
ElectroCat: Platinum-Group-Metal-Free Engineered Framework Nano-Structure Catalyst

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Contract Number: DE-EE0008077

Subcontractors:

- Savannah River National Laboratory, Aiken, SC
- Northwestern University, Evanston, IL

Project Start Date: September 1, 2017

Project End Date: December 31, 2020

Overall Objectives

- Develop catalysts based on high-surface-area polymers.
- Synthesize platinum group metal (PGM)-free electrocatalysts with well-defined functional groups and structures.
- Characterize PGM-free electrocatalysts to probe any possible correlation between their physical and chemical attributes and their electrochemical performance.
- Active site modeling: model PGM-free engineered framework nano-structure catalyst with ideal structure.
- Conduct membrane electrode assembly (MEA) optimization and fuel cell testing.
- Meet DOE's 2020 activity target: 30 mA cm⁻² at 0.90 V_{IR-free} in an H₂-O₂ fuel cell.
- Deliver six or more MEAs to the Electrocatalysis Consortium (ElectroCat), each with active area ≥50 cm² for independent testing and evaluation.

Fiscal Year (FY) 2018 Objectives

- Greenway Energy, LLC (GWE), Savannah River National Laboratory (SRNL), and Northwestern University (NU) will collaborate to prepare PGM-free engineered framework nano-structure catalysts using a rational catalyst design with well-defined structures and functional groups consisting of “phen”-type coordination sites (e.g., CTFs, MOFs) and porphyrinic type sites (MOFs, POPs).
- Down-select polymeric materials with high surface area, pore volume, and pyridinic N.
- Demonstrate rotating ring-disk electrode (RRDE) performance >1.5 mA cm⁻² at 0.8 V versus reversible hydrogen electrode (RHE) in 0.1 M HClO₄ acid at a loading of 0.6 mg cm⁻².
- GWE consultant Dr. Anderson, in collaboration with Dr. Holby (Los Alamos National Laboratory [LANL] ElectroCat consortium lab), will align modeling tasks with relevant experimental results.
- Initial MEA optimization and fuel cell performance testing will be performed by SRNL and GWE respectively, in collaboration with LANL ElectroCat consortium lab.
- Demonstrate catalyst activity of 20 mA cm⁻² at 0.9 V_{IR-free} in hydrogen/oxygen fuel cell.

Technical Barriers

This project addresses the following technical barriers from Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

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

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

Technical Targets

Progress toward technical targets for catalyst activity for the oxygen reduction reaction (ORR) is shown in Table 1.

FY 2018 Accomplishments

- Optimized synthesis protocol and scale-up to prepare >400 mg of “phen”-type chelating polymers, porphyrinic polymers, and high N-containing carbon-based materials per batch parameters.
- Down-selected polymeric materials for high-throughput synthesis based on RRDE screening experiments. The three materials selected are azo-polyporphyrin, phenyl-polyporphyrin, and ZIF-8 based catalysts.
- Achieved RRDE performance of 2.78 mA cm⁻² for a phenyl-polyporphyrin-based catalyst.
- Aligned the modeling tasks performed by the LANL ElectroCat consortium laboratory with the ongoing experimental research at GWE, SRNL, and NU.
- Initiated MEA optimization and fuel cell testing studies at GWE, SRNL, and LANL (ElectroCat consortium lab). Significant progress has been made toward achieving the go/no-go metrics demonstrating H₂/O₂ fuel cell performance of 16 mA cm⁻² at 0.9 V_{IR-free} (this is 80% of the target of 20 mA cm⁻²).

Table 1. Progress Toward Technical Targets for Catalyst Activity for the ORR

Metric	Units	Current Status ^a	FY18 Target	2020 DOE Target
Fuel Cell Test: Catalyst Activity	mA cm ⁻² @ 900 mV _{IR-free}	16 ^c 32 ^b	≥20 ^c	≥44 ^b
Fuel Cell Test: Catalyst Activity	mA cm ⁻² @ 800 mV	52.8	NA	NA
RRDE Test: Catalyst Activity	mA cm ⁻² @ 800 mV	2.78	≥1.5 ^d	NA

^a Current status denotes performance measurements recorded up to September 30, 2018.

^b 80 °C H₂/O₂ MEA; fully humidified, total outlet pressure 150 kPa_{abs.}; anode stoich. 2; cathode stoich. 9.5.

^c 80 °C H₂/O₂ in an MEA; total outlet pressure of 100 kPa_{abs.}.

^d 0.1 M HClO₄ acid; catalyst loading of 0.6 mg cm⁻².

INTRODUCTION

Traditional synthesis methodologies that produce durable, highly active PGM-free electrocatalysts typically consist of a top-down approach utilizing a nitrogen-coordinating precursor, a metal precursor, and a support material. Nitrogen-coordinated transition metal complexes typically are absorbed onto a support material, which is then activated via high-temperature pyrolysis. Selection of the support and the nitrogen coordinating precursor has long been the focal point of efforts to maximize the number of accessible, catalytically active sites.

In this project, GWE in collaboration with SRNL and NU will develop durable, highly active, low-cost, PGM-free electrocatalysts for polymer electrolyte membrane fuel cells designed and synthesized using a unique, bottom-up, rationally designed approach. Electrocatalysts are produced via polymerization reaction followed by a high-temperature pyrolysis step. Additionally, this project focuses on catalyst site and ORR mechanistic modeling to better understand the structure-property relationship.

APPROACH

To achieve the overall objectives, the project is divided into three main tasks that encompass the following.

- Task 1. Catalyst development and characterization. Novel electrocatalysts are produced via polymerization reactions using well-defined functional groups and structures. A rational approach is used to better understand PGM-free active site morphology and to enhance the performance of the electrocatalyst by improving active site quantity and morphology.
- Task 2. Active site modeling. Catalyst site and ORR mechanistic modeling will be performed more effectively as we incorporate data on chemical and physical characteristics gained through the bottom-up approach taken in Task 1.
- Task 3. MEA optimization and fuel cell testing. The project will culminate in internal and independent fuel cell tests (deliver six or more MEAs, each with active area ≥ 50 cm², to an ElectroCat core lab for independent testing and evaluation) demonstrating the capability of the novel catalyst materials of achieving DOE project targets and advancing the state of the art.

RESULTS

Task 1.0: Catalyst Development Based on High-Surface-Area Polymers (Month 1–36)

During the first year of the project, a large number of electrocatalysts with well-defined functional groups and structures have been synthesized via polymerization reactions and characterized. Distinct nitrogen functionalities vary among the different material families to rationally target the discovery of the active sites. Possible correlations between physical attributes and electrochemical performance have been examined. Initially, 17 families of materials consisting of “phen”-type chelating polymers, porphyrinic polymers, and high-nitrogen-containing carbon-based materials were synthesized, characterized, and screened by RRDE for oxygen-reduction activity. Subsequently, three materials that met our first year internal ORR activity target measured by RRDE (Table 1), were down-selected for further study and optimization: azo-polyporphyrin, phenyl-polyporphyrin, and ZIF-8 (Figure 1).

Polyporphyrins synthesized using pyrrole and terephthalaldehyde demonstrated the highest performance for catalyzing the ORR and have received the most focus during Budget Period 1 (BP 1). Characterization of phenyl-polyporphyrin by scanning electron microscopy and X-ray photoelectron spectroscopy shows spherical particles of ~200 nm to 300 nm in diameter (Figure 2) with nitrogen content (predominantly pyrrolic) of 11 at%. Following pyrolysis, the Brunauer-Emmett-Teller surface area increases from 16 m²/g to ~1,200 m²/g. Average particle size appears unchanged, but an increase in surface roughness is observed. Additionally, overall N content decreases by half, from 11 at% to about 5.5 at%. After pyrolysis, there is a significant increase in the fraction of pyridinic-N, and Fe content increases from 0.08 at% to about 0.35 at%. RRDE

screening indicates the polyporphyrin-based catalysts exhibit high activity for the ORR, with $E_{1/2}$ typically ranging from 0.78 V to 0.82 V. The highest performance measured for the ORR at 0.8 V versus RHE is 2.78 mA cm^{-2} .

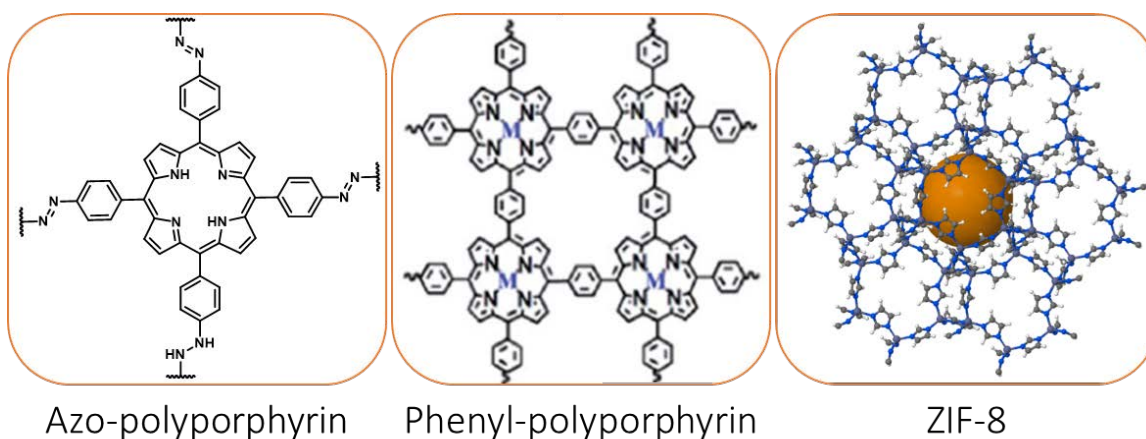


Figure 1. Structures of down-selected polymer-based catalyst precursors

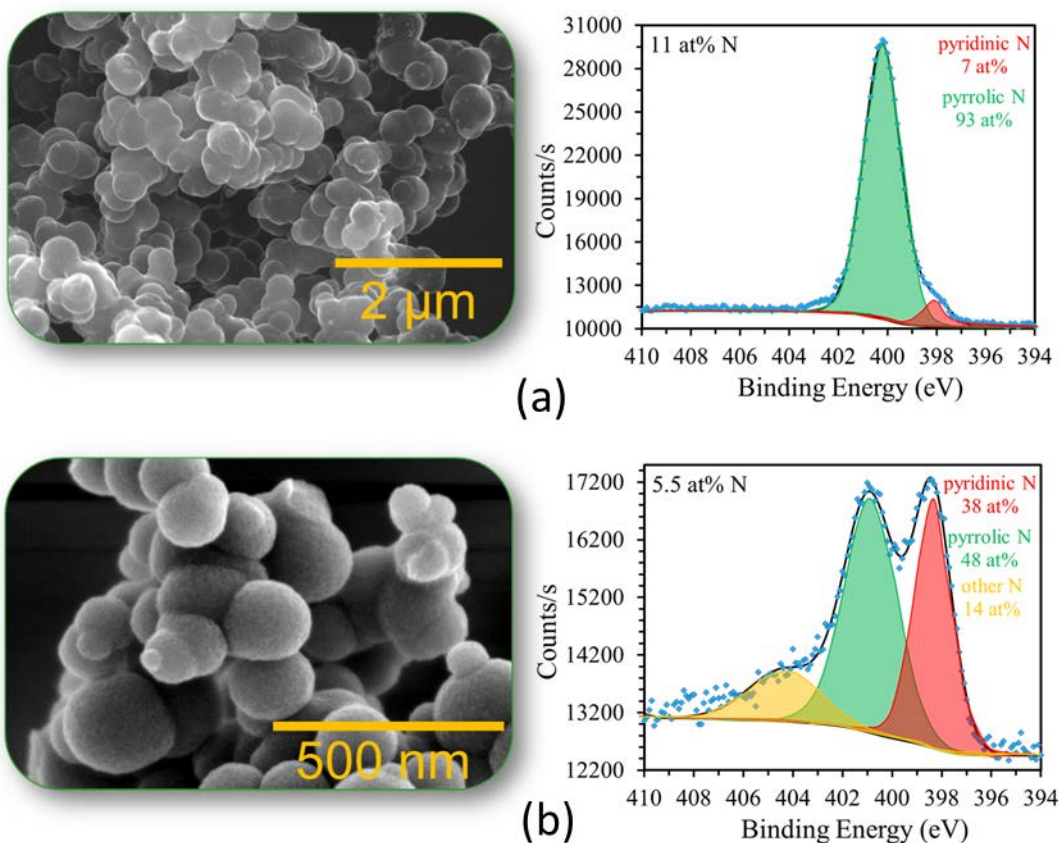


Figure 2. Scanning electron microscopy images and X-ray photoelectron spectroscopy analysis of (a) as-synthesized and (b) heat-treated polyporphyrin materials

Task 2.0: Active Site Modeling (Month 1–30)

The modeling program began with plausible Fe-N-C catalyst structures and H₂O molecules to calculate reversible potentials for steps in the pathway for the oxygen reduction reaction using adsorption energies and the linear Gibbs energy relationship. In coordination with the rational design of catalyst preparation, reactive site modeling will provide insight into the electrochemical mechanisms for the ORR and provide reversible potentials for intermediate steps and overpotentials. For the linear Gibbs energy relationship calculations of approximate reversible potentials for these reactions with intermediates adsorbed on the electrode surfaces, we used the standard experimental reversible potentials for the solution phase potentials and the corresponding Gibbs energy changes shown in Table 2.

Table 2. Solution Phase Potentials and the Corresponding Gibbs Energy Changes for Different ORR Intermediates

Reaction	$U^0(\text{V})$	$\Delta G^0(\text{eV})$
$\text{O}_2(\text{g}) + \text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{OOH}(\text{aq})$	-0.125	0.125
$\text{OOH}(\text{aq}) + \text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{O}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	0.21	-0.21
$\text{O}(\text{aq}) + \text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{OH}(\text{aq})$	2.12	-2.12
$\text{OH}(\text{aq}) + \text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{H}_2\text{O}(\text{l})$	2.72	-2.72
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23	-4.92

We assume FeN₄ when substituted into graphene is isoelectronic to Fe^{II} in iron porphyrin. Studies of reactions 1–4 over two Fe^{II} sites, two Fe^{III} sites, and two Fe^{IV} sites are the subject of this report. The Fe^{II}, Fe^{III}, and Fe^{IV} sites had the structures as shown in Figure 3. Looking down the columns of adsorption energies tabulated in Figure 3, a trend is evident; all adsorbates bond to the surfaces increasingly weakly as the Fe oxidation state increases. In past work, Dr. Anderson deduced that the ideal adsorption energies for the intermediates during the four-electron reduction of O₂ would be 0.0 eV for O₂ and H₂O and -1.35 eV, -2.49 eV, and -1.38 eV for OOH, O, and OH respectively [2]. Adsorption energies for Fe^{III} edge, Fe^{IV} bulk, and Fe^{IV} edge sites look most promising in this regard. To predict reversible potentials, however, we must use the adsorption energies of both the reactant, for example O, and product, for example OH, simultaneously. The adsorption energies of the H₂O molecule are ~ 0.5 eV, but this energy barrier will be partially offset by the interaction with water because the enthalpy of condensation for H₂O(g) is 0.45 eV.

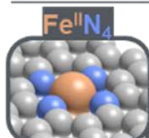
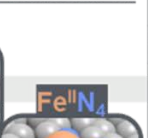

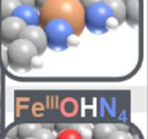

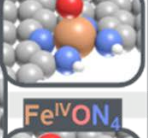

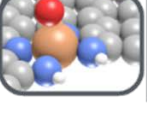
Active sites considered		O ₂	OOH	O	OH	H ₂ O
	Site	Adsorption Energy				
	Fe ^{II} bulk	-1.300	-2.160	-4.825	-3.074	-0.536
	Fe ^{II} edge	-1.053	-1.784	-4.273	-3.033	-0.490
	Fe ^{III} bulk	0.480	-2.429	-3.367	-2.095	-0.807
	Fe ^{III} edge	-0.207	-1.288	-2.864	-2.314	-0.365
	Fe ^{IV} bulk	-0.092	-1.058	-2.543	-1.616	-0.475
	Fe ^{IV} edge	-0.123	-0.805	-2.139	-1.625	-0.371
	Ideal	0.0	-1.35	-2.49	-1.38	-0.0

Figure 3. Schematic representation of various bulk and edge Fe^{II}, Fe^{III}, and Fe^{IV} active sites and adsorption energies (eV) of intermediates over Fe sites

To summarize, of the six catalyst sites explored, bulk Fe^{IV} shows the greatest promise for catalyzing four-electron reduction of O_2 to water because its predicted overpotential 0.29 V is the lowest. Edge Fe^{III} is a close second with its 0.43 predicted overpotential. No other sites are active. An issue is stabilizing Fe^{IV} against reduction to Fe^{III} . Although the calculated reversible potentials are approximate, we think our findings provide helpful guidance for catalyst development. They also correspond nicely to the ~ 0.90 V onset potential for O_2 reduction in the polarization plot for (CM+PANI)-Fe-C catalysts in the work by Chung et al. [1]. The dissociated structure of $\text{OOH}(\text{ads})$ with OH binding to C and O to Fe seen for bulk Fe^{III} and Fe^{IV} sites has not been discussed previously for carbon-based catalysts. The kinetic treatment on the combined electron transfer and bond rearrangement presents a challenge. This form of $\text{OOH}(\text{ads})$ may be important to understanding active site degradation and poisoning.

Task 3.0: MEA Optimization and Fuel Cell Testing (Month 4–36)

Selected catalysts have been successfully synthesized using a scaled-up procedure. Scale-up was necessary for producing the quantities needed for MEA fabrication and optimization. MEA optimization and fuel cell performance evaluation is in progress at LANL, in parallel with in-house fuel cell testing at SRNL and GWE. Fuel cell test results for H_2/O_2 are shown in Figure 4. Evaluation of a polyporphyrin based catalyst at LANL shows 16 mA cm^{-2} at $900 \text{ mV}_{\text{IR-free}}$, at 80°C in an MEA, with a total outlet pressure of 100 kPa (interim FY18 fuel cell target testing parameters). MEAs prepared at SRNL using the same catalyst resulted in a slightly lower performance of 12 mA cm^{-2} with the same testing conditions (Figure 4 [a and b]). Using the 2020 DOE performance target parameters (see Table 1) a current density of 32 mA cm^{-2} was measured (Figure 4 [c and d]).

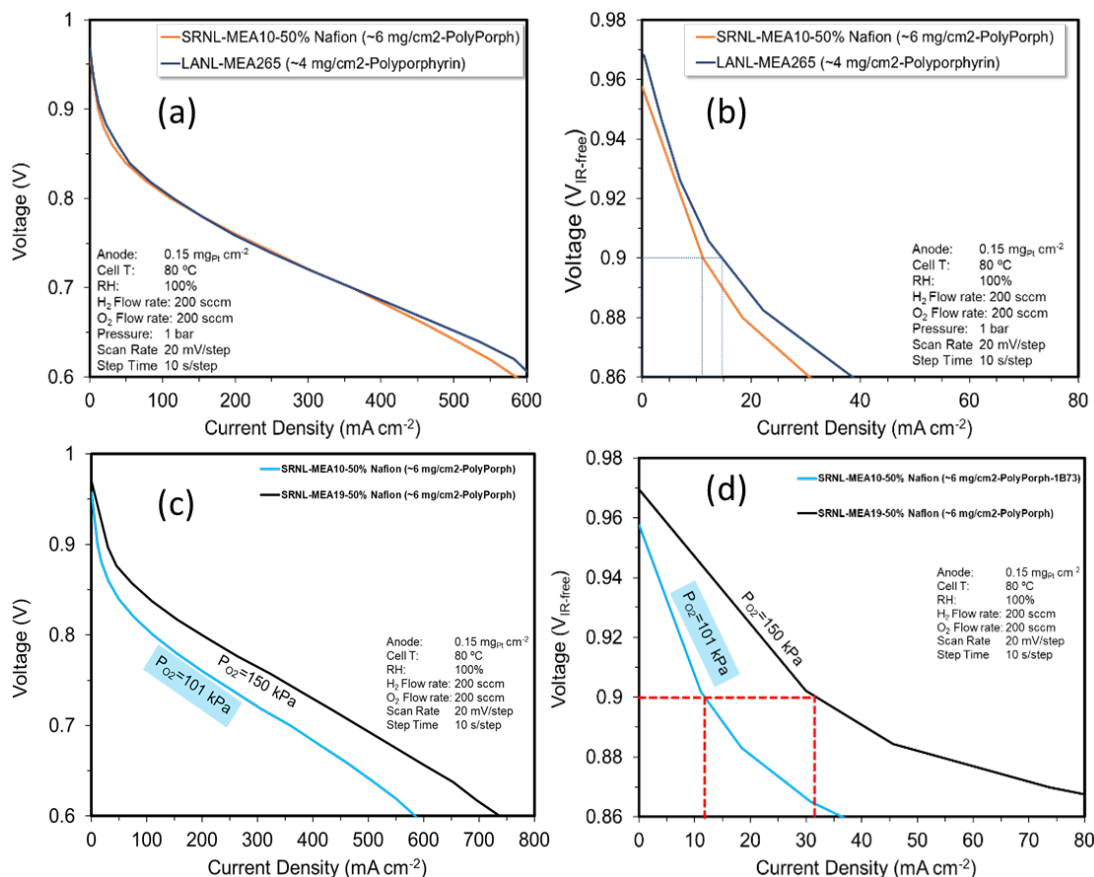


Figure 4. H_2/O_2 fuel cell performances of polyporphyrin-based catalysts at LANL and SRNL/GWE. (a) Uncorrected polarization curves, (b) IR-corrected polarization curves, (c) uncorrected polarization curves obtained at $101 \text{ kPa}_{\text{abs}}$ and $150 \text{ kPa}_{\text{abs}}$ back pressure, and (d) IR-corrected polarization curves obtained at $101 \text{ kPa}_{\text{abs}}$ and $150 \text{ kPa}_{\text{abs}}$ back pressure.

CONCLUSIONS AND UPCOMING ACTIVITIES

A wide range of metal-organic frameworks and covalent-organic frameworks were synthesized using a rational design to impart catalytic activity for the ORR. This was accomplished through the incorporation of FeN₂ moieties, or “phen”-type sites, and FeN₄ moieties, typically porphyrinic functionalities. Of the 17 families of materials screened, polyporphyrins synthesized using pyrrole and terephthalaldehyde demonstrated the highest performance for catalyzing the ORR and were down-selected for further study.

The polyporphyrin-based catalysts, unique to our research team among the ElectroCat consortium core labs and participating project teams, will be the focus during Budget Period 2 (BP 2). The ZIF-8 based catalysts will be utilized as a baseline catalyst for comparison of chemical, electrochemical, and physical properties and in MEA fabrication techniques. Additional analysis of polyporphyrin-based catalysts planned for BP2 includes detailed electron tomography (at Oak Ridge National Laboratory ElectroCat consortium lab), and X-ray techniques such as extended X-ray absorption fine structure and X-ray absorption near edge structure, to better understand the catalyst composition before and after pyrolysis, especially as it pertains to Fe moieties.

Polyporphyrins synthesized using a variety of different precursors, such as those containing 2, 3, and 4 aldehyde functional groups, will be explored during BP2, as well as the effect of different metal centers, especially Mn and Co. Heteroatom addition will be explored to address polymer stability at high potential and to tune hydrophobicity of the catalyst layer. Catalyst performance will be evaluated in H₂/O₂ and H₂/air fuel cell testing with the primary objective of achieving the BP 2 go/no-go metrics of 25 mA cm⁻² at 0.90 V_{IR-free}. Catalyst and MEA stability testing also will be initiated during BP 2.

Models developed during BP 1 will continue to be optimized during BP 2. The kinetic treatment on the combined electron transfer and bond rearrangement presents a challenge. This form of OOH(ads) could be important to understanding active site degradation and poisoning.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. “PGM-Free Engineered Framework Nano-Structure Catalysts,” 2018 DOE Hydrogen Program Fuel Cell Project Progress Report, January 4, 2018, WebEx.
2. “PGM-Free Engineered Framework Nano-Structure Catalysts,” 2018 DOE Hydrogen Program Fuel Cell Project Progress Report, March 27, 2018, Aiken SC.
3. “PGM-Free Engineered Framework Nano-Structure Catalysts,” DOE Hydrogen and Fuel Cells Program Review Presentation, June 13–15, 2018, Washington DC.
4. “PGM-Free Engineered Framework Nano-Structure Catalysts,” Go/No-Go Milestone Presentation, September 06, 2018, Aiken, SC.

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1. H.T. Chung, D.A. Cullen, D. Higgins, B.T. Sneed, E.F. Holby, K.L. More, and P. Zelenay, *Science* 357 (2017): 479.
2. A.B. Anderson, *Phys. Chem. Chem. Phys.* 14 (2012): 1330.