

## V.B.2 FC-PAD Fuel Cell – Performance and Durability Electrocatalysts and Supports

Debbie Myers<sup>1</sup> (Primary Contact), Nancy Kariuki,<sup>2</sup>  
Xiaoping Wang,<sup>2</sup> Dennis Papadias,<sup>2</sup>  
Rajesh Ahluwalia,<sup>2</sup> Shyam Kocha,<sup>3</sup> KC Neyerlin,<sup>3</sup>  
Jason Christ,<sup>3</sup> Jason Zack,<sup>3</sup> Rangachary Mukundan,<sup>4</sup>  
Rod Borup,<sup>4</sup> Yu Seung Kim,<sup>4</sup> Karren More,<sup>5</sup> and  
David Cullen<sup>5</sup>

<sup>1</sup>Argonne National Laboratory  
9700 S. Cass Avenue  
Lemont, IL 60439  
Phone: (630) 252-4261  
Email: dmyers@anl.gov

### Subcontractors:

<sup>2</sup> Argonne National Laboratory, Argonne, IL  
<sup>3</sup> National Renewable Energy Laboratory, Golden, CO  
<sup>4</sup> Los Alamos National Laboratory, Los Alamos, NM  
<sup>5</sup> Oak Ridge National Laboratory, Oak Ridge, TN

### DOE Managers:

Dimitrios Papageorgopoulos  
Phone: (202) 586-5463  
Email: Dimitrios.Papageorgopoulos@ee.doe.gov

Greg Kleen  
Phone: (240) 562-1672  
Email: Gregory.Kleen@ee.doe.gov

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- Impact of catalyst degradation on the properties defining the performance of the cathode catalyst layer (e.g., oxygen and water transport)

### Fiscal Year (FY) 2016 Objectives

The technical objectives for FC-PAD are covered by the individual thrust areas, and are found in the separate annual reports for those thrust areas.

- Quantify, by ex situ measurements, the steady state concentration and dissolution rates of dissolved Pt and base metal from state-of-the-art Pt alloy catalysts.
- Measure the impact of transition metal dissolution on oxygen permeability of ionomer.
- Determine the effects of carbon type (e.g., high, medium, and low surface area) on catalyst durability and degradation mechanisms.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (A) Durability
- (B) Cost
- (C) Performance

Specifically, this FC-PAD thrust area addresses the following issues related to Technical Barriers A, B, and C:

- Lack of high performance at high current densities for cathodes utilizing low loadings of advanced Pt-based cathode electrocatalysts which have oxygen reduction reaction (ORR) mass activities exceeding the DOE target ( $>0.44$  A/mg-Pt).
- Loss of electrochemically active surface area (ECA) and oxygen reduction reaction activity of the cathode electrocatalyst during fuel cell operation.
- Degradation in fuel cell performance due to instability of Pt and alloying components.

### Technical Targets

This project develops membrane electrode assemblies that meet the following DOE membrane electrode assembly targets (Table 1).

### Overall Objectives

- Achieve durable and high performance at both low and high current densities for membrane electrode assemblies based on low precious group metal cathode catalysts/supports with the following targets:
  - Loading: 0.125 mg Pt/cm<sup>2</sup> (cathode + anode)
  - Performance at 0.8 V: 300 mA/cm<sup>2</sup>
  - Performance at rated power: 1,000 mW/cm<sup>2</sup>
  - Durability: 5,000 hours by 2020, 8,000 hours ultimate
- Develop the knowledge base for more durable and high-performance cathode catalysts and supports, by studying:
  - Catalyst and catalyst support durability and degradation mechanisms
  - Catalyst/support interactions

**TABLE 1.** Technical Targets: Membrane Electrode Assemblies for Transportation Applications

Characteristic	Units	2020 Targets
Cost	\$/kW <sub>net</sub>	14
Durability with cycling	Hours	5,000
Start-up/shutdown durability	Cycles	5,000
Performance @ 0.8 V	mA/cm <sup>2</sup>	300
Performance @ rated power (150 kPa <sub>abs</sub> )	mW/cm <sup>2</sup>	1,000
Robustness (cold operation)		0.7
Robustness (hot operation)		0.7
Robustness (cold transient)		0.7

## FY 2016 Accomplishments

- Determined potential and potential cycling dependence of Pt and Co dissolution from several Pt<sub>3</sub>Co alloys and Pt oxide formation kinetics and thermodynamics and developed a model based on these data for the thermodynamics and kinetics of Pt and Co loss from catalyst particles.
- Initiated solid-state cell measurements of oxygen permeability in ionomer thin films.
- Developed a model for the corrosion of the cathode catalyst carbon support during drive cycles.



## INTRODUCTION

The FC-PAD consortium's mission is to advance the performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) at a pre-competitive level to further enable their commercialization. The performance of the cathode electrocatalyst, primarily at high current densities, and the durability of the electrocatalyst and support under load cycling and start-stop conditions are major challenges to the widespread and cost competitive commercialization of PEMFC systems. Current research is focused on achieving high performance and durability in low Pt-loaded PEMFCs utilizing advanced Pt alloy catalysts.

## APPROACH

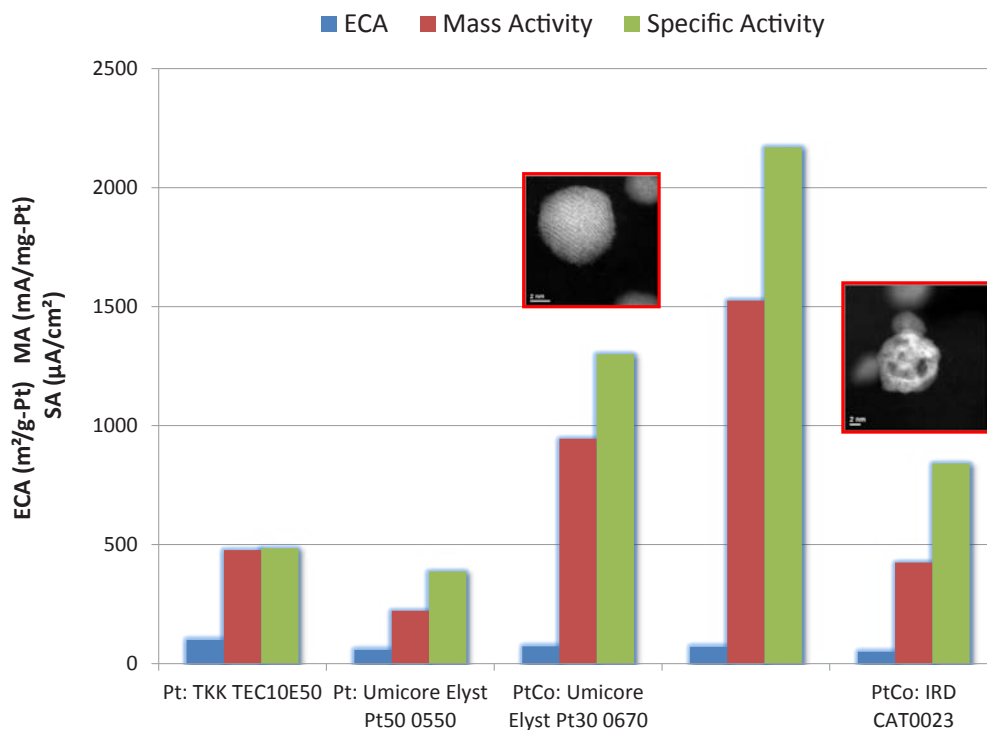
The Electrocatalyst and Support thrust area's approach is to provide foundational understanding of cathode electrocatalyst activity, performance, and durability by studying the following: (1) catalyst and catalyst support durability and degradation mechanisms, (2) catalyst/support interactions, and (3) the effects of catalyst instability on cathode-catalyst-layer properties. More specifically, the first area focuses on elucidating the degradation mechanisms of

the catalyst and support as a function of catalyst/support physicochemical properties, and defining the impact of cell operating conditions and catalyst/support types on degradation rates and mechanisms utilizing ex situ and operando measurements. The second area focuses on understanding the interplay between the catalyst and support properties and their mutual interactions, determining the effects of carbon type (e.g., high, medium, and low surface area) and carbon dopants on the strength of the catalyst/support and ionomer/support interactions, and investigating the impact of these interactions on catalyst and support stability, durability, and performance. The third area focuses on quantifying the impact of catalyst degradation on the properties defining the performance of the cathode catalyst layer (e.g., impact of base metal leaching from Pt alloy catalyst on proton conductivity, oxygen permeability, and water uptake in ionomer). These three areas, especially areas (1) and (2), rely extensively on the capabilities of the cross-cutting thrust areas of FC-PAD.

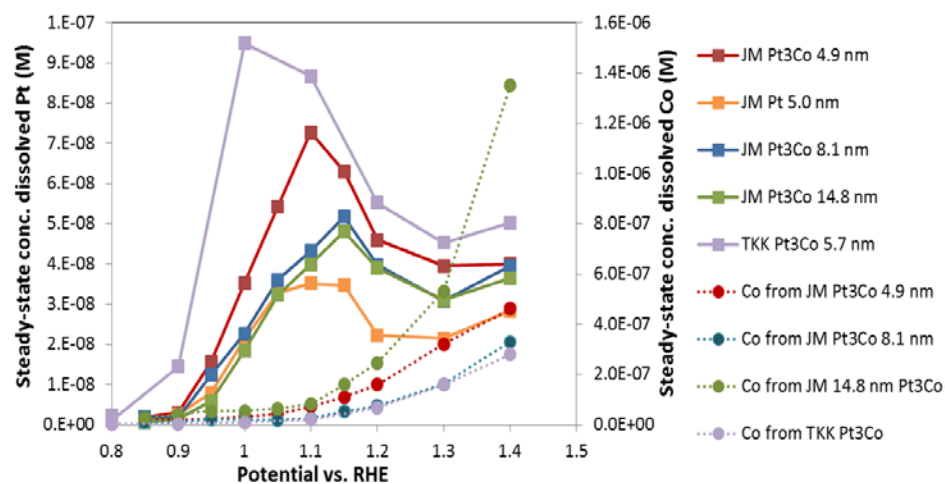
## RESULTS

Several state-of-the-art Pt alloy electrocatalysts were acquired from commercial sources for use by FC-PAD: 30.5 wt% 4.4 nm Pt<sub>7</sub>Ni<sub>3</sub>/C (Umicore); 55 wt% 6.0 nm PtCo/C (IRD); 46.5 wt% 5.7 nm Pt<sub>3</sub>Co/C (Tanaka Kikinzoku Kogyo [TKK]); and 4.9 nm, 8.7 nm, and 14.3 nm 40 wt% Pt<sub>3</sub>Co/C (Johnson Matthey). For comparison, two Pt/C catalysts were also acquired: 46 wt% 5.5 nm Pt/C (Umicore) and 47.5 wt% 2.5 nm Pt/C (TKK). The morphology of all the catalysts could be classified as "solid," with the exception of the IRD PtCo catalyst which had a "spongy" morphology (Figure 1). The ORR activity of these catalysts was screened using the thin-film rotating disk electrode (RDE) technique. The RDE-determined specific surface areas and ORR mass and specific activities of a selection of these catalysts are shown in Figure 1 along with representative transmission electron microscopy images for the alloy catalysts. All but one set of these data were taken utilizing perfluorosulfonic acid (PFSA) binder. The alloys were found to have higher ORR activities than the Umicore Pt/C baseline catalyst and to meet or exceed the DOE 2020 mass activity target of 0.44 A/mg-Pt. These data also illustrate the detrimental impact of PFSA ionomer on ORR activity; the ORR activity was suppressed by 40% in the presence of PFSA for the Umicore Pt<sub>7</sub>Ni<sub>3</sub>/C catalyst.

The Pt and Co dissolution behavior of the TKK Pt<sub>3</sub>Co/C was determined as a function of potential, potential cycling, time, and number of cycles, utilizing an aqueous electrochemical cell and inductively-coupled plasma-mass spectrometry detection of dissolved Pt and Co concentrations, to determine the thermodynamics and kinetics of metal dissolution. The oxide formation kinetics and thermodynamics were also determined as a function of potential. These data and previously acquired data for the three Johnson Matthey Pt<sub>3</sub>Co/C catalysts, shown in Figure 2,



**FIGURE 1.** The RDE-determined specific surface areas and ORR mass and specific activities of a selection of catalysts being studied by FC-PAD and representative transmission electron microscopy images for the alloy catalysts. All except one set of these data, as indicated, were taken utilizing PFSA binder for the RDE catalyst thin film.



RHE – Reference hydrogen electrode; JM – Johnson Matthey

**FIGURE 2.** Dissolved concentrations of Pt and Co in room-temperature perchloric acid electrolyte after holding the potential on the catalysts indicated for 72 hr

were utilized to develop a model for the thermodynamics and kinetics of Pt and Co loss from catalyst particles. The rate constants for Pt dissolution were derived from the potentiostatic dissolution data as a function of time and were used to interpret the behavior observed in the potential cycling tests. Findings from the modeling of the dissolution

data, correlation with the oxide formation and reduction kinetics, and comparison with similar studies of Pt catalysts are as follows.

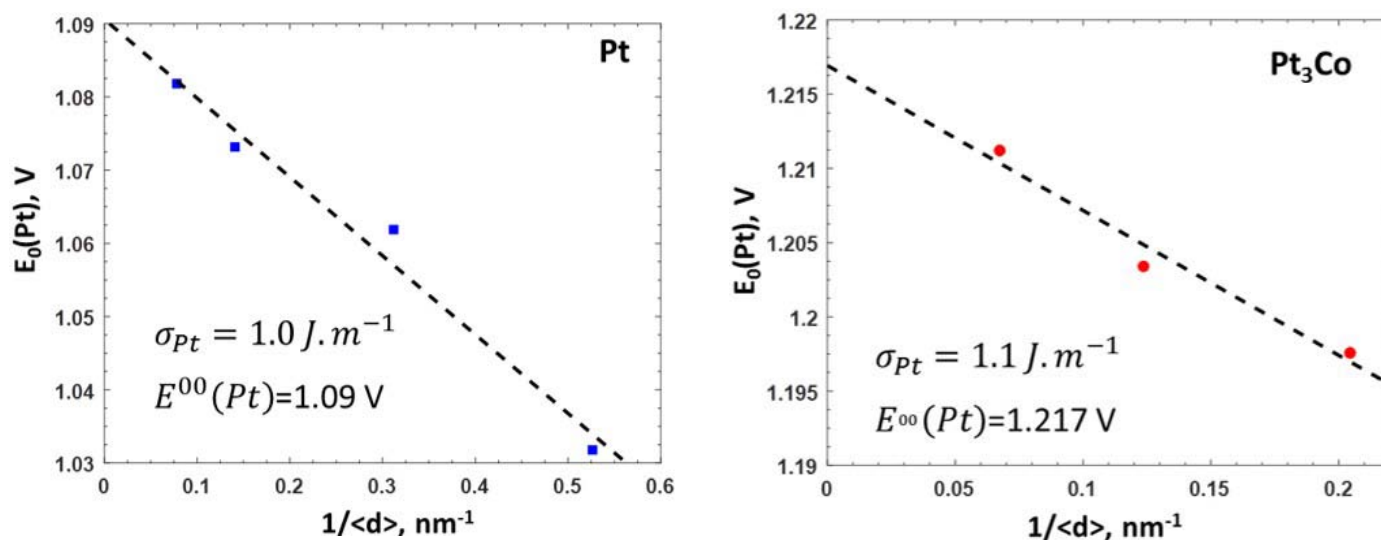
- The standard potential ( $E^0$ ) for Pt dissolution from  $Pt_3Co$  is higher than that from Pt which results in the Pt in

Pt<sub>3</sub>Co being more stable at potentials <~1.0 V, but less stable at higher potentials due to higher extents of Pt oxide formation in the alloys (Figure 3).

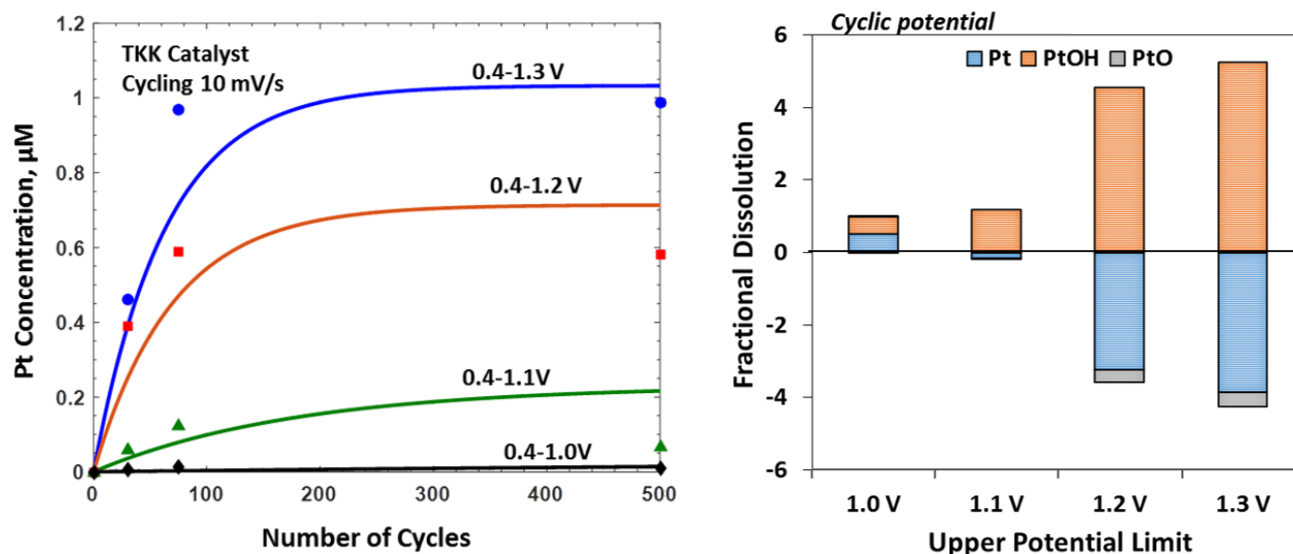
- Under potential cycling conditions and with upper potential limits <1.1 V, Pt dissolves as Pt and PtOH and there is no significant re-deposition during the cathodic sweep of the potential cycle.
- Under potential cycling conditions and with upper potential limits >1.1 V, Pt dissolves as PtOH and Pt<sup>2+</sup> re-deposits as Pt during the cathodic sweep (Figure 4).

- Surface Co is thermodynamically unstable ( $E^0 = 0.28$  V) and dissolves during pre-treatment to create a core-shell structure. Subsurface Co (SS-Co) is thermodynamically stable with a dissolution potential ( $E^0$ ) of 1.158 V which increase with increasing Pt skin thickness.

Experiments were initiated to determine the impact of transition metal dissolution on the oxygen permeability using a solid state Pt microelectrode electrochemical cell. These initial measurements, taken at room temperature and at 100% relative humidity, showed a substantial decrease in



**FIGURE 3.** Standard potential ( $E^0$ ) for Pt dissolution ( $\text{Pt} = \text{Pt}^{2+} + 2\text{e}^-$ ) from Pt<sub>3</sub>Co alloy and Pt nanoparticles and its dependence on particle diameter. Derived from Pt potentiostatic dissolution data at 0.85 V.



**FIGURE 4.** Dissolved Pt concentrations as a function of number of triangle potential cycles from 0.4 V to the potentials indicated at a scan rate of 10 mV/s for the TKK Pt<sub>3</sub>Co catalyst. Identity of species dissolved as a fraction of the total Pt dissolved. Negative fractions indicate re-deposition.

both oxygen permeability (15%) and ORR kinetics with  $\text{Ni}^{2+}$  doping of an ionomer film over the Pt microelectrode. These results qualitatively agree with previous RDE measurements of oxygen permeability through an ionomer thin film [1].

A model for carbon corrosion was developed based on a series of in-cell  $\text{CO}_2$  evolution measurements during voltage cycling using cells with TTK Pt catalysts cathode catalysts supported on either high surface area Ketjen carbon (E), graphitized low surface area carbon (EA), and intermediate surface area Vulcan (V) [2]. The experimental data were modeled using four potential-dependent processes: (1) formation of active ( $\text{C}^{\#}\text{OH}$ ) and passive ( $\text{C}^{\#}\text{O}_x$ ) carbon surface oxide species, (2) formation of OH and oxide surface species on Pt, (3) oxidation of active carbon surface species ( $\text{C}^{\#}\text{OH}$ ) with OH spill-over from Pt at intermediate potentials, and (4) oxidation of active carbon surface species ( $\text{C}^{\#}\text{OH}$ ) with  $\text{H}_2\text{O}$  at high potentials. The modeling effort showed that the extents of corrosion are linked to formation of carbon oxides and interaction of these oxides with Pt hydroxide and oxide and water. The corrosion mechanism during drive cycles and the corrosion rates for the three carbon types can be summarized as follows.

- Formation of surface oxides on carbon defect sites ( $\text{C}^{\#}$ )
  - Defect sites hydrolyze to form active oxides ( $\text{C}^{\#}\text{OH}$ ) at cathode potentials  $>0.3$  V.
  - $\text{C}^{\#}\text{OH}$  converts to passive oxides ( $\text{C}^{\#}\text{O}_x$ ) at  $E > 0.8$  V.
- Carbon corrosion is catalyzed by PtOH
  - PtOH begins to form at  $E > 0.6$  V.
  - PtOH converts to PtO at  $E > 0.9$  V.
- Steady-state corrosion mechanism
  - Corrosion rate peaks at  $\sim 0.6$  V cathode potential, small at 0.95 V.
  - Corrosion is primarily due to oxidation of  $\text{C}^{\#}\text{OH}$  by  $\text{H}_2\text{O}$ .
  - All three carbons (Ketjen [E-type], Vulcan [V-type], and graphitized Ketjen [EA-type]) show similar steady-state corrosion rates.
- Carbon corrosion under transient potentials can be much higher
  - Spikes in corrosion rates while transitioning from high (0.95 V) to low cell potentials (0.4 V) are due to formation of  $\text{C}^{\#}\text{OH}$  and its reaction with PtOH.
  - Larger spikes in corrosion rates while transitioning from low (0.4 V) to high cell potentials (0.95 V) are due to accelerated oxidation of  $\text{C}^{\#}\text{OH}$  by  $\text{H}_2\text{O}$  at elevated potentials.
- Transient corrosion rates: E-Type  $\sim$  V-Type  $\gg$  EA-Type

## CONCLUSIONS AND FUTURE DIRECTIONS

### Conclusions

- For catalyst particles with solid morphology and over the particle size studied (5–14 nm),  $\text{Pt}_3\text{Co}$  alloy nanoparticles are more stable against Pt dissolution than Pt nanoparticles with potential holds at  $<1.0$  V, but less stable at  $>1.0$  V.
- Subsurface Co in PtCo nanoparticles with a core-shell morphology is stabilized against dissolution with a Co dissolution potential  $\sim 880$  mV higher than the standard potential for Co dissolution.
- Dissolved  $\text{Co}^{2+}$  decreases the oxygen permeability of PFSA thin films.
  - Carbon corrosion is primarily due to oxidation of activated carbon oxides, formed on defect sites in the carbon, by  $\text{H}_2\text{O}$  and is catalyzed by PtOH.

### Future Directions

This FC-PAD thrust area will continue to focus on the impact of catalyst and support type on performance and durability and the impact of the degradation of these components on the performance impacting properties of other electrode layer components through the following research activities:

- Experimentally determine and model the effects of alloy catalyst morphology on Pt and alloying element dissolution rates (i.e., IRD spongy PtCo and Umicore solid  $\text{Pt}_7\text{Co}_3$ ).
- Provide additional data needed for to catalyst degradation model: measurements of Pt re-deposition rates as a function of potential.
- Application of catalyst corrosion model to cell data using transmission electron microscopy-energy dispersive X-ray and X-ray fluorescence quantification of Pt and Co in cell components.
- Correlate changes in Pt and alloying element coordination numbers, bond distances, and surface Pt strain with changes in ORR activity resulting from application of accelerated stress tests.
- Determine impact of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  on the oxygen permeability of PFSA thin films as a function of relative humidity and temperature using solid state microelectrode apparatus.
- Determine rates and mechanisms of carbon corrosion for Pt alloy catalysts vs. Pt catalysts of similar particle size distribution.
- Determine effects of carbon type on Pt dissolution rates.



## FY 2016 PUBLICATIONS/PRESENTATIONS

Publications/Presentations Relevant to FC-PAD from Thrust Members

1. James A. Gilbert, A. Jeremy Kropf, Nancy N. Kariuki, Stacy DeCrane, Xiaoping Wang, Somaye Rasouli, Kang Yu, Paulo J. Ferreira, Dane Morgan, and Deborah J. Myers, "In-Operando Anomalous Small-Angle X-Ray Scattering Investigation of Pt<sub>3</sub>Co Catalyst Degradation in Aqueous and Fuel Cell Environments," *Journal of The Electrochemical Society*, 162 (14) (2015) F1487–F1497.
2. Deborah J. Myers, James Gilbert, Nancy N. Kariuki, Xiaoping Wang, A. Jeremy Kropf, Zhiwei Yang, Mallika Gummalla, Mike Perry, Sarah Ball, Jonathan Sharman, Brian Theobald, Alex Martinez, Dash Fongalland, Somaye Rasouli, Kang Yu, and Paulo J. Ferreira, "Mechanisms of PEMFC Cathode Catalyst Dissolution and Degradation X-ray scattering and absorption studies of polymer electrolyte fuel cell cathode electrocatalysts," 3rd International Workshop on Degradation Issues of Fuel Cells and Electrolysers, Santorini, Greece, September 30, 2015. (Invited)
3. Rodney L. Borup, D.D. Papadias, Rangachary Mukundan, Dusan Spornjak, David Langlois, R. Ahluwalia, Karren More, and Steve Grot, "Carbon Corrosion in PEM Fuel Cells During Drive Cycle Operation," *ECS Transactions*, 69 (17) 1029–1038 (2015).
4. F. Cetinbas, R. Ahluwalia, N. Kariuki (Argonne National Laboratory), K.L. More, D.A. Cullen, B. Sneed (Oak Ridge National Laboratory), R.P. Winarski, J. Ilavsky, V. De Andrade, and D.J. Myers (Argonne National Laboratory), "Structural Characterization and Transport Modeling of Pt and Pt alloy Polymer Electrolyte Fuel Cell Cathode Catalyst Layers," Submitted to the 230th Meeting of the Electrochemical Society.

## REFERENCES

1. D. Myers, "Rationally Designed Catalyst Layers for PEMFC Performance Optimization," U.S. Department of Energy, Fuel Cell Technologies Office, 2015 Annual Merit Review and Peer Evaluation. [https://www.hydrogen.energy.gov/pdfs/review15/fc106\\_myers\\_2015\\_o.pdf](https://www.hydrogen.energy.gov/pdfs/review15/fc106_myers_2015_o.pdf).
2. R. Borup, "V.E.1. Durability Improvements through Degradation Mechanism Studies," U.S. Department of Energy, Fuel Cell Technologies Office, 2015 Annual Progress Report, [https://www.hydrogen.energy.gov/pdfs/progress15/v\\_e\\_1\\_borup\\_2015.pdf](https://www.hydrogen.energy.gov/pdfs/progress15/v_e_1_borup_2015.pdf).