

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)
- Nissan Technical Center, North America (NTCNA), Detroit, MI (Dr. Kev Adjemian)
- BASF fuel cells, Somerset, NJ (BASF) (Dr. Emory De Castro)
- Los Alamos National Laboratory, Los Alamos, NM (LANL) (Dr. Piotr Zelenay)

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- (B) Cost (reduce 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	2015 Target	NEU 2011 status
Specific Activity @ 80°C, 0.1 M HClO ₄	A/cm ³	150/300	30
Specific Activity @ 80°C, 150 kPa, H ₂ /O ₂ , 100% relative humidity (RH)	A/cm ³	150/300	130
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

FY 2011 Accomplishments

- Current efforts focus on synthesis of non-PGM metals contained in unique liganded environments (mostly using N or O) and its incorporation onto carbon supports for effecting improved oxygen reduction reaction (ORR) performance and stability. Such as those shown by the LANL group.
- Our effort encompasses development of novel bi-dentate and tetra-dentate complexes where tandem electron transfer to oxygen can be facilitated using two or three transition metals with different oxidation states.
- Successful implementation of these strategies has been done at NEU as well as partner institutions which include UTK, UNM and MSU.
- One such rendition of a ligand Fe-based catalyst has also been extensively tested at NTCNA for both fuel cell activity as well as durability. The latter tests involved both catalysts and support stability tests incorporating DOE mandated cycling tests.
- Current status of the non-PGM field puts the volumetric power density at 130 A/cm³ this however needs to be translated to actual fuel cell performance levels which requires redesign of electrode structures. In addition, excellent durability of the tested catalysts is reported.

Fiscal Year (FY) 2011 Objectives

The objective of this project is to design non-platinum group (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:



Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are promising candidates as an alternative to traditional energy converters. A primary technical challenge faced in the development of the technology is the sluggish kinetics of the ORR on the cathode. Pt and Pt alloy electrocatalysts remain the choice of electrocatalysts for PEMFCs due to the so called “stability criterion.” However, recent reports have shown good activity and stability for alternative non-PGM-based electrocatalysts [1] and Dodelet [2] for the more challenging ORR.

Approach

The objective of this project is to design non-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 PEMFCs. 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.

Results

UNM explored the effect of support material for the catalyst. It was shown that templating catalysts onto a sacrificial layer of hierarchically structured silica (HSS) or fumed silica allows synthesis of materials with well developed porosity, this cannot be achieved with synthesis methods based on use of carbon black. These HSS materials also offer higher surface areas when compared to catalysts supported on carbon blacks. After etching silica, the cavities left by the vacated silica create an open-framed structure that upon addition of catalysts allows for internal transport of electrolyte and reactant, providing additional surface area for the active sites. Two classes of catalysts were synthesized and characterized: Fe-cyanamide and Fe-4-aminoantipyrene diethanolamine. It was found that heat treatment conditions including ramp rates, durations, and temperatures can have dramatic effects on final catalytic activity, and should be optimized for every combination of Fe and C-N precursors. Furthermore, the density functional theory computations show that nitrogen may play a dual role in non-Pt ORR electrocatalysts: on the one hand it provides a stabilizing coordination environment for transition metals such as cobalt or iron. On the other hand, the ability to stabilize narrow channels due to balancing nitrogen and cobalt content indicates that nitrogen can help stabilize microstructures. The investigated catalysts show significant activity towards oxygen reduction and can be used as inexpensive substitutes for Pt.

The effect of the nitrogen precursor was explored by the team from MSU. Metal-nitrogen-carbon cathode catalysts for the ORR in low temperature fuel cells were synthesized by pyrolysis of iron-acetate, Ketjen black and various nitrogen precursors of varying nitrogen content, including carbon-free nitrogen precursors. In collaboration with UNM a surface analysis was carried out to determine the surface nitrogen content produced by the various precursors. These results were combined with ORR activity results to determine what type of nitrogen precursor produced the best performing catalyst.

In addition, two sample catalysts from MSU that were prepared from melamine and ammonium carbamate precursors were sent to NTCNA Fuel Cell Laboratory for ex situ and in situ characterization.

Understanding the selectivity of the catalyst towards two or four electron pathways is very important for oxygen reduction catalysts. Rotating ring disk electrode (RRDE) experiments were performed for the melamine-based catalyst to verify the formation of peroxide. Peroxide formation was observed to be less than 2% (DOE Target).

Fuel cell testing was carried out and current-voltage (I-V) performance was measured at both atmospheric and 1 bar pressure, 80°C, 100% RH. The high frequency resistance of this MEA was very high due to the amount of ionomer in the catalyst layer and the catalyst layer's thickness. As expected, HFR measured at 1 bar was higher than at atmospheric pressure. These are shown as I-V curves both on a linear and corresponding semi-logarithmic Tafel plots in Figures 1 and 2, respectively. Volumetric activity or volumetric current density is calculated at 0.8 V internal resistance-free voltage and an effective carbon density of 0.4 g/cm³ was assumed for these calculations. Volumetric current densities of 31 and 131 A/cm³ were obtained for the melamine-based catalyst MEA without pressure and with

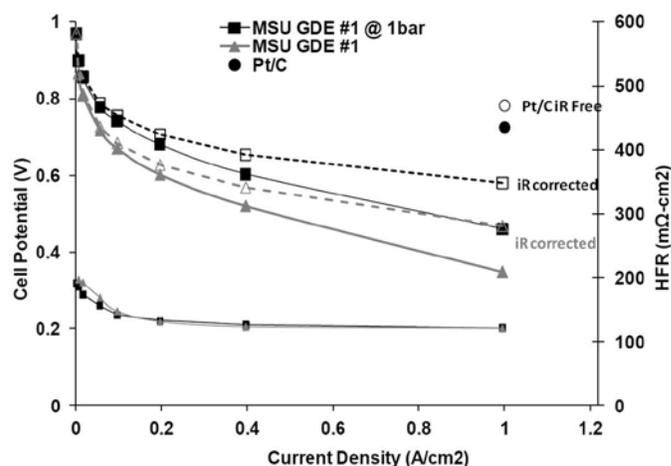


FIGURE 1. I-V performance for Fe-N_x-based catalysts using melamine precursors with (■ and □) and without (▲ and △) back-pressure (100 kPa) conditions under 100% RH, 80°C, and H₂/O₂.

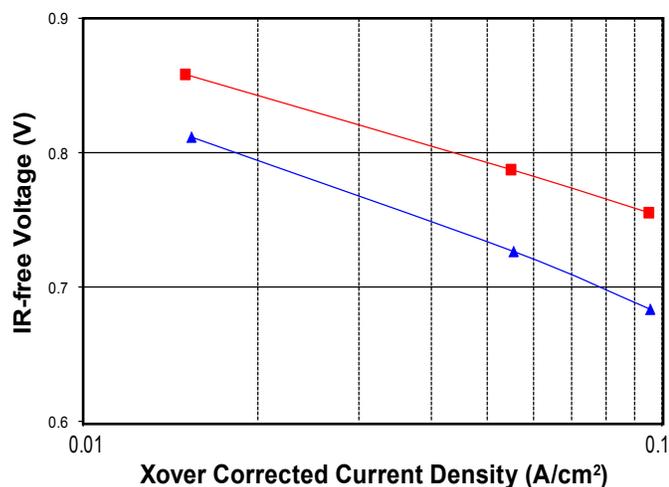


FIGURE 2. Corresponding Tafel Plots for Fe-N_x catalysts prepared using melamine precursors, with (red) and without (blue) back pressure (150 kPa). Plots reflect internal resistance correction and adjustment for hydrogen cross over.

back-pressure of 1 bar, respectively. However, at 80°C under H₂/air with 100% RH or 50% RH, this MEA showed very poor performance.

In situ durability tests were performed on the same MEA (Fe-N_x melamine precursor sample) which was used to evaluate I-V performance (Figures 1 and 2). Two types of in situ durability tests, namely load cycling and start-stop cycling (10,000 cycles) were performed. The first referred to as catalyst durability test (or Pt dissolution protocol in NTCNA parlance) involved square wave potential cycling tests in the range of 0.6 and 1.0 V with 3 s on and 3 s off periods (Figure 3). The same MEA used for support durability tests, here cycling were used in the range of 1.0 and 1.5 V in a triangular profile (Figure 3) referred to as carbon corrosion test. In this case, the open circuit voltage value did change due to the potential cycling resulting in carbon loss.

The I-V performance curves were recorded before and after these durability tests. Catalyst durability cycling showed minimal effect on I-V performance with and without back-pressure. However, carbon corrosion test cycling

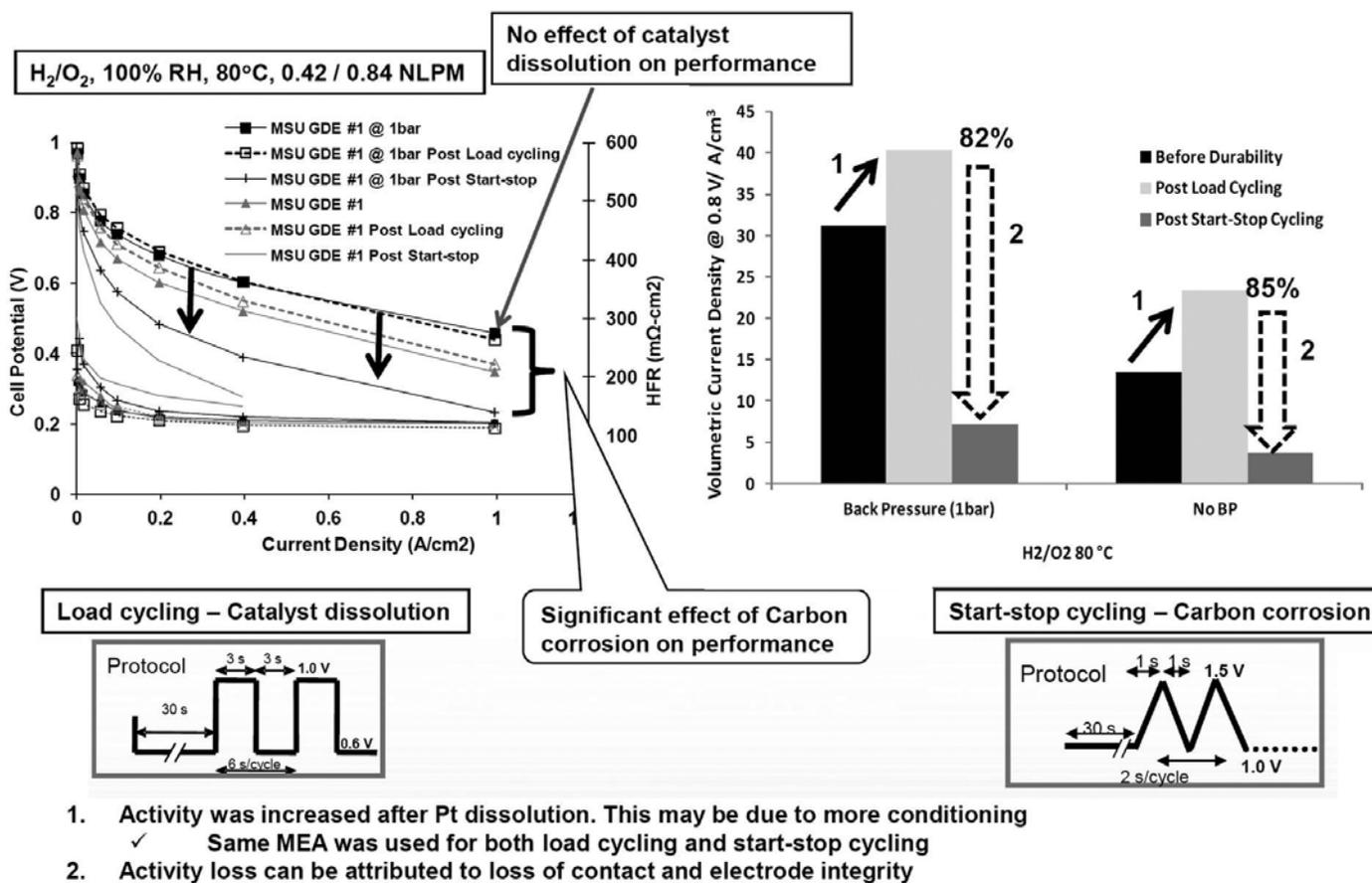


FIGURE 3. Durability tests in single cells (80°C, 100% RH, with and without backpressure, 150 kPa). Two protocols were (a) catalysts durability involving cycling between 0.6 and 1.0 V in a square wave profile with 3 s on and 3 s off periods and (b) carbon corrosion tests between 1.0 and 1.5 V in a triangular profile.

showed significant drop in performance under both pressure conditions. The drop in performance due to start-stop cycling can be attributed to formation of surface oxides on the carbon surface making it hydrophilic in nature. Also, loss in carbon causes a decrease in the electronic conductivity resulting in lower performance which can be observed in the kinetic region.

Conclusions and Future Directions

- A multipronged effort involving several different chemistries is being pursued for the effective development of a non-PGM-based oxygen reduction catalyst.
- Initial results have shown good performance both in RRDE as well as fuel cell test conditions. Performance of 130 A/cm³ is reported based on projections in a single-cell test conducted at NTCNA. This is close to the 2010 DOE non-PGM target.
- Excellent catalyst durability is reported using NTCNA/DOE cycling protocols, however significant carbon corrosion is measured which needs to be addressed via modifications in pretreatments to carbon blacks, use of grapheme-based materials as well as stable transition metal oxide supports.

FY 2011 Publications/Presentations

1. “Unveiling N-Protonation and Anion-Binding Effects on Fe/N/C-Catalysts for O₂ Reduction in PEM Fuel Cells”, Herranz, Juan; Jaouen, Frederic; Lefevre, Michel; Kramm, Ulrike; Proietti, Eric; Dodelet, Jean-Pol; Bogdanoff, Peter; Fiechter, Sebastian; Abs-Wurmbach, Irmgard; Bertrand, Patrick; Arruda, Thomas; Mukerjee, Sanjeev, *J. Phys. Chem. C* (In Press).

References

1. Wu, G.; More, K.L.; Johnston, C.M.; Zelenay, P. *Science* **2011**, *332*, 443.
2. Lefevre, M.; Proietti, E.; Jaouen, F.; Dodelet, J.P. *Science* **2009**, *324*, 71.