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

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## Fiscal Year (FY) 2012 Objectives

- Quantify and understand the role of Pt-Co alloy composition and acid leaching of these alloys in the degradation of polymer electrolyte membrane fuel cell (PEMFC) performance,
- Establish dominant catalyst and cathode degradation mechanisms for Pt, Pt-Co alloys, and $Pt_3Sc$,
- 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

The Argonne-led team 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 (≤80ºC) and 5,000 hours (>80ºC)
- ≤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/cm² after 30,000 cycles between 0.6 and 1.0 V

## FY 2012 Accomplishments

- Prepared Pt/alternative carbons, Pt/C with different levels of Cl impurities. Fabricated and tested membrane electrode assemblies (MEAs) of $Pt_xCo_{(1-x)}$, acid-leached $Pt_xCo_{(1-x)}$, $Pt_3Sc$, and various Pt/C.
- Established relationship between loss of electrochemically-active surface area (ECA), mass activity, and particle size for Pt and Pt alloys.
- Determined that the operating parameters of upper potential limit and anodic sweep rate have the most significant impact on cell degradation.
- Established most significant factors governing cycling-induced changes in catalyst particle size distribution (PSD) and ECA loss.

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## 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, especially the Pt-based cathode catalyst. The project's primary focus is elucidation of the effects of cathode catalyst and support physicochemical properties and cell operating conditions on the rates and mechanisms of cathode catalyst degradation. 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 identify the degradation modes and factors contributing to cathode catalyst degradation by utilizing: (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 atomistic and macroscopic kinetic and transport modeling. The catalysts studied are benchmark Pt on carbon supports with varying properties, Pt alloys, acid-leached Pt alloys, and 3M's Pt-based nano-structured thin film catalysts. In the experimental aspects of the project, we utilize accelerated stress tests of membrane-electrode assemblies (MEAs) containing various catalysts and supports and in situ and ex situ dissolution, microscopic, structural, and chemical characterization of these catalysts, which are input into the catalyst and cell models. These measurements provide complementary information and, in the case of the aqueous studies, information such as catalyst component dissolution rates, that are not accessible in the MEA environment.

The goal of the project is to elucidate the effects of catalyst physicochemical properties on catalyst and cell performance degradation by systematically varying these properties (particle size, catalyst oxophilicity, catalyst type, surface area of carbon support, and effect of catalyst impurity). The effects of the various properties are decoupled by either controlling or carefully determining the catalyst particle size and particle size distributions.

## Results

The focus of this year's effort has been on determining the effects of potential profile on Pt catalysts, compositional studies of Pt-Co alloy catalysts, cell studies of $Pt_3Sc$, effects of acid leaching and dissolution studies of Pt-Co alloys, dissolution studies of 3M's Pt NSTF catalyst, Kinetic Monte Carlo-based modeling of Pt-Co alloys, and modeling of PSD and ECA evolution.

Four cycling profiles sweeping between 0.6 and 1.0 V with 16 s periods were applied to MEAs containing a 3.2 nm mean diameter Pt catalyst. These profiles, illustrated in Figure 1, were square wave (SW), triangle wave (TW), 25 mV/s anodic sweep and a cathodic step to 0.6 V denoted slow/fast (SF), and a step to 1.0 V and a 25 mV/s sweep back to 0.6 V denoted fast/slow (FS). After 10,000 cycles, these four MEAs were cross-sectioned and analyzed for Pt content in the membrane using scanning electron microscopy (SEM) and electron microprobe analysis. The trends of performance loss on air, ECA loss, oxygen reduction reaction (ORR) mass activity (MA) loss, and amount of Pt in the membrane were found to be SW≅FS>>TW≅SF. The anodic sweep rate had the most impact on the rates of performance, ECA, and MA loss and on the amount of Pt found in the membrane (Figure 1).

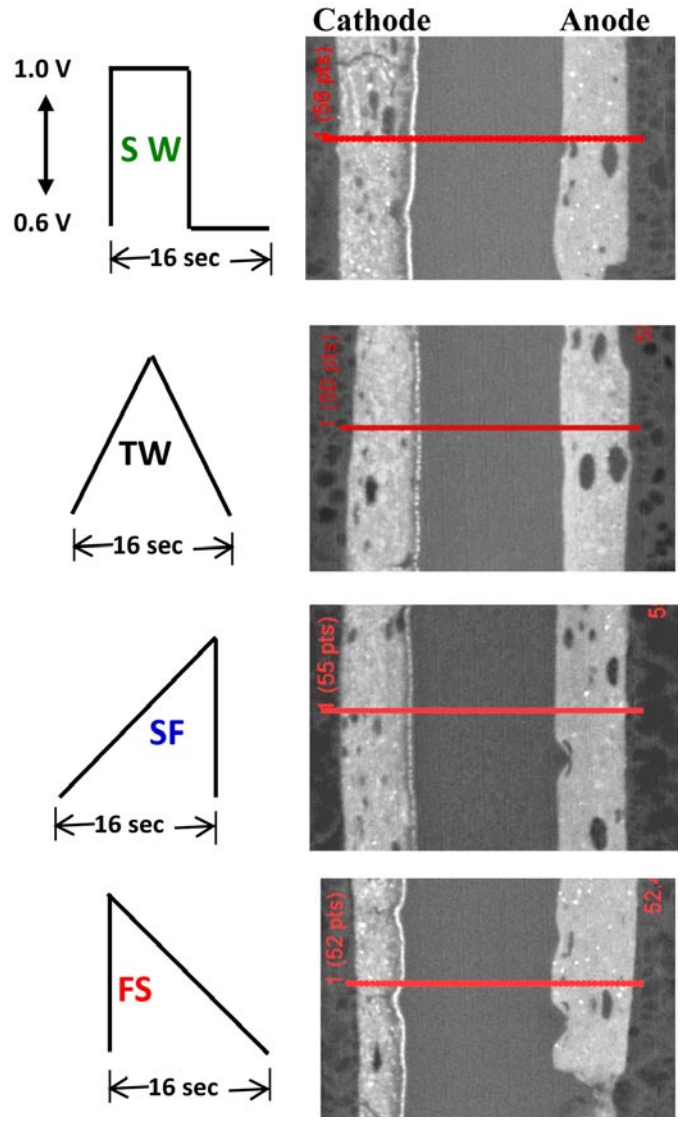


**FIGURE 1.** Potential profiles applied to MEAs containing the 3.2 nm mean diameter Pt cathode catalyst and SEMs of cross-sections of the MEAs after application of 10,000 of the respective cycles. These images show that the amount of Pt in the membrane (bright vertical band near the cathode) is highest for the SW and FS profiles.

Catalysts were prepared containing 40 wt% $Pt_3Co$ nanoparticles with a mean diameter of 5.6 nm and 35 wt% PtCo with a mean diameter of 4.1 nm on high-surface-area Ketjen black carbon support ($Pt_3Co$/C and PtCo/C). These materials were acid treated by soaking in 80°C 0.5 M $H_2SO_4$ for two days. The resulting catalysts are designated AL $Pt_3Co$ and AL PtCo and were found to have Pt:Co atomic ratios of 80:20 and 71:29, respectively. These catalysts were incorporated into the cathodes of MEAs and subjected to the DOE cycling protocol (0.6 to 1.0 V, 50 mV/s). Following fabrication, an MEA containing the non-acid-leached $Pt_3Co$ was also acid-treated (AT $Pt_3Co$) for comparison with both the as-prepared $Pt_3Co$ MEA and the MEA prepared from AL $Pt_3Co$. Cell diagnostics of cathode catalyst ECA, ORR MA, and air and oxygen polarization curves were performed after 1,000, 3,000, 5,000, 10,000, and 30,000 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 AL $Pt_3Co$ and AL PtCo and an AT $Pt_3Co$ MEA.

The initial low current density oxygen and high current density air performances of MEAs containing all the catalysts studied in this project are summarized in Figure 2. Specific to the studies performed this year, this figure shows that: (1) AL PtCo has lower initial ORR activity than AL $Pt_3Co$, but comparable initial performance on air at high current densities, (2) catalyst leaching and MEA acid treatment decrease the ORR activity of the $Pt_3Co$ catalyst, resulting in ~10 mV lower MEA $O_2$ performance (at 0.8 A/cm$^2$), and (3) acid leaching of $Pt_3Co$ and acid treatment of the $Pt_3Co$ MEA increases the $H_2$/Air performance at high currents (~25-30 mV at 1.5 A/cm$^2$) due to a decrease in the resistance to proton transport in the cathode. Figure 2 also summarizes the effect of potential cycling using the DOE protocol. It was found that ECA, MA, ORR specific activity (SA, activity per square centimeter of ECA), and $O_2$ performance decay trends are the same for $Pt_3Co$, AL $Pt_3Co$, and AT $Pt_3Co$. Acid-leached PtCo shows the highest loss of both ORR activity and air performance. Parametric studies on these catalysts showed that $Pt_3Co$, as compared to AT $Pt_3Co$ and AL $Pt_3Co$, has a greater decay in high current density performance when subjected to 0.4 V to 0.95 V SW cycling. This was attributed to a higher increase in resistance to proton transport in the cathode. However, acid leaching of $Pt_3Co$ did not affect the decay trends of ECA, MA, SA, and performance with cycling. For all catalysts, cycling to 1.05 V, rather than 0.95 V, had the most detrimental impact on ORR activity and air performance of all cell operating conditions tested. Lower RH on the cathode (30% RH versus 100% RH) decreased this degradation.

A summary of the ECA and ORR MA losses of all the cathode catalysts studied in this project when subjected to 10,000 cycles of the DOE protocol (0.6 to 1.0 V, 50 mV/s triangle) in the MEA environment is shown in Figure 3. This plot shows that all catalysts fall along the same trendline of loss versus initial particle size, irrespective of the catalyst composition, indicating that this is the dominant factor controlling cycling-induced catalyst losses.

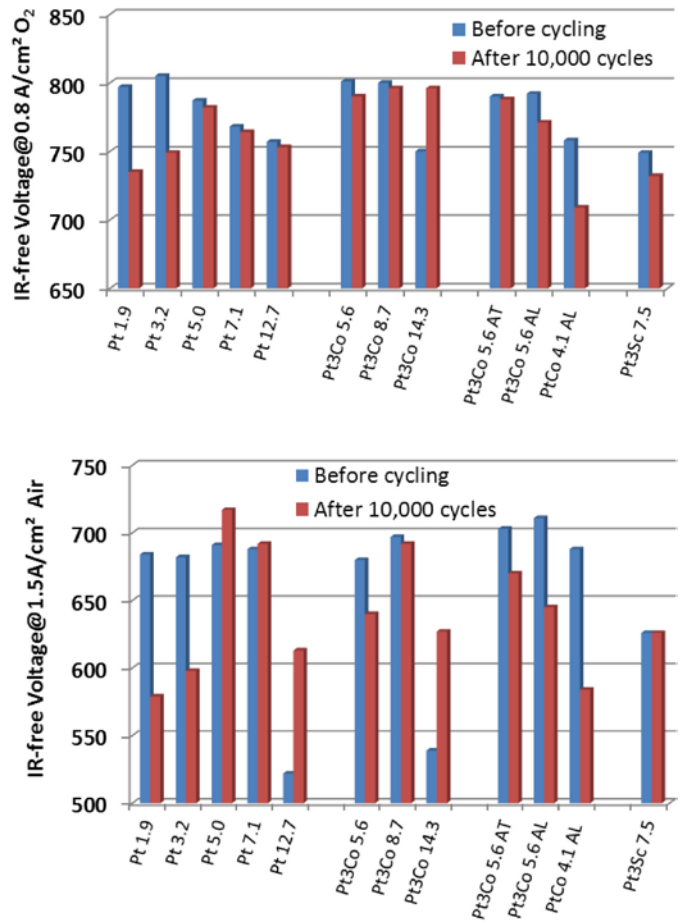


**FIGURE 2.** Initial and post-cycling low current density oxygen and high current density air performances of MEAs containing all the catalysts studied in this project. Cycling profile: 0.6 to 1.0 V, 50 mV/s triangle.

This year's effort in the ex situ characterization tasks included TEM and anomalous small-angle X-ray scattering (ASAXS) analyses of the $Pt_3Co$ MEAs after 30,000 DOE protocol cycles. These analyses, summarized in Figure 4, showed that cycling decreases the fraction of smaller particles in the PSDs and increases the fraction of larger particles, which increases the tailing of the PSDs toward larger particle sizes. The extent of growth in the mean particle size and the extent of changes in the PSDs increased with decreasing initial $Pt_3Co$ particle size, as was reported last year for the Pt catalysts.

The in situ characterization task included a study of the 3.2 nm Pt in an MEA using ASAXS. This catalyst was subjected to 1,500 square wave cycles between 0.4 to 1.05 V (20 s period). The ASAXS-derived Pt PSDs (Figure 5)

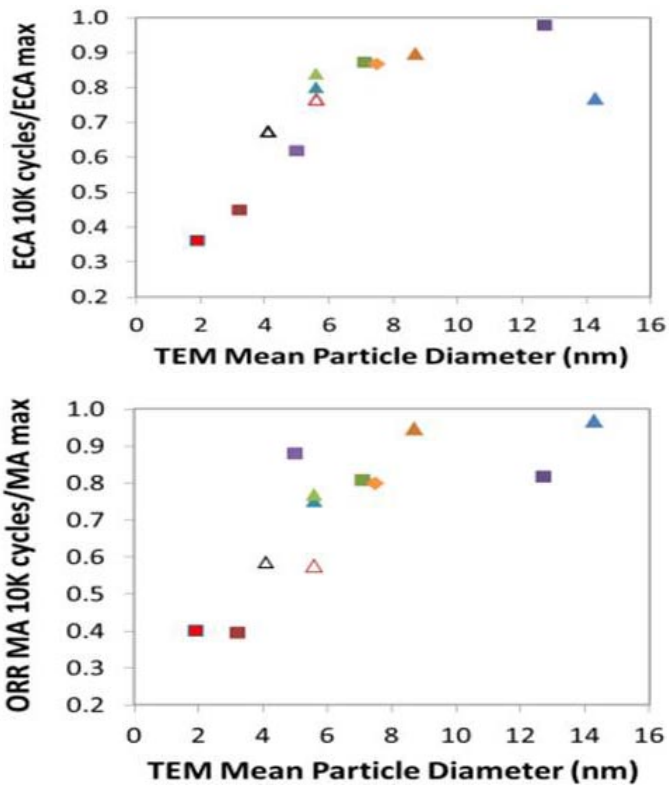


**FIGURE 3.** Fraction of ECA (top) and ORR MA (bottom) remaining after 10,000 DOE protocol cycles as a function of initial mean diameter of the catalysts. Squares: Pt, Triangles: $Pt_3Co$, Hollow triangles: Acid-leached $Pt_3Co$, Hollow black triangle: Acid-leached PtCo, Diamond: $Pt_3Sc$.

illustrate that the main impact of cycling on the PSD in the MEA environment is loss of particles <3.7 nm in diameter, with a minor contribution from an increase in the number of particles >3.7 nm. Comparison of ECA losses to the changes in geometric surface area calculated from the ASAXS data illustrate that the catalyst lost geometric surface area even while the ECA was increasing during the initial cycling (i.e., during the well-known MEA conditioning period).

In the fundamental out-of-cell studies task, the effect of potential and particle size on the steady-state dissolved concentration of Pt and Co in perchloric acid electrolyte was determined for the $Pt_3Co$ catalysts (5.6, 8.7, and 14.3 nm). These studies, illustrated in Figure 6, showed that: (1) the steady-state dissolved Pt concentration increases with decreasing mean particle size, as was observed for Pt catalysts, (2) the loss of cobalt from catalyst is potential independent at potentials >0.85 V and <~1.0 V corresponding with the potential region with decreased platinum dissolution, (3) the fraction of total cobalt leached from catalyst decreases with increasing particle size corresponding with decreased fraction of total cobalt on the surface and in the sub-surface layer of the particle, and (4) the largest loss of cobalt is observed during electrode preparation and wet-up.

In the theoretical task of the project, the model for Pt cyclic voltammetry and Pt dissolution under steady-state and cycling conditions was further refined using additional Pt dissolution data and oxide coverage as a function of Pt particle size. The model assumes formation of a non-ideal solid solution between Pt and Pt oxide and that this oxide decreases the surface activity of Pt and thus the concentration of dissolved Pt. The kinetics for oxide formation were determined using cyclic voltammetry experiments and were utilized to model the effects of potential cycling rates, upper potential limits, and lower potential limits on the loss of Pt due to dissolution and on Pt re-deposition. The resulting model was utilized to calculate the evolution of the PSD and ECA with number of DOE protocol potential cycles (shown in Figure 7 for the 3.2 nm Pt catalyst). It was determined that the experimental ECA losses cannot be explained solely on the basis of Pt dissolution or change in PSD due to preferential dissolution of smaller particles and re-deposition on larger particles. It was necessary to include particle coalescence due to Pt re-deposition between particles and not particle migration to accurately model the ECA loss data.

In the atomistic modeling tasks of the project, a Kinetic Monte Carlo model was further developed to determine the effect of initial alloy composition, particle size, and potential on the extent of Pt and base metal loss from the particles and the effect on particle size and shape. The Kinetic Monte Carlo model predicts rapid de-alloying of $Pt_{1-x}Co_x$ nanoparticles at x>0.35 and that the maximum retention of Co in the particles, and thus maximum retention of ORR activity, is achieved with initial Co concentrations near this value.

## Conclusions and Future Directions

The major conclusions from this work are:

- The predominant catalyst physicochemical property in defining the extent of ECA and ORR activity loss of Pt and Pt alloy nanoparticle catalysts induced by potential cycling is the initial size of the catalyst particles.
- The operating parameters of upper potential limit and anodic sweep rate have the most significant impact on cathode performance degradation.
- Acid leaching of Pt-Co alloys decreases the initial ORR activity, but increases high current density fuel cell performance due to loss of Co and increase in proton conductivity in cathode, respectively.
- The best overall cathode catalyst performance and performance durability with cycling of all catalysts studied in this project was achieved for the $Pt_3Co$ catalyst with initial mean particle size of ~8.5 nm. This catalyst achieves the DOE cathode catalyst durability targets of ≤40% loss of initial catalytic mass activity and <30 mV loss at 0.8 A/cm² after 30,000 cycles between 0.6 and 1.0 V (24% and 14 mV, respectively).

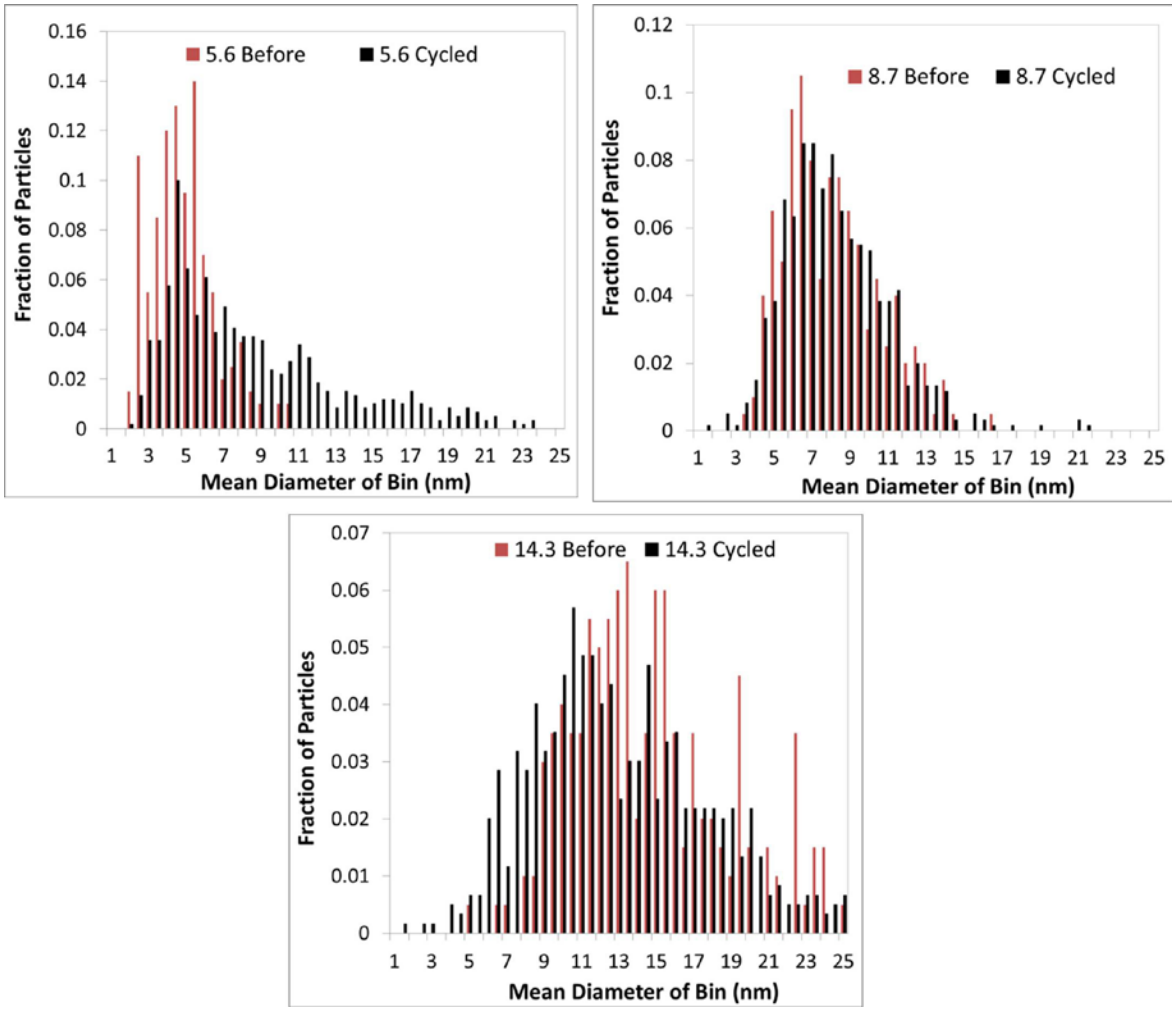


**FIGURE 4.** PSDs, determined using TEM characterization, of the three $Pt_3Co$ catalysts with initial mean diameters of 5.6, 8.7, and 14.3 nm before and after 30,000 DOE protocol cycles.

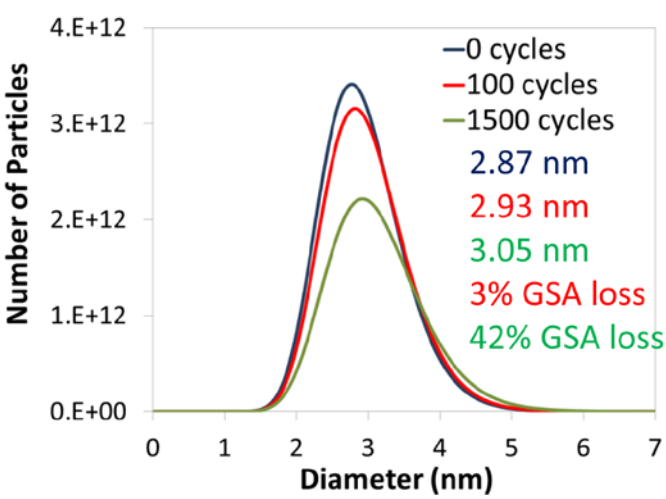


**FIGURE 5.** PSDs, determined using ASAXS, of a Pt catalyst with nominal initial mean diameter of 3.2 nm, during DOE protocol cycling in an MEA.

- The most significant factors governing cycling-induced change in PSD and ECA loss are competition between Pt dissolution and oxide formation and coalescence of particles via Pt re-deposition.
- Kinetic Monte Carlo modeling indicates that the maximum retention of Co in $Pt_{1-x}Co_x$ nanoparticles, and thus maximum retention of ORR activity upon exposure to the MEA environment, is achieved with initial Co concentrations (x) near 0.35.

Future plans for the remainder of this project are:

- Prepare, characterize, and test MEAs containing Pt-Ni catalysts; characterize and test MEAs containing Pt/alternative carbons and Pt/Ketjen carbon with $Cl^-$ impurities.
- Complete analysis of ASAXS and XAFS data for Pt and $Pt_3Co$ MEAs.

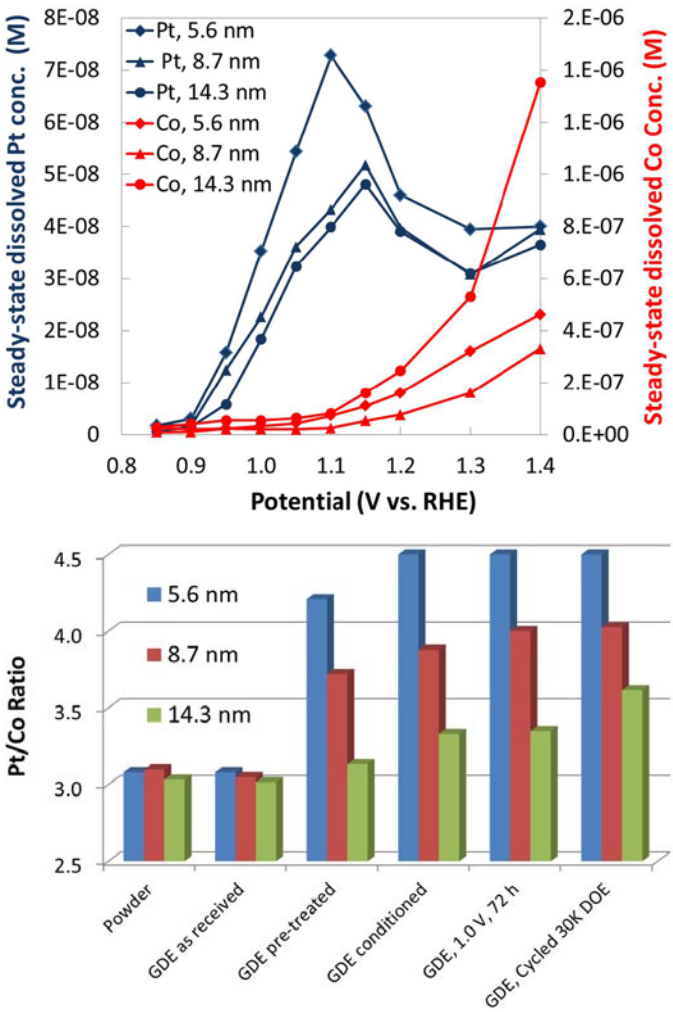


**FIGURE 6.** Potential dependence of the steady-state dissolved Pt and Co concentrations in perchloric acid electrolyte for the three $Pt_3Co$ catalysts. Evolution of the Pt to Co atomic ratio with electrode preparation stages. GDE pre-treated: soaking in room temperature water; Conditioning: potential cycling from 0.05 to 1.1 V, 15-20 cycles; 1.1 V, 72 h: held for 72 h in room temperature perchloric acid electrolyte.

- Study the effect of temperature on extent of oxide formation and on dissolution.

## FY 2012 Publications/Presentations

### Publications

**1.** Z. Yang, S. Ball, D. Condit, M. Gummalla, "Systematic Study on the Impact of Pt Particle Size and Operating Conditions on PEMFC Cathode Catalyst Durability", *J. Electrochem. Soc.,* 158 (11), B1439-B1445 (2011).

**2.** D.J. Groom, S. Rajasekhara, S. Matyas, Z. Yang , M. Gummalla, S. Ball, P.J. Ferreira, "Influence of Pt Catalyst Nanoparticle Size on the Electrochemical Performance of PEM Fuel Cells", *Electrochem. Soc. Trans.*, 41 (1) 933-936 (2011).

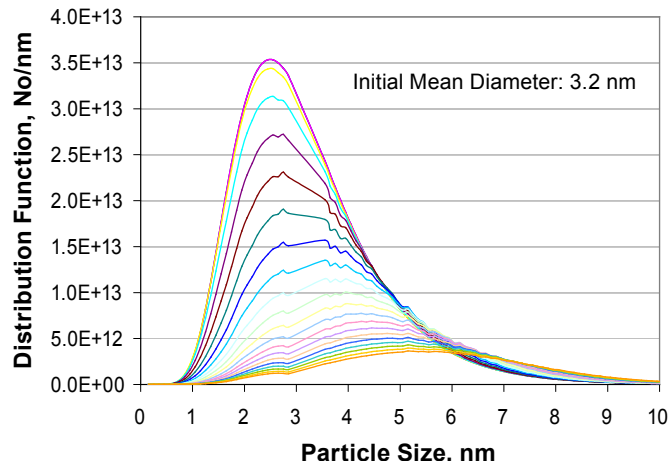


**FIGURE 7.** Modeled evolution of the PSD of 3.2 nm mean diameter Pt with DOE protocol cycling.

**3.** D. Myers, J. Gilbert, X. Wang, N. Kariuki, S. Niyogi, A.J. Kropf, D. Morgan, S. Ball, J. Sharman, B. Theobald, and G. Hards, "*In situ* X-ray absorption and scattering studies of PEFC cathode electrocatalysts", *Prep. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, 57 (1), 414-416, (2012).

**4.** J.A. Gilbert, N.N. Kariuki, R. Subbaraman, A.J. Kropf, M.C. Smith, E.F. Holby, D. Morgan, and D.J. Myers, "*In-situ* Anomalous Small Angle X-Ray Scattering Studies of Platinum Nanoparticle Fuel Cell Electrocatalyst Degradation", *J. Am. Chem. Soc.,* 134, 14823-14833 (2012).

**5.** B. Puchala, S.-K. Lin, L. Wang, D. Morgan, "PEMFC Nanoparticle Dealloying from Kinetic Monte Carlo Simulations", *Electrochem. Soc. Trans.*, accepted.

**6.** J. Gilbert, N. Kariuki, A.J. Kropf, D. Morgan, D. Myers, S. Ball, J. Sharman, B. Theobald, G. Hards, "In Situ Anomalous Small-Angle X-ray Scattering Study of Fuel Cell Catalyst Degradation in Aqueous and Membrane Electrode Assembly Environments", *Electrochem. Soc. Trans.*, accepted.

### Presentations

**1.** R. Subbaraman, X. Wang, X. Wang, N.Kariuki, D.Myers, and R.K. Ahluwalia, "Ex-situ Potentiostatic and Potentiodynamic Durability of Low Pt Loading fuel cell MEAs", 220th Electrochemical Society Meeting, Boston, MA, Oct. 9 -14, 2011.

**2.** D.J. Groom, S. Rajasekhara, S. Matyas, Z. Yang , M. Gummalla, S. Ball, P.J. Ferreira, "Influence of Pt Catalyst Nanoparticle Size on the Electrochemical Performance of PEM Fuel Cells", 220th Electrochemical Society Meeting, Boston, MA, Oct. 9–14, 2011.

**3.** E. Holby, S.-K. Lin, B. Puchala, L. Wang, D. Morgan, "Modeling Pt and Pt-alloy Degradation in PEMFC Cathodes", DOE Fuel Cell Technologies Program Durability Working Group Meeting", Boston, MA, Oct. 13, 2011. [Invited]

**4.** X. Wang, D. Myers, and N. Kariuki, "Investigation of PEFC Electrocatalyst Degradation", IEA-AFC Annex 22 Fall 2011 Workshop, Jülich, Germany, December 12–13, 2011.

**5.** D. Myers, J. Gilbert, X. Wang, N. Kariuki, S. Niyogi, A.J. Kropf, Dane Morgan, Sarah Ball, Jonathan Sharman, Brian Theobald, and Graham Hards, "In situ X-ray absorption and scattering studies of PEFC cathode electrocatalysts", 243rd American Chemical Society National Meeting and Exposition, San Diego, CA, March 25–29, 2012. [Invited]

**6.** D.J. Myers, J.A. Gilbert, N.N. Kariuki, X. Wang, A.J. Kropf, S. Niyogi, M.C. Smith, and D. Morgan, S.C. Ball, J. Sharman, B. Theobald, E. Christian, and G. Hards, "In Situ Anomalous Small Angle X-ray Scattering and X-ray Absorption Studies of Fuel Cell Catalysts", 221st Electrochemical Society Meeting, Seattle, WA, May 6–10, 2012. [Invited]

**7.** P.J. Ferreira, "Seeing Small: Enabling new discoveries in Li-ion batteries and Fuel Cells Through Advanced Transmission Electron Microscopy", G-COE Special Lecture, Kyushu University, Japan, June 12, 2012.

**8.** X. Wang, D. Myers, N. Kariuki, S. DeCrane, T. Nowicki, S. Arisetty, and R. Ahluwalia, "Polymer Electrolyte Fuel Cell Lifetime Limitations: The Role of Electrocatalyst Degradation", IEA-AFC Annex 22 Spring 2012 Workshop, Daejeon, Korea, June 21–22, 2012.

**9.** P.J Ferreira, "Seeing Small: Enabling new discoveries in Energy Materials Through Advanced Transmission Electron Microscopy", HVEM Seminar, Kyushu University, Japan, June 24, 2012.

**10.** D. Morgan, Y.-L. Lee, B. Puchala, L. Wang, and S.-K. Lin, "Atomistic-Based Approaches For Modeling Activity and Degradation in Fuel Cell Catalysts", 244th American Chemical Society National Meeting and Exposition, Philadelphia, PA, August 19–23, 2012. [Invited]

**11.** D. Morgan, B. Puchala, E. Holby, Y. Shao-Horn, L. Wang, S.-K. Lin, J. Gilbert, and D. Myers, "Computational Studies of Fuel Cell Electrocatalysts", Gordon Research Conference on Fuel Cells, Smithfield, RI, August 5–10, 2012. [Invited]

**12.** D. Morgan, B. Puchala, E. Holby, Y. Shao-Horn, L. Wang, S.-K. Lin, J. Gilbert, and D. Myers, "Evolution of Pt and Pt-Alloy Nanoparticles under PEMFC Conditions: Insights from Modeling", Energy Materials Center at Cornell Annual Energy Materials Symposium, Ithaca, NY, USA, August 10, 2012. [Invited]