V.D.11 Development of Novel Non-PGM Electrocatalysts for Proton Exchange Membrane Fuel Cell Applications

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• Michigan State University, East Lansing, MI (MSU) (Prof. Scott Barton)
• University of Tennessee, Knoxville, TN (UTK) (Prof. Thomas Zawodzinski)
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• BASF Fuel Cells, Somerset, NJ (BASF) (Dr. Emory De Castro)
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Fiscal Year (FY) 2012 Objectives

The objective of this project is to design non platinum group metal (PGM)-based materials and supporting gas transport layer, both in the interfacial reaction layer between the electrode and membrane as well as in the underlying gas diffusion medium, for meeting and exceeding DOE goals for application in solid polymer electrolyte fuel cells. This project is focused on materials development and is assisted by advanced analytical tools, computation, and testing for improving the design via critical understanding of electrocatalysis in these novel structures.

Technical Barriers

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

(B) Cost (eliminate precious metal loading of catalysts)
(C) Performance (increase the specific and mass activities of catalysts)
(A) Durability (increase the durability/stability of catalysts with cycling)

Technical Targets

TABLE 1. Progress towards Meeting Technical Targets for Non-PGM Electrocatalysts for Transportation Applications

Characteristic	Units	2017 Target	NEU 2012 status
Specific Activity @ 80°C, 150 kPa, H_2/O_2, 100% relative humidity (RH)	A/cm^3 A/cm^2	300 A/cm^3 (internal resistance free) 100 mA/cm^2 (internal resistance free)	130 A/cm^3 105 mA/cm^2
Durability at 80°C Cycling: Catalyst Durability	% loss of activity	5%	<1%
Durability at 80°C Cycling: Carbon Corrosion Durability	% loss of activity	10%	<50% Partially recoverable

FY 2012 Accomplishments

• Cross laboratory measurement of a wide variety of samples emanating from diverse choice of polymer precursors at MSU, NEU, UNM indicate a confluence in terms of performance; these are very close (within the errors inherent in these measurements) to the current state-of-the-art materials recently reported by our partners at LANL [1]. One of the most recent samples reported by LANL under the label LANL-2 however shows a ~49 mV lower overpotential loss as compared to the other materials.

• Wide variety of polymeric precursors indicating such confluence of inherent oxidation reduction reaction (ORR) activity strongly suggests, at least qualitatively, evolution of a common active site as a result of pyrolysis conditions.

• Extrapolation of fuel cell derived internal resistance (iR) corrected data currently indicates volumetric performance in the range of 160-175 A/cm^3. Geometric area activity (iR-free) is currently 105 mA/cm^2.

- Durability measurements conducted in one of such samples derived from Melamine polymeric precursor and iron acetate followed with plasma pyrolysis shows excellent tolerance to catalysts stability tests (based on Nissan protocol, similar to DOE protocol). Carbon corrosion tests which involves load cycling to 1.5 V vs. the reference hydrogen electrode (RHE) however indicated significant losses; this however was recoverable over 1,600 cycles beyond which irreversible losses occurred.

- Understanding of the nature of the active site was significantly advanced in this reporting period with identification of a dual site mechanism wherein the N_{2+2} site was responsible for the initial adsorption and reduction of oxygen to peroxide moieties followed with a second cascade step of further reduction of the peroxide in closely surrounding $Fe-N_2$ sites. Such formulation of the mechanism was supported with in situ X-ray absorption spectroscopy (XAS) and targeted electrochemical probe measurements.

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Introduction

Recent reports [1-2] have clearly demonstrated the significant advancements made in enabling good oxygen reduction activity by Fe-based non-PGM catalysts. These so called $Fe-N_x$ based systems have evolved over several decades of intense work leading up to the current state of the art, reported recently in references [1-2]. This report provides for the first time a comprehensive view of (a) confluence of ORR activity derived from materials prepared using a variety of polymeric precursor materials viz. the current state of the art [1-2] by three different university groups (b) excellent durability in terms of catalyst stability (via DOE and Nissan protocols) and recovery of losses incurred during carbon corrosion measurement when placed under load (c) detailed understanding of nature of active site and electrocatalytic pathway as distinct from the parallel pathway in alkaline electrolytes.

Approach

The approach adopted in this reporting period involved (a) material preparation using of a wide variety of polymer precursor materials in conjunction with Fe-containing salts pyrolyzed up to temperatures of 700-800°C under inert atmosphere followed with repeated steps (up to three) of etching (in acid) and repyrolysis. Rotating ring disc electrode (RRDE) and fuel cell tests using well established protocols for cross laboratory performance comparison and extrapolation of volumetric activity (from iR-corrected fuel cell data). Durability measurements using two well

established protocols (catalyst durability) and carbon corrosion tests (both DOE protocols) and investigation on the nature of active site and ORR electrocatalysis steps as measured using in situ synchrotron spectroscopy at the Fe K edge under actual cell operational conditions.

Results

Figure 1 shows three different polymer precursor starting materials, namely poly aniline (LANL), poly vinyl guanidine (NEU) and 1 amino anti-pyrine (UNM). These were polymerized on either Ketjen black 600 (LANL and NEU) or templated on high surface area silica moieties. All of the polymerizations were initiated using well known procedures reported in our July interim report. Extent of polymerization has been previously calibrated using reference molecular weight measurements conducted with the aid of mass spectrometry. All the polymerization steps were conducted in the presence of Fe salts (typically acetate) and in one case also with Co salt (also acetate). Following polymerization with simultaneous incorporation of the metal salt, each sample was pyrolyzed under inert gas (Ar) in a temperature range of (700 to 800°C); this was followed by a series of acid leach (0.5 M H_2SO_4) and repyrolysis steps (up to three times) before final formation of the catalyst material. In the case of the Si template materials from UNM, the initial pyrolysis step was followed with an acid etch step using dilute HF (0.05 M). This provided for an in situ open framework carbon structure to form along with the evolution of the $Fe-N_x$ structure as was the goal of the LANL and NEU samples albeit without the Si template. In the MSU sample case shown in Figure 3, a single high-pressure pyrolysis step was adopted using nitrogen precursor (Melamine), carbon (Ketjen black or Vulan XC-72) and the metal salt Fe^{2+} acetate. Figure 2, shows a cross laboratory ORR measurement using a glassy carbon-based RRDE experiment with high loading of catalysts mentioned above (600 $\mu g/cm^2$). Also shown are the results of samples obtained from LANL, namely the new sample referred to as LANL-2 and the previously reported material [1] referred to as PANI-Fe-Co derived using preparation conditions mentioned above. As can be seen from Figure 2, measured using 0.1 M $HClO_4$ (900 rpm) under oxygen saturation conditions, room temperature, all samples with the exception of a new hitherto unreported material from LANL labeled as LANL-2 performed similarly. The LANL-2 material showed a ~40 mV initial lower ORR overpotential. In addition to the materials mentioned above, Figure 2 also shows the performance of an earlier reported material referred to as PEIbFe from NEU, which constitutes the poly ethylene imine polymer in conjunction with Fe acetate prepared in exactly similar conditions as reported above. Such close performance levels observed for a wide variety of samples prepared using different procedures, LANL, NEU vs. UNM and MSU samples strongly indicates possible evolution of common active site as a result of such
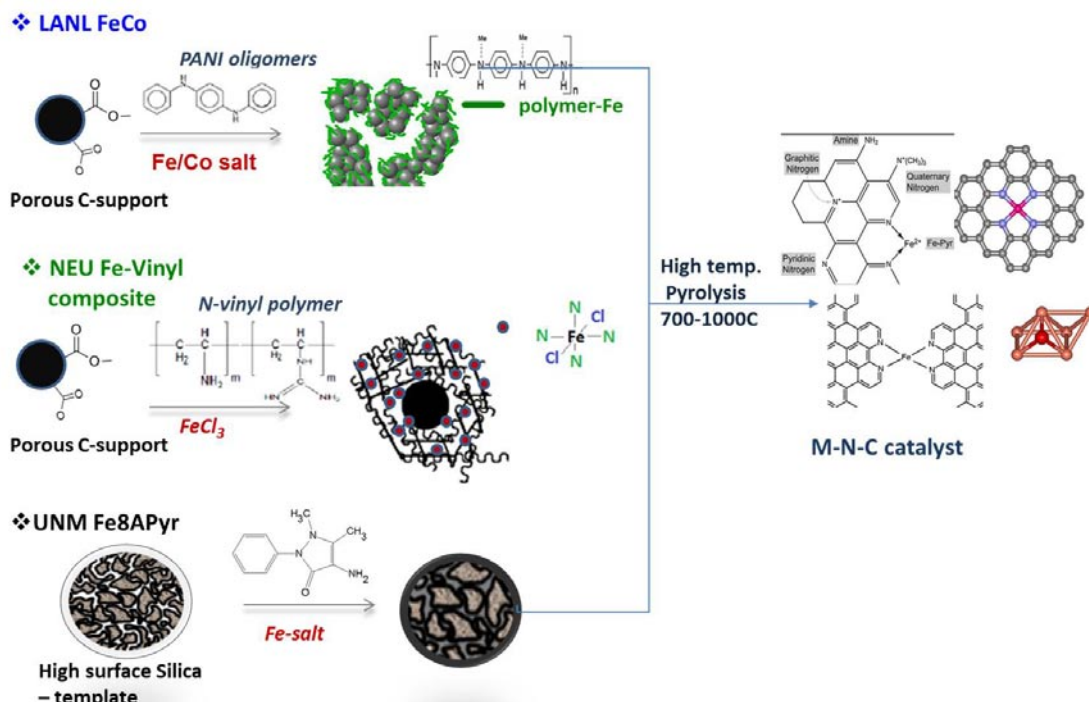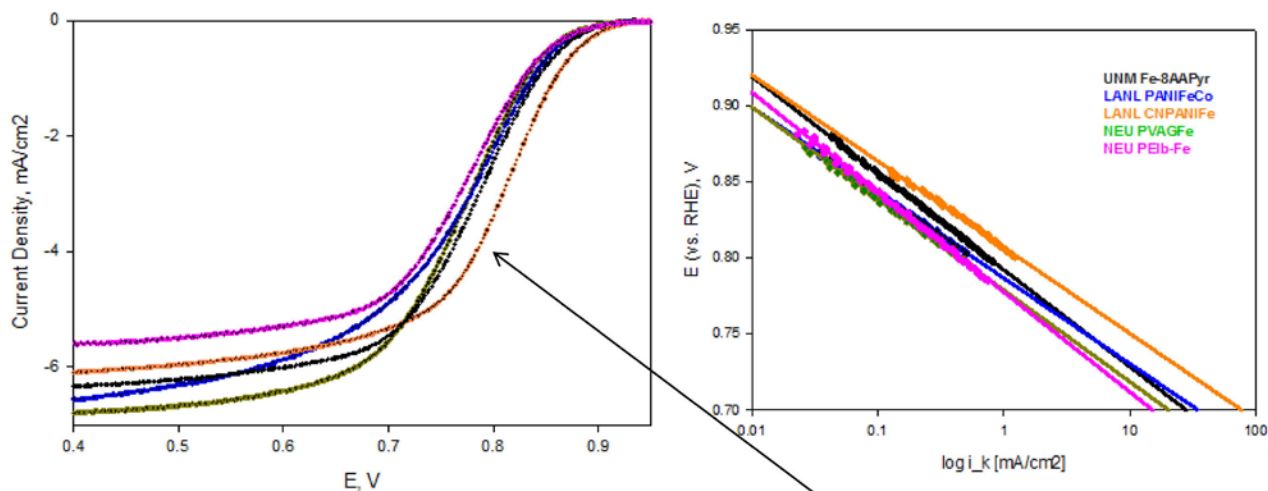
Figure 1. Representation of chemistry and pyrolysis conditions used by cross laboratory partners, UNM, LANL, and NEU

Cross Laboratory Materials Characterization

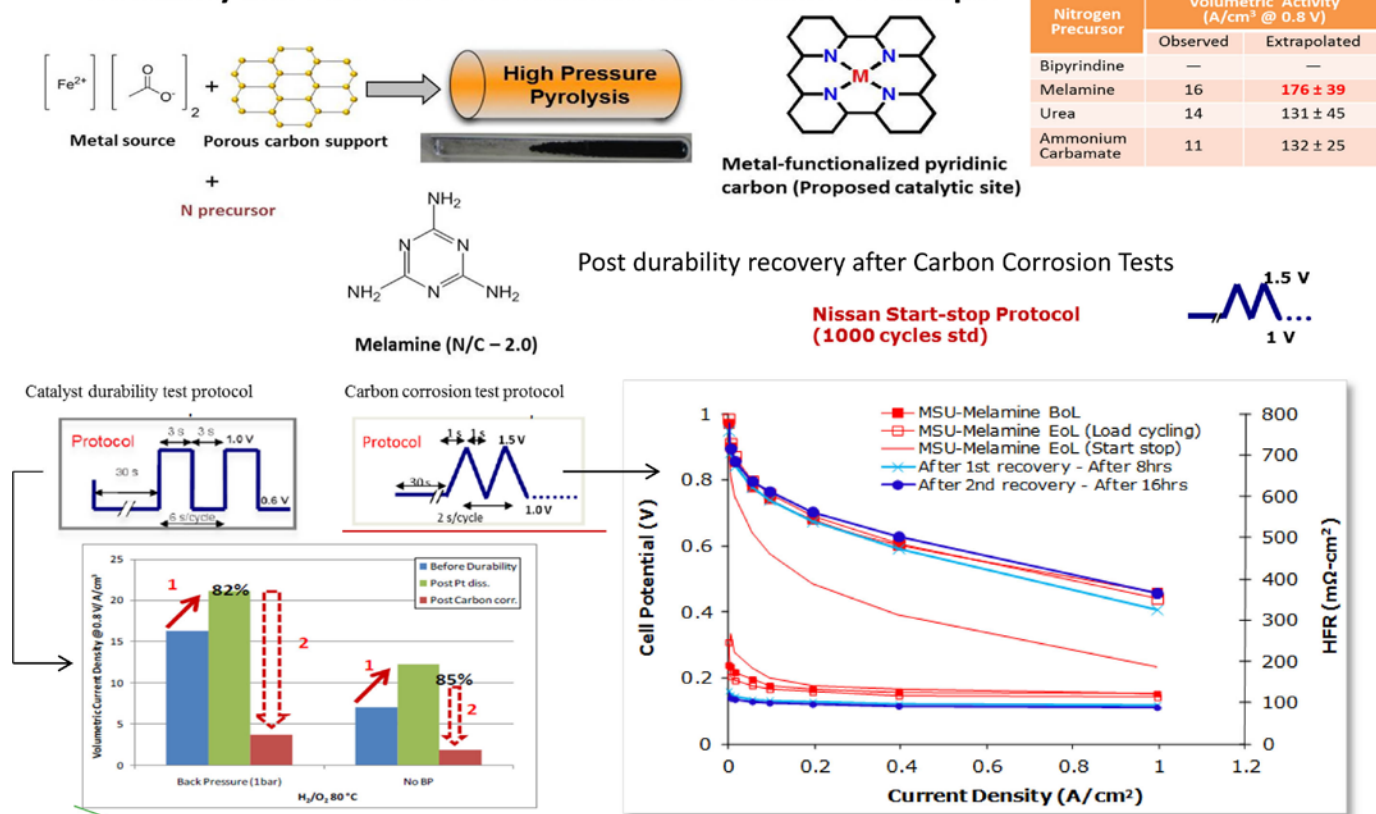|	I at 0.8[V] [mA/cm^2]	E$_{1/2}$ [V]	Tafel Slops, [mV/dec]
UNM Fe-AAPyr	2.5	0.78	63
PANIFeCo	2.3	0.77	56
LANL-2	3.4	0.80	56
PVAGFe	2.2	0.77	60
PEIbFe	1.87	0.77	65

Highest Onset Potential of All Samples

Figure 2. Cross laboratory comparison of ORR activity measured using rotating ring disk electrode technique, performance comparison shown at 900 rpm. Electrolyte is 0.1 M HClO$_4$, room temperature with standard catalyst loading of ~600 µg/cm^2. Corresponding Tafel slopes and kinetic activity are shown in associated plot and table.

pyrolysis. It should be noted that attempts to prepare such Fe-based (most likely Fe-N$_x$) type materials have a three decade history of evolution in activity. One important distinction between the current materials and the wealth of data reported earlier is the use of starting materials. Most of the earlier work used metal heme type macrocycles such as Fe or Co containing phthalocyanines or porphyrins. In the current evolution of materials showing true enhancement of both onset of ORR as well as inherent activity emanate from slow evolution of Fe-N$_x$ structures via pyrolysis of polymeric precursors with no existing Fe-N structures. This is an important distinction to make as this will be later used to explain the reason for enhanced performance of such metal polymer composite pyrolysis derived materials as opposed to previous attempts involving heme-containing macrocycles. Figure 3 provides a snapshot of durability and fuel cell performance reported via MSU prepared sample, wherein the extrapolated volumetric activity (A/cm^3) shows values in the range of 160-170 A/cm^3. While not stellar this is within the DOE mandated target of 300 A/cm^3. More importantly

however the catalyst degradation measurements conducted using Nissan protocols (square waves with 3 second on and 3 sec off periods between a potential range of 0.6 and 1.0 V) indicated no degradation; in fact over the short range of time (1,600 cycles) there was a slight improvement of performance (Figure 3). Subjecting the same membrane electrode assembly (MEA) to carbon corrosion test using DOE protocols (1.0 to 1.5 V load cycling tests) showed immediate lowering of performance, an occurrence not surprising considering the most likely active site formation involving a local graphene structure. Most surprising observation however was the recovery observed when the MEA was left under load at 400 mA/cm^2. This recovery lasted through till 1,600 cycles after which irrecoverable losses were observed. Figure 4 represents a proposed mechanism drawing distinction between the observed activity differences observed between the two extreme ends of the pH scale, at high pH ORR activity (900 rpm) is always better with a ~150-200 mV lower overpotential (see lower left hand plot). This is clearly observed in the rotating disk electrode profiles

Figure 3. Preparation conditions for sample prepared by MSU using high pressure pyrolysis of nitrogen precursor Melamine in conjunction with carbon support (Ketjen black 300) and Fe salt (acetate), iR-free fuel cell performance projections to 0.8 V is also made for obtaining volumetric activity (Table 1). Durability measurements are shown for this sample measured at the Nissan technical center North America using DOE protocols for both catalyst stability and carbon corrosion. As shown, this sample showed excellent durability for catalyst stability test; carbon corrosion test however exhibited losses which however were recoverable till 1,600 cycles.

Oxygen Reduction Mechanism on Fe-N₄ Sites
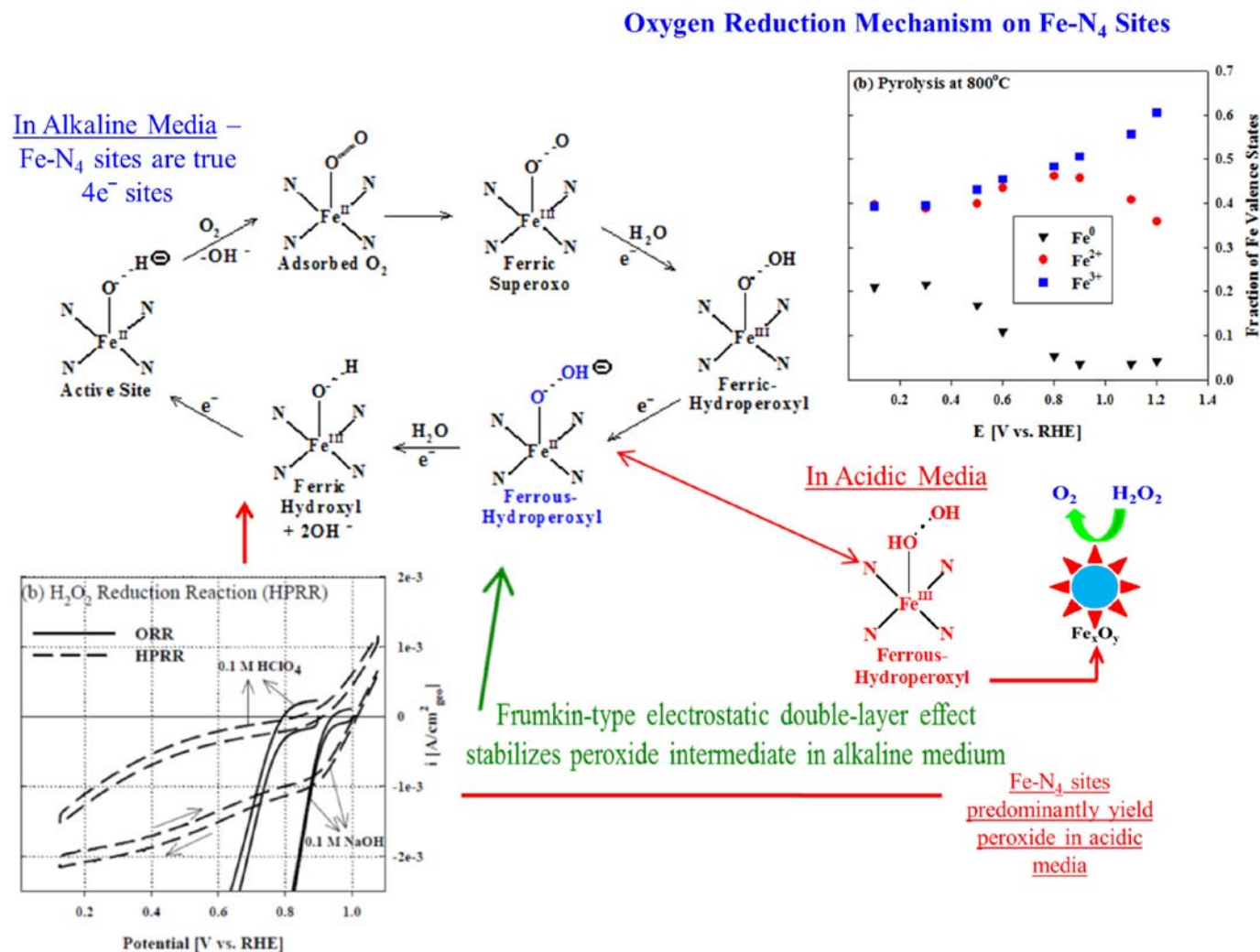
Figure 4. Mechanistic interpretation of the active site based on RDE measurements at acid and alkaline pH with O_2 and peroxide and in situ and *operando* synchrotron measurements conducted at Fe K edge (not shown) which explains the important distinction of observed activities at the two pH scales and need for a dual site mechanism in the acidic environment.

of a representative Fe-TPP (tetraphenyl porphyrin) sample pyrolyzed at $800^{\circ}C$ on Ketjen black (600) support. When the electrolyte is instead dosed with 0.1 M H_2O_2, the higher pH response is better than O_2. Corresponding behavior at lower pH scale represents only initial decomposition of the peroxide. Detailed XAS measurements (not shown) support the mechanism shown in Figure 4, wherein this difference in activity over the pH scale is explained on the basis of the fact that the initial turnover number for the adsorption of molecular oxygen on $F-N_{2+2}$ is extremely fast both in acid and alkaline pH; however it is only in the alkaline pH that the peroxy-anion is stabilized and allows for the further reduction to water. In the acid pH the inability of such stabilization therefore requires an additional site where peroxy-anion can be further reduced.

Conclusions and Future Directions

Conclusions

- Cross-laboratory studies of materials emanating from the pyrolysis of diverse polymer precursors in conjunction of Fe and Co salts indicate a common evolution of active sites for ORR reduction.

- Detailed durability studies indicate excellent tolerance to catalyst stability tests, and relatively poor resistance to carbon corrosion test protocols, the latter however is recoverable over several cycles.

- Mechanism for an active site is proposed which is supported by activity observations at both ends of the spectrum.

Future Directions

- Principal focus of the group will include meeting and exceeding DOE targets for ORR activity in terms of both volumetric and geometric areas (see Table 1).
- Meet and exceed DOE durability milestones for more diverse materials.
- Further test the validity of the proposed mechanism using final set of in situ and *operando* synchrotron XAS data in conjunction with density functional theory calculations.

FY 2012 Publications/Presentations

1. 'Fundamental Mechanistic Understanding of Electrocatalysis of Oxygen Reduction on Pt and Non Pt Surfaces: Acid vs. Alkaline Medium', N. Ramaswamy and S. Mukerjee, Advances in Physical Chemistry, Vol. 2012, Article ID 491604, (2012).

References

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2. Lefevre, M.; Proietti, E.; Jaouen, F.; Dodelet, J.P. *Science* **2009**, *324*, 71.