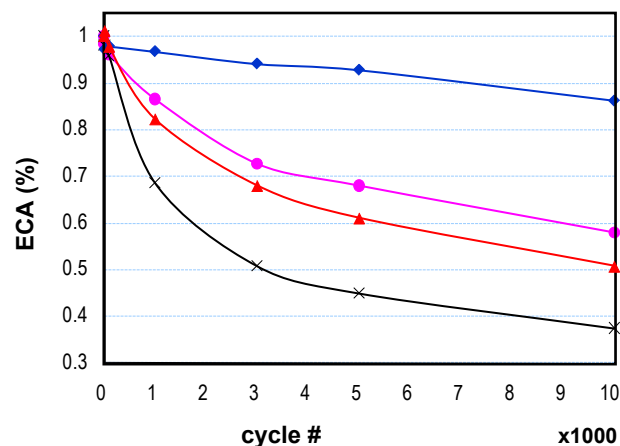


FIGURE 3. Normalized loss of electrochemically-active surface area as a function of cycle number for square wave potential cycling. (●) Baseline conditions: square wave of 10 s at 0.4 V-10 s at 0.95 V, cell temperature of 80°C, anode/cathode RH of 100%, atmospheric pressure, fuel/oxidant of 4%hydrogen and nitrogen, respectively. (◆) Same as baseline, except anode and cathode RH of 30%. (▲) Same as baseline, except cell temperature of 90°C. (x) Same as baseline, except upper potential limit of cycling of 1.05 V.

- In addition to causing a loss of ECA, cycling to high potentials (1.05 V) increases cathode transport losses.
- Low anode/cathode inlet RH decreases cathode catalyst degradation (30% RH versus 100% RH).
- Increased cell temperature increases cathode catalyst degradation (90°C versus 80°C).

These studies on Pt/C provide the background for on-going studies of platinum alloy (e.g., Pt₃Co/C) cathode electrocatalyst degradation modes.

In the modeling tasks of the project, a KMC model has been developed that can predict Pt nano-particle evolution under fuel cell conditions. As a first step of the validity of this tool, the evolution of a 3.1 nm Pt particle from a spherical particle with random atomic orientation to its thermodynamic equilibrium structure in vacuum at 300 K was determined. As shown in Figure 4, the KMC tool correctly predicts the evolution of the particle to a cubo-octahedra structure, as observed experimentally. This model is being further developed to follow the shape and structure evolution of Pt alloy nano-particles and the changes in the nano-particles in the fuel cell environment due to various processes, such as dissolution and surface migration of atoms. This KMC tool will enable the identification of the causes of the stability/instability of nano-particle alloys in the

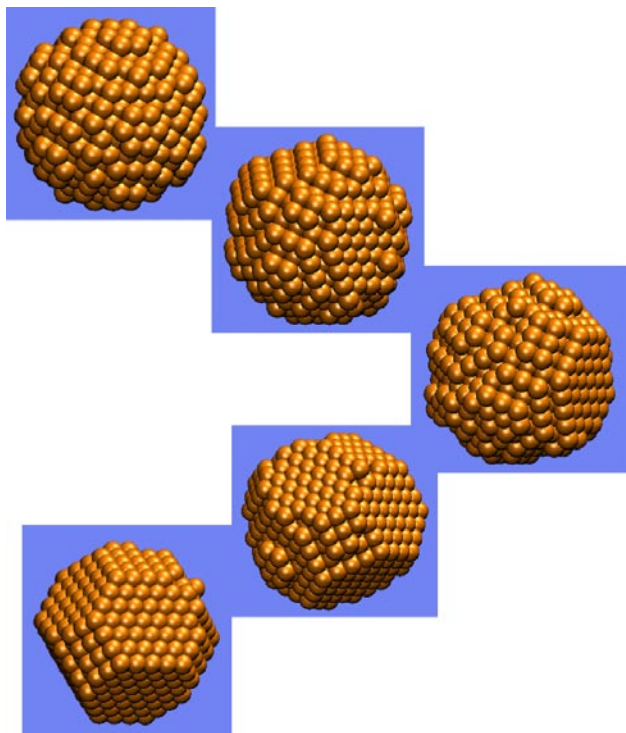


FIGURE 4. KMC model prediction of the evolution of a 3.1 nm Pt spherical particle in vacuum at 300 K to its equilibrium structure, a cubo-octahedra.

fuel cell environment and to identify properties and mechanisms that control degradation.

Conclusions and Future Directions

The following interim conclusions can be made from our initial studies of the degradation of baseline Pt/C electrocatalysts:

- Initial fuel cell performance increases with decreasing cathode electrocatalyst mean Pt particle size, however degradation of performance with potential cycling increases with decreasing particle size.
- Potential cycling (0.4 to 1.0 V; 50 mV/s) causes Pt catalysts of $< \sim 4$ nm initial mean diameter to evolve to specific surface areas comparable to those of 7-12 nm particles (20-30 m²/g).
- Performance degradation with potential cycling can be attributed to increased rates and extent of ECA loss with decreasing Pt particle size for electrocatalysts with mean Pt particle sizes $< \sim 4$ nm.
- Extent of loss of ~ 3 nm Pt nano-particle cathode electrocatalyst performance, caused by loss of ECA, increases with increasing cell temperature, increasing RH, and increasing upper limit of potential cycling.

The immediate future direction of the experimental portion of the project is to complete characterization of the Pt/C class of catalysts, including acquiring additional data needed for the nano-particle degradation modeling effort, such as Pt dissolution rates and extent of oxidation as a function of potential. Immediate future work on advanced catalysts will focus on characterization of platinum-cobalt alloy nano-particles of varying initial particle size.

Future Directions

- Characterize Pt dissolution as a function of particle size for Pt and Pt₃Co.
- Determine effect of temperature on Pt dissolution rates for “benchmark” Pt/C catalyst (3.2 nm mean diameter).
- Determine ORR activity of Pt₃Co/C catalysts of varying particle size and evolution of activity with potential cycling.
- Quantify Pt₃Co catalyst performance loss in a fuel cell as a function of initial particle size and cell parameters.
- Extend KMC code development to alloy nano-particles.
- Model aqueous cell and MEA mean particle size and particle size distribution evolution with cycling.

- Develop model for Pt nano-particle voltammetry, including states of oxide as a function of potential to predict Pt dissolution rates.
- Synthesize and characterize nano-particles of advanced Pt alloy electrocatalysts (e.g., Pt₃Sc and Pt₃Y).

FY 2010 Publications/Presentations

1. Dane Morgan, Edward Holby, Wenchao Sheng, Yang Shao-Horn, "Understanding Pt Surface Area Loss in PEMFC Cathodes – Size and Oxidation Effects", 217th Meeting of the Electrochemical Society, Vancouver, Canada, April 25–30, 2010. (Invited)
2. Debbie Myers, Xiaoping Wang, Rajesh Ahluwalia, Xiaohua Wang, Matt Smith, and James Gilbert, "Degradation Mechanisms of Pt-based Oxygen Reduction Reaction Electrocatalysts", 2010 Gordon Research Conference on Fuel Cells, Bryant University, Smithfield, Rhode Island, August 1–6, 2010. (Invited)

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1. J. Garbak, "Technology Validation", 2010 Department of Energy Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 8, 2010.
2. K. Wipke, S. Sprik, J. Kurtz, T. Ramsden, "Controlled Hydrogen Fleet and Infrastructure Analysis", 2010 Department of Energy Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 10, 2010.
3. F.A. de Bruijn, V.A.T. Dam, G.J.M. Janssen: "Durability and degradation issues of PEM fuel cell components", *Fuel Cells* **8** (2008) 3-22.