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# Highly Accessible Catalysts for Durable High-Power Performance

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#### Subcontractors:

- 3M Company, St. Paul, MN
- Carnegie Mellon University, Pittsburgh, PA
- Cornell University, Ithaca, NY
- Drexel University, Philadelphia, PA
- National Renewable Energy Laboratory, Golden, CO

Project Start Date: April 1, 2016  
Project End Date: June 30, 2019

## Overall Objectives

- Reduce overall stack cost by improving high-current-density (HCD) performance in H<sub>2</sub>/air fuel cells appropriate to meet DOE heat rejection and Pt-loading targets.
- Maintain long-term high electrocatalytic mass activities.
- Mitigate catalyst HCD degradation.

## Fiscal Year (FY) 2018 Objectives

- Optimize PtCo catalyst on accessible carbon supports for durable kinetic activity.
- Evaluate effects of electrolyte on electrode kinetics and transport.

- Quantify performance loss terms and degradation mechanism on low-platinum-group-metal (low-PGM) catalysts.

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan<sup>1</sup>:

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

## Technical Targets

Table 1 shows the DOE technical targets and current project status.

## FY 2018 Accomplishments

- Improved overall fuel cell performance by 10%–20% over last year's PtCo on accessible carbon catalysts by optimizing the catalyst preparation process.
- Demonstrated HCD fuel cell performance on porous carbon catalysts with ionic liquid and new ionomer.
- Reduced catalyst degradation nearly 50% by optimizing PtCo nanocrystal ordered intermetallic structure.

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<sup>1</sup> <https://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

Table 1. Progress Toward Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

Metric	Units	PtCo/HSC-en	PtCo/HSC-f	Ordered-PtCo/KB	DOE 2025 Target
		2018-1	2018-2	2018-3	
PGM total loading [cathode/anode]	mg/cm <sup>2</sup>	0.125 [0.10/0.025]	0.088 [0.063/0.025]	0.125 [0.10/0.025]	<0.125
Mass activity @ 900 mV <sub>IR-free</sub>	A/mg <sub>PGM</sub>	0.6 <sup>a</sup>	0.7 <sup>a</sup>	0.53 <sup>a</sup>	>0.44
Loss in catalytic (mass) activity	% loss	42 <sup>b</sup>	54 <sup>b</sup>	15	<40
Performance at 0.8 V (150 kPa, 80 °C)	A/cm <sup>2</sup>	0.363	0.382	0.301	>0.3
Power at rated power (150 kPa, 94 °C)	W/cm <sup>2</sup>	tbd	0.93	tbd	>1.0
Power at rated power (250 kPa, 94 °C)	W/cm <sup>2</sup>	1.31	1.26	1.15	-
PGM utilization (150 kPa, 94 °C)	kW/g <sub>PGM</sub>	tbd	10.6	tbd	>8
PGM utilization (250 kPa, 94 °C)	kW/g <sub>PGM</sub>	10.5	14.3	9.2	-
Catalyst AST (0.6–0.95 V)	mV loss at 0.8 A/cm <sup>2</sup>	34	47	8	<30
Support AST (1.0–1.5 V)	mV loss at 1.5 A/cm <sup>2</sup>	>500	>500	tbd	<30

MEA – membrane electrode assembly

HSC – high-surface-area carbon

KB – Ketjen Black

AST – accelerated stability testing

Green: meets target; Red: did not meet target

<sup>a</sup> Mass activity at 0.9 V<sub>RHE</sub> in cathodic direction

<sup>b</sup> Meets target in absolute term (i.e., >0.26 A/mg<sub>PGM</sub>)

## INTRODUCTION

The amount of platinum used in the oxygen reduction reaction (ORR) catalyst in fuel cells must be lowered by at least 4-fold to enable proton exchange membrane fuel cells cost-competitiveness with other vehicular propulsion power sources. In our previous DOE-funded project, we demonstrated that carbon-supported Pt-alloy catalysts (PtNi/HSC and PtCo/HSC) exhibited very high ORR electrocatalytic activity and impressive durability, exceeding DOE targets [1]. However, their high-power performance fell short of the target.

As the Pt content is lowered in the cathode, approaching  $<0.1 \text{ mg}_\text{Pt}/\text{cm}^2$ , large oxygen and proton fluxes must be supplied to the Pt surface, causing a performance loss due to a relatively high local transport resistance in the state-of-the-art electrodes. The local resistance was associated with the electrolyte-Pt interface and Pt location/distribution [2]. In addition, the non-precious transition metal in the catalyst, such as Ni or Co, could dissolve and migrate into the ionomer phase, replacing protons and consequently lowering the ionomer proton conductivity and causing hydrodynamic performance loss. Although these Pt-alloy catalysts exhibit excellent durable high catalytic activity, the target performance at high power has not been realized, limiting its cost reduction benefit.

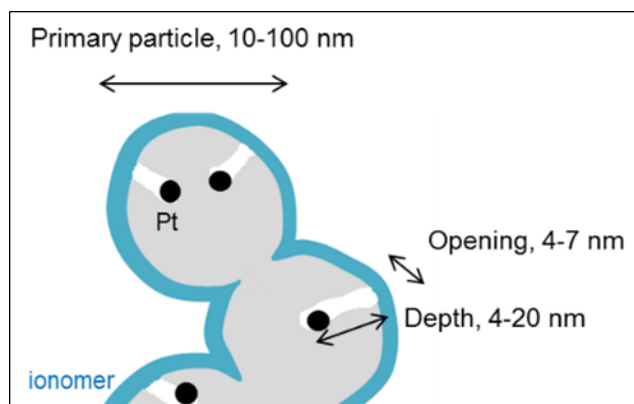
## APPROACH

The general approach for this project is to develop and select carbon supports and electrolytes that have favorable transport properties, and subsequently develop a high-performance Pt-alloy electrode using these subcomponents. The efforts can be divided into four thrusts: (1) development of carbon support, (2) selection of electrolyte (ionomer or ionic liquid), (3) development of stable highly dispersed Pt alloy nanoparticles, and (4) understanding the effects of the transition metal on performance.

## RESULTS

It was shown that the carbon support morphology has a pronounced effect on how electrocatalysts perform. Catalysts made from compact, solid carbon have most of their Pt particles on the carbon surface in contact with ionomer. The adsorption of ionomer onto Pt was shown to decrease its ORR activity and increase the local transport resistance. On the other hand, a majority of the deposited Pt particles on catalysts made with porous carbon are embedded inside the carbon pores. While this mitigates ionomer adsorption, thus increasing the ORR activity, it also can make it difficult for protons and  $\text{O}_2$  to access the electrocatalyst sites. Last year, we showed that with the proper carbon internal pore morphology, one could obtain high ORR activity with acceptable proton and  $\text{O}_2$  resistance in carbon's internal pores. These accessible, porous carbon catalysts have shown fuel cell performance metrics that meet DOE targets at both low and high current densities.

This year, we continued our efforts to further understand proton and  $\text{O}_2$  transport within carbon's internal pores. Cornell University (Cornell) used high-resolution transmission electron microscope (TEM) tomography to identify the location of Pt and to measure the carbon internal pore morphology. General Motors (GM) and the National Renewable Energy Laboratory (NREL) used MEA diagnostics to distinguish the relative resistances between proton and  $\text{O}_2$  transport in the pores. Carnegie Mellon University (CMU) performed ex situ proton and  $\text{O}_2$  conductivity measurements on carbon black and thin ionomer films, respectively. CMU also continued to develop a mesoscale particle-pore model to delineate the fuel cell performance sensitivity, using a catalyst layer morphology consistent with the microscopy results from Cornell. From our experimental and modeling results, a preliminary guideline for an ideal catalyst morphology for optimal performance is shown in Figure 1. It is preferable to have all Pt particles within the carbon shielded away from the ionomer layer to optimize ORR activity and local transport. The primary particle size and internal pore morphology of carbon particles are also important to provide sufficient/appropriate proton and  $\text{O}_2$  conduction.



**Figure 1. Illustration of cathode catalyst layer morphology to achieve optimal fuel cell performance**

Voltage-cycling AST was employed on PtCo catalysts made from different carbon support types. As shown in Figure 2, PtCo on solid carbon (Vulcan) not only showed lower initial ORR activity and ECSA, but also a higher degradation rate compared to porous carbons (HSC or KB). Unsurprisingly, catalysts made with accessible carbons, having more open pore structures, showed higher degradation rates than inaccessible porous carbon. Still, the HCD benefit from better local transport could be realized on accessible carbon catalysts even after the stability test.

Cornell investigated the mechanisms of electrochemical active surface area (ECSA) loss underlying this trend using TEM of post-mortem MEA cross-sections (Figure 2b). Energy-dispersive X-ray spectroscopy quantification of the Pt mass loss through the formation of a Pt band found similar losses of around 15% for all catalysts. The degree of catalyst coarsening, however, varied significantly among the different catalysts. Vulcan-supported catalysts showed more severe surface area loss through coarsening, especially through the formation of large, irregularly shaped particles, as seen in the heavy tail in the size distributions. Such irregular particles and a distribution tail of larger particles were generally absent for HSC-supported catalysts. Electron energy loss spectroscopy (EELS) composition mapping confirmed that the large, irregular particles in aged PtCo/Vulcan frequently contained multiple PtCo cores, a signature of particle coalescence (Figure 2c). Multi-core PtCo particles were rarely observed in aged PtCo/HSC MEAs. Both catalysts also showed growth of smaller, more spherical particles, exhibiting an increase in Pt shell thickness in EELS measurements of PtCo samples, suggesting that these particles grew via Ostwald ripening. The electrochemically observed ECSA loss was quantitatively consistent with the combined expected loss due to Pt mass loss to the Pt band and catalyst coarsening, measured with scanning transmission electron microscopy techniques, indicating that these are likely the dominant ECSA degradation mechanisms under these test conditions. Together, these results indicate that Ostwald ripening is a significant coarsening mechanism for all catalysts, regardless of the support morphology, while particle coalescence only contributes significantly for catalysts with solid carbon supports. Thus, porous carbon supports suppress coalescence, likely by restricting the migration of particles embedded in carbon pores. This is an encouraging result, as it demonstrates that design of the catalyst support morphology can provide an effective strategy for mitigating catalyst degradation through particle coalescence.

Pre-project results by Cornell and other groups suggested that increase in atomic level ordering of a Pt binary alloy, a so-called ordered intermetallic, could improve both ORR activity and stability of the catalyst, yet realization of the effect in an MEA has not been obtained. Further, the heat treatment required for the high level of ordering generally results in particle sintering and loss of Pt surface area, reducing fuel cell performance. This year, Cornell used in situ techniques including heating synchrotron X-ray diffraction and heating TEM to maximize the formation of ordered intermetallic without excessive particle sintering (Figure 3a). Using this, GM was able to further improve the stability of its best catalyst. Figure 3b shows that the annealing conditions mitigate the losses in ORR activity and Pt surface area by a factor of two. The differences in catalyst decay are being studied by microscopy. The ordered intermetallics are being prepared on other accessible porous carbons in order to achieve both good fuel cell HCD performance and durability.

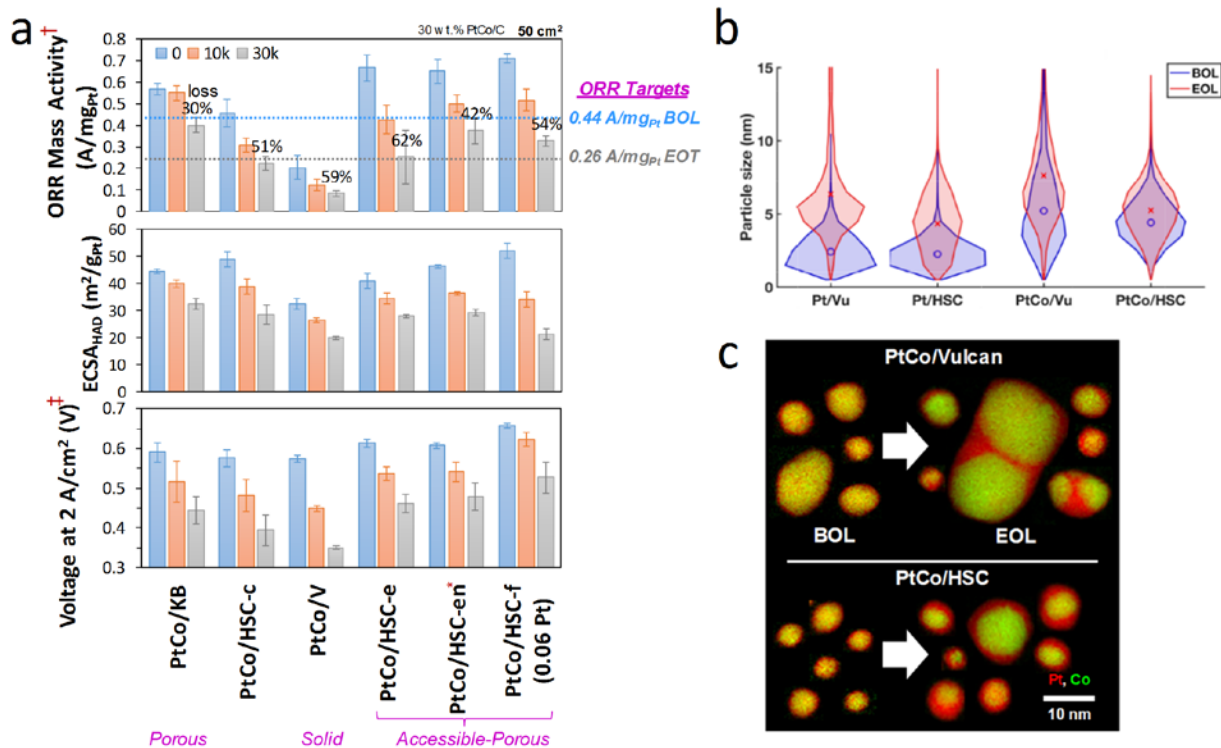


Figure 2. (a) ORR activity, Pt surface area, and voltage at 2 A/cm<sup>2</sup> of PtCo catalysts with different carbon supports during AST. (b) Particle size distribution of Pt and PtCo before and after AST. (c) TEM-EELS showing changes in Pt and Co distribution during AST.

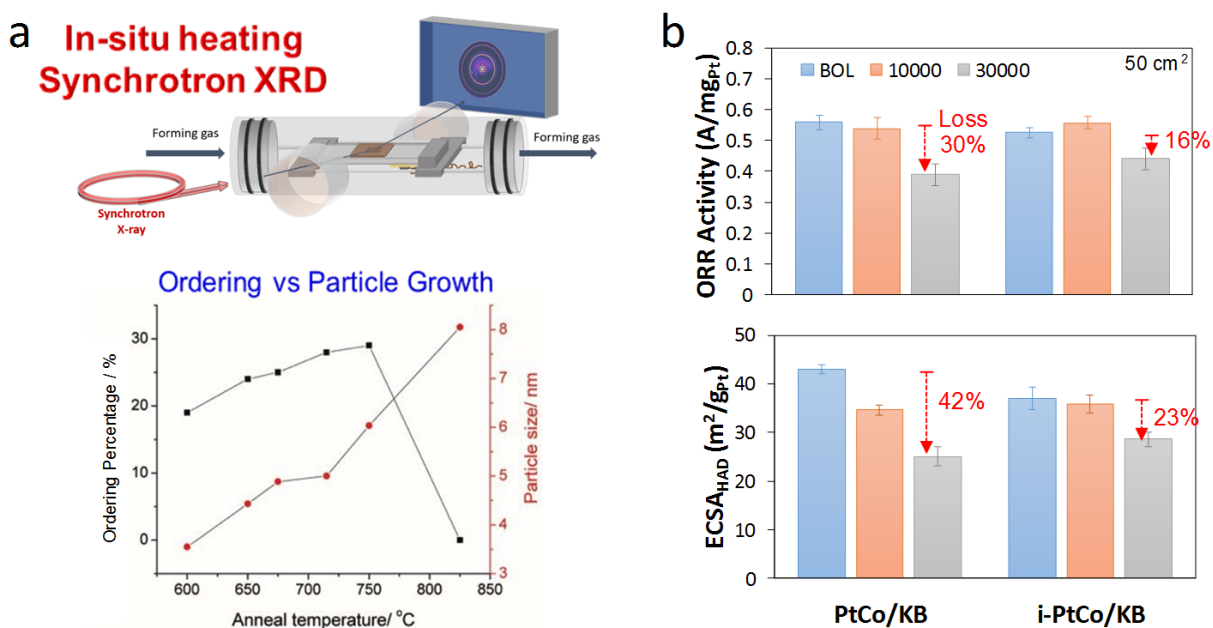


Figure 3. (a) In situ heating synchrotron X-ray diffraction experiment to study the degree of ordering and particle sintering as a function of heat-treatment conditions. (b) Improved retention of ORR activity and Pt surface area after AST by the heat treatment.

Although ionic liquids have been shown in rotating disk electrode to enhance ORR activity of Pt alloy catalyst, enhancement in a fuel cell has not been reproducibly demonstrated. This year, we established a procedure by adding the ionic liquid to the cathode after the layer was formed to prevent ionic liquid loss during application. A Pt/V cathode doped with ionic liquid showed improved fuel cell performance. Interestingly, the enhancement increases with current density, up to ~50 mV at 2.5 A/cm<sup>2</sup> (Figure 4a). Sub-ambient MEA diagnostics at NREL reveal that the increase is predominantly due to a potential-dependent kinetic enhancement, hypothetically as a result of competitive adsorption between the perfluorosulfonic acid ionomer and the ionic liquid. Similar, but somewhat smaller, improvement was observed with PtCo/KB. When measuring the proton accessibility of Pt on the porous carbon using CO stripping, it was found that the anion in the ionic liquid (beti) facilitates proton conduction into the carbon internal pores at low relative humidity (Figure 4b). This opens up a way to improve fuel cell performance of porous carbon catalysts under relatively dry conditions.

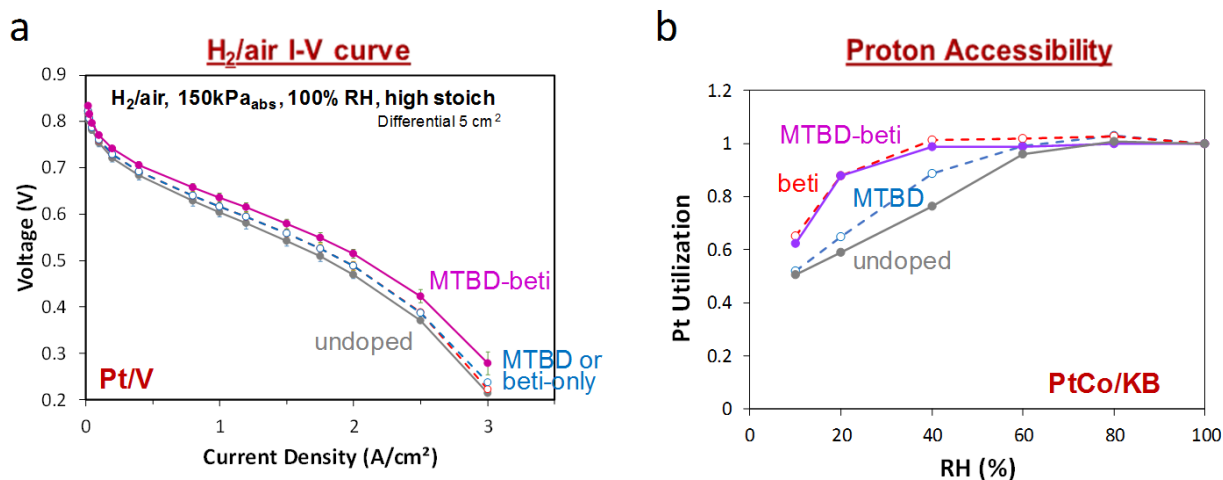


Figure 4. (a) Improved fuel cell performance by ionic liquid doping on Pt/V cathode. (b) Effect of ionic liquid ions on the proton accessibility as a function of relative humidity on PtCo/KB cathode.

## CONCLUSIONS AND UPCOMING ACTIVITIES

- Promising new materials provide paths to better activity and durability:
  - Ordered intermetallic PtCo showed exceptional stability.
  - Improved ORR activity can be obtained with ionic liquid in MEAs.
  - Continual improvement in durability of accessible carbons.
- Improved understanding of low-PGM electrodes:
  - Identified that proton transport in internal pores is sufficient and that local-O<sub>2</sub> transport is the primary focus area to improve performance.
  - Internal pore size (opening) is the key factor for good ORR activity and transport properties.
- Upcoming activities include:
  - Implement with accessible carbons, the intermetallic alloy for better stability, and ionomer and ionic liquid for better activity.
  - Optimize intermetallic PtCo catalysts for HCD performance and durability.

- Develop and validate fundamental performance model including dissolved transitional metal cations.
- Provide MEAs for DOE validation.

## SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. “Editors’ Choice” recognition by the *Journal of The Electrochemical Society* for excellent publication.
2. Selected as “Energy Focus” article by *ACS Energy Letters* for excellent publication.
3. Two patent applications submitted.
4. Prof. Héctor D. Abruña was elected to the National Academy of Sciences.
5. Prof. Héctor D. Abruña received the A. J. Bard Award for 2019 from The Electrochemical Society.

## FY 2018 PUBLICATIONS/PRESENTATIONS

### Publications

1. Yin Xiong, Li Xiao, Yao Yang, Francis J. DiSalvo, and Héctor D. Abruña, “High-Loading Intermetallic Pt<sub>3</sub>Co/C Core-shell Nanoparticles as an Enhanced Activity Catalyst towards the Oxygen Reduction Reaction (ORR),” *Chem. Mater.* 30, no. 5 (2018): 1532–1539
2. J. Braaten, A. Kongkanand, and S. Litster, “Oxygen Transport Effects of Cobalt Cation Contamination of Ionomer Thin Films in Proton Exchange Membrane Fuel Cells,” *ECS Transactions* 80 (2017): 283.
3. S. Ogawa, V. Yarlagadda, A. Kongkanand, and S. Litster, “Nano-scale simulation of platinum particle dissolution, re-deposition, and transport,” *ECS Transactions* 80, no. 8 (2017): 231–239.
4. [Invited Encyclopedia Entry] Anusorn Kongkanand, Wenbin Gu, and Mark F. Mathias, “Proton-Exchange Membrane Fuel Cells with Low-Pt Content,” In *Encyclopedia of Sustainability Science and Technology*, R.A. Meyers, Ed. (Springer, 2018), [https://doi.org/10.1007/978-1-4939-2493-6\\_1022-1](https://doi.org/10.1007/978-1-4939-2493-6_1022-1).
5. [Energy Focus] Venkata Yarlagadda, Michael K. Carpenter, Thomas E. Moylan, Ratandeep Singh Kukreja, Roland Koestner, Wenbin Gu, Levi Thompson, and Anusorn Kongkanand, “Boosting Fuel Cell Performance with Accessible Carbon Mesopores,” *ACS Energy Lett.* 3 (2018): 618.
6. [Editors’ Choice] Elliot Padgett, Nina Andrejevic, Zhongyi Liu, Anusorn Kongkanand, Wenbin Gu, Koji Moriyama, Swami Kumaraguru, Thomas E. Moylan, Ratandeep Kukreja, Yi Jiang, and David A. Muller, “Connecting nanostructure with utilization of hydrogen fuel cell catalysts using quantitative cryo-STEM tomography,” *J. Electrochem. Soc.* 165 (2018): F173.
7. Yun Cai, Joseph M. Ziegelbauer, Andrew M. Baker, Wenbin Gu, Ratandeep S. Kukreja, Anusorn Kongkanand, Mark F. Mathias, Rangachary Mukundan, and Rod L. Borup, “Electrode Edge Cobalt Cation Migration in an Operating Fuel Cell: An In Situ Micro-X-Ray Fluorescence Study,” *J. Electrochem. Soc.* 165 (2018): F3132.

### Presentations

1. A. Kongkanand, “Highly-Accessible Catalysts for Durable High-Power Performance,” US Drive Fuel Cell Tech Team, Southfield, MI, April 2017.
2. H. Abruña, “Compositional and Structural Effects on ORR Electrocatalysis,” DOE CWG workshop, Argonne National Laboratory, Lemont, IL, May 3, 2017.
3. A. Kongkanand and V.R. Yarlagadda, “Recent Capabilities for Developing Low-PGM Electrodes,” DOE CWG workshop, Argonne National Laboratory, Lemont, IL, May 3, 2017.
4. C. Gittleman, A. Kongkanand, and S. Kumaraguru, “Ionomer in Catalyst Layer and Unresolved Issues,” DOE DWG workshop, Argonne National Laboratory, Lemont, IL, May 4, 2017.

5. H.D. Abruña, “Compositional and Structural Effects on ORR Electrocatalysis,” Nankai University, May 8, 2017.
6. H.D. Abruña, “Operando Methods for the Study of Energy Materials,” Huazhong University of Science and Technology, Wuhan, May 12, 2017.
7. H.D. Abruña, “Compositional and Structural Effects on ORR Electrocatalysis,” Wuhan University, May 12, 2017.
8. “Operando Methods for the Study of Energy Materials,” Dept. Chem., Univ. Buenos Aires, May 18, 2017.
9. H.D. Abruña, “Compositional and Structural Effects on ORR Electrocatalysis,” INQUIMAE, Univ. Buenos Aires, May 19, 2017.
10. H.D. Abruña, “Operando Methods for the Study of Energy Materials,” XVII Encuentro de Superficies y Materiales Nanoestructurados, Bariloche, Argentina, May 24, 2017.
11. [Invited] W. Gu, A. Kongkanand, V.R. Yarlagadda, P.T. Yu, and M.F. Mathias, “The Importance of the Cathode Catalyst Support in the Pursuit of Low-Cost PEM Fuel Cells,” ECS 231st Meeting, New Orleans, LA, May 28–June 1, 2017.
12. Venkata Yarlagadda, Samuel E. McKinney, Cristin L. Keary, Levi Thompson, Barr Halevi, and Anusorn Kongkanand, “Preparation of PEMFC Electrodes from Milligram-Amount Catalysts,” ECS 231st Meeting, New Orleans, LA, May 28–June 1, 2017.
13. Venkata Yarlagadda, Elliot Padgett, Ratandeeep Kukreja, Joseph M. Ziegelbauer, Jonathan Braaten, Shohei Ogawa, Siddharth Komini Babu, Srikanth Arisetty, Wenbin Gu, Levi Thompson, Shawn Litster, David A. Muller, and Anusorn Kongkanand, “Effects of Carbon Supports on the Stability of Pt and PtCo Nanoparticles in PEMFC Cathodes,” ECS 231st Meeting, New Orleans, LA, May 28–June 1, 2017.
14. [Invited] S. Arisetty, S. Alia, J. Zack, J.M. Ziegelbauer, N.N. Kariuki, V.R. Yarlagadda, D.J. Myers, K.C. Neyerlin, and A. Kongkanand, “Dealloying of Binary Catalysts in Hydrogen Fuel Cell,” ISE 68<sup>th</sup> Meeting, Providence, RI, August 27–September 1, 2017.
15. [Invited] S. Ogawa, S. Komini Babu, H. T. Chung, P. Zelenay, E. Padgett, D.A. Muller, A. Kongkanand, and S. Litster, “Microstructural Modeling of PEFC Catalyst Layer Performance and Durability,” ECS 232nd Meeting, National Harbor, MD, October 1–5, 2017.
16. [Invited] K.C. Neyerlin, L. Anderson, A. Chuang, K.L. More, R. Ahluwalia, S.A. Mauger, G. Bender, B.S. Pivovar, W. Gu, S. Kumaraguru, A. Kongkanand, and S.S. Kocha, “Methods for Understanding and Mitigating High Current Density Performance Losses in Low Loaded Pt-Based PEMFCs,” ECS 232nd Meeting, National Harbor, MD, October 1–5, 2017.
17. S. Ogawa, V. Yarlagadda, A. Kongkanand, and S. Litster, “Nano-Scale Simulation of Platinum Particle Dissolution, Re-Deposition, and Transport,” ECS 232nd Meeting, National Harbor, MD, October 1–5, 2017.
18. J. Braaten, A. Kongkanand, and S. Litster, “Oxygen Transport Effects of Cobalt Cation Contamination of Ionomer Thin Films in Proton Exchange Membrane Fuel Cells,” ECS 232nd Meeting, National Harbor, MD, October 1–5, 2017.
19. S. Arisetty, S.M. Alia, J.W. Zack, A. Kongkanand, V. Yarlagadda, R.S. Kukreja, J.M. Ziegelbauer, K.C. Neyerlin, N. Kariuki, D.J. Myers, B. Lakshmanan, “Catalyst Dissolution Rates during PEM Fuel Cell Operation,” ECS 232nd Meeting, National Harbor, MD, October 1–5, 2017.
20. Y. Li and J. Snyder, “Improved Activity and Durability of Ionic Liquid Composite Nanoporous Nanoparticle Electrocatalysts for Oxygen Reduction Reaction,” AIChE Fall Meeting, Minneapolis, MN, October 31, 2017.
21. Y. Li and J. Snyder, “Mitigation of Structural and Compositional Instability in 3-Dimensional, Nanoporous Electrocatalysts,” ECS Fall Meeting, Washington, DC, October 3, 2017.



22. J. Snyder and Y. Li, “Electrocatalytic Interface Engineering with Ionic Liquids,” ECS Fall Meeting, Washington, DC, October 3, 2017.
23. [Invited] J. Ziegelbauer, Y. Cai, and A. Kongkanand, “Synchrotron-based Research for Zero-emission Transportation Applications at General Motors,” CHESS/CLASSe Seminar, Cornell University, October 2017.
24. [Invited] A. Kongkanand, “Catalysts for Sustainable Fuel Cell Electric Vehicles,” Technology Collaboration Programme on Advanced Fuel Cells by the International Energy Agency (IEA), Berlin, Germany, November 15, 2017.

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1. B. Han et al., “Record Activity and Stability of Dealloyed Bimetallic Catalysts for Proton Exchange Membrane Fuel Cells,” *Energy Environ. Sci.* 8, no. 1 (2015): 258-266.
2. Anusorn Kongkanand, Wenbin Gu, and Mark F. Mathias, “Proton-Exchange Membrane Fuel Cells with Low-Pt Content,” In *Encyclopedia of Sustainability Science and Technology*, R.A. Meyers, Ed. (Springer, 2018), [https://doi.org/10.1007/978-1-4939-2493-6\\_1022-1](https://doi.org/10.1007/978-1-4939-2493-6_1022-1).