

# V.A.8 High-Throughput Synthesis, ORR Activity Modeling, and Testing of non-PGM PEMFC Cathode Catalysts

Deborah J. Myers (Primary Contact),  
Xiaoping Wang, Sheldon Lee, Magali Ferrandon,  
Nancy N. Kariuki, and Theodore Krause

Argonne National Laboratory (ANL)  
9700 S. Cass Avenue  
Lemont, IL 60439  
Phone: (630) 252-4261  
Email: dmyers@anl.gov

## DOE Manager

Dimitrios Papageorgopoulos  
Phone: (202) 586-5463  
Email: Dimitrios.Papageorgopoulos@ee.doe.gov

## Collaborators

Piotr Zelenay, Hoon Chung, Ulises Martinez, Edward Holby,  
and Samrat Choudhury, Los Alamos National Laboratory  
(LANL), Los Alamos, NM

Project Start Date: August 14, 2014  
Project End Date: September 30, 2015

## Overall Objectives

- Accelerate the development of high activity and stable non-platinum group metal (PGM) cathode catalysts for proton exchange membrane fuel cells (PEMFCs)
- Develop tools for the rapid synthesis, fabrication, composition characterization, and activity and durability screening of non-PGM PEMFC cathode catalysts
- Identify a non-PGM cathode catalyst and synthesis conditions for catalysts in the polyaniline-Fe,(Co)-carbon (PANI-Fe,(Co)-C) class with higher oxygen reduction reaction (ORR) activity than the current best-in-class of PANI-Fe-C pyrolyzed at 900°C
- Achieve a current density of  $>200 \text{ mA/cm}^2$  at  $0.8 \text{ V}_{\text{iR-free}}$  for a fuel cell with a PANI-Fe,(Co)-C cathode catalyst

## Fiscal Year (FY) 2015 Objectives

- One year project. See Overall Objectives.

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cell section of the Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration (MYRDD) Plan:

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

## Technical Targets

The DOE technical targets relating to this project are shown in Table 1.

**TABLE 1.** Technical Targets from FCTO MYRDD Plan

Barrier	Target
<b>C. Performance</b>	Catalyst activity in $\text{H}_2/\text{O}_2$ at $0.044 \text{ A cm}^{-2}$ ( $80^\circ\text{C}$ ): $\geq 0.87 \text{ V}$ (iR-free)
<b>B. Cost</b>	$< \$7/\text{kW}_e$ MEA cost target
<b>A. Durability</b>	$< 40\%$ performance loss at $0.80 \text{ A cm}^{-2}$ after 30,000 accelerated stress test cycles in nitrogen

MEA – membrane electrode assembly

## FY 2015 Accomplishments

- Developed a high-throughput (HT) method for synthesizing and characterizing high surface area (HSA) non-PGM ORR catalysts
- Applied a commercial combinatorial method/cell, a multi-electrode channel flow double electrode (m-CFDE) cell, to screening the ORR activity of HSA catalysts simultaneously; the ORR activity trends from the m-CFDE cell for the HT-synthesized catalysts were identical to those from rotating disk electrode (RDE) tests of large, single batches of catalysts, validating the HT methods.
- Designed, built, and utilized an m-CFDE cell which has improved performance and ease of use compared to the commercial m-CFDE
- Achieved ORR half-wave potential agreements between m-CFDE and RDE results of 9 mV for commercial Pt/C and 80 mV for PANI-Fe<sub>4</sub>Co-C catalyst
- Identified a PANI-Fe,Co-C catalyst with higher ORR activity than the previous best catalyst in this class (PANI-Fe-C, pyrolyzed at 900°C) and synthesized sufficient quantities of this catalyst for MEA tests
- Developed a density functional theory (DFT) model to screen non-PGM ORR activity and stability, screened 22 possible sites, and down-selected the eight most probable sites based on activity



## INTRODUCTION

The goal of this project was to accelerate the development of high activity and stable non-PGM cathode catalysts for PEMFCs. The means for achieving this overall goal and a secondary goal of the project was to develop generally applicable methods for the rapid throughput synthesis of non-PGM catalysts and the rapid throughput screening of ORR activity of catalysts in an aqueous environment. The non-PGM catalyst class studied was the iron and iron-cobalt-containing materials derived from a composite of the metal salts, polyaniline (carbon, nitrogen-containing polymer), and HSA carbon. This class of material was first discovered in the LANL-led project entitled “Advanced Cathode Catalysts” [1]. In that project, it was determined that variables such as metal, polymer, and carbon content, as well as the temperature and atmosphere in which the composites are pyrolyzed, are important in determining the activity and activity stability of the resulting catalysts. Changing these variables and testing their effects on the resulting catalyst properties is a very time consuming process and only a limited portion of the composite composition and temperature space have been explored.

Another aspect of the project was the development of computational means for determining the energetically most favored active sites in Fe,Co-carbon-nitrogen catalysts by calculating formation energies and computationally screening the ORR activity of potential activity sites.

## APPROACH

The overall approach of the project was to develop and utilize the capability for HT synthesis and ORR activity testing of non-PGM PEMFC cathode catalysts, with a specific application of the approach to rapidly explore the compositional and temperature space for the PANI-Fe,Co-C class of catalysts. This approach involved the rapid throughput (1) synthesis of the precursor composites; (2) pyrolysis of catalyst precursors in a multi-sample tube furnace; (3) physical and chemical characterization of catalysts using multi-sample, automated X-ray diffraction (XRD) and X-ray fluorescence (XRF); and (4) screening of the catalysts’ ORR and ORR activity stability in a hydrodynamic aqueous cell. The approach also included determining the validity of the combinatorial hydrodynamic aqueous cell using RDE, developing the capability for high-throughput screening of possible Fe-N-C active site moieties for activity and stability using DFT-based descriptors, and scaling up the best base metal-PANI-C catalyst for MEA fabrication and testing. The computational aspect of this project also involved calculating the formation energies of potential sites collected from the literature and calculating a structure predominance diagram as a function of N and Fe/Co chemical potentials (representing varied synthesis conditions).

## RESULTS

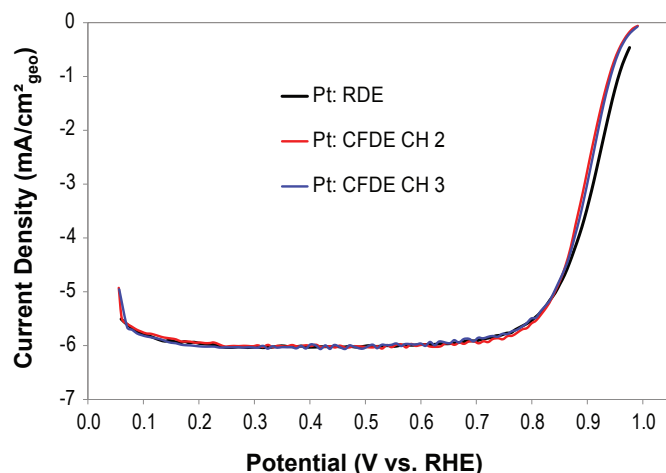
The synthesis of PANI-Fe,Co-C non-PGM PEMFC cathode catalysts involves the following steps: (1) polymerizing aniline in the presence of dissolved cobalt and iron and HSA carbon, (2) driving off the solvent, (3) grinding the precipitate, (4) pyrolyzing the precipitate in an inert atmosphere at temperatures between 800°C and 1,000°C, (5) acid treating the powder at an elevated temperature, (6) removing the acid from the powder, and (7) pyrolyzing the powder at the same temperature as the first pyrolysis [1]. In this project, the single batch, single composition procedure developed by Zelenay et al. [1] was adapted into an HT fabrication process, where feasible. Methods were developed and utilized for synthesizing the PANI-Fe,Co-C composite catalyst precursor with nine different Fe to Co ratios using a robotic platform (CM3, FreeSlate Inc.) and for pyrolyzing, acid treating, and rinsing these samples in an HT manner. For example, the acid treatment was performed using a multi-port reflux system and the catalysts powders were separated from the supernatant acid using a multi-sample centrifuge rather than filtering. The samples were pyrolyzed at five temperatures between 800°C and 1,000°C to yield 45 different catalysts. The phase compositions of the catalysts were determined by a multi-sample HT XRD after the first pyrolysis step and after the second pyrolysis step. The Fe and Co weight percentages in the catalysts after the second pyrolysis were also determined by XRF.

The ORR activities of these catalysts were screened in a high throughput fashion using two multi-electrode channel flow double electrode cells, one purchased from Eiwa Corporation and the other designed and built at ANL. Both of these cells allow ORR activity testing of four catalyst samples simultaneously in a hydrodynamic aqueous environment with operating principles similar to those of RDE. The “double electrode” refers to an upstream glassy carbon electrode on which catalyst-ionomer inks are deposited and a downstream Pt electrode on which reaction products (e.g., peroxide) can be detected similar to the ring electrode in rotating ring disc electrode measurements. Figure 1 shows pictures of the Eiwa and ANL cells. The most significant difference between the two cells is that the Eiwa cell’s electrodes are permanently imbedded in the bottom plate of the cell, whereas in the ANL cell each set of glassy carbon-platinum electrodes is mounted in a removal electrode “plug.” The removable plugs facilitate the quick changing of the catalyst on the glassy carbon electrode and also replacement of damaged electrodes.

The validity of the two cells in providing data similar or equivalent to that obtained using RDE was first tested using a commercial Pt/C catalyst which was extensively tested in the project FC111 “Best Practices and Benchmark Activities for ORR Measurements by the Rotating Disk Electrode Technique” [2]. As shown in Figure 2, the half-



**FIGURE 1.** Pictures of the Eiwa m-CFDE, cell showing the glassy carbon and platinum electrodes imbedded in the cell wall, and of the ANL m-CFDE showing the electrodes imbedded in removal “plugs”

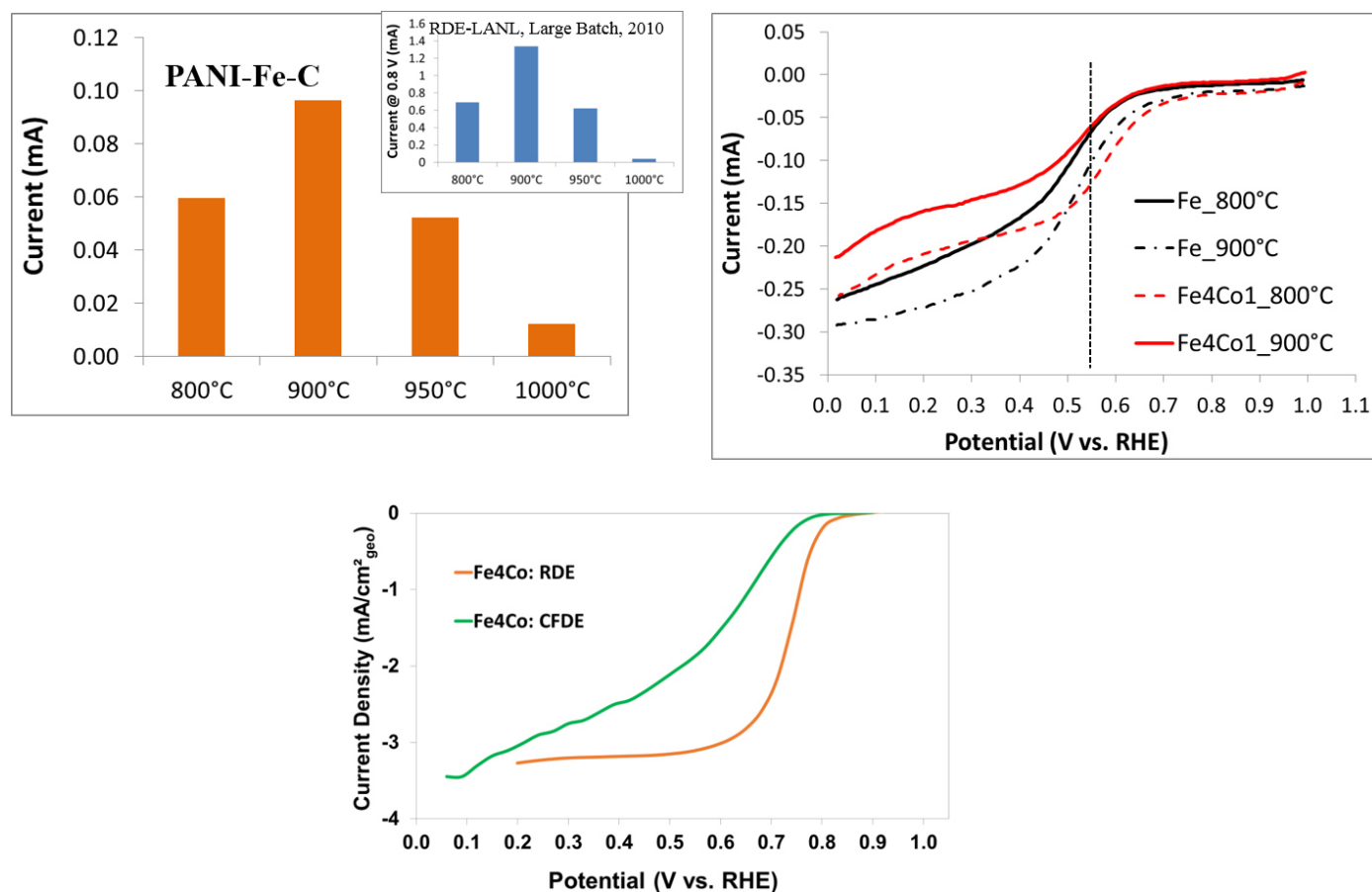


RHE – Reference hydrogen electrode

**FIGURE 2.** ORR voltammograms for a Tanaka Pt/C catalyst in 0.1 M HClO<sub>4</sub> electrolyte using RDE (from FC111 project) and using the ANL m-CFDE cell (two m-CFDE electrodes shown for comparison)

wave potentials for the ORR, a comparative measure of ORR activity when using identical Pt loadings (18 μg/cm<sup>2</sup>), agree within 9 mV when comparing the ANL RDE results from FC111 [2] and the m-CFDE (ANL-built cell) results for the same catalyst.

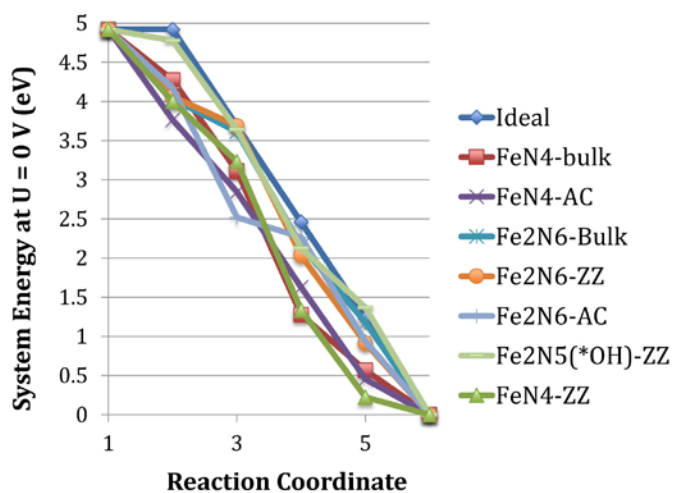
Select results from the ORR activity screening of the 45 PANI-Fe<sub>4</sub>Co-C catalysts using the m-CFDE are shown in Figure 3. The m-CFDE screening of the PANI-Fe-C HT-produced catalysts showed the same activity trends with pyrolysis temperature as the single large batch-RDE results from LANL [1], validating both the HT synthesis method and the m-CFDE screening technique. The most active catalyst for ORR in these screening was found to be the PANI-Fe<sub>4</sub>Co-C catalyst pyrolyzed at 800°C. This catalyst composition was scaled up and the effect of total metal loading on the support was determined. The highest ORR activity of this class was found for the material that had a total metal molar loading that was half that of the standard metal loading. The RDE and m-CFDE results for this catalyst at a loading of 0.6 mg/cm<sup>2</sup> are also compared in Figure 3.



**FIGURE 3.** Select results from the ORR activity screening of the 45 PANI-Fe,Co-C catalysts using the m-CFDE, comparison of m-CFDE ORR activity trends with pyrolysis temperature for HT PANI-Fe-C with RDE activity trends for LANL's large batch PANI-Fe-C; comparison of m-CFDE and RDE results for HT PANI-Fe<sub>4</sub>Co-C

This comparison shows that while the m-CFDE is able to screen relative ORR activity of non-PGM at these high loadings, further work is necessary to determine absolute half-wave potentials for non-PGM catalysts with high loadings on the glassy carbon m-CFDE electrode.

In the computational modeling aspect of the project at LANL, 22 initial structures were considered and eight were down-selected based on the activity descriptor, OH\* binding energy. Full ORR reaction pathways have been calculated, using DFT, on the down-selected catalyst structures (Figure 4) developing the first ORR catalyst/activity library for iron-carbon-nitrogen ORR catalysts. Of these structures, the Fe<sub>2</sub>N<sub>5</sub>(\*OH) structure on the zig-zag edge has the highest calculated thermodynamic limiting potential, U<sub>1</sub> (0.76 V vs. computational hydrogen electrode, [CHE]). This value serves as the ORR activity figure of merit and a higher value represents a higher calculated ORR activity. This value of 0.76 V vs. CHE is the highest calculated Fe-based ORR activity value to date (though still below that calculated for a Fe/Co structure). This suggests that selection of ligand species and geometry is a valuable tool in optimizing future



**FIGURE 4.** ORR reaction pathway on Fe<sub>x</sub>N<sub>y</sub>-C active site structures from DFT. Reaction coordinates are: (1) \* + 4H<sup>+</sup> + 4e<sup>-</sup> + O<sub>2</sub>, (2) \*OO + 4H<sup>+</sup> + 4e<sup>-</sup>, (3) \*OOH + 3H<sup>+</sup> + 3e<sup>-</sup>, (4) \*O + 2H<sup>+</sup> + 2e<sup>-</sup> + H<sub>2</sub>O, (5) \*OH + H<sup>+</sup> + e<sup>-</sup> + H<sub>2</sub>O, (6) \* + 2H<sub>2</sub>O. \* represents the active site structure with or without adsorbate. Fe2N5-bulk is not included as \*OO and \*OOH were found to not bind to this structure.

non-PGM ORR catalyst structures. Additionally, the  $\text{FeN}_4$  and  $\text{Fe}_2\text{N}_6$  structures show that host C material (zig-zag [ZZ] edge, arm-chair [AC] edge, or bulk graphene) can also significantly modify the ORR reaction pathway.

## CONCLUSIONS AND FUTURE DIRECTIONS

### Conclusions

- Non-PGM catalysts can be synthesized and characterized using an HT approach.
- A PANI- $\text{Fe}_4\text{Co}$  catalyst pyrolyzed at 800°C can potentially have a higher ORR activity than the highest activity PANI-Fe<sub>4</sub>Co-C catalyst known to date.
- A combinatorial technique for screening the ORR activity of catalysts in an aqueous environment, the m-CFDE technique, can achieve half-wave potentials approaching those of RDE and can provide relative ORR activity of non-PGM catalysts.

### Future Directions

- RDE screening of select HT PANI-Fe<sub>4</sub>Co-C samples, in addition to the PANI-Fe<sub>4</sub>Co-C samples, to further validate m-CFDE and HT synthesis approach
- Fabrication, performance testing, and durability testing of MEAs containing the PANI-Fe<sub>4</sub>Co-C catalyst fabricated using the HT approach
- Correlation of ORR activity trends with phase composition and metal content of numerous HT PANI-Fe<sub>4</sub>Co-C samples
- Diagnosis of sources of half-wave discrepancy between RDE and m-CFDE results for non-PGM catalysts (i.e., for thick electrocatalyst layers)
- Development of techniques for HT/robotic deposition of catalyst-ionomer inks on the m-CFDE glassy carbon electrodes
- Code development for automation of catalyst active site screening using a DFT Monte Carlo search program
- Development of HT, fully-automated non-PGM-based MEA electrode fabrication

## FY 2015 PUBLICATIONS/PRESENTATIONS

1. Holby, E.F. and Taylor, C.D. “Activity of N-coordinated multi-metal-atom active site structures for Pt-free oxygen reduction reaction catalysis: Role of \*OH ligands.” *Sci. Rep.* 5, (2015).

## REFERENCES

1. Zelenay, P., FC-003, “Advanced Cathode Catalysts,” 2007-2011.
2. Kocha, S., FC-111, “Best Practices and Benchmark Activities for ORR Measurements by the Rotating Disk Electrode Technique,” 2014.