

V.A.8 Development of Novel Non-PGM Electrocatalysts for Proton Exchange Membrane Fuel Cell Applications

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- Nissan Technical Center, North America (NTCNA), Detroit, MI (Nilesh Dale)
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Overall Objectives and Objectives for Fiscal Year (FY) 2014

The objective of this project is to design non-platinum group metal (PGM)-based catalysts 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. The principal target for the reporting FY was to take the project beyond the first phase, where the project's Go/No-Go milestone of 100 mA/cm² @ 0.8 V (internal resistance-free, iR-free) at 80°C, pure H₂/O₂, with 1.5 bar total pressure was met. This reporting period, the principal objective was to transition the project from H₂/O₂ to H₂/air with slated target of 30 mA/cm²

@ 0.8 V, 2.5 bar total pressure and an end-of-the-project target of 1 A/cm² @ 0.4 V (same total pressure), both under 100% relative humidity (RH). In a quarterly timeline basis, the target for scale up was to achieve 50 gm batch size by the 3rd quarter and 100 gm batch size at the end of the project (5th quarter). Both these scale-up targets had a quality control milestone of less than 5% variation of activity measured with H₂/air (2.5 bar total pressure) at 0.8 V. In addition, the project aimed at arriving at a unified understanding of the nature of active sites in these catalysts as well as some preliminary understanding of the mechanistic pathway.

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 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

The technical targets for this project are listed in Table 1.

FY 2014 Accomplishments

1. Following our Go/No-Go decision target (successfully met in July 2013), our down-selected catalyst was from University of New Mexico, referred to as UNM-CTS (mechano-chemical approach using water insoluble nicarbazin) catalyst. In order to transition to areal performance with air, blends were prepared of this down-selected catalyst with previously developed catalyst from University of New Mexico referred to UNM-CBDZ (prepared using non-metal chelating approach using carbendazim material) to improve mass transport and durability. As per our milestones for areal activity in H₂/air (Table 1), we have successfully surpassed the low current density target (30 mA/cm² @ 0.8 V). Our current state of the art for high-current-density performance stands at 850 mA/cm² using the above-mentioned blends. In addition, emerging catalysts prepared using an Fe-encapsulated metal organic framework (MOF) chemistry approach referred to as NEU-Fe-MOF (from Northeastern University) show great promise for an alternative approach. Preliminary

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

Characteristic	Units	2015 Target	NEU 2014 status
Specific activity @ 80°C, 1.5 bar total pressure, H ₂ /O ₂ , 100% RH	A/cm ³	Volumetric activity of 300 A/cm ³ @ 0.8 V (iR-free) projected from ~10 mA/cm ² Un-projected volumetric activity (no target set)	400 A/cm ³ 95 A/cm ³
2013 Go/No-Go target	A/cm ²	100 mA/cm ² (iR-free)	100 mA/cm ²
Specific activity @ 80°C, 2.5 bar total pressure, H ₂ /Air, 100% RH 2014 target	A/cm ²	Areal activity of 30 mA/cm ² @ 0.8 V Areal activity of 1 A/cm ² @ 0.4 V	70 mA/cm ² 800 mA/cm ²
Scale-up of catalyst Intra- and inter-batch variability	gms percent	50 gms 5% variation for both inter- and intra-batch	Target successfully met Target successfully met
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

measurements indicate that this has the potential of meeting both the low- and high-current-density areal activity targets in air. However, this is data using small batch synthesis (below 1 gm batch size). Our current efforts include approaches for scaling up the synthesis using low-cost precursors.

- Our current efforts toward scale up performed by Pajarito Powders are on target based on the timelines for the slated milestones. At the end of the second quarter in the second phase of this project, we have successfully demonstrated less than 5% variability in performance at the low current density target potential (0.8 V) and approximately 5% variability at the higher current density (0.6 V). These variabilities include materials, reflecting both inter- and intra-batch measurements. This data is exclusively from areal activity measurements using single-cell data in air as per this project's slated operating conditions (2.5 bar total pressure in air, 100% humidification at 80°C).
- Durability measurements conducted on the down-selected UNM-Fe-CTS catalysts show excellent tolerance to catalyst stability tests. Carbon corrosion tests, which involve load cycling to 1.5 V vs. the reference hydrogen electrode, however, indicated significant losses, similar to the losses with a PGM cathode.
- Understanding of the nature of the active site was significantly advanced in this reporting period with identification of a dual site mechanism wherein the N₂₊₂ site was responsible for the initial adsorption and reduction of oxygen to peroxide moieties followed by a second cascade step of further reduction of the peroxide in closely surrounding Fe-N₂ sites. Such formulation of the mechanism was supported with in situ X-ray absorption spectroscopy and targeted electrochemical probe measurements.



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 oxygen reduction reaction (ORR) activity derived from materials prepared using a variety of polymeric precursor materials viz. the current state of the art by three different university groups, (b) successful transition from previous operations in oxygen to air, (c) excellent durability in terms of catalyst stability (*vide* DOE and Nissan protocols), and (d) detailed understanding of the 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 blends of materials derived using two separate approaches under the common ambit of the University of New Mexico group's silica templating methodology, referred to as the UNM-CTS and UNM-CBDZ. The former material (UNM-CTS) was derived using a mechano-chemical approach of ball milling an organic charge transfer salt (nicarbazin) in the presence of Fe salt and the latter using an aqueous formulation of a non-chelating material, carbendazim, with Fe salt, both in conjunction with silica support followed by several steps of pyrolysis and etching. Typical blends comprised a 1:1 mixture. The Northeastern University approach involved a one-pot synthesis of an MOF material

referred to as Zif8 in conjunction with chelated metal salt encapsulation.

These derived materials were tested in single cells (5 cm^2) using a commercial anode electrode (Alfa Aesar) containing 0.3 mg/cm^2 Pt loading. Typical cathode loading was 2 mg/cm^2 , and the membrane used was Nafion[®] 211, with 50% Nafion[®] loading at the cathode. Tests were conducted under steady-state potentiostatic conditions with each point measured for a minimum of 60 s. Common test protocols are replicated at NTCNA and NEU. In this annual report, the data related to scale up efforts were exclusively conducted at Pajarito Powders Corp. Durability studies were performed on pre-scale-up catalysts at the Nissan Technical Center. Investigation of the nature of active site and ORR electrocatalysis steps was accomplished using in situ synchrotron spectroscopy at the Fe-K edge under actual cell *operando* conditions.

RESULTS

Pajarito Powder has scaled up formulations of the charge transfer salt (CTS) catalyst and a previously reported (Phase 1) derived UNM catalyst referred to as UNM-CBDZ in a 1:1 ratio. The approaches for both these catalysts are briefly described above in the approach section. The key purpose for this formulation was to (a) improve mass transport to meet the areal activity target in H_2/air as well as (b) provide higher durability under the two above-mentioned (see approach section) DOE-mandated protocols. The chemically intensive approach for scale up involved several key steps requiring optimization. The initial scale up effort was focused on a 10-20-gram batch (Phase 1, reported in the 2012-13 report), with the goal that the methods developed can be applied towards 30-50 gr, with trajectory towards 100-gram batches.

Demonstration of trajectory towards 100 grams per batch of the original Fe-CTS catalyst involved pretreatment of precursors to reduce and eliminate precursors source and batch consistency effects on manufacturing. As mentioned above, the milestone was to meet the H_2/air areal performance target of $30 \text{ mA @ } 0.8 \text{ V}$ and $1,000 \text{ mA @ } 0.4 \text{ V}$ in 2.5 bar air, 80°C , 100% humidification.

The trajectory towards 100-gram batches was established through use of larger volume processing equipment, processing vessel materials changes, and tuning of processing parameters such as the pyrolysis temperature trajectory, etching times and agitations, and mixing times and intensity.

Increased manufacturability and production robustness due to pretreatment and conditioning of precursors is demonstrated in the performance of a 50-gram batch made using a 10-kg aliquot from a 100-kg key precursor conditioned and pretreated so the final catalyst matches catalysts made from different batches of the same key precursor sold in 100-gram containers.

A brief summary illustrating these developments is presented, showing a nearly 80% improvement in performance in air (compared to previous reporting period) with $70 \text{ mA @ } 0.8 \text{ V}$ and $800 \text{ mA @ } 0.4 \text{ V}$ achieved using 2.2 mg/cm^2 loading gas diffusion electrodes. Figure 1(a) shows two separate formulations (Gen 1 and Gen 2, blends) using variations in silica templates. Comparison of Gen 2 (100% CTS batch) and Gen 2A (CTS/CBDZ blend) with variation of the silica template shows remarkable inter-batch reproducibility in H_2/air . The low current density target of 30 mA/cm^2 at 0.8 V (uncorrected) has been met and exceeded with current state-of-the-art 70 mA/cm^2 current density. The higher current density target of 1 A/cm^2 at 0.4 V (uncorrected) (quarter 5, end-of-project target) is not yet met, with current activity at 0.8 A/cm^2 . These performance figures are better delineated in the corresponding Tafel (semi-log) plot shown in Figure 1(b). Both these are reported without any internal resistance correction. Figure 1(c) reports intra-batch variations in performance using Gen 2 catalyst formulations. Over the upcoming period, further improvements to performance will continue, and modeling predictions from MSU will be combined with impedance and helium-oxygen testing at NEU to determine transport issues. In addition, NTCNA will be testing the improved Gen 2 catalyst.

A brief introduction to the NEU catalyst synthesis methodology is provided in Figure 2(a), wherein an iron-based non-PGM ORR electrocatalyst utilizes a MOF-based support that hosts a chelated iron complex within its pores. The MOF support was chosen in order to take advantage of the porosity and high surface area that are key features known to improve the catalytic activity and mass transport. A one-pot encapsulation procedure developed by NEU uses a zinc metal organic framework (ZIF-8 MOF) synthesized in the presence of the chelated Fe (or Co) precursors. The final product was dried in a vacuum oven for 4 hours at 70°C , followed by either one or two heat-treatments in argon at $1,050^\circ\text{C}$ and ammonia at 950°C . Preliminary rotating disk electrode analysis, shown in Figure 2(b), shows performance exceeding that of Pt in alkaline electrolyte (0.1 M KOH) and a half-wave potential difference of 70 mV compared to Pt in acidic pH (0.1 M HClO_4). Non-Fe-containing MOF shows comparatively a 400 mV over-voltage, indicating predominant peroxide generation. Preliminary fuel cell measurements made using H_2/O_2 (1.5 bar total pressure), 80°C , 100% humidification indicated performance in excess of the DOE Phase 1 target of 100 mA/cm^2 at 0.8 V (iR corrected) with current state of the art at 170 mA/cm^2 . More importantly, the H_2/air performance meets both the low (0.8 V iR uncorrected) and high current density (0.4 V iR uncorrected) values with current state of the art at 75 mA/cm^2 (at 0.8 V) and 1 A/cm^2 (at 0.4 V).

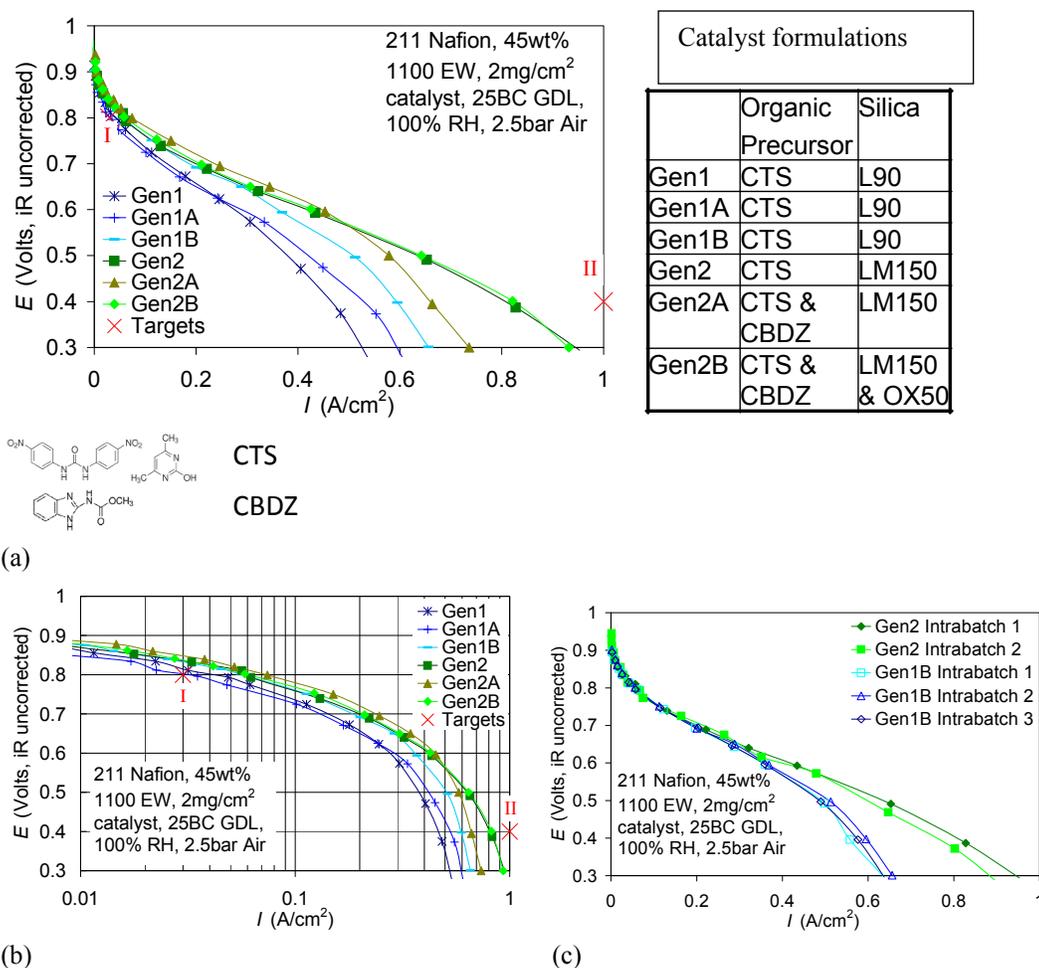


Figure 1 (a-c). Areal activity measured using 5-cm² single cells in H₂/air (2.5 bar total pressure), 80°C, 100% humidity, 2.2 mg/cm² non-PGM catalyst loading at the cathode and anode comprising a commercially obtained electrode (Alfa Aesar, 0.5 mg/cm² Pt loading on SGL substrate). The non-PGM catalyst depicted comprised both a pure UNM-CTS (Gen 1) and a formulation (1:1) of UNM-CTS and UNM-CBDZ (Gen 2) using different formulations of silica support (resultant pore formation). Here the batch sizes used were in excess of 50 gms. (a) Inter-batch variations between Gen 1 and Gen 2 and internal formulation effects using variation of silica support. (b) The corresponding Tafel slope showing performance in lieu of this project's milestones for both low- and high-current-density operation. (c) Intra-batch variations for both Gen 1 and 2 catalysts.

CONCLUSIONS

- Catalyst blends (1:1) prepared by Pajarito Powders using 50+ gms batch sizes with UNM catalysts (UNM-CTS and UNM-CBDZ) show inter- and intra-batch variations below 5%. They also meet and exceed the low-current-density areal activity target in H₂/air (2.5 bar total pressure, 80°C, 100% RH). The high-current-density target of 1 A/cm² at 0.4 V (quarter 5, end-of-project target) is currently at 800 mA/cm². A separate MOF-based approach from NEU shows excellent areal activity under these performance metrics, exceeding the low-current-density benchmark and meeting the high-current-density target.

- Detailed durability studies reported earlier on the UNM catalysts measured by NTCNA indicate excellent tolerance to catalyst stability tests and relatively poor resistance to carbon corrosion test protocols; the latter, however, is on par with those observed for PGM catalysts.

FUTURE DIRECTIONS

- The principal focus of the group will be to meet the high-current-density areal activity target at 0.4 V (iR uncorrected) using both UNM blend formulations. Correlate impedance and helium-oxygen experiments with modeling to identify dominant polarization effects.

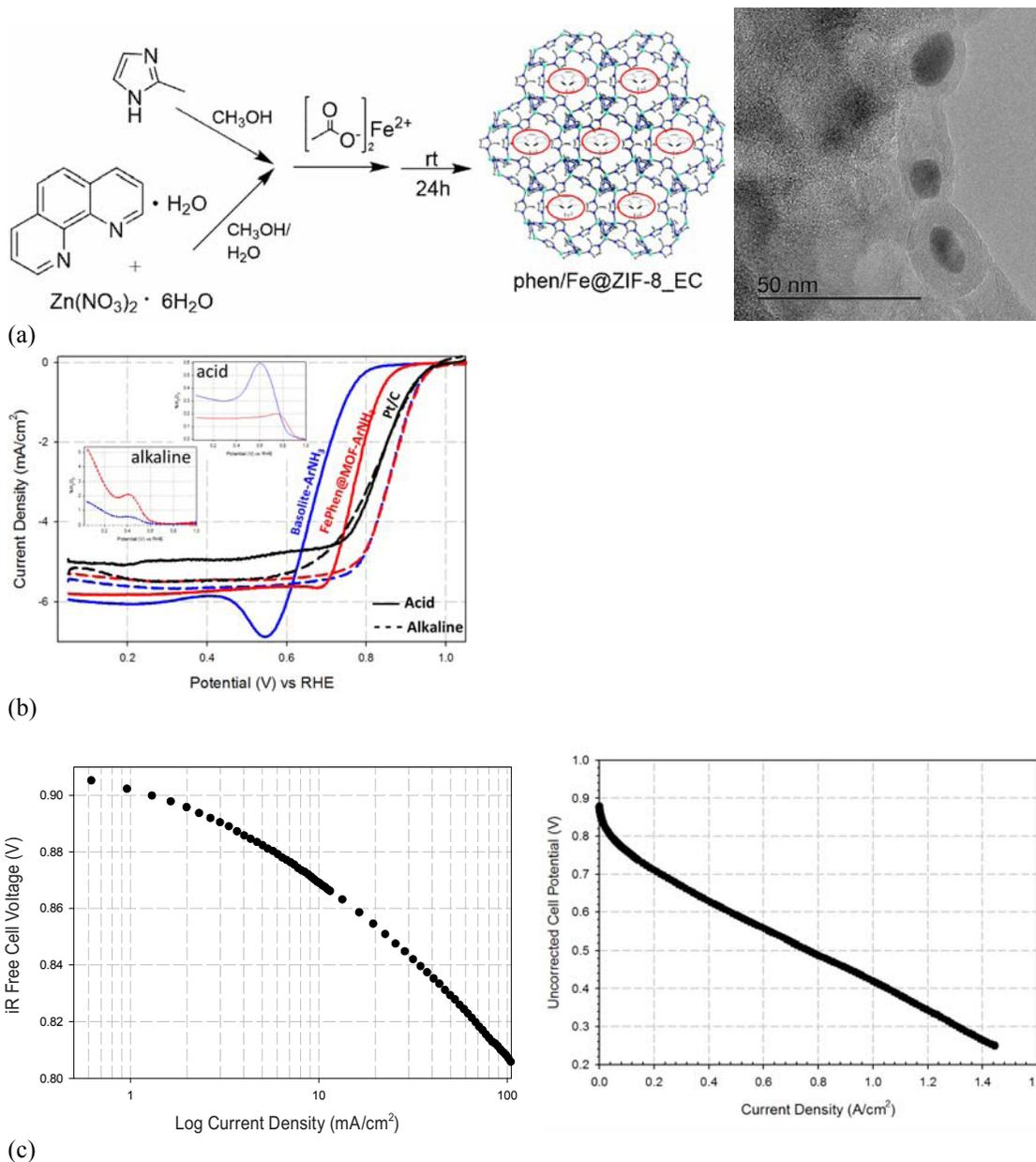


Figure 2 (a-c). (a) Schematic showing the one-pot synthetic approach for NEU MOF-based Fe-encapsulated catalysts. Scanning electron micrograph shows encapsulation and carbon fiber formation. (b) Rotating disk electrode comparison with Pt/C (Tanaka 30% Pt/C) in both acid and alkaline pH (0.1 M KOH and HClO₄). Also plotted is a non-Fe-containing catalyst referred to as Basolite. (c) Tafel plot for single-cell data (5 cm²) in H₂/O₂ with 1.5 bar total pressure, 100% RH, 80°C. Also shown is the corresponding linear polarization data (iR uncorrected) in H₂/air showing the concomitant low- and high-current-density performance using 2.5 bar total pressure.

2. Optimize scale up and MEA fabrication for MOF-based catalysts from NEU.
3. Validate durability under DOE protocols with tests conducted at NTCNA.
4. Further test the validity of the proposed mechanism using final set of in situ and *operando* synchrotron X-ray absorption spectroscopy data in conjunction with density

functional theory calculations. In addition, use the in situ spectroscopy to probe degradation pathways.

FY 2014 PUBLICATIONS

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3. 'Catalytic activity of Co-N_x/C electrocatalysts for oxygen reduction reaction: a density functional theory study', P. Atanassov, and B. Kiefer, *Phys. Chem. Chem. Phys.*, **15**, 148-153 (2013).

4. 'Mechanistic studies of oxygen reduction Fe-PEI derived non PGM electrocatalysts, A. Serov, U. Tylus, K. Kartyushkova, S. Mukerjee and P. Atanassov, *App. Catal. B.*, **150-151**, 179-186 (2014).

5. 'Elucidating oxygen reduction active sites in pyrolyzed metal nitrogen coordinated non precious metal electrocatalysts systems', U. Tylus, Q. Jia, K. Strickland, N. Ramaswamy, A. Serov, P. Atanassov and S. Mukerjee, *J. Phys. Chem. C.*, **118 (17)**, 8999-9008 (2014).

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7. 'Activity descriptor identification for oxygen reduction on non precious electrocatalysts: linking surface science to coordination chemistry', N. Ramaswamy, U. Tylus, Q. Jia and S. Mukerjee, *J. Amer***135(41)**, 15443-15449 (2013).

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9. 'Impact of transition metal on nitrogen retention and activity of iron-nitrogen-carbon oxygen reduction catalysts.', S. Ganesan, N. Leonard and S.C. Barton, *Phys. Chem. Chem. Phys.*, **16**, 4576-4585 (2014). doi:10.1039/c3cp54751e.

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