ElectroCat (Electrocatalysis Consortium)

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Overall Objectives

- Expedite the development of platinum-group-metal-free (PGM-free) catalysts, electrodes, and membrane electrode assemblies (MEAs) for fuel cell applications by facilitating collaboration between national laboratories.

- Foster the development of necessary capabilities.

- Create an interface for making those capabilities available to industry and academic partners.

Fiscal Year (FY) 2019 Objectives

Argonne National Laboratory (ANL)

- Synthesize 25 unique Fe,TM-N-C (iron-(transition metal)-nitrogen-carbon) catalysts using high-throughput methodology and evaluate their oxygen reduction reaction (ORR) activity and durability using hydrodynamic, high-throughput techniques. The goal for area-specific ORR activity is 70 $\mu A/mF$ at 0.8 V.

- Fully define the structure of PGM-free electrodes and agglomerates by supplementing nano-computed tomography (nano-CT) data with information from other techniques, such as small angle X-ray scattering, porosimetry, and transmission electron microscopy (TEM).

- Determine the sources of high-current-density performance limitations for PGM-free electrodes.

- Publish a database of density functional theory (DFT) calculations and the raw input and output files; make openly available the curated data gathered in high-temperature synthesis and characterization efforts; and create and ingest containerized models into the Data and Learning Hub for Science with links to data in the Materials Data Facility to promote reuse and replicability.

- Define catalyst composition, synthetic procedure, and electrode composition that will achieve a 20% improvement in cathode performance lifetime versus the 2018 ElectroCat status (duration over which current density at 0.7 V with hydrogen-air shows <5% decay).

Los Alamos National Laboratory (LANL)

- Propose modifications to the electrode structure to improve mass transport in the high-current-density region based on studies of ionomer-loading gradient and improved porosity using catalyst layer pore formers.

- Identify the relationship between metal organic framework (MOF) synthesis conditions and ORR activity through a systematic study and propose a possible synthesis pathway(s) to improve the catalyst ORR activity and durability. Demonstrate the MEA durability decay rate of ≤ 1 mA/(cm^2 h) at 0.7 V at 0.2 bar partial pressure of O_2 (oxygen) and cell temperature 80°C.

- Demonstrate the ability of *adaptive design* to utilize input data from ANL curated data format and output DFT data to ANL curated data format. This will enable concurrent evolution of the experimental and theoretical databases with all appropriate metadata.

- Complete X-ray and vibrational spectra calculations for FeN_4 (iron atom coordinated to four nitrogen atoms), $OHFeN_4$ (iron atom

coordinated to four nitrogen atoms and one hydroxyl group), and OFeN$_4$ (iron atom coordinated to four nitrogen atoms and one oxygen atom) hosted at zig-zag edge, arm-chair edge, and in the bulk, as well as N- and C-degraded OHFeN$_4$ active site structures with and without NO (nitric oxide) probe molecule. Compare calculation results to experimental signatures: X-ray absorption near edge structure (XANES), nuclear resonance vibrational spectroscopy (NRVS), electron energy loss spectroscopy (EELS), and others.

- Identify mechanisms of Fe de-metalation based on the systematic analysis proposed in Task 6. Provide a complete analysis of the kinetic degradation model at varied voltage, partial pressures, and relative humidity conditions. Demonstrate improved durability of PGM-free electrocatalysts during fuel cell operation based on mitigation mechanisms developed from the knowledge gained from the mitigation of catalyst degradation task.

National Renewable Energy Laboratory (NREL)

- Complete the X-Ray Diffraction Analysis tool, to be integrated into the Data Hub and available as an analysis tool for X-ray diffraction (XRD) data. Work with ElectroCat researchers to confirm applicability of the tool using at least two XRD datasets in the ElectroCat Data Hub.

- Characterize bulk electrode transport resistance as a function of electrode fabrication conditions. Improve bulk electrode transport resistance by at least 10% when compared to ultrasonically sprayed catalyst-coated membranes deposited at 80°C (our current standard).

- Elucidate trends in drying rate on in situ MEA performance and durability utilizing the segmented cell. Down-selected high-performing regimes will be assessed for transport and proton resistance.

- In accordance with the annual ElectroCat milestone in Q4 of FY19, demonstrate the ability to reduce bulk electrode transport resistance by 10% over ultrasonically sprayed electrodes when utilizing ink and/or processing methodologies.

- For an identical catalyst material, loading, and operating condition, demonstrate that electrospun fabricated electrodes exhibit a 10% improvement in performance, as determined at constant potential (between 0.6 and 0.4 V), when compared to electrodes fabricated via ultrasonic spray or hand-painting.

- Compute onset potentials for ORR on FeN$_4$ structure (with and without OH ligands) on graphene. Calculate a potential value for where the OH (hydroxyl group) occupied site is favored vs. the computational hydrogen electrode prediction. Determine the source of deviations and analyze the effect of different contributions (e.g., entropic effects, solvent effects). If differences in the potential value are obtained vs. the computational hydrogen electrode and the differences due to different contributions can be understood, then the capability is a go.

Oak Ridge National Laboratory (ORNL)

- Initiate scanning transmission electron microscopy (STEM) imaging and spectroscopy for at least three electrospun PGM-free catalysts, before and after incorporation into an MEA. The progress measure will be coordinated with NREL to assess structure and uniformity of catalyst layers fabricated and to correlate morphological observations with measured performance.

- Characterize at least three MOF-based PGM-free catalysts incorporated in the cathode catalyst layer of MEAs before and after durability testing using high-resolution analytical electron microscopy. Coordinate the analysis effort and MEAs with tasks for implementing PGM-free catalyst test protocols at LANL and tasks for X-ray scattering and nano-CT at ANL.

- Report on effort to measure Fe de-metalation in several PGM-free MEAs after fuel cell operation/testing using STEM/EELS/EDS (EDS – energy-dispersive X-ray spectroscopy) and X-ray photoelectron spectroscopy. This effort will be highly coordinated with LANL and ANL to quantify the loss of Fe relating directly to loss of Fe-based catalytic sites in

polyaniline- (PANI-) and MOF-derived catalysts.

ElectroCat Annual Milestone

- Achieve PGM-free cathode MEA performance in a hydrogen-oxygen fuel cell of 29 mA/cm^2 at 0.90 V (iR-corrected) at 1.0 bar partial pressure of O_2 and cell temperature 80°C; define performance-limiting catalyst and electrode properties to guide the synthesis of PGM-free catalysts and fabrication of electrodes/MEAs (LANL, ANL, ORNL, NREL).

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[1]:

- (A) Durability (catalyst, MEA)

- (B) Cost (catalyst)

- (C) Performance (catalyst, MEA).

Technical Targets

This project focuses on the development and implementation of high-performance PGM-free cathode catalysts for polymer electrolyte fuel cells (PEFCs), following DOE technical targets outlined in Table 3.4.7 in the Fuel Cells section of the Multi-Year Research, Development, and Demonstration Plan. The overall goal is durable PGM-free ORR catalysts that achieve an activity of 0.044 A/cm^2 at 0.90 V in a PEFC MEA by 2025.

FY 2019 Accomplishments

ElectroCat Development and Communication

- Supported four existing and six new funding opportunity announcement (FOA) projects with 10 capabilities.

- Held a consortium-wide semi-annual meeting on January 30–31, 2019, in Santa Fe, New Mexico, to kick off new FOA projects. Information was distributed to consortium members and select information is available through the public website and data

management hub (https://www.electrocat.org, https://datahub.electrocat.org).

- Was issued one patent.

- Published 12 papers and gave 20 presentations (10 invited).

Performance and Durability Improvement

- Exceeded the ElectroCat FY 2018 annual milestone of PGM-free cathode MEA performance of 25 mA/cm^2 at 0.90 V, H_2/O_2, iR-free (voltage corrected for cell resistance): high current density value of 36 mA/cm^2, average for four MEAs of 33 mA/cm^2.

- Developed an (Fe,Zn)-ZIF (iron and zinc zeolitic imidazolate framework) catalyst precursor with Fe exclusively in FeN_4 sites, which after heat treatment resulted in a catalyst with no detectable Fe spectator species.

- Addressed "shelf-life" durability of the (AD)Fe-N-C (atomically-dispersed iron-nitrogen-carbon) catalyst powder.

- Improved performance stability and decreased CO_2 emissions of cyanamide+polyaniline-Fe(Zn)-C cathodes under steady-state holds in oxygen using a radical scavenger (in close collaboration with the Pacific Northwest National Laboratory-led FOA project).

Characterization and Capability Development

- Determined that performance loss of (AD)Fe-N-C cathode with accelerated stress test (AST) cycling is predominantly due to loss of catalyst activity.

- Determined using NRVS and Mössbauer spectroscopy that NO, the surface molecular probe, can bind to Fe^{3+} and Fe^{2+}; quantified the amount of NO adsorbed at high and low potentials using voltammetric stripping and temperature-programmed desorption.

- Used STEM-EELS and X-ray absorption to characterize Fe species and structure evolution during heat treatment, obtaining guidance for improved catalyst synthesis.

- Characterized ORR activity and atomic structure of 75 high-throughput-synthesized Fe-dopant-phenanthroline-ZIF catalysts using

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[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

X-ray absorption and multi-channel flow double electrode cell, identifying materials with half-wave potential ($E_{1/2}$) greater than 0.80 V.

- Developed and utilized methods to characterize Fe speciation as a function of cell potential using in situ Mössbauer spectroscopy.

- Acquired MEA performance and kinetic data for (AD)Fe-N-C cathode as a function of the number of AST cycles and applied the distributed ORR model to determine the kinetic losses, number of active sites remaining, and the mass transport losses.

- Defined advances needed in catalyst activity and electrode properties to achieve 1,000 mW/cm^2 power density while meeting the Q/dT target.

ORR Active-Site Activity and Durability Modeling

- Calculated DFT database of vibrational spectra with and without probe molecules for identification of stretching frequencies observed using nuclear resonance vibrational spectroscopy.

- Calculated DFT database of isomer shift and quadrupole splitting values for identification of doublets in Mössbauer spectra of PGM-free catalysts.

Table 1. Progress toward Meeting Technical Targets for PGM-Free Electrocatalysts and MEAs for Transportation Applications

Characteristic	Units	DOE 2025 Electrocatalyst and MEA Targets	ElectroCat Status
H_2-air fuel cell performance	mA/cm^2 @ 800 mV (measured)	300	107
PGM-free catalyst activity	mA/cm^2 @ 900 $mV_{iR-free}$	≥ 44	33

INTRODUCTION AND APPROACH

ElectroCat, a DOE Energy Materials Network (EMN) consortium, uses the EMN approach to accelerate the development and implementation of PGM-free fuel cell materials. The EMN consortia leverage the existing relevant capabilities of the DOE national laboratories and develop missing strategic capabilities to accelerate core research toward discovery, development, and scale-up of materials. The EMN consortia also aid competitively selected projects led by industry, academia, and other national laboratories. Critical aspects of the EMN approach are the use of predictive simulation across all scales, high-throughput materials synthesis, screening, and characterization, and rapid data mining, correlation, and publication. In the materials discovery and development arena, ElectroCat is focused on developing and implementing PGM-free catalysts and electrodes for PEFCs. In addition to the development of PGM-free catalysts, ElectroCat focuses on creating the tools and catalyst information database critical to industrial deployment of PGM-free catalyst fuel cells.

RESULTS

Consortium Development

ElectroCat comprises four core national laboratories contributing their expertise in characterization, materials and electrode synthesis/fabrication testing and diagnostics, and modeling. These existing and demonstrated capabilities were utilized in 2019 to support the R&D efforts in the four ElectroCat 2017 FOA projects. This year, four new capabilities were developed and evaluated: temperature-programmed desorption of probe molecules, wetting properties of catalysts, refined calculation of reaction energetics, and electrospinning of electrodes. Detailed information on all ElectroCat capabilities, including the ones added recently, are available on the consortium website: https://www.electrocat.org.

PGM-Free Catalyst Development and Characterization

Catalysts with High Microporosity

Performance of highly porous PGM-free catalysts synthesized using Zn salts (e.g., zinc chloride), cyanamide, and polyaniline was further improved by varying the ionomer-to-catalyst ratio and the ionomer equivalent weight in the cathode. A maximum hydrogen-oxygen fuel cell performance of 36 mA/cm^2 (33 mA/cm^2 value from four independent experiments) at 0.90 V (*iR*-free) and a hydrogen-air fuel cell performance of 107 mA/cm^2 at 0.80 V (as measured) were achieved using this approach. The hydrogen-oxygen performance exceeded the ElectroCat annual milestone of 25 mA/cm^2 (Figure 1).

Catalysts with Atomically Dispersed Transition-Metal Sites

Nitrogen-doped PGM-free catalysts containing atomically-dispersed Fe, (AD)Fe-N-C, were synthesized using bimetallic (Fe,Zn)-ZIFs as the precursor structure. The formation of the active sites and development of porosity were examined using TEM, with EDS quantification of N, Zn, and Fe content, and using X-ray absorption fine structure (XAFS) analysis during heat treatment. The TEM/EDS and XAFS show that mesoporosity emerges during pyrolysis at temperatures as low as 500°C concurrent with significant loss of Zn. XAFS shows that an FeN$_4$ square planar structure is formed at temperatures as low as 650°C. Temperatures above 1,000°C are needed to completely remove the Zn to trace levels and to increase support graphitization. However, these temperatures result in an undesirable loss of pyridinic nitrogen, which has been associated with ORR activity of this class of catalysts.

Anode: 0.2 mg$_{Pt}$ cm^{-2} Pt/C H$_2$, 200 sccm, 1.0 bar H$_2$ partial pressure; **Cathode:** *ca*. 6.8 mg cm^{-2}, CM-PANI-Fe-C(Zn), Aquivion® D83 55 wt%, 200 sccm, 1.0 bar O$_2$ partial pressure; **Membrane:** Nafion® 211; **Cell:** 5 cm^2
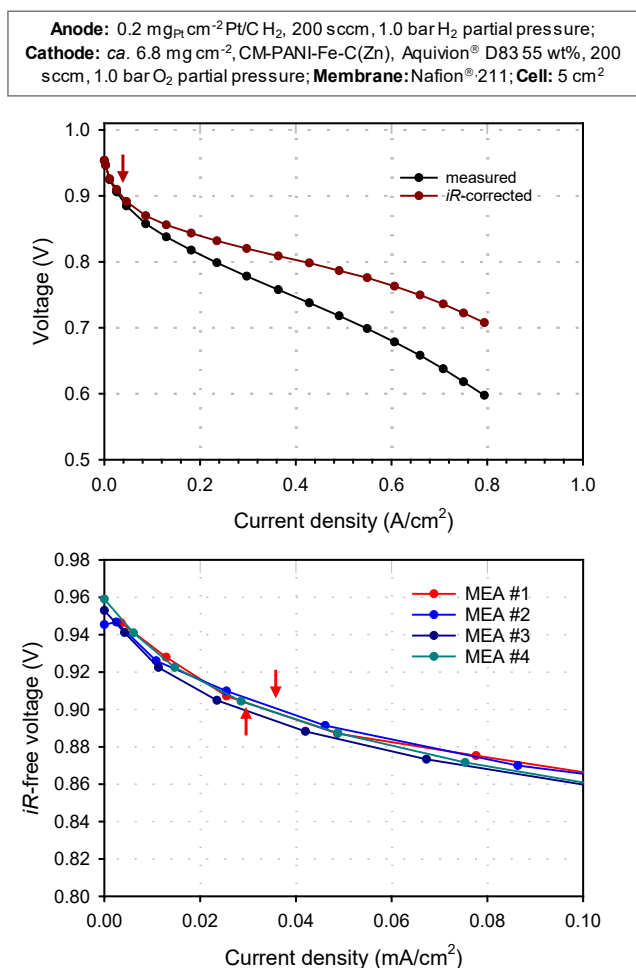

Figure 1. Hydrogen-oxygen performance of CM-PANI-Fe(Zn)-N-C catalyst meeting the ElectroCat FY 2018 activity milestone in an MEA of 25 mA/cm² at 0.90 V (*iR*-free).

Active Site Characterization

Experiments using probe molecules coupled with NRVS, Mössbauer spectroscopy, and in situ Mössbauer spectroscopy were utilized to elucidate the nature of the active site in the (AD)Fe-N-C class of catalysts. Mössbauer spectroscopy experiments performed in 0.5 M H_2SO_4 with ^{57}Fe-enriched (AD)Fe-N-C catalyst reveal strong potential dependence of Fe speciation on electrode potential (Figure 2). The content of doublet 1 (D1) species, assigned to Fe^{3+} in either square-pyramidal or octahedral coordination, decreases as potential decreases from 0.6 V to 0.1 V. At the same time, Fe species represented by doublet 2 (D2), usually assigned to Fe^{2+} in distorted square planar coordination, increases. Unlike these two species, the iron species responsible for doublet 3 (D3), often assigned to Fe^{2+} species in octahedral coordination, appears immune to potential changes, suggesting their location in the bulk of the catalyst phase rather than on the surface. The accompanying potential-dependent XANES data indicate the presence of two major Fe species in the (AD)Fe-N-C catalyst, with the ratio of the two species dependent on potential (isosbestic points in Figure 2, lower left): predominantly octahedral at high potentials and predominantly four-coordinate at low potentials. Ex situ Mössbauer experiments with NO as a molecular probe of the ORR active sites indicate that, in addition to inducing quadrupole splitting in the spectra assigned to both Fe^{3+} and Fe^{2+} sites, the probe-site interaction results in a decrease in the Fe^{3+}/Fe^{2+} ratio.
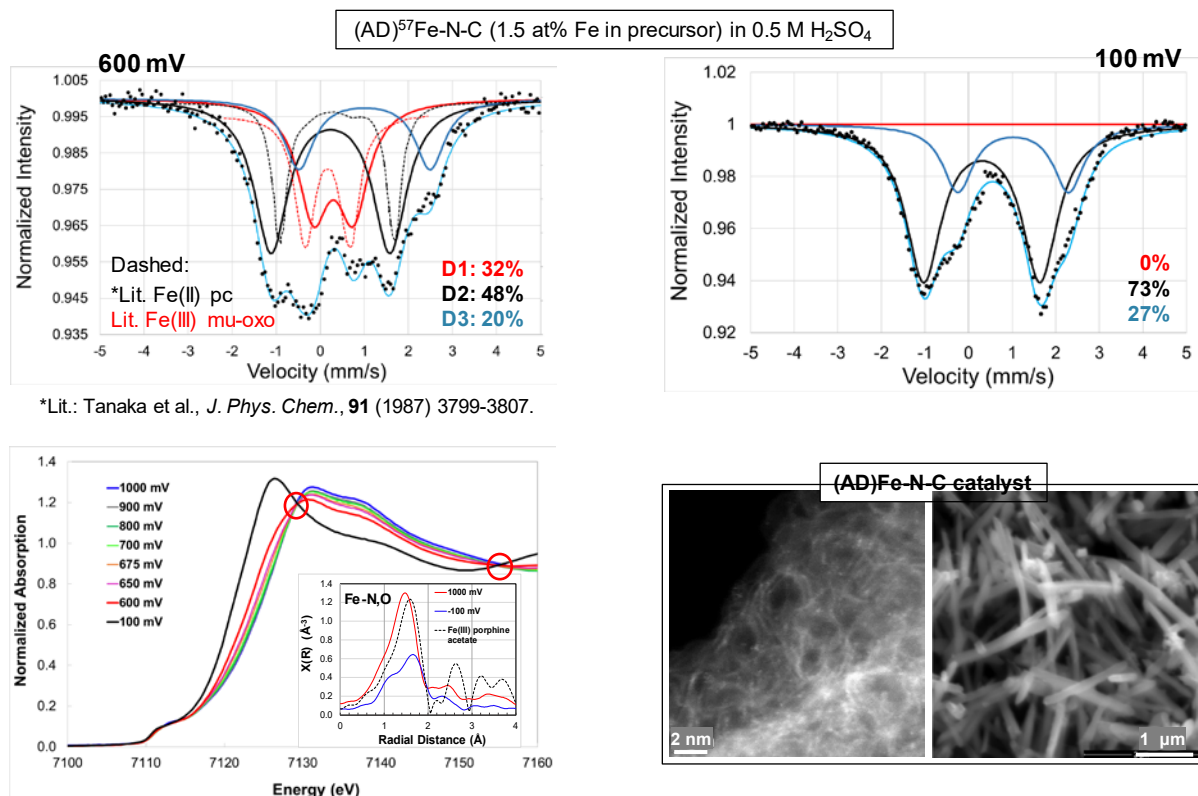

Figure 2. In situ Mössbauer and XANES data as a function of potential for an (AD)Fe-N-C catalyst in de-aerated 0.5 M H_2SO_4 electrolyte and STEM micrographs of the (AD)Fe-N-C catalyst.

Unambiguous proof for the presence of Fe sites on the surface of iron-derived PGM-free catalysts was obtained in NRVS experiments involving NO as surface probe and both as-synthesized (i.e., oxidized) and reduced, fully ^{57}Fe-enriched (AD)Fe-N-C catalyst. The NRVS spectra in Figure 3 reveal new vibrational modes upon NO treatment of the catalysts. Based on literature data and in-house DFT modeling (example shown for reduced NO-treated catalyst in Figure 3), a broad band in the range 400–600 cm^{-1} can be assigned to Fe-NO stretch vibration and a band below 200 cm^{-1} to an acoustic mode involving overall translation of the entire Fe site. The changes to the spectra in that range suggest that NO adsorption is capable of modifying the entire acoustic mode of Fe. The NRVS experiments provide the very first evidence of NO probe binding to

both Fe^{3+} and Fe^{2+} surface sites in a PGM-free catalyst. Ongoing DFT calculations are designed to provide complete interpretation of the recorded spectra.
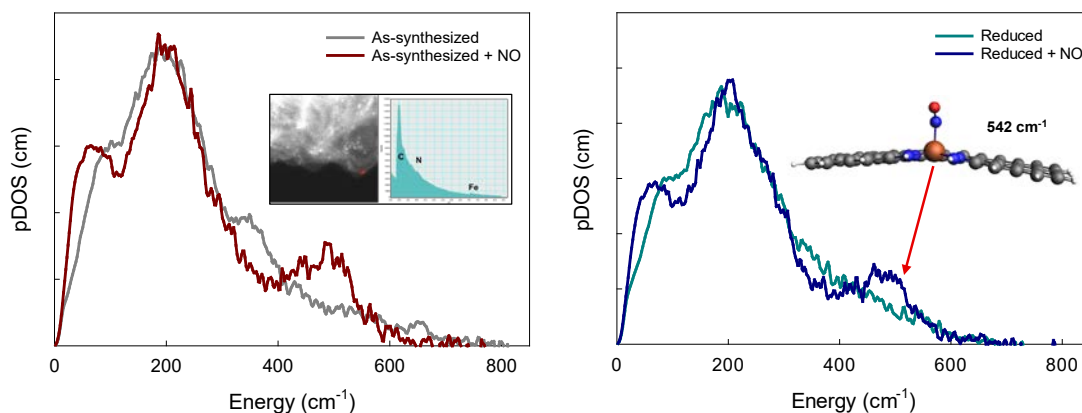

Figure 3. NRVS spectra of as-synthesized (left) and reduced (AD)[57]Fe-N-C catalyst without and with NO probe. Inset: HR-STEM and EELS spectra of (AD)[57]Fe-N-C catalyst highlighting atomic dispersion of Fe-N sites.

The use of NO_2^- (nitrite anion) as an alternative molecular probe, which unlike NO can be used in situ, shows strong potential dependence of ORR poisoning and stripping charge (Figure 4). Stripping charges of nitrite adsorbed at 0.90 V and 0.43 V differ by a factor of approximately three, ca. 1.3×10^{13} NO molecules/cm^2 and ca. 3.0×10^{12} NO molecules/cm^2, respectively (Figure 4, top left). This very significant difference in the number of adsorbed NO was confirmed by temperature-programmed desorption experiments (Figure 4, top right). DFT calculations reveal high affinity of NO to Fe, as well as to some local epoxides, expected to form at higher electrode potentials. The normalized stripping charge of NO_2^- correlates well with change in the oxidation state of Fe, as determined from XANES linear combination fitting (Figure 4, bottom). It also agrees with potentials of the Faradaic couple in the cyclic voltammogram in the same figure, which is typically assigned to the Fe^{2+}/Fe^{3+} redox process.
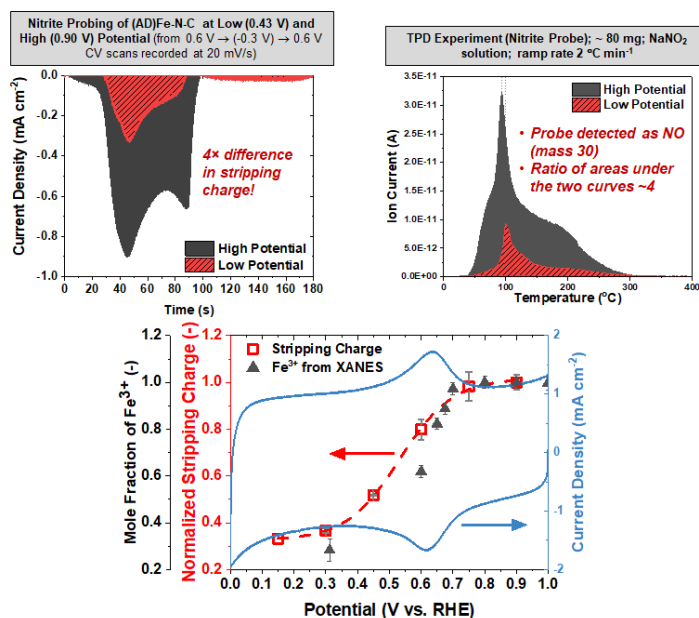

Figure 4. (Upper left) Stripping current of the nitrite probe at 0.43 V and 0.90 V vs. reversible hydrogen electrode as a function of time. (Upper right) Temperature-programmed desorption experiments with NO adsorbed at the two potentials. (Bottom) Potential dependence of probe stripping charge and mole fraction of Fe^{3+} in the catalyst (from XANES). Voltammetry highlights good correlation of the stripping charge with the redox potential for the Fe^{2+}/Fe^{3+} couple.

High-Throughput Synthesis of Catalysts

Catalyst development and characterization via high-throughput approach is one of ElectroCat's main pillars. In this research period, the approach was used to study the effect of carbon source and Fe content on ORR activity of catalysts derived from either Black Pearls (BP) or ZIF-8 as the primary carbon sources, phenanthroline as a primary nitrogen precursor, and iron acetate as a source of Fe (at a constant weight percent of 0.5) (Figure 5). The highest ORR activity was found with ZIF as a carbon source and phenanthroline content of 40 wt % ($E_{1/2}$ = 0.81 V) (Figure 5, top). Fourier transformed extended X-ray absorption fine structure (EXAFS) data in Figure 5 (bottom) show that, in the absence of phenanthroline or ZIF in the precursor, the product of the high-temperature treatment was iron carbide. The desirable FeN_x sites (i.e., sites containing iron atom coordinated to different number of nitrogen atoms) were formed with ZIF as precursor or with 25%–60% phenanthroline with BP carbon. High phenanthroline contents promoted carbide formation, too. The high-throughput approach was also used to determine (1) the effect of 12 metal dopants on performance of ZIF- and phenanthroline-derived Fe-based catalysts, (2) the effect of dopant-metal content on catalytic activity, and (3) the activity of manganese (Mn)-based (rather than Fe-based) catalysts as a function of the wt % of Mn in the precursors. Several catalysts in the study showed high activity, yielding $E_{1/2}$ values in the 0.80–0.81 V range. Mn-based catalysts consistently exhibited lower ORR activity than Fe-based catalysts at all tested loadings.
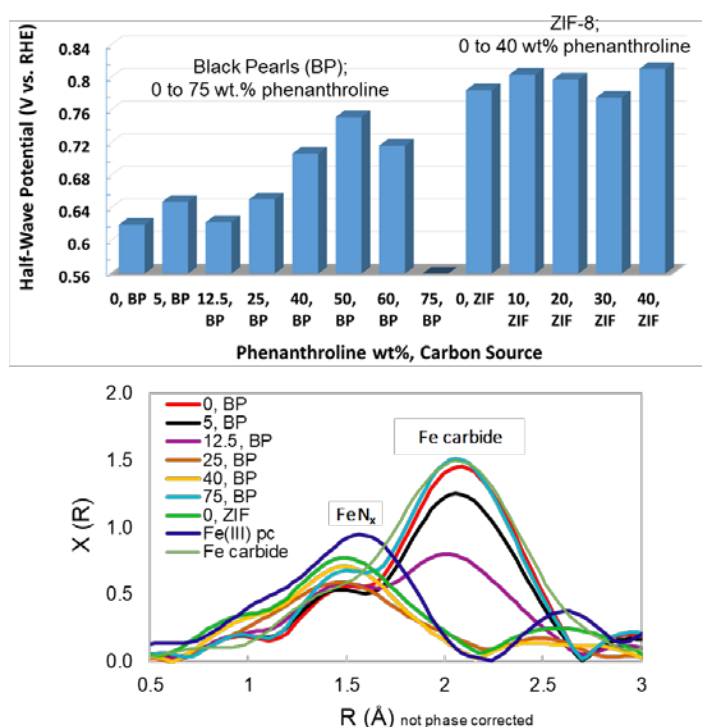

Figure 5. High-throughput synthesis of catalysts (with fixed 0.5 wt % Fe content in precursor): effect of carbon source and Fe content on ORR activity (top). Fourier transformed EXAFS data for catalysts synthesized using different phenanthroline contents and carbon sources. Catalyst synthesis: iron acetate; precursors ball-milled, heat-treated at 1,050°C (5°C/min) in Ar for 1 h; heat-treated at 950°C in ammonia for 5 min. Rotating disk electrode evaluation of ORR activity: catalyst loading 0.6 mg/cm², O₂-saturated 0.5 M H₂SO₄, steady-state current measurements, carbon-rod counter electrode.

Catalyst Durability

In spite of several reports of poor shelf stability of many, especially the most ORR-active MOF-derived catalysts, the (AD)Fe-N-C catalyst showed no performance loss when stored under ambient conditions for as long as nine months. However, both this and the CM-PANI-Fe-C(Zn) catalyst noted fast loss in their initial activity during operation in a hydrogen-oxygen cell. The drop in current occurred across the entire range of studied voltages, from the open cell voltage (ca. 1.0 V at the beginning of testing) to ca. 0.2 V. Significant loss in the current density at the reference voltage of 0.90 V (44% after three polarization cycles) implied

considerable active site loss. Operando XAFS experiments involving CM-PANI-Fe(Zn)-C catalyst pointed to FeN_x site oxidation during 0.70 V hold in oxygen, coincident with the loss in performance. It was possible to reduce Fe back to its original state during cathode purge with helium but without a recovery in fuel cell performance. These results pointed to irreversible loss of active sites, rather than structural or chemical alteration of the Fe-N/O sites, as the cause of the overall performance loss.

Because free radicals (e.g., ·OOH [hydroperoxyl radical]) formed via Fenton reactions are likely one of the causes of PGM-free catalyst degradation, the durability of the (CM+PANI)-Fe-C(Zn) catalyst was studied with and without a ceria-based radical scavenger physically mixed into the catalysts (Figure 6). Experiments (in collaboration with the Pacific Northwest National Laboratory-led FOA project) were carried out using a system designed for parallel studies of F^- (fluoride), CO_2 (carbon dioxide), and transition metal emissions from the cathode of an MEA during fuel cell operation. Following initial CO_2 emissions, most likely due to the removal of oxygen-functionalized carbons, the cathode with 5 wt % of radical scavenger in the catalyst layer showed stable performance during 0.30 V hold, lower CO_2 emissions, and nearly negligible fluoride emissions. Fe and Zn were detected in the effluent water (0.09 $\mu g_{Fe}/cm^2$ h and 0.56 $\mu g_{Zn}/cm^2$ h) during break-in, but CO_2 and fluoride emissions remained relatively low. These results suggest the use of radical scavengers as one possible route toward stabilizing PGM-free ORR catalysts in the PEFC cathode during fuel cell operation.

Paths toward Power Density Improvement for PGM-Free Cathodes

Even the highest-to-date demonstrated performance of PGM-free catalysts in PEFC cathodes is insufficient to meet power requirements of a fuel cell power system for automotive applications. Systematic improvements are thus needed in catalyst activity and electrode structure to reach 1,000 mW/cm^2 power density in a 90 kW_e stack while meeting Q/dT = 1.45 kW/°C target at 2.5 bar inlet pressure, 95°C coolant exit temperature, and 1.5 cathode stoichiometry. Relative to the current (AD)Fe-N-C catalyst, the needed advances, depicted in Figure 7, include (1) reduction in kinetic losses by a 12-fold increase in the catalyst mass activity, (2) reduction in cathode catalyst layer ohmic losses via a 2-fold increase in the active site density and engineered electrode structure for 50% lower sheet resistance, and (3) management of mass transfer losses via 50% reduction in the electrode thickness.
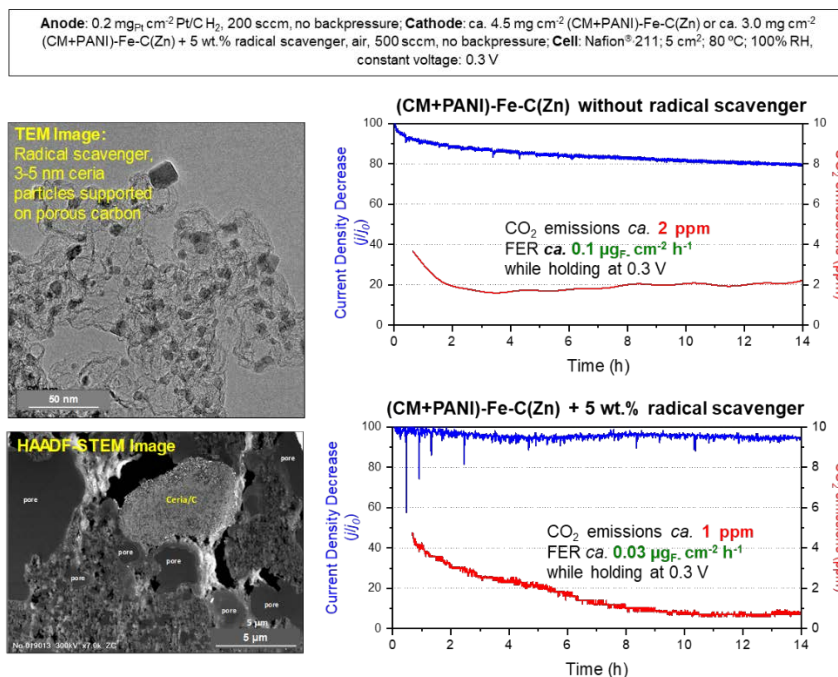

Figure 6. Catalyst durability testing of the (CM+PANI)-Fe(Zn)-C catalyst with and without a ceria-based radical scavenger. The TEM and HAADF-STEM (high-angle annular dark field–scanning transmission electron microscopy) images of the catalyst are shown on the left.
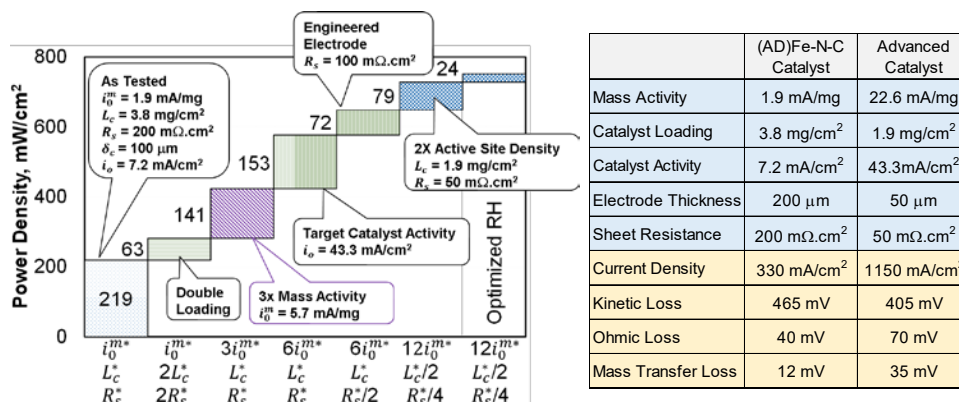
	(AD)Fe-N-C Catalyst	Advanced Catalyst
Mass Activity	1.9 mA/mg	22.6 mA/mg
Catalyst Loading	3.8 mg/cm²	1.9 mg/cm²
Catalyst Activity	7.2 mA/cm²	43.3mA/cm²
Electrode Thickness	200 μm	50 μm
Sheet Resistance	200 mΩ.cm²	50 mΩ.cm²
Current Density	330 mA/cm²	1150 mA/cm²
Kinetic Loss	465 mV	405 mV
Ohmic Loss	40 mV	70 mV
Mass Transfer Loss	12 mV	35 mV

Figure 7. Paths toward power density improvement for PGM-free cathodes.

CONCLUSIONS AND UPCOMING ACTIVITIES

The following are the main conclusions from ElectroCat activities in the period covered by this report and preceding research:

- The existing challenges notwithstanding, very significant improvements to ORR activity of PGM-free electrocatalysts have been achieved in merely one decade of research (Figure 8).

- PGM-free catalyst activity in an MEA of 33 mA/cm² at 0.90 $V_{iR\text{-free}}$ (an average from four independent experiments) and hydrogen-air performance of 107 mA/cm² was achieved using the CM-PANI-Fe(Zn)-C catalyst.

- Further improvement to the power density of PGM-free cathodes is necessary to meet automotive fuel cell stack power requirements.

- While noticeable enhancements to catalyst stability, especially during storage, have been demonstrated, performance durability represents a major challenge for PGM-free electrocatalysis. In response to this challenge, significant progress in the understanding of causes of performance loss under the fuel cell operating conditions have been accomplished. The results point to carbon corrosion, especially at high voltages (high cathode potentials), and de-metalation, especially at low voltages (low cathode potentials).

- Preliminary studies involving radical remediation attest to reduced degradation rates in the presence of a radical scavenger.

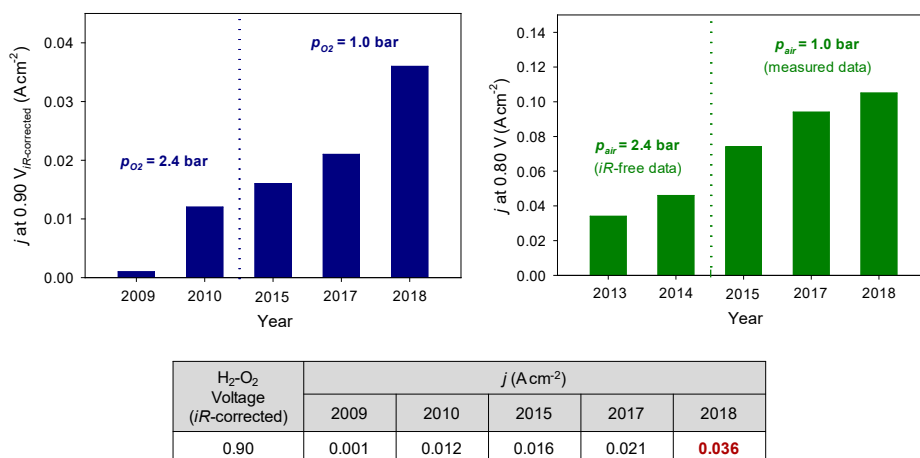| H₂-O₂ Voltage (iR-corrected)	j (A cm⁻²)				
	2009	2010	2015	2017	2018
0.90	0.001	0.012	0.016	0.021	**0.036**

Figure 8. Progress in fuel cell performance of PGM-free ORR catalysts from 2008 to 2018 (H₂-air performance not recorded before 2013).

The following are the remaining challenges and barriers in the development and implementation of PGM-free ORR catalysts:

- Limited stability of PGM-free electrodes under steady-state and load-cycling conditions and under AST cycling, especially in air

- Still inadequate understanding of the catalyst and electrode degradation mechanism(s)

- PGM-free catalyst ORR activity in need of further improvement (12x over the current status)

- Improved electrode design and catalyst-ionomer integration to provide adequate ionic, electronic, and mass transport to and from active sites

- Materials and synthetic techniques to increase active site density while avoiding spectator species formation (e.g., Fe metal clusters and carbides)

- Further development of radical scavengers and methods of their incorporation into the catalyst layer to mitigate the effects of hydroperoxyl radical formation, likely responsible for ionomer and/or carbon matrix degradation.

With the above challenges in mind, ElectroCat efforts in the immediate future will focus on improvements in performance and durability of catalysts and electrodes, including:

- Further identification of primary factors governing the durability of PGM-free catalysts and electrodes and continued development of means to prevent performance degradation

- Advancements in fuel cell performance of catalysts by maximizing volumetric density and accessibility of active sites, through (1) the development of novel synthesis approaches using information from in situ characterization techniques; and (2) optimization of hierarchical pore-size and ionomer distribution using information from imaging, X-ray scattering, and multi-scale modeling efforts

- Determination and optimization of fuel cell performance of high-throughput-synthesized materials with the highest activity; further exploration of synthetic conditions, dopants, and non-Fe metals

- Correlation of probe desorption temperatures with site identity and poisoning of ORR activity.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. H.T. Chung and P. Zelenay, "Non-Precious Metal Catalysts Prepared from Precursors Comprising Cyanamide and Polyaniline," U.S. Patent 9,979,026 issued on May 22, 2018.

FY 2019 PUBLICATIONS/PRESENTATIONS

Publication 1 (APR Reference). The following are lists of ElectroCat publications and presentations in the period covered by this report (May 2018–May 2019).

Publications

1. Y. Shao, J.-P. Dodelet, G. Wu, and P. Zelenay, "PGM-Free Cathode Catalysts for PEM Fuel Cells: A Mini-Review on Stability Challenges," *Adv. Mater.* 31 (2019): 1807615.

2. Y. He, S. Hwang, D.A. Cullen, M. A. Uddin, L. Langhorst, B. Li, S. Karakalos, A.J. Kropf, E.C. Wegener, J. Sokolowski, M. Chen, D. Myers, D. Su, K. L. More, G. Wang, S. Litster, and G. Wu, "Highly Active Atomically Dispersed CoN_4 Fuel Cell Cathode Catalysts Derived from Surfactant-assisted MOFs: Carbon-shell Confinement Strategy," *Energy Environ. Sci.* 12, no. 1 (2019): 250–260.

3. U. Martinez, S. Komini Babu, E. F. Holby, H. T. Chung, X. Yin, and P. Zelenay, "Progress in the Development of Fe-based PGM-free Electrocatalysts for Oxygen Reduction Reaction," *Adv. Mater.* 31 (2019): 1806545.

4. J. Li, M. Chen, D.A. Cullen, S. Hwang, M. Wang, B. Li, K. Liu, S. Karakalos, M. Lucero, H. Zhang, C. Lei, H. Xu, G.E. Sterbinsky, Z. Feng, D. Su, K. L. More, G. Wang, Z. Wang, and G. Wu, "Atomically Dispersed Manganese Catalysts for Oxygen Reduction in Proton-exchange Membrane Fuel Cells," *Nature Catal.* 1, no. 12 (2019): 950.

5. I.A. Rutkowska, A. Wadas, S. Zoladek, M. Skunik-Nuckowska, K. Miecznikowski, E. Negro, V. Di Noto, A. Zlotorowicz, P. Zelenay, and P.J. Kulesza, "Activation of Reduced-Graphene-Oxide Supported Pt Nanoparticles by Aligning with WO_3^- Nanowires toward Oxygen Reduction in Acid Medium: Diagnosis with Rotating-Ring-Disk Voltammetry and Double-Potential-Step Chronocoulometry," *J. Electrochem. Soc.* 165, no. 15 (2018): J3384–J3391.

6. D.J. Myers and P. Zelenay, "ElectroCat (Electrocatalysis Consortium)," *Hydrogen and Fuel Cells Program 2018 Annual Progress Report*, Fuel Cells / Catalysts & Electrodes (Washington, DC: U.S. Department of Energy Hydrogen and Fuel Cells Program, 2019); 13 pp.

7. D. Kim, N.P. Zussblatt, H.T. Chung, S.M. Becwar, P. Zelenay, B.F. Chmelka, "Highly Graphitic Mesoporous Fe,N-doped Carbon Materials for Oxygen Reduction Electrochemical Catalysts," *ACS Appl. Mater. Interfaces* 10 (2018): 25337–25349.

8. X. Yin and P. Zelenay, "Kinetic Models for the Degradation Mechanism of the PGM-Free ORR Catalysts," *ECS Trans.* 85, no. 13 (2018): 1239–1250.

9. P.J. Kulesza, J.K. Zak, I.A. Rutkowska, B. Dembinska, S. Zoladek, K. Miecznikowski, E. Negro, V. Di Noto, and P. Zelenay, "Elucidation of Role of Graphene in Catalytic Designs for Electroreduction of Oxygen," *Curr. Opin. Electrochem*. 9 (2018): 257–264.

10. U. Martinez, S. Komini Babu, E.F. Holby, and P. Zelenay, "Durability Challenges and Perspective in the Development of PGM-free Electrocatalysts," *Curr. Opin. Electrochem.* 9 (2018): 224–232.

11. S. Mukherjee, D.A. Cullen, S. Karakalos, K. Liu, H. Zhang, S. Zhao, H. Xu, K.L. More, G. Wang, and G. Wu, "Metal-Organic Framework-Derived Nitrogen-Doped Highly Disordered Carbon for Electrochemical Ammonia Synthesis using N_2 and H_2O in Alkaline Electrolytes," *Nano Energy* 48 (2018): 217–226.

12. S.T. Thompson, A.R. Wilson, P. Zelenay, D.J. Myers, K.L. More, K.C. Neyerlin, and D. Papageorgopoulos, "ElectroCat: DOE's Approach to PGM-Free Catalyst and Electrode R&D," *Solid State Ionics* 319 (2018): 68–76.

Presentations

1. P. Zelenay, "Oxygen Reduction at PGM-free Electrocatalysts: Coming of Age?" (invited lecture), 3rd International Fuel Cells Workshop, Tel Aviv–Ramat Gan, Israel, October 29–November 1, 2018.

2. U. Martinez, S. Komini Babu, E.F. Holby, X. Yin, B.T. Manard, and P. Zelenay, "Identification of Possible Degradation Mechanisms of PGM-Free Electrocatalysts during Fuel Cell Operation," AiMES 2018 and 234th Meeting of The Electrochemical Society, Cancun, Mexico, September 30–October 4, 2018.

3. H.T. Chung, D.A. Cullen, X. Yin, S. Komini Babu, K.L. More, D.J. Myers, and P. Zelenay, "Activity and Durability Insights for Atomically Dispersed (AD)Fe-N-C Oxygen Reduction Catalysts," AiMES 2018 and 234th Meeting of The Electrochemical Society, Cancun, Mexico, September 30–October 4, 2018.

4. D.J. Myers, A.J. Kropf, D. Yang, C. Yang, H. Mistry, F. Cetinbas, R. Ahluwalia, J. Park, N. Kariuki, S. Komini Babu, H.T. Chung, and P. Zelenay, "X-Ray Absorption Spectroscopy, Scattering, and Tomography Characterization of Platinum Group Metal-Free Oxygen Reduction Reaction Catalysts and Electrodes," AiMES 2018 and 234th Meeting of The Electrochemical Society, Cancun, Mexico, September 30–October 4, 2018.

5. J. Park, N. Kariuki, D.J. Myers, H.T. Chung, U. Martinez, and P. Zelenay, "High-Throughput Performance Testing in 25-Electrode Array Fuel Cell for Platinum Group Metal-Free Catalysts," AiMES 2018 and 234th Meeting of The Electrochemical Society, Cancun, Mexico, September 30–October 4, 2018.

6. D.A. Cullen, K.L. More, D.J. Myers, G. Wu, S. Litster, H. Xu, H.T. Chung, and P. Zelenay, "Formation of Metal-Nitrogen Sites in Atomically-Dispersed Catalysts Observed by *in situ* Microscopy," AiMES 2018 and 234th Meeting of The Electrochemical Society, Cancun, Mexico, September 30–October 4, 2018.

7. S. Komini Babu, U. Martinez, E.F. Holby, N. Kariuki, K.P. Ramaiyan, K. Artyushkova, G.M. Purdy, H.T. Chung, D.J. Myers, and P. Zelenay, "Molecular Probes for the Identification and Quantification of Active Sites in PGM-free ORR Catalysts," AiMES 2018 and 234th Meeting of The Electrochemical Society, Cancun, Mexico, September 30–October 4, 2018.

8. P. Zelenay, U. Martinez, S. Komini Babu, H.T. Chung, X. Yin, and E.F. Holby, "Recent Advances in PGM-Free Electrocatalysis of Oxygen Reduction" (invited plenary lecture), International Symposium on Electrocatalysis, Szczyrk, Poland, August 29–September 1, 2018.

9. D.J. Myers, "Performance and Durability of Low Platinum and Platinum Group Metal-free Polymer Electrolyte Fuel Cells" (invited plenary lecture), International Conference on Electrochemical Energy Science and Technology, Niagara Falls, Ontario, Canada, August 16, 2018.

10. D.A. Cullen and K.L. More, "Direct Observation of Atomically Dispersed Catalysts for Oxygen Reduction" (invited lecture), 256th ACS National Meeting, Boston, MA, August 19–23, 2018.

11. D.J. Myers, "X-Ray Scattering, Spectroscopy and Tomography Characterization of PEFC Cathode Catalysts, Inks, and Electrodes" (invited lecture), 2018 Gordon Research Conference–Fuel Cells, Smithfield, Rhode Island, July 29–August 3, 2018.

12. S. Komini Babu, U. Martinez, E.F. Holby, D. Myers, H.T. Chung, and P. Zelenay, "ORR Active Site Probing on PGM-Free Catalysts" (poster presentation; **best poster award**), 2018 Gordon Research Conference–Fuel Cells, Smithfield, Rhode Island, July 29–August 3, 2018.

13. D.J. Myers and P. Zelenay, "ElectroCat (Electrocatalysis Consortium)" (DOE invited lecture). DOE Hydrogen and Fuel Cells Program 2018 Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 13–15, 2018.

14. D.J. Myers, A.J. Kropf, and D. Yang, "In Situ X-ray Absorption Spectroscopy Characterization of Iron-Carbon-Nitrogen Oxygen Reduction Reaction Catalysts during Pyrolysis" (invited lecture), 233rd Meeting of the Electrochemical Society, Seattle, Washington, May 13–17, 2018.

15. L. Osmieri, X. Wang, F. Cetinbas, H.T. Chung, X. Yin, S. Kabir, D.J. Myers, P. Zelenay, R. Ahluwalia, and K.C. Neyerlin, "Operando Determination of Oxygen Reduction Reaction Kinetics on PGM-Free Electrocatalysts in a PEFC," 233rd Meeting of the Electrochemical Society, Seattle, Washington, May 13–17, 2018.

16. X. Yin, U. Martinez, S. Komini Babu, H.T. Chung, G.M. Purdy, and P. Zelenay, "Kinetic Insight into the Degradation Mechanism of PGM-Free ORR Catalysts" (invited lecture), 233rd Meeting of the Electrochemical Society, Seattle, Washington, May 13–17, 2018.

17. P. Zelenay, "The Progress and Challenges in Oxygen Reduction Electrocatalysis without Precious Metals" (invited keynote lecture), 233rd Meeting of the Electrochemical Society, Seattle, Washington, May 13–17, 2018.

18. J. Park, N. Kariuki, D.J. Myers, B.T. Hohman, S. Lee, H.T. Chung, U. Martinez, and P. Zelenay, "High-Throughput Activity and Performance Screening Methods for PGM-Free Catalysts," 233rd Meeting of the Electrochemical Society, Seattle, Washington, May 13–17, 2018.

19. D. Cullen, B. Sneed, K. More, H. Chung, E. Holby, P. Zelenay, J. Spendelow, and G. Wu, "Atomic-Level Transformations in Platinum Group Metal-Free Electrocatalysts Observed during *in situ* Annealing," 2018 Materials Research Society Spring Meeting and Exhibit, Phoenix, Arizona, April 2–6, 2018.