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

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Subcontractors:

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

Industrial Partner:

Ballard Power Systems

Collaborator:

California State University-Northridge, Northridge, CA

Project Start Date: September 1, 2017

Project End Date: December 31, 2020

Overall Objectives

- **Catalyst development based on high-surface-area polymers:** Synthesize platinum group metal (PGM)-free electrocatalysts with well-defined functional groups and structures; characterize these materials to probe any possible correlation between their physical/chemical attributes and electrochemical performance.
- **Active site modeling:** Model PGM-free engineered framework nano-structure catalyst with ideal structure.
- **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 a H₂-O₂ fuel cell.
 - Deliver six or more MEAs, each with active area ≥50 cm², to an Electrocatalysis Consortium (ElectroCat)

lab for independent testing and evaluation.

Fiscal Year (FY) 2019 Objectives

- Greenway Energy, LLC (GWE), Savannah River National Laboratory (SRNL), and Northwestern University will continue development of PGM-free engineered framework nano-structure catalysts using a rational catalyst design.
- The project team will improve oxygen reduction reaction (ORR) performance of down-selected polyporphyrin-based catalyst materials through heteroatom addition and through addition of peripheral functionalities.
- GWE consultant Dr. Anderson, in collaboration with Dr. Holby of Los Alamos National Laboratory (LANL) (an ElectroCat lab), will focus on proposing new ORR reaction pathways for the Fe-porphyrin and graphene-hosted FeN₄-type active sites.
- SRNL and GWE will perform MEA optimization and fuel cell performance testing of optimized catalysts, respectively, in collaboration with LANL.
- The project team will demonstrate catalyst activity of 25 mA cm⁻² at 0.9 V_{IR-free} in an H₂/O₂ fuel cell.

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 Plan¹:

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

Technical Targets

The DOE 2020 technical targets and our current project status are listed in Table 1 for comparison.

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

FY 2019 Accomplishments

- High-throughput synthesis of down-selected catalysts, including polyazoporphyrin, polyphenylporphyrin, and zeolitic imidazolate framework (ZIF-8) based catalysts, was performed.
- X-ray absorption spectroscopy (XAS) analysis showed single-atom Fe sites in polyporphyrin-based catalysts with Fe-N₄ sites in the “as prepared” material, and similar absorption energy to a Fe-porphine reference. Lower symmetry was observed in pyrolyzed polyporphyrin indicating some Fe-N_x (x <4) present.
- Electron microscopy studies indicated the “as prepared” particles are dense, have smooth surfaces, are mostly amorphous, and contain no Fe clusters or particles. Heat treated particles are porous/rough and meso-graphitic, exhibit some nano-porosity, and contain atomically dispersed iron.
- A new multi-valent reaction pathway was proposed based on calculations of multiple structures and multiple methods. The calculations suggest using polymerization approaches that maintain the open, 2-D nature of the applied molecules during pyrolysis to enable such pathways and to obtain high ORR activities.
- MEA optimization and fuel cell testing studies at GWE, SRNL, and LANL (ElectroCat lab) have shown significant progress. The FY 2019 and FY 2020 go/no-go H₂/O₂ fuel cell performance metrics have been met, demonstrating ORR current density of 30 mA cm⁻² at 0.9 V_{IR-free}.

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

Metric	Units	Current Status ^a	FY 2019 Target	2020 DOE Target
Fuel cell test: catalyst activity	mA cm ⁻² @ 900 mV _{IR-free}	30 ^c	≥25 ^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

RRDE – rotating ring-disk electrode

^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 are typically 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 Northwestern University is developing 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 reactions followed by a high-temperature pyrolysis step. In addition, this project also focuses on catalyst site and ORR mechanistic modeling to understand better the structure-property relationship.

APPROACH

To achieve the overall objectives, the project is divided into three main tasks which 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 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 lab for independent testing and evaluation) demonstrating the capability of the novel catalyst materials to achieve the DOE project targets and advance the state of the art.

RESULTS

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

During the first year of the project, 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. Three materials (polyazoporphyrin, polyphenylporphyrin, and ZIF-8-based catalysts) were down-selected for further optimization and analysis to take place during the second year of the project. Characterization included XAS and electron microscopy/tomography.

XAS was performed on the conventional polyphenylporphyrin catalyst (Figure 1). The “as prepared” and heat-treated materials were analyzed to provide insight on metal oxidation state and metal bonding and/or coordination environment before and after heat treatment. Rising edge absorption energy of the Fe K-edge indicates Fe was in the +3 oxidation state for both “as prepared” and pyrolyzed polyporphyrin samples. Analysis of the pre-edge peak located at $\sim 7,114$ eV shows high symmetry, a fingerprint of D_{4h} symmetry, for the “as prepared” sample. This is indicative of the Fe-N₄ moiety. The “as prepared” sample’s absorption energy is a good match to the Fe-porphine reference indicating a high likelihood the “as prepared” sample is in fact an Fe-porphine-based material. Lower symmetry is observed in the pyrolyzed sample indicating some Fe-N_x (x < 4) is present, which may be due to conversion of some Fe-N₄ moieties to Fe-N_x (x < 4) during pyrolysis. Fe K-edge extended X-ray absorption fine structure (EXAFS) analysis shows an absorption at approximately 1.5 Å for both the “as prepared” and pyrolyzed samples, which is attributed to the Fe-N scattering path. The spectrum shows the absence of a Fe-Fe signal, located at 2.13 Å, for both samples. This signifies that no Fe metallic particles are present, therefore all Fe present is composed of single atom sites like Fe-N_x (x \leq 4).

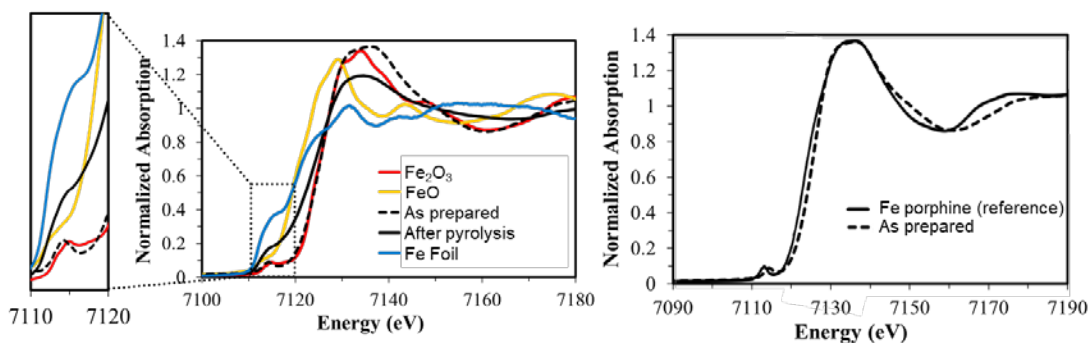


Figure 1. Fe K-edge X-ray absorption near edge structure (XANES) for conventional polyphenylporphyrin “as prepared” and after pyrolysis compared to other Fe moieties in +2 and +3 oxidation states (left), and a comparison of “as prepared” polyphenylporphyrin and an Fe-porphine reference spectrum (right).

Scanning transmission electron microscope (STEM)-based electron tomography and electron energy loss spectrometry (EELS) were performed at Oak Ridge National Laboratory (ORNL) (an ElectroCat lab). STEM-based 3-D electron tomography provided structure and composition analysis of two polyphenylporphyrin-based catalyst samples. An “as prepared” polyphenylporphyrin sample and a pyrolyzed sample were analyzed. Micrograph images show the “as prepared” and heat-treated particles are approximately the same size, around 150 to 200 nm in diameter. “As prepared” particles are dense, have smooth surfaces, and are mostly amorphous (Figure 2, left image). In addition, “as prepared” particles show evidence of Fe atoms with no Fe-containing clusters or particles observed. In contrast, heat-treated particles are meso-graphitic and exhibit nanoporosity (Figure 2, right image). The EELS study shows the presence of Fe atoms (inset in Figure 2, right) in the heat-treated particles with no Fe-containing clusters observed. The heat-treated particles show atomically dispersed Fe, with the Fe atoms associated with the basal plane edges/steps.

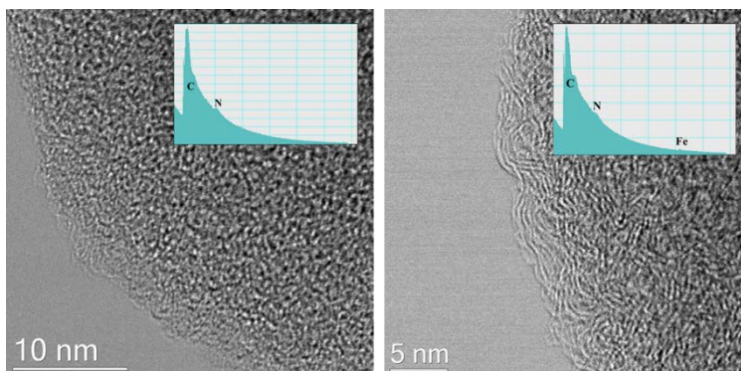


Figure 2. STEM-based electron tomography of optimized polyphenylporphyrin “as prepared” (left), and after pyrolysis (right). Inset shows EELS analysis

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

In Budget Period (BP) 2, the theory component has focused on two main areas: (1) quantifying impacts of theoretical methodology (computational hydrogen electrode [CHE] vs. linear Gibbs energy relation [LGER] thermochemical models, density functional theory methods such as exchange and correlation functionals, etc.); and (2) consideration of a variety of previously unexplored ORR pathways possible when both sides of an Fe atom as well as neighboring C binding site are included for a variety of “FeN₄”-type structures with both O and OH intermediates possibly acting as ligand modifiers.

In Figure 3, two proposed pathways within the LGER and CHE thermochemical approaches with two different exchange-correlation functionals (PBE and RPBE) for a Fe-porphyrin type catalyst are shown. In this novel pathway, a spontaneously evolved OH ligand is formed (as previously proposed) and then acts as an intermediate with the OH/O ligation effectively changing sides of the molecule during cycles of ORR. Activity is uniformly quite high across all methodologies employed.

The graphene-hosted FeN₄ structure (Figure 4) is also shown to have a fairly high ORR activity for this newly proposed pathway that only utilizes Fe binding and thus is not susceptible to C-based poisoning as suggested in literature. If such pathways are to occur, both sides of the Fe must remain accessible to the environment and not form stacked layers that could sterically block these high-activity pathways. As a result, theoretical input to the synthesis efforts suggest using polymerization approaches that maintain the open, 2-D nature of the applied molecules during pyrolysis to enable such pathways and to obtain high ORR activities.

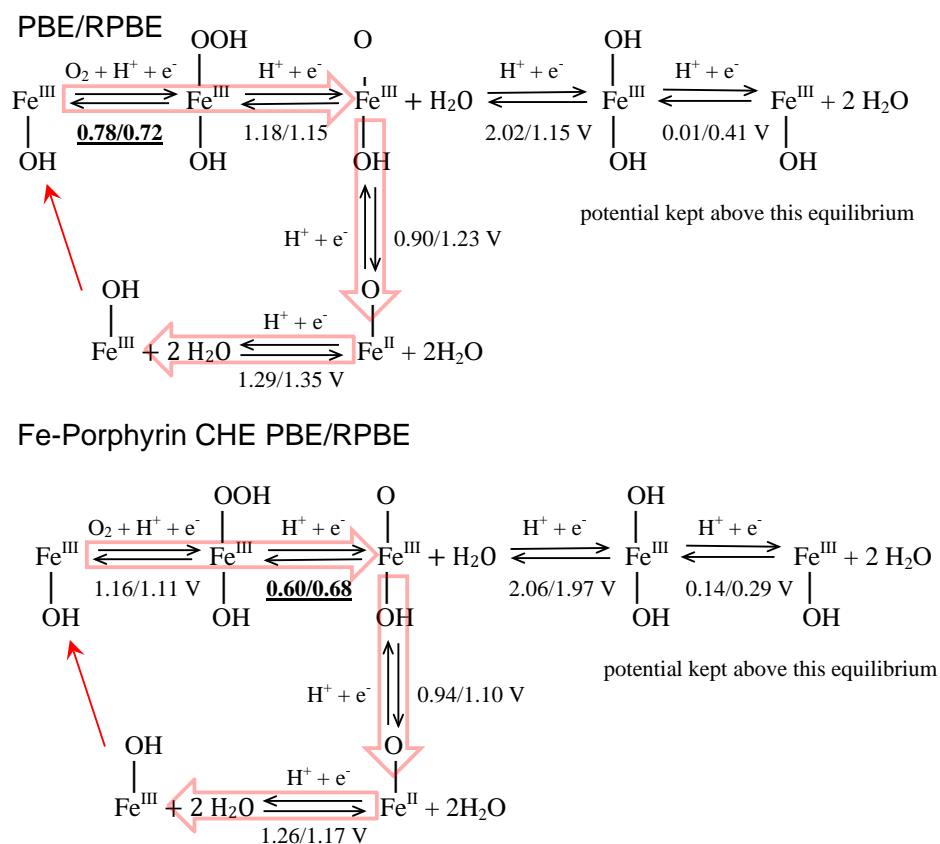


Figure 3. Proposed ORR reaction pathways in the Fe-porphyrin type active sites

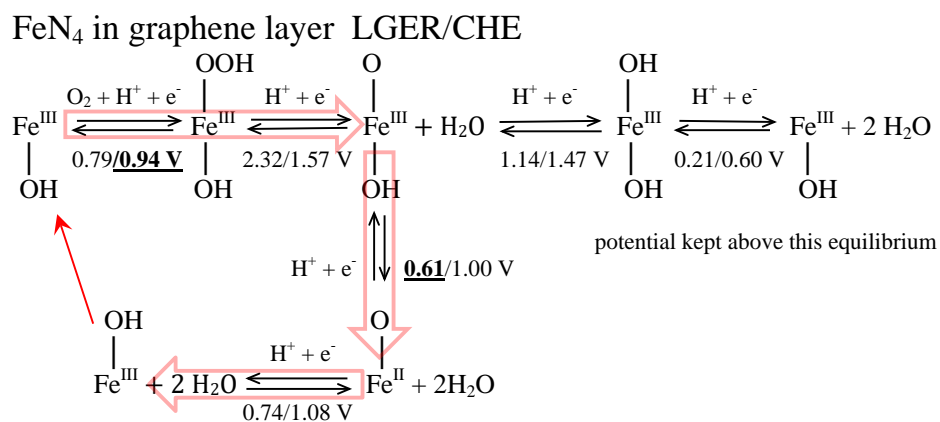


Figure 4. Proposed ORR reaction pathways for FeN₄ in graphene layer

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

During the second year, oxygen reduction performance evaluation has shifted from mostly rotating disk electrode (RDE)-based fuel cell performance-based analysis. The shift in focus has revealed certain modified polyporphyrin-based catalysts have improved fuel cell performance despite equivalent or slightly lower RDE performance. MEAs prepared with the modified polyphenylporphyrin catalyst shows improved intrinsic

activity with open circuit potentials as high as 0.986 V. Oxygen reduction performance in an H₂/O₂ (1 bar) fuel cell at 0.9 V_{IR-free} is 30 mA cm⁻², which meets the end-of-project activity target (Figure 5).

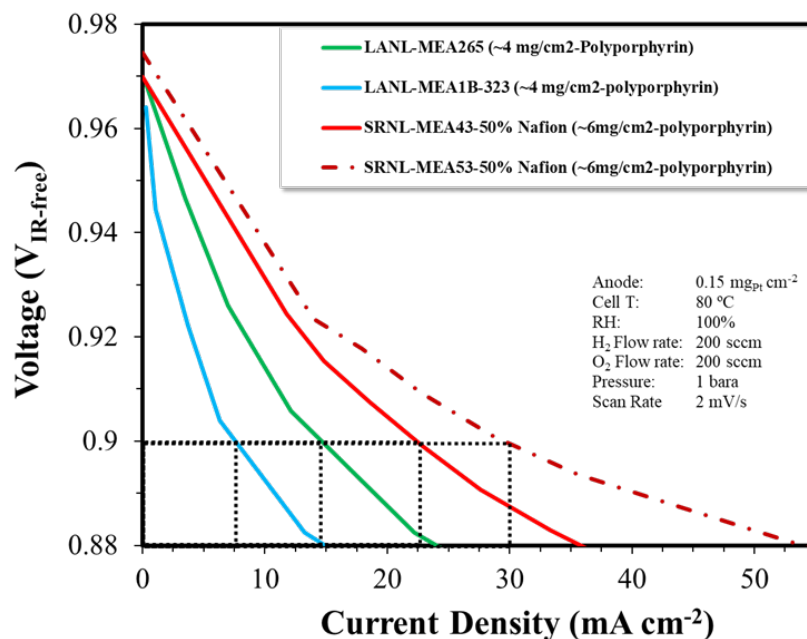


Figure 5. H₂/O₂ fuel cell performance of modified polyphenylporphyrin catalyst compared with conventional polyphenylporphyrin catalyst.

CONCLUSIONS AND UPCOMING ACTIVITIES

During Year 1 of the project 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. Of the materials screened, polyporphyrins synthesized using pyrrole and terephthalaldehyde demonstrated the highest performance for catalyzing the ORR and were down-selected for further study. Analysis of polyporphyrin-based catalysts performed during Year 2 included detailed electron tomography (performed at ORNL, an ElectroCat lab) and XAS techniques, such as EXAFS and XANES, to better understand the catalyst composition before and after pyrolysis, especially as it pertains to Fe moieties.

A summary of the XAS analysis shows single-atom Fe sites in polyporphyrins with Fe-N₄ sites in “as prepared” polyporphyrin, with similar absorption energy to an Fe-porphine reference. Lower symmetry was observed in pyrolyzed polyporphyrin samples, indicating some Fe-N_x (x <4) present. XAS also shows an Fe-N scattering path and the absence of an Fe-Fe signal for both samples, which signifies that no Fe metallic particles are present. All Fe present is composed of single-atom sites of the form Fe-N_x (x ≤4). Further analysis is necessary to exclude the possible presence of Fe oxides in the pyrolyzed catalyst. Electron microscopy studies show “as prepared” particles are dense, have smooth surfaces, are mostly amorphous, and contain no Fe clusters or particles. Heat-treated particles are porous and meso-graphitic, exhibit some nanoporosity, and contain atomically dispersed iron.

Catalyst performance was evaluated in H₂/O₂ 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}. MEAs prepared using optimized polyphenylporphyrin-based catalysts showed open circuit potentials as high as 0.986 V with greatly improved oxygen reduction performance of 30 mA cm⁻² in an H₂/O₂ (1 bar) fuel cell at 0.9 V_{IR-free}, which meets the end-of-project activity target. MEA stability testing was also initiated during BP 2, consisting of an alternating potential hold at 0.7 V for 1 h (more realistic operating V) followed by polarization to 0.3 V. Performance at 0.9 V_{IR-free} shows a logarithmic decay.

Models developed during BP 2 show a new multivalent reaction pathway based on calculations of multiple structures and multiple methods. The proposed reaction pathway suggests a synthesis strategy designed to keep both Fe axial sites open.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. “PGM-Free Engineered Framework Nano-Structure Catalysts,” 2018 DOE Hydrogen and Fuel Cells Program Fuel Cell Project Progress Report, WebEx, January 4, 2018.
2. “PGM-Free Engineered Framework Nano-Structure Catalysts,” 2018 DOE Hydrogen and Fuel Cells Program Fuel Cell Project Progress Report, Aiken, SC, March 27, 2018.
3. “PGM-Free Engineered Framework Nano-Structure Catalysts,” DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting Presentation, Washington, DC, June 13–15, 2018.
4. “PGM-Free Engineered Framework Nano-Structure Catalysts,” Go/No-Go Milestone Presentation, Aiken, SC, September 6, 2018.
5. “PGM-Free Engineered Framework Nano-Structure Catalysts,” DOE Hydrogen and Fuel Cells Program Review Presentation, Washington, DC, April 29–May 1, 2019.
6. Alfred B. Anderson and Edward F. Holby, “Pathways for O₂ Electroreduction over Substitutional FeN₄, HOFeN₄, and OFeN₄ in Graphene Bulk Sites: Critical Evaluation of Overpotential Predictions Using LGER and CHE Models,” *J. Phys. Chem. C* 123, no. 30 (2019): 18398–18409; doi: 10.1021/acs.jpcc.9b03703

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