

# ElectroCat (Electrocatalysis Consortium)

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Project Start Date: February 1, 2016

Project End Date: September 30, 2020

## Consortium 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 capabilities available to industry and academic partners.

## Fiscal Year (FY) 2018 Objectives

### Argonne National Laboratory (ANL)

- Identity of X-ray absorption near-edge structure (XANES) spectroscopy and extended region features that are correlated with oxygen reduction reaction (ORR) activity for the atomically dispersed iron-nitrogen-carbon ((AD)Fe-N-C) catalysts using X-ray absorption fine structure (XAFS) spectroscopy data acquired from ex situ samples, in situ electrochemical experiments, and in situ pyrolysis experiments. Select and prepare six PGM-free electrode specimens and obtain 3-D micro-structures using synchrotron X-ray computed tomography (XCT).

- Automated deposition of catalyst-ionomer inks on multichannel flow double electrode (m-CFDE) glassy carbon electrodes demonstrated to result in ORR half-wave potentials within 10 mV of those measured using rotating disk electrode (RDE).
- Hydrogen-oxygen and hydrogen-air polarization curves measured for 25 electrodes simultaneously with different catalyst and ionomer-to-carbon ratios in the 25 cathode catalyst layers. Catalysts will include catalysts in the (AD)Fe-N-C class arising from high-throughput synthesis task.

### Los Alamos National Laboratory (LANL)

- Demonstrate five-fold (400%) improvement in fuel cell performance of (AD)Fe-N-C catalysts at 0.80 V (measured) at 0.2 bar partial pressure of O<sub>2</sub> and cell temperature of 80°C.
- Evaluate active-site specificity of molecular probe methodology for PGM-free catalysts; compare binding motifs (structures and energies) of three different probe molecules adsorbed at no less than three sites local for selected Fe-based sites in activity/durability library via density functional theory.
- Identify possible degradation mechanisms via experiment and theory. Validation and publication on durability descriptor calculation automation (DDCA)-based modeling approach and calculation of activity descriptor for locally degraded structures (addition to calculated active-site library); qualification and comparison of empirical activity-loss reaction kinetic model to DDCA atomic-scale model; corroboration from active-site probe methodology and CO<sub>2</sub>/F<sup>-</sup>/transition-metal emission measurements.

### National Renewable Energy Laboratory (NREL)

- Demonstrate that the powder sputter and implant system (PSIS)-prepared PGM-free catalyst (e.g., deposited Fe<sub>x</sub>N<sub>y</sub> on black pearl) is capable of achieving a half-wave potential 0.70 V versus reversible hydrogen electrode (RHE) for the ORR with 85% selectivity.
- Demonstrate homogeneous current distribution in a subset of 6 to 7 segments located between

the bend regions and along a straight channel section in segmented cell. The current densities of all segments in this subset must be within 10% of those in a standard 5 cm<sup>2</sup> test cell while using identical PGM-free electrode compositions in both cells.

- Demonstrate the capability to fabricate PGM-free electrodes with ionomer or electrocatalyst gradients in x, y, and z dimensions.
- Separate the pressure dependent (Fickian) and independent (non-Fickian) transport resistances for at least two types of PGM-free electrocatalyst/electrode combinations.

#### Oak Ridge National Laboratory (ORNL)

- Conduct high-resolution scanning transmission electron microscopy (TEM) imaging and spectroscopy on at least three new (AD)-Fe-N-C catalysts and at least three metal organic framework/zeolitic imidazolate framework (ZIF)-derived catalysts in coordination with synthesis efforts at LANL and high-throughput methods at ANL. These studies will focus on understanding morphological aspects of catalysts in addition to identification of potential active sites.
- Characterize at least four PGM-free MEAs before and after degradation testing using analytical electron microscopy and tomography. This effort will be highly coordinated with efforts at LANL to develop protocols to assess performance and durability of PGM-free catalysts and with XCT and XAFS efforts at ANL.
- Complete evaluation of ORNL's new "pixel array detector" combined with cryo-electron microscopy (imaging and spectroscopy) to image/analyze thin ionomer layers in optimized PGM-free electrode morphologies.

#### ElectroCat Annual Milestone

- Achieve PGM-free cathode MEA performance in an H<sub>2</sub>-O<sub>2</sub> fuel cell of 25 mA cm<sup>-2</sup> at 0.90 V (*iR*-corrected) at 1.0 bar partial pressure of O<sub>2</sub> 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.

#### 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>:

- (A) Durability (catalyst, MEA)
- (B) Cost (catalyst)
- (C) Performance (catalyst, MEA).

#### Technical Targets

This project focuses on the development and implementation of high-performing and durable PGM-free cathode catalysts for polymer electrolyte fuel cells (PEFCs), following DOE technical targets outlined in the Fuel Cells section of the Multi-Year Research, Development, and Demonstration Plan.<sup>1</sup> The overall goal is durable PGM-free ORR catalysts that achieve an activity of 0.044 A/cm<sup>2</sup> at 0.90 V in a PEFC MEA by 2020.

#### FY 2018 Accomplishments

##### ElectroCat Development and Communication

- National laboratories are supporting four federal funding opportunity announcement (FOA) projects with 10 capabilities.
- New national laboratory capabilities were submitted, reviewed, and selected by DOE and the Steering Committee in April 2018.
- A publicly accessible data-management hub for national laboratory and FOA project datasets was developed and launched (<https://datahub.electrocat.org>).
- Nine papers were published, including one in *Science*, and 28 presentations were given (11 invited).

##### Performance Improvement

- Accomplished and exceeded ElectroCat FY 2017 annual milestones of 20 mA cm<sup>-2</sup> at 0.90

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

V (H<sub>2</sub>/O<sub>2</sub>, *i*<sub>R-free</sub>) and 100 mA cm<sup>-2</sup> at 0.80 V (H<sub>2</sub>/air).

- Achieved four-fold improvement of the H<sub>2</sub>-air fuel cell performance at 0.80 V of the (AD)Fe-N-C catalyst, from 9 mA cm<sup>-2</sup> to 36 mA cm<sup>-2</sup> since the 2017 report.
- Reached half-wave potential (*E*<sub>1/2</sub>) of 0.85 V with (AD)Fe-N-C in RDE testing, an increase of 0.02 V over the 2017 status.
- Improved PGM-free catalyst activity in an MEA: 21 mA/cm<sup>2</sup> at 0.90 V<sub>*i*<sub>R-free</sub></sub> and 0.044 A/cm<sup>2</sup> at 0.88 V (H<sub>2</sub>-O<sub>2</sub> fuel cell).

#### Characterization and Capability Development

- Correlated ORR activity with FeN<sub>4</sub> content; identified spectroscopic signatures of FeN<sub>4</sub> content.
- Determined that FeN<sub>x</sub> site is formed and zinc is removed from Fe-Zn-ZIF at temperatures as low as 900°C.
- Successfully used NO and NO<sub>2</sub><sup>-</sup> as molecular probes for ORR-active surface sites.
- Obtained further direct evidence of a majority of Fe sites being atomically dispersed and on the (AD)Fe-N-C catalyst surface using TEM, a molecular probe, and X-ray spectroscopy.
- Used TEM and XAFS to characterize Fe species and structure evolution during heat treatment, obtaining guidance for improved catalyst synthesis.

- Characterized the atomic structure and ORR activity of 40 combinatorial (Zn<sub>1-x</sub>Fe<sub>x</sub>)ZIF-F catalysts using XAFS and m-CFDE cell, identifying materials with potentially >5x ORR activity of baseline composition.
- Developed system for automated deposition of multiple inks resulting in *E*<sub>1/2</sub> agreement between m-CFDE and RDE of 5 mV for PGM-free catalysts.
- Further refined the capability to characterize by XAFS the atomic structure of catalysts during heat treatment, determining the evolution of Fe species.
- Acquired MEA kinetic data for (AD)Fe-N-C cathode and applied the distributed ORR model to determine reaction order, activation energy, and the potential dependence of active site availability.

#### ORR Active-Site Activity and Durability Modeling

- Calculated binding energies of potential probes/poisons to various active-site structures.
- Utilized model descriptors to determine that N loss is likely responsible for PGM-free catalyst activity decrease.
- Developed and utilized logistic decay model to describe autocatalytic degradation mechanism 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 <sub>2</sub> -air fuel cell performance	mA/cm <sup>2</sup> @ 800 mV (measured)	300	105
PGM-free catalyst activity	mA/cm <sup>2</sup> @ 900 mV <sub><i>i</i><sub>R-free</sub></sub>	≥44	21

## 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 is comprised of four core national laboratories contributing their expertise in characterization, materials, and electrode synthesis/fabrication testing and diagnostics, modeling, and fabrication. These existing and demonstrated capabilities were utilized in 2018 to support the R&D efforts in the four ElectroCat 2017 FOA projects. Critical aspects of the EMN consortia are the evaluation of the utility of existing capabilities and the influx of new capabilities. This year, two capabilities were discontinued and four capabilities were added. These new capabilities—currently under evaluation—are in the areas of temperature-programmed desorption of probe molecules, wetting properties of catalysts, refined calculation of reaction energetics, and electrospinning of electrodes.

### PGM-Free Catalyst Development and Characterization

**Catalysts with improved microporosity:** Highly porous PGM-free catalysts developed from a simple synthesis process using Zn salts (zinc chloride) and cyanamide and polyaniline as the sources of carbon and nitrogen, were further improved by using magnetic separation to decrease the content of undesired iron species prior to a final heat treatment in an inert atmosphere. Catalyst performance in the fuel cell also was improved by tuning the ionomer content and ionomer type utilized in the cathode catalyst layer. A hydrogen-oxygen fuel cell performance of 21 mA cm<sup>-2</sup> at 0.90 V (*iR*-free) and a hydrogen-air fuel cell performance of 105 mA cm<sup>-2</sup> were achieved using this approach. The hydrogen-oxygen performance exceeded the ElectroCat annual milestone of 20 mA cm<sup>-2</sup> and the hydrogen-air performance represents an increase of 28% over that reported in the 2017 ElectroCat Annual Progress Report (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 Zn-derived ZIFs as the parent structures. The synthesis of the catalyst precursor has been tuned to achieve a fibrous structure with the goal of enhancing the porosity of the resulting catalyst. By tuning the catalyst synthesis procedure and the electrode composition, the hydrogen-air fuel cell performance of the (AD)Fe-N-C catalyst was improved four-fold (9 mA cm<sup>-2</sup> to 36 mA cm<sup>-2</sup> at 0.80 V) since publication of the ElectroCat 2017 Annual Progress Report (Figure 2). The ORR activity of these catalysts has been correlated with their FeN<sub>x</sub> content using linear combination fitting of the XANES spectra. XAFS analyses of these materials during the heat-treatment synthetic step shows that the proposed FeN<sub>x</sub> active sites are formed between 650°C and 885°C (Figure 3), concurrent with Zn evaporation. The XAFS analyses also showed that FeN<sub>x</sub> can be converted to iron carbide and metal during the heat treatment step of holding at 1,000°C. The purpose of these studies is to guide the synthetic effort in maximizing the volumetric density of FeN<sub>x</sub> sites to enhance the ORR activity of this class of catalysts.

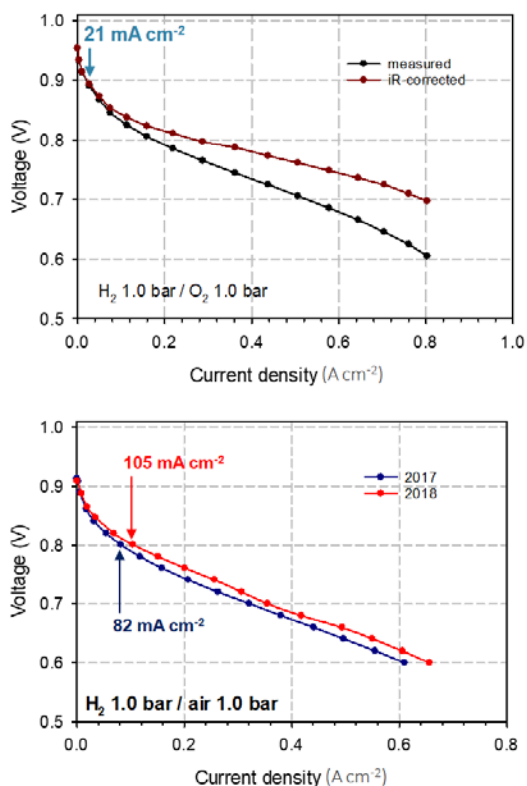


Figure 1. Hydrogen-oxygen performance and improvement in hydrogen-air fuel cell performance of (CM+PANI)-Fe-C(Zn) PGM-free catalyst compared to 2017 performance reported at the DOE 2017 Annual Merit Review

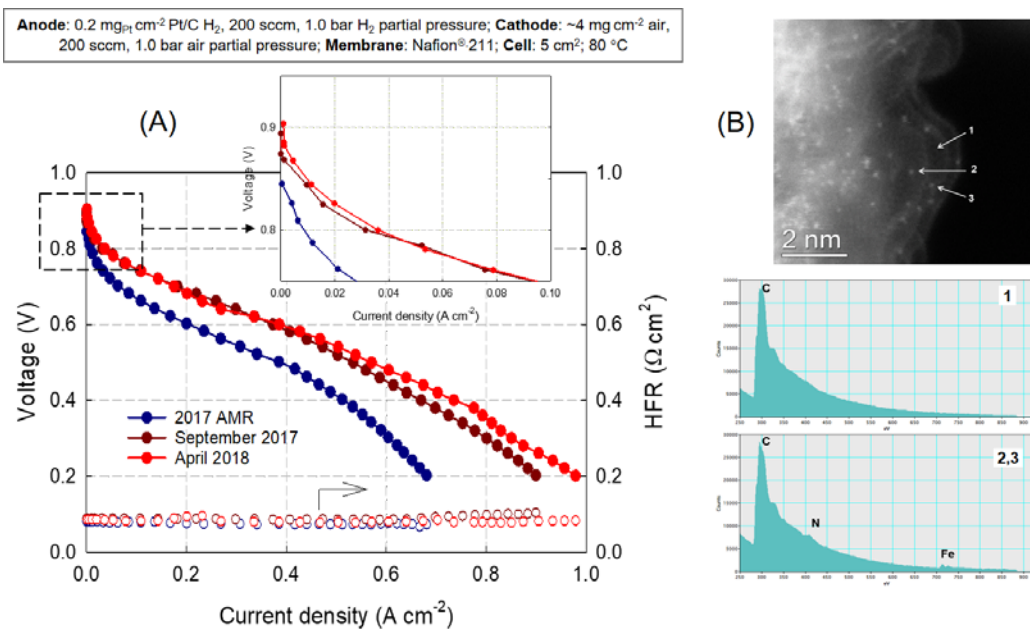


Figure 2. (A) Improvement of hydrogen-air fuel cell performance of (AD)Fe-N-C catalyst (red curve) compared to September 2017 and performance reported at DOE 2017 Annual Merit Review. (B) High-resolution TEM image and electron energy loss spectra of the (AD)Fe-N-C catalyst.

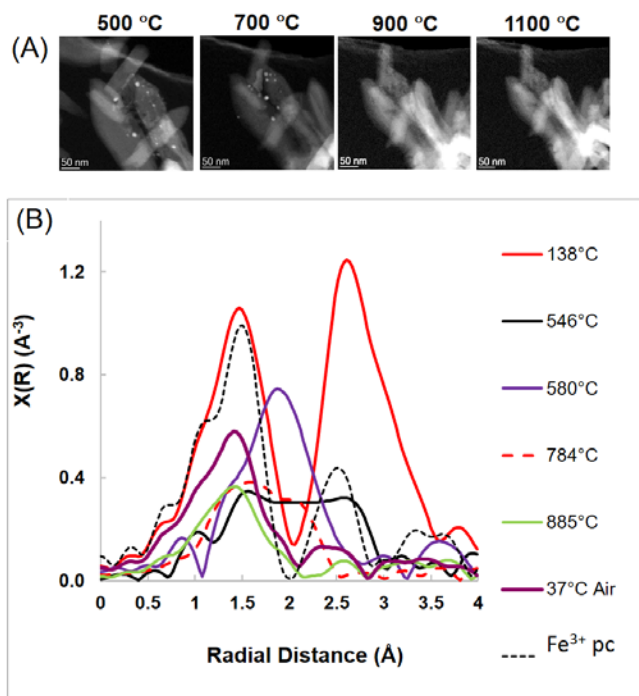


Figure 3. (A) TEM micrographs of (AD)Fe-N-C precursor during heat treatment. (B) Fourier transforms of iron K-edge XAFS showing evolution of iron speciation in the (AD)Fe-N-C catalyst precursor during high temperature heat treatment. The Fourier transform of an  $\text{FeN}_4$  standard ( $\text{Fe}^{3+}$  phthalocyanine,  $\text{Fe}^{3+}$  pc) is shown for comparison (dotted line).

**Direct detection of active sites:** Spectroscopic and electrochemical experiments with probe molecules were utilized to determine the density of active sites in the (AD)Fe-N-C class of catalysts (Figure 4). These experiments—utilizing nitrite as a source of the nitric oxide probe molecule—showed that the active site density is approximately  $3 \times 10^{12}$  sites  $\text{cm}^{-2}$  (approximately 0.5/Fe atom) and that the turnover frequency for ORR on these sites at 0.80 V is  $1.7 \text{ e}^- \text{ site}^{-1} \text{ s}^{-1}$ . The accompanying potential-dependent XAFS data indicate that poisoning of the ORR occurs both with and without coordination of nitric oxide to the Fe center, pointing to a complex multi-atom active site or multiple active sites, beyond  $\text{FeN}_x$  alone. Accompanying density functional theory calculations have identified that probe molecules bind to Fe and to the graphene only in the presence of defects or epoxides local to the  $\text{FeN}_x$  sites.

**ORR kinetics:** Multiple MEAs with (AD)Fe-N-C cathode catalysts were tested under a variety of oxygen partial pressures and temperatures and the results were utilized as input to a distributed ORR kinetic model to derive the ORR reaction order and activation energy. These data also were fit to a potential-dependent active site availability model, based on a reduced form of the Fe center being the active site. This fit showed that near the open circuit less than 10% of the active sites are available; 100% availability is achieved at approximately 0.65 V; and the redox potential for the Fe center is 0.79 V, agreeing well with voltammetric results (Figure 5). The effective number of electrons transferred in this redox transition was calculated to be 0.7, which agrees with that calculated from linear combination fitting of potential-dependent XAFS data.

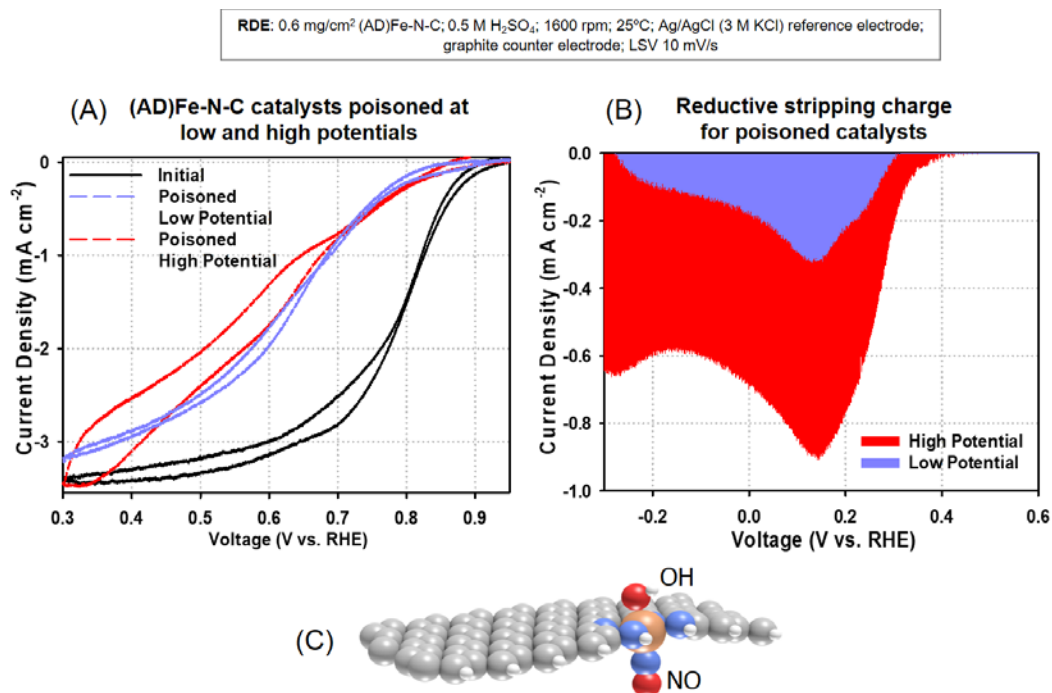


Figure 4. (A) Rotating disk electrode ORR traces of the (AD)Fe-N-C catalyst before and after exposure to nitrite probe at low and high potentials. (B) Voltammetric stripping charge for NO adsorbed from a nitrite solution at high and low potentials. (C) Depiction of active site poisoned by NO probe molecule.

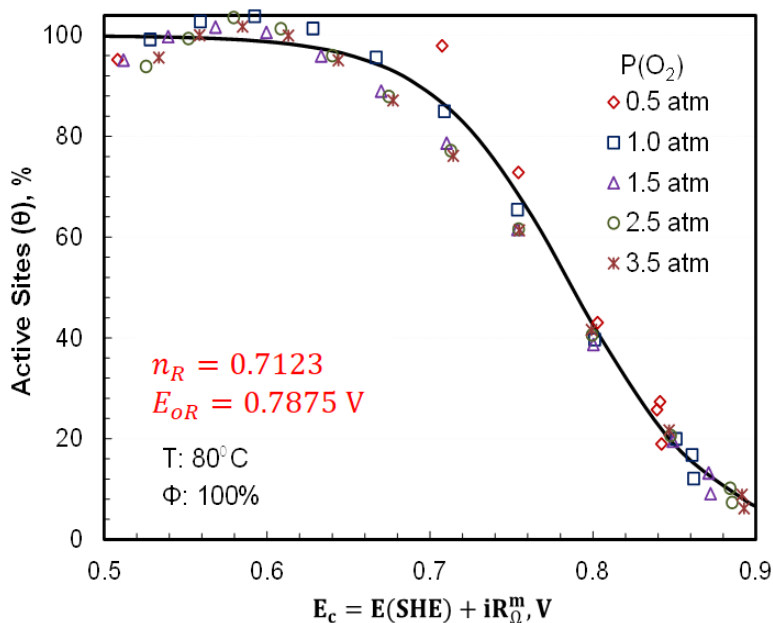


Figure 5. Fitting of the performance data for cells with (AD)Fe-N-C cathode catalyst taken with different cathode gas oxygen partial pressures to extract the availability of active sites as a function of  $iR$ -corrected cathode potential

**Catalyst durability:** A system was implemented for the parallel studies of F<sup>-</sup>, CO<sub>2</sub>, and transition metal emissions from the cathode of an MEA at various operating conditions to gain better understanding of the possible degradation mechanisms of PGM-free catalysts. Degradation studies of the (CM+PANI)-Fe(Zn)-C catalyst operating on air showed low CO<sub>2</sub> and F<sup>-</sup> emissions over all cell voltages. Carbon dioxide generation

increased when operating on oxygen instead of air, with the accompanying low fluoride emission rate pointing to the catalyst rather than the membrane being the source of the detected CO<sub>2</sub>. Post-test characterization by scanning electron microscopy, EDX, and X-ray photoelectron spectroscopy (XPS) suggest that demetallation—likely following the loss of nitrogen coordination—is the main mechanism for activity loss of (CM+PANI)-Fe-C(Zn) catalysts (Figure 6). Kinetic models for MEA performance degradation suggest a two-step autocatalytic degradation mechanism where a deactivation agent, such as peroxide, is produced from the reactants.

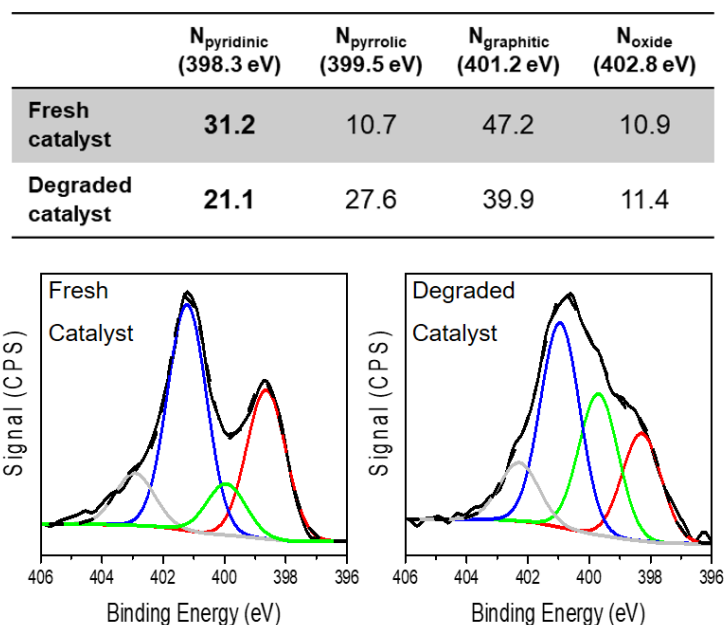


Figure 6. XPS spectra and XPS fitting results of a fresh (CM+PANI)-Fe-C(Zn) catalyst and of the same catalyst that has been degraded in an MEA

**High-throughput synthesis, characterization, and performance evaluation of PGM-free catalysts and electrodes:** A high-throughput and, where possible, combinatorial approach to synthesis, characterization, ORR-activity measurement, electrode fabrication, and fuel cell performance testing has been utilized to expedite progress toward achieving the ElectroCat goals. A robotic system was used to synthesis the (Zn<sub>x</sub>Fe<sub>1-x</sub>)ZIF-F catalyst precursors with five different iron contents and three different iron salts, and these precursors were heat-treated in a multi-sample tube furnace at three different temperatures to produce 40 unique samples. The ORR activities of the resulting catalysts were screened using a combinatorial hydrodynamic cell. The fuel cell performance was evaluated using 25-electrode combinatorial fuel cell hardware. The atomic structure, phase composition, and near-surface composition were characterized using X-ray diffraction, X-ray spectroscopy, electron energy loss spectroscopy, and XPS, respectively. The characterization showed that the fraction of Fe present as an FeN<sub>x</sub> species was highest at the lowest heat-treatment temperature and with a Fe-to-Zn atomic ratio in the precursor of 2.5:97.5 (Figure 7). Higher heat-treatment temperatures and Fe contents favored formation of graphite-encased iron carbide species at the expense of FeN<sub>x</sub> sites, and a reduction of near-surface Fe, pyridinic N, C/N, and clustering of atomically dispersed Fe and an increase in the degree of graphitization of the carbon matrix. The highest ORR activities were achieved using the iron nitrate and sulfate precursors, pyrolysis temperatures of 900°C and 1,000°C, and intermediate Fe-to-Zn atomic ratios (2.5:97.5 and 5:95).



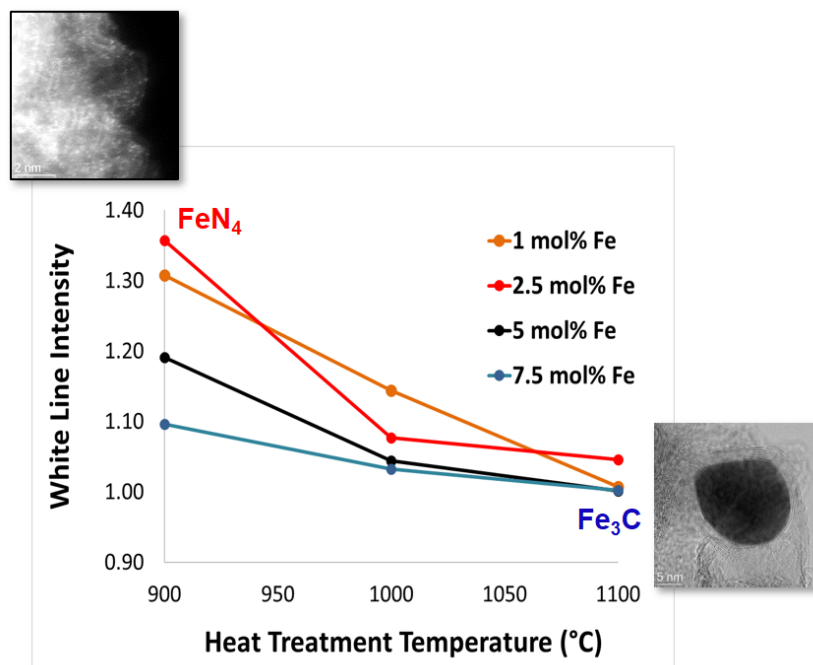


Figure 7. White line intensity in the Fe K-edge XAFS of (AD)Fe-N-C catalysts as a function of initial Fe content in the ZIF precursor and the heat-treatment temperature. The white line intensity has been shown to be proportional to the fraction of Fe in the  $\text{FeN}_4$  coordination environment. Insets: atomic dispersion of Fe-N sites in catalyst (upper left) and graphite encased iron carbide particle (lower right).

### Capability Development

ElectroCat is developing several capabilities that show potential to impact PGM-free electrocatalyst development. Examples of these capabilities are the combinatorial screening of catalyst activity using an m-CFDE cell and combinatorial fuel cell testing using segmented cell hardware. These capabilities were further developed and demonstrated this year. An automated deposition system using a programmable XY stage and a nanoliter injector was developed to deposit catalyst-ionomer inks on the 1-mm by 3-mm glassy carbon electrodes of the m-CFDE. An ORR half-wave potential agreement with RDE results of 5 mV was achieved using this deposition, versus the 30 mV agreement achieved last year with non-automated deposition. A system was developed for fabrication of electrodes with a gradient of catalyst/ionomer ratio and demonstrated for an 8-cm-long deposition. A Kelvin probe was validated as a quick screening tool to quantify ionomer gradients in electrodes. This deposition system is being used in concert with a segmented cell to accelerate the optimization of catalyst/ionomer ratio for improved performance of PGM-free electrodes and to evaluate the effects of electrode composition on durability.

### CONCLUSIONS AND UPCOMING ACTIVITIES

The following are highlighted conclusions from the ElectroCat activities thus far.

- An Fe-N-C catalyst, (AD)Fe-N-C, was further developed and characterized this year resulting in a 20 mV increase in ORR half-wave potential in RDE testing versus last year's status, and a four-fold improvement in fuel cell performance at 0.80 V ( $36 \text{ mA cm}^{-2}$  versus  $9 \text{ mA cm}^{-2}$ ). This catalyst has the majority of Fe sites on the surface of the catalyst and able to adsorb probe molecules and oxygen with a representative active site density of approximately  $3 \times 10^{12} \text{ sites cm}^{-2}$  and an ORR turnover frequency of  $1.7 \text{ e}^- \text{ site}^{-1} \text{ s}^{-1}$ . ORR activity was correlated with  $\text{FeN}_x$  species content in the catalyst.

- The proposed FeN<sub>x</sub> active sites are formed at temperatures as low as 900°C, with higher temperatures causing formation of inactive carbide species and clustering of the atomically-dispersed Fe sites but formation of the more stable graphitic versus amorphous carbon.
- Availability of the (AD)Fe-N-C active sites in a fuel cell electrode was correlated with reduction of the Fe center with a fit redox potential of 0.79 V and ORR reaction order and activation energy of 0.70 kJ/mol and 62 kJ/mol, respectively.
- PGM-free catalyst activity in an MEA of 21 mA cm<sup>-2</sup> at 0.90 V<sub>iR-free</sub> and hydrogen-air performance of 105 mA cm<sup>-2</sup> were achieved using the CM-PANI-Fe-C(Zn) catalyst.
- Loss of PGM-free electrode performance is primarily due to loss of catalyst ORR activity, with results thus far suggesting activity loss is related to demetallation, likely following the loss of nitrogen coordination through a two-step autocatalytic degradation mechanism.

The following are the remaining challenges and barriers in developing and implementing PGM-free ORR catalysts.

- Insufficient stability of metal organic framework–based catalyst powders and electrodes.
- Limited stability of PGM-free electrodes under steady-state and load-cycling conditions.
- Inadequate understanding of the catalyst and electrode degradation mechanism.
- ORR activity of PGM-free catalysts in continued need of further improvement to reduce cathode thickness and lower cost of other stack components.
- Development of surface-specific characterization techniques and molecular probes for carbon-based materials.
- Electrode design and catalyst-ionomer integration to provide adequate ionic, electronic, and mass transport to and from active sites.
- Replacement of Fe in catalyst with another PGM-free transition metal not catalyzing hydroperoxyl radical formation and ionomer degradation.
- Integration with existing automotive fuel cell stack and system technology.

The focus of future work to address these challenges includes the following.

### **ElectroCat Development**

- Demonstrate or utilize recently selected national laboratory capabilities.
- Incorporate collaborators from DE-FOA-0001874 into ElectroCat and coordinate activities of all ElectroCat partners.
- Populate Data Hub with datasets from national laboratory and FOA partners; implement automated methods for data capture and publication.
- Develop automated artificial intelligence and machine learning techniques for data correlation and experimental design.

### Improvement in Performance and Durability of Catalysts and Electrodes

- Further identify primary factors governing the durability of PGM-free catalysts and electrodes, and develop means to prevent performance degradation.
- Advance fuel cell performance of catalysts by maximizing volumetric density and accessibility of active sites, through the development of novel synthesis approaches, using information from in situ characterization techniques; and optimization of hierarchical pore-size and ionomer distribution, using information from imaging, X-ray scattering, and multi-scale modeling efforts.
- Verify synthesis and activity of promising materials (e.g., 900°C, 5 at% Fe) identified in initial screening, scale up synthesis, and test fuel cell performance and durability.
- Continue to develop surface-specific methods for ORR active-site determination (e.g., probe molecules).

### SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. 2017 R&D 100 Award for *Clean-Energy Electrocatalysts Without Precious Metals*, Los Alamos National Laboratory, P. Zelenay (PI) (joint entry with Pajarito Powder, LLC).

### FY 2018 PUBLICATIONS/PRESENTATIONS

#### Publications

1. Chung, H.T., D.A. Cullen, D. Higgins, B.T. Sneed, E.F. Holby, K.L. More, and P. Zelenay. "Direct Atomic-Level Insight into the Active Sites of a High-Performance PGM-Free ORR Catalyst." *Science* 357 (6350), 479–484, 2017.
2. Dekel, D.R., M. Page, C. Bae, Y. Yan, P. Zelenay, Y.S. Kim, and S. Gottesfeld. "Anion Exchange Membrane Fuel Cells: Current Status and Remaining Challenges." *J. Power Sources* 375, 351–360, 2018.
3. Kneebone, J.L., S.L. Daifuku, J.A. Kehl, G. Wu, H.T. Chung, M.Y. Hu, E.E. Alp, K.L. More, P. Zelenay, E.F. Holby, and M.L. Neidig. "A Combined Probe-Molecule, Mössbauer, Nuclear Resonance Vibrational Spectroscopy and Density Functional Theory Approach for Evaluation of Potential Iron Active Sites in an Oxygen Reduction Reaction Catalyst." *J. Phys. Chem. C* 121 (30), 16283–16290, 2017.
4. Komini Babu, S., H.T. Chung, P. Zelenay, and S. Litster. "Modeling Electrochemical Performance of the Hierarchical Morphology of Precious Group Metal-Free Cathode for Polymer Electrolyte Fuel Cell." *J. Electrochem. Soc.* 164 (9), F1037–F1049, 2017.
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7. Mukherjee, S., D.A. Cullen, S. Karakalos, K. Liu, H. Zhang, S. Zhao, K.L. More, G. Wang, and G. Wu. "Metal-Organic Framework-Derived Nitrogen-Doped Highly Disordered Carbon for Electrochemical Ammonia Synthesis Using N<sub>2</sub> and H<sub>2</sub>O in Alkaline Electrolytes." *Nano Energy* 48, 217–226, 2018.
8. Thompson, S.T., A.R. Wilson, P. Zelenay, D.J. Myers, K.L. More, K.C. Neyerlin, and D. Papageorgopolous. "ElectroCat: DOE's Approach to PGM-Free Catalyst and Electrode R&D." *Solid State Ionics* 319, 68–76, 2018.
9. Yin, X., L. Lin, H.T. Chung, S. Komini Babu, U. Martinez, G.M. Purdy, and P. Zelenay. "Effects of MEA Fabrication and Ionomer Composition on Fuel Cell Performance of PGM-Free ORR Catalyst." *ECS Trans.* 77 (11) 1273–1281, 2017.

**Presentations**

1. Cetinbas, C.F., X. Wang, R.K. Ahluwalia, N.N. Kariuki, R. Winarski, V.J. De Andrade, and D.J. Myers. “PEFC Cathode Catalyst Layer Electrode Microstructure Analysis and Transport Modeling” (invited lecture). 21st International Conference on Solid State Ionics (SSI-21), Padua, Italy, June 18–23, 2017.
2. Cetinbas, F., N. Kariuki, R. Ahluwalia, H.T. Chung, P. Zelenay, and D.J. Myers. “PGM-Free Electrode Microstructure Analysis and Transport Modeling.” 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1–5, 2017.
3. Chung, H., D.A. Cullen, B.T. Sneed, H.M. Meyer III, L. Lin, X. Yin, K.L. More, and P. Zelenay. “Atomically Dispersed (AD)Fe-N-C Oxygen Reduction Catalysts for Polymer Electrolyte Membrane Fuel Cells.” 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1–5, 2017.
4. Cullen, D.A., B.T. Sneed, and K.L. More. “Overcoming the Challenges of Beam-Sensitivity in Fuel Cell Electrodes.” Microscopy & Microanalysis 2017, St. Louis, Missouri, August 6–10, 2017.
5. Cullen, D.A., B.T. Sneed, G. Wu, J. Spendelow, H.T. Chung, P. Zelenay, and K.L. More. “Electron Microscopy Observations of Catalyst-Support Interactions in Polymer Electrolyte Membrane Fuel Cells.” 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1–5, 2017.
6. Holby, E.F., U. Martinez, H.T. Chung, and P. Zelenay. “Modeling Durability of PGM-Free Active Site Structures at the Atomic Scale.” 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1–5, 2017.
7. Komini Babu, S., S. Ogawa, H.T. Chung, P. Zelenay, and S. Litster. “Porous Electrode Engineering for Platinum Group Metal-Free Oxygen Reduction Reaction Catalysts” (invited lecture). 231st Meeting of the Electrochemical Society, New Orleans, Louisiana, May 28–June 1, 2017.
8. Komini Babu, S., U. Martinez, H. Chung, L. Lin, X. Yin, and P. Zelenay. “Influence of Transition Metal and Synthesis Methodology on the Active Site Density on the Surface of PGM-Free Catalysts.” 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1–5, 2017.
9. Martinez, U., S. Komini Babu, H.T. Chung, L. Lin, G.M. Purdy, and P. Zelenay. “Structure-Activity-Durability Relationships of (CM+PANI)-Me-C PGM-free Catalysts.” 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1–5, 2017.
10. Myers, D. “Activity, Performance, and Durability of Polymer Electrolyte Fuel Cell Catalysts and Electrodes” (invited lecture). 2nd International Fuel Cells Workshop, Ramat Gan, Israel, October 30–31, 2017.
11. Myers, D., J. Park, N. Kariuki, M. Ferrandon, A.J. Kropf, D. Yang, H. Lv, A. Zakutayev, G. Bender, and H. Dinh. “High-Throughput Experimental Activities in ElectroCat.” ElectroCat Modeling Workshop, Washington, D.C., September 20, 2017.
12. Myers, D.J., M. Ferrandon, A.J. Kropf, D. Yang, N.N. Kariuki, J. Park, and S. Lee. “High-Throughput Synthesis and Characterization of PGM-Free Oxygen Reduction Reaction Electrocatalysts.” 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1–5, 2017.
13. Ogawa, S., S. Komini Babu, E. Padgett, H.T. Chung, P. Zelenay, A. Kongkanand, and S. Litster. “Microstructural Modeling of PEFC Catalyst Layer Performance and Durability.” 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1–5, 2017.
14. Wilson, A.R., D.C. Papageorgopoulos, D.J. Myers, P. Zelenay, H.N. Dinh, and K.L. More. “The Electrocat (Electrocatalysis) Consortium” (invited lecture). 231st Meeting of the Electrochemical Society, New Orleans, Louisiana, May 28–June 1, 2017.
15. Yin, X., H.T. Chung, L. Lin, G.M. Purdy, U. Martinez, and P. Zelenay. “High-Performance PGM-Free Electrocatalysts for the Polymer Electrolyte Fuel Cell Cathode” (invited lecture). 231st Meeting of the Electrochemical Society, New Orleans, Louisiana, May 28–June 1, 2017.

16. Yin, X., L. Lin, H.T. Chung, S. Komini Babu, U. Martinez, G.M. Purdy, and P. Zelenay. “Effects of Porosity and Ionomer Composition on Fuel Cell Performance of PGM-Free ORR Catalysts.” 231st Meeting of the Electrochemical Society, New Orleans, Louisiana, May 28–June 1, 2017.
17. Yin, X., L. Lin, U. Martinez, H.T. Chung, and P. Zelenay. “Organic Molecular Catalyst for Electrochemical Production of Hydrogen Peroxide.” 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1–5, 2017.
18. Zelenay, P. “ElectroCat Overview” (invited lecture). ElectroCat Modeling Workshop, Washington, D.C., September 20, 2017.
19. Zelenay, P. “Electrocatalysis of Oxygen Reduction at Platinum Group Metal-Free Catalysts” (invited lecture). University of California Merced, School of Natural Sciences, Chemistry and Chemical Biology, Merced, California, October 20, 2017.
20. Zelenay, P. “Electrocatalysis Without Precious Metals” (invited lecture). American Chemical Society National Meeting and Exposition, March 18–22, 2018.
21. Zelenay, P. “Introduction to PGM-Free Catalysis and Protocols.” DOE Catalysis-Durability Working Group Meeting, Argonne National Laboratory, Lemont, Illinois, May 2–3, 2017.
22. Zelenay, P. “Oxygen Reduction at Platinum Group Metal-Free Electrocatalysts: Progress in Performance and Understanding of Reaction Mechanism” (invited lecture). Colorado School of Mines, Golden, Colorado, December 8, 2017.
23. Zelenay, P. “PGM-Free Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells: State of the Art and Challenges” (invited lecture). University of California Santa Cruz, Chemistry and Biochemistry, Santa Cruz, California, October 23, 2017.
24. Zelenay, P. “PGM-Free ORR Electrocatalysis: Progress and Challenges on the Path to Viability” (invited lecture). Israel Research Center for Electrochemical Propulsion (INREP) Energy Conference, Bar-Ilan University, Ramat Gan, Israel, May 9–10, 2017.
25. Zelenay, P. “Platinum Group Metal-Free Electrocatalysts for Oxygen Reduction in Fuel Cells” (invited lecture). Milan Polytechnic, Milan, Italy, June 27, 2017.
26. Zelenay, P. “Recent Developments in PGM-Free Electrocatalysis of Oxygen Reduction” (invited lecture). 2nd International Fuel Cells Workshop, Ramat Gan, Israel, October 30–31, 2017.
27. Zelenay, P., and D.J. Myers. “ElectroCat (Electrocatalysis Consortium).” U.S. Department of Energy, Energy Efficiency and Renewable Energy, Fuel Cell Technologies Program, 2017 Merit Review and Peer Evaluation Meeting, Washington, D.C., June 5–9, 2017.
28. Zhang, H., H.T. Chung, D.A. Cullen, K.L. More, P. Zelenay, and G. Wu. “Metal-Organic Framework-Derived Atomic Iron-Dispersed Carbon Electrocatalysts for Oxygen Reduction in Acidic Polymer Electrolyte Fuel Cells.” 231st Meeting of the Electrochemical Society, New Orleans, Louisiana, May 28–June 1, 2017.