

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

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## Fiscal Year (FY) 2011 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.
- 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 5,000 hours (>80°C).
- <40% loss of initial catalytic mass activity after 30,000 cycles between 0.6 and 1.0 V.
- <30 mV loss at 0.8 A/cm<sup>2</sup> after 30,000 cycles between 0.6 and 1.0 V.

## FY 2011 Accomplishments

- Completed parametric and particle size studies comparing membrane electrode assembly (MEA) performance degradation for Pt<sub>3</sub>Co and Pt cathodes with similar initial particle sizes.
- Determined that voltage cycling from 0.6 to 1.0 V causes Pt particles of <~7 nm to grow to ~9.5 nm, irrespective of initial particle size, with evidence for both dissolution and coalescence growth mechanisms.
- Determined that Pt dissolution increases with decreasing Pt particle size and is correlated with oxide formation.
- Developed Pt cyclic voltammetry and dissolution models and Kinetic Monte Carlo (KMC) model of alloy nanoparticle dissolution for defining the alloy nanoparticle parting limit.



## 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. The observed performance degradation has reversible and irreversible components. The topic of this project is the irreversible degradation of Pt-based cathode catalysts,

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. The results of this project will define the operating conditions and catalyst types/structures that will mitigate performance loss and allow PEMFC systems to achieve the DOE lifetime targets.

## Approach

The project approach is to perform: (1) systematic cell degradation tests, (2) in situ and ex situ structural characterization of the catalysts, (3) fundamental out-of-cell studies, and (4) theoretical modeling to identify the degradation modes and factors contributing to cathode catalyst degradation. The catalysts 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 are systematically varying the particle size of Pt and one Pt alloy (Pt<sub>3</sub>Co) on a standard support. To elucidate the effect of catalyst type and catalyst oxophilicity, we are studying four classes of catalysts: Pt, Pt alloys, acid-leached alloys, and core-shell catalysts while either controlling or carefully determining the particle size and particle size distributions. To elucidate support effects, we are studying Pt on carbon supports with varied surface area, pore size, and relative proportions of micro- and mesopores. We are also determining the effects of a catalyst precursor impurity on degradation rates by post-synthesis doping of a Pt/C catalyst with varying levels of a precursor impurity (e.g., Cl).

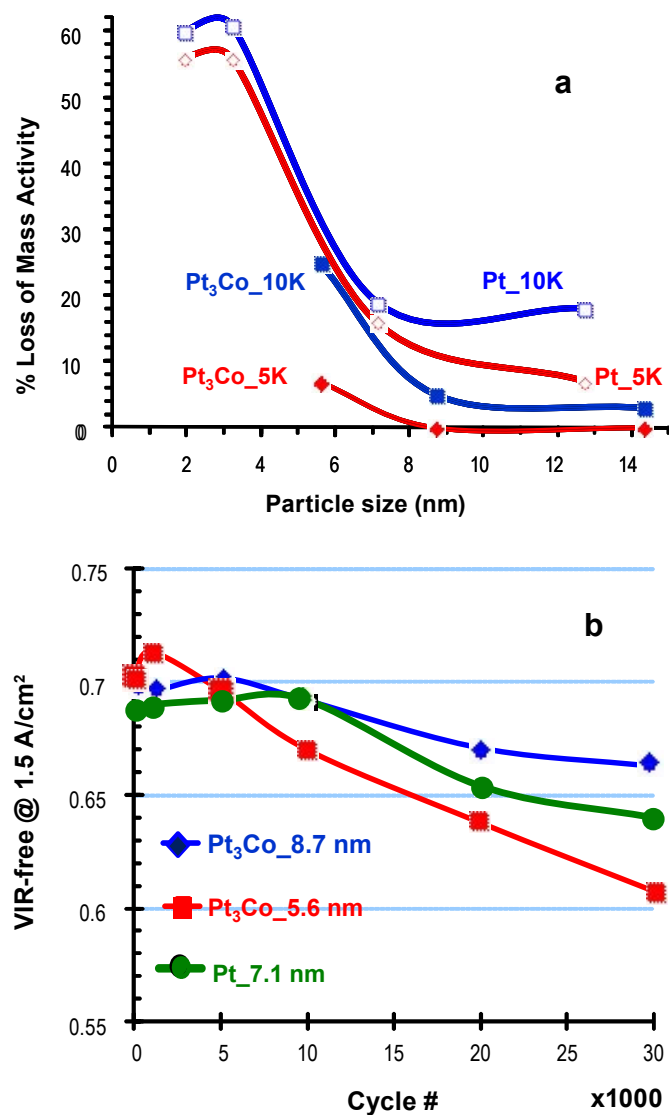
The results of the experimental efforts feed into coupled models at various levels of complexity from atomic-level, *ab initio* oxidation and dissolution calculations, to catalyst degradation models, to cell kinetic and transport models. The modeling effort also defines the experiments necessary to complete 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), 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

The focus of this year's effort has been on parametric and particle size studies of MEAs with Pt<sub>3</sub>Co cathode electrocatalysts, comparison with identical studies of Pt MEAs, electron microprobe (EMPA) and STEM analysis of cycled Pt MEAs, degradation mechanism experiments and modeling of Pt cathode catalysts, and *ab initio*-based modeling of Pt-Co alloys. Catalysts were prepared containing 40 wt% Pt<sub>3</sub>Co nanoparticles with a mean diameter of 5.6 nm on high-surface-area Ketjen black carbon support (Pt<sub>3</sub>Co/C). This material was heat treated to form catalysts with mean particle sizes of 8.7 and 14.3 nm. These catalysts were also incorporated into the cathodes of MEAs and subjected to the DOE cycling protocol (0.6 to 1.0 V, 50 mV/s) in the fuel cell environment. Cell diagnostics of cathode catalyst electrochemically active surface area (ECA), oxygen reduction reaction (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 with MEAs containing the 5.6 nm Pt<sub>3</sub>Co/C. The results of the particle size and parametric studies on the Pt<sub>3</sub>Co and comparison with the Pt results shown in last year's report are summarized in the following.

- Increasing the upper limit of voltage cycling increases cathode catalyst surface area and mass activity loss.
- Low inlet relative humidity decreases cathode catalyst degradation.
- ECA loss: Depends on catalyst particle size. No statistically meaningful difference was observed between Pt and Pt<sub>3</sub>Co MEAs.
- ORR mass activity loss: Depends on catalyst particle size. The mass activity of Pt<sub>3</sub>Co is more stable than the mass activity of Pt (Figure 1).
- Initial performance: Pt<sub>3</sub>Co-based MEAs showed better beginning of life performance than Pt-based MEAs (~20 mV in H<sub>2</sub>/O<sub>2</sub> or ~15 mV in H<sub>2</sub>/Air @ 1 A/cm<sup>2</sup>).
- Performance degradation: At high currents, the performance loss depends on catalyst particle size, no statistically meaningful difference was observed between Pt and Pt<sub>3</sub>Co MEAs (Figure 1).
- The ionic resistance in the electrode is higher for cycled Pt<sub>3</sub>Co cells than cycled Pt cells, which offsets the improved mass activity stability of the alloy.

This year's effort in the ex situ characterization tasks included post-cycling EMPA of the Pt<sub>3</sub>Co and Pt-containing MEAs and STEM analysis of the Pt-containing MEAs. These MEAs had varying initial Pt particle size (1.9, 3.2, 7.1, and 12.7 nm) and were subjected to the DOE cycling protocol for 10,000 cycles (30,000 for the 7.1 nm particle



**FIGURE 1.** (a) Loss of oxygen reduction reaction mass activity after 5,000 (Pt\_5K and Pt<sub>3</sub>Co\_5K) and 10,000 (Pt\_10K and Pt<sub>3</sub>Co\_10K) cycles in an MEA (DOE protocol) as a function of initial mean particle size of Pt and Pt<sub>3</sub>Co catalysts and (b) Internal resistance-free cell voltage at 1.5 A/cm<sup>2</sup> on air as a function of cycling in an MEA for Pt<sub>3</sub>Co (5.6 and 8.7 nm) and Pt (7.1 nm).

size). MEAs with the 3.2 nm Pt/C cathode catalyst used in the parametric studies mentioned above were also analyzed.

The EMPA results showed that Pt migrated into the membrane for all of the Pt and Pt<sub>3</sub>Co MEAs, with the exception of the cells tested at lower relative humidity (30% vs. 100%) and the cell with the largest Pt particle size (12.7 nm). The trends in Pt migration into the membrane observed were the same for Pt and Pt<sub>3</sub>Co MEAs, including:

- Lower Pt content in the membranes with larger catalyst particle sizes.
- Lower Pt content in the membrane for low RH cycled cell.

- Higher Pt content in the membrane for high voltage and high temperature cycled cell.

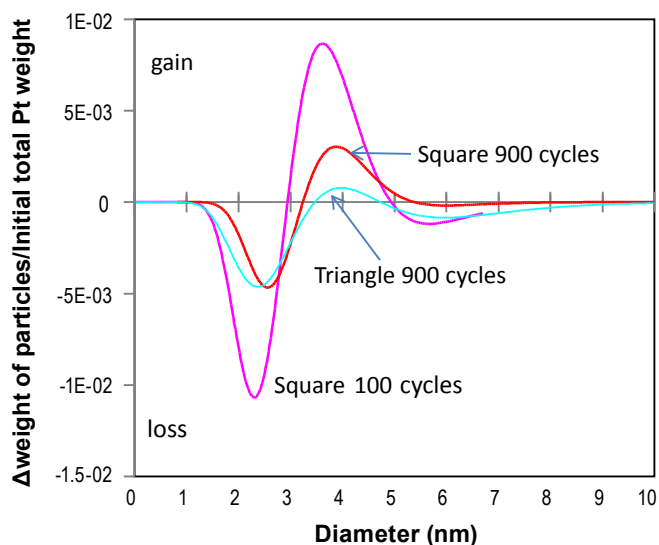
The Pt MEA (7.1 nm) had a higher Pt content in the membrane than the Pt<sub>3</sub>Co MEAs (5.6 nm and 8.7 nm) after 30,000 DOE protocol cycles.

TEM analyses of the Pt MEAs after 30,000 DOE protocol cycles showed that the extent of growth in the mean particle size and size distribution depend on position in electrode, that dendrites were formed, indicative of the dissolution/re-precipitation mechanism of particle growth, and that coalesced particle shapes were formed. The quantification of the extent of each of the two particle growth mechanisms (dissolution/re-precipitation and coalescence) is underway. The three smallest particle sizes (1.9, 3.2, and 7.1 nm) evolve to approximately the same average particle size (9.5 nm) after extended potential cycling. The largest particle size (12.7 nm) showed no loss of ECA, but did show particle growth in the region of the electrode closest to the membrane due to formation of a few very large particles.

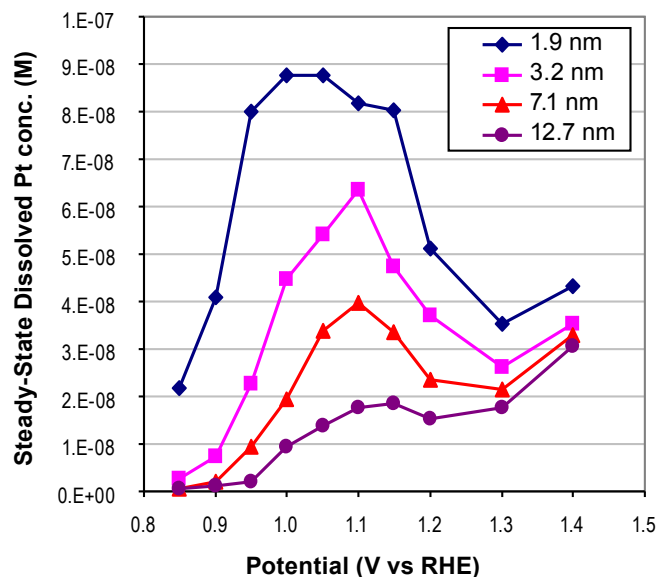
The ex situ characterization task also included a study of the 3.2 nm Pt/C in an aqueous electrochemical environment (0.1 M HClO<sub>4</sub> electrolyte) using anomalous small-angle X-ray scattering (ASAXS). This catalyst was subjected to 900 cycles of two potential cycling protocols: the DOE protocol and 0.4 to 1.05 V square waves (0.4 to 1.05 V, 10 s each potential). The Pt subjected to the DOE cycling protocol only grew by 0.09 nm over 900 cycles, whereas the Pt subjected to the square wave cycling grew by 0.33 nm. Analyses of the change in the particle size distributions for these two sets of data (Figure 2) showed that the mechanism for growth of the mean particle size is similar for the two cycling protocols: loss of particles <3.2 nm and >5 nm, accompanied by an increase in the number of particles in the 3.2-5 nm range, differing only in extent for the two cycling protocols. The largest contributor to surface area loss is loss of particles in the 1.5-3.2 nm diameter range. The majority of the change occurred during the first 100 cycles. Analysis of the ASAXS intensities also shows that there is an overall loss of Pt from the electrodes, with the square wave showing higher loss rates.

In the fundamental out-of-cell studies task, the effect of potential and particle size on the steady-state dissolved concentration of Pt was determined for the Pt/C catalysts (1.9, 3.2, 7.1, and 12.7 nm). This was correlated with the extent of Pt oxide formation, as determined by cyclic voltammetry. These studies, illustrated in Figure 3, showed that the:

- Steady-state dissolved Pt concentration increases with decreasing mean particle size.
- Oxide coverage at constant potentials >0.9 V increases with decreasing particle size.
- Dissolved Pt concentration peaks at an oxide coverage of ~1 O/Pt, decreasing with increasing oxide coverage above a monolayer.



**FIGURE 2.** Change in the weight of Pt at all particle sizes in the particle size distribution as a result of DOE protocol cycling (0.6 to 1.0 V triangle cycles, 50 mV/s) or square wave cycling (0.4 to 1.05 V, 10 s each potential) in 0.1 M HClO<sub>4</sub> electrolyte. The initial mean particle size of the catalyst was 3.2 nm. Weight changes were derived from ASAXS-determined particle size distributions; spherical nanoparticles were assumed to calculate weights.



**FIGURE 3.** Steady-state dissolved Pt concentration in perchloric acid electrolyte as a function of potential for Pt/C of initial mean particle size of 1.9, 3.2, 7.1, and 12.7 nm.

In the theoretical modeling task of the project, a model was developed for Pt cyclic voltammetry and Pt dissolution under steady-state and cycling conditions. A non-ideal solid solution between PtO<sub>x</sub> and Pt was assumed where oxide decreases the effective surface activity of Pt. Under steady-state conditions, it was found that: (1) there is a balance

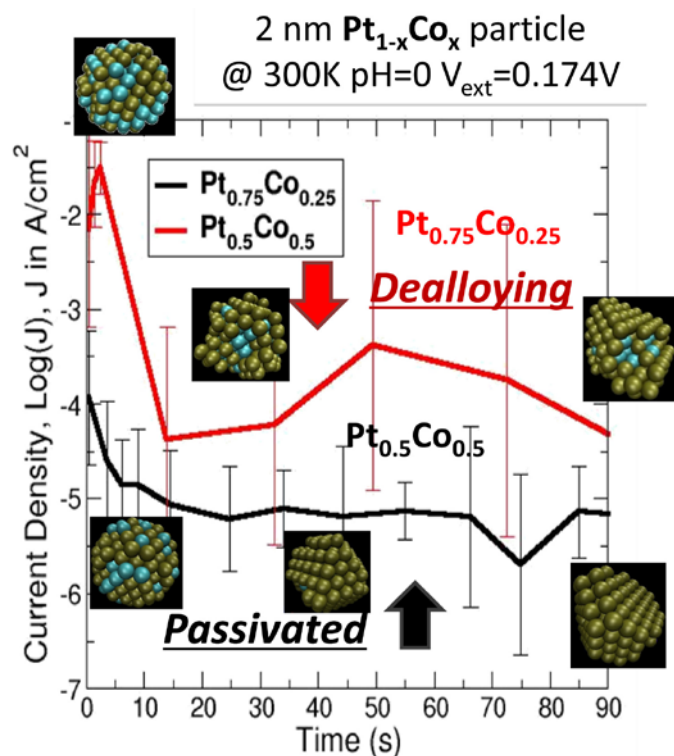
between Pt dissolution and protective oxide formation at >0.8 V, (2) the activity of Pt is strongly dependent on oxide coverage, which is strongly dependent on potential at >0.8 V, and (3) the potential dependence of the dissolved Pt concentration is lower than that expected for a two-electron electrochemical reaction due to non-unit activity of Pt caused by formation of oxide. Under cycling conditions, the kinetic constants for Pt dissolution were determined from potentiostatic concentration-time data at 0.9 V and 72-h equilibrium data for other potentials, the kinetic constants for re-deposition from potential cycling data. Conclusions from this work are: (1) at <0.9 V deposition is competitive with dissolution and (2) at >1 V, cycling accelerates Pt dissolution compared to potentiostatic conditions due to incomplete protection of the oxide.

Also in the modeling aspect of the project, the KMC model developed last year for Pt was extended to include Pt alloys and was applied to the evolution of Pt<sub>3</sub>Co nanoparticles under fuel cell conditions. An effective bond-energy Hamiltonian was developed from density functional theory fits, which were then implemented in the KMC model of alloy nanoparticle dissolution. The KMC model predicts rapid Pt<sub>1-x</sub>Co<sub>x</sub> nanoparticle de-alloying at 0.25 < x < 0.5, which suggests that the concentration limit for retaining some Co in the nanoparticle is less than the 0.55 observed for bulk structures (Figure 4).

## Conclusions and Future Directions

The following conclusions can be made from our studies of the degradation of Pt<sub>3</sub>Co and Pt/C electrocatalysts:

- Initial fuel cell performance increases with decreasing cathode electrocatalyst mean Pt and Pt<sub>3</sub>Co particle size, however degradation of performance with potential cycling increases with decreasing particle size.
- Potential cycling (0.6 to 1.0 V; 50 mV/s) causes Pt catalysts of ≤ 7 nm initial mean diameter to evolve to mean particle sizes and specific surface areas of 9.5 nm.
- Performance degradation with potential cycling can be attributed to increased rates and extent of ECA loss with decreasing Pt and Pt<sub>3</sub>Co particle size, with ECA loss rates being the same for Pt and Pt<sub>3</sub>Co. Despite better ORR mass activity stability than Pt, the Pt<sub>3</sub>Co MEAs showed approximately the same performance loss with cycling due to decreased cathode proton conductivity (possibly due to Co<sup>2+</sup> poisoning of proton-conducting sites in electrode).
- Extent of Pt and Pt<sub>3</sub>Co nanoparticle cathode electrocatalyst performance loss, caused by loss of ECA, increases with increasing cell temperature, increasing relative humidity, and increasing upper limit of potential cycling; preliminary analyses indicate a correlation of performance loss with extent of Pt dissolution and loss of Pt from the cathode.



**FIGURE 4.** Corrosion current density as a function of time for 2 nm  $Pt_{0.75}Co_{0.25}$  and  $Pt_{0.5}Co_{0.5}$  particles, as derived from Kinetic Monte Carlo calculations. This plot illustrates that  $Pt_{0.75}Co_{0.25}$  reaches a stable state, retaining Co in the core, whereas the  $Pt_{0.5}Co_{0.5}$  nanoparticle does not passivate before losing all of its Co.

The immediate future direction of the experimental portion of the project is to complete characterization of the  $Pt_3Co$  catalysts and cycled MEAs, including acquiring additional data needed for the nanoparticle 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 cell fabrication and cycling of MEAs containing  $Pt_3Sc/C$ ,  $PtCo/C$  and  $PtCo_3/C$  cathode catalysts.

#### Near-Term Future Directions

- Characterize Pt dissolution as a function of particle size for  $Pt_3Co$ .
- Characterize evolution of  $Pt_3Co$  particle size during potential cycling in an MEA using anomalous small-angle X-ray scattering.
- Evaluate the impact of Pt:Co ratio, catalyst leaching, alloying with Sc, alternative carbon support, and impurity doping on degradation.
- Quantify ECA loss due to particle coalescence and Pt dissolution/re-deposition processes by modeling TEM images.
- Complete cyclic voltammetry and dissolution models.

#### FY 2011 Publications/Presentations

1. “Behavior of Pt and  $Pt_3Co$  Nanoparticles in PEM Fuel Cells Observed by High-Resolution TEM, Aberration-Corrected STEM and In-situ TEM”, Conference, 17<sup>th</sup> International Microscopy Congress, Rio de Janeiro, Brazil, September 2010. [Invited]
2. “Atomic Structure and Defect Behavior of Nanoparticles through Aberration-Corrected STEM, High-Resolution TEM and In-situ TEM, Materials Science and Engineering Program”, Texas A&M University, College Station, TX, October 2010. [Invited]
3. “Influence of Pt catalyst nanoparticle size on the electrochemical performance of PEM fuel cells”, S. Rajasekhara, D.J. Groom, S. Matyas, M. Gummalla, S. Ball, P.J. Ferreira, MRS Spring Meeting, San Francisco, California, April, 2011.
4. “New Understanding of Pt Surface Area Loss in PEMFCs”, D. Morgan, E. Holby, and L. Wang, 216th ECS Meeting, Las Vegas, NV, USA Oct. 10-15 (2010). [Invited]
5. “New Approaches to Modeling Fuel Cells: Catalytic Activity and Stability in PEMFC and SOFC”, D. Morgan, Drexel University, PA, USA, Nov. 10, 2010. [Invited]
6. “New Approaches to Modeling Fuel Cells: Catalytic Activity and Stability in PEMFC and SOFC”, D. Morgan, Columbia University, New York, NY, 2010. [Invited]