V.A.5 Development of Novel Non-PGM Electrocatalysts for Proton Exchange Membrane Fuel Cell Applications

Sanjeev Mukerjee (Primary Contact)
Department of Chemistry and Chemical Biology
Northeastern University (NEU)
Boston, MA 02115
Phone: (617) 373-2382
Email: S.mukerjee@neu.edu

DOE Managers
Donna Lee Ho
Phone: (202) 586-8000
Email: Donna.Ho@ee.doe.gov
David Peterson
Phone: (720) 356-1747
Email: David.Peterson@ee.doe.gov

Contract Number: DE-EE0000459

Subcontractors
- University of New Mexico (UNM), Albuquerque, NM (Prof. Plamen Atanassov)
- Michigan State University (MSU), East Lansing, MI (Prof. Scott Barton)
- Nissan Technical Center, North America (NTCNA), Detroit, MI (Dr. Nilesh Dale)
- Pajarito Powder, LLC (PPC), Albuquerque, NM (Dr. Bar Halevi)

Project Start Date: August 1, 2010
Project End Date: July 31, 2015

Overall Objectives and Objectives for Fiscal Year (FY) 2014-2015

The objective of this project is to design non-platinum group metal (non-PGM)-based catalysts and supporting gas transport layers, and optimize both the interfacial reaction zone between the electrode and membrane as well as the underlying gas diffusion medium to meet and exceed DOE goals for application in solid polymer electrolyte fuel cells. This project is focused on materials development and is assisted by employing advanced analytical tools, computation, and testing to improve overall design by gaining a critical understanding of the the electrocatalysis pathway in these novel structures. The principle 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/cm^2 at 0.8 V (internal resistance-free, iR-free) at 80°C, in pure H_2/O_2, and with 1.5 bar total pressure was met. For this reporting period, the principle objectives were to (a) transition the project from hydrogen/oxygen to hydrogen/air with a slated target of 30 mA/cm^2 at 0.8 V, 2.5 bar total pressure and (b) reach an end-of-project target of 1 A/cm^2 at 0.4 V (same total pressure), both under 100% relative humidity. On a quarterly timeline basis, the target for scale-up was to achieve 50 g batch size by the fourth quarter FY 2014 and 100 g batch size at the end of the program (second quarter FY 2015). Both of these scale-up targets had a quality control milestone of less than 5% variation of activity as measured with hydrogen/air (2.5 bar total pressure) at 0.8 V. In addition, the project aimed to arrive 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:

(A) Durability (increase the durability/stability of catalysts with cycling)

(B) Cost (eliminate precious metal loading of catalysts)

(C) Performance (increase the specific and mass activities of catalysts)

Technical Targets

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

FY 2015 Accomplishments

Since achieving our go/no go decision target (July 2013), our down-selected catalysts were obtained from University of New Mexico and were referred to as UNM-CTS (mechano-chemical approach using water insoluble nicarbazin) catalysts. In order to transition to areal performance in air, several blends of the down-selected catalysts were made by combining them with a previously developed catalyst from UNM referred to as UNM-CBDZ (prepared using a nonmetal chelating approach using carbendazim material). As per our milestones for areal activity in hydrogen/air (Table 1), we have successfully surpassed the low current density target (30 mA/cm^2 at 0.8 V). Our current state-of-the-art for high current density performance stands at 1,050 mA/cm^2 using the above-mentioned blends. These results correspond to a 200 g batch size well in excess of the end of the program metrics. In addition, emerging catalysts prepared using an iron-encapsulated metal organic framework (MOF) chemistry approach referred to as NEU-Fe-MOF (from Northeastern

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

Characteristic	Units	2015 Target	NEU 2015 Status
Specific Activity @ 80°C, 1.5 bar total pressure, H_2/O_2, 100% relative humidity (RH) 2013 Go/No-Go Target	A/cm^3 A/cm^2	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) 100 mA/cm^2 (iR-free)	400 A/cm^3 95 A/cm^3 100 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	100 mA/cm^2 1,050 mA/cm^2
Scale-Up of Catalyst Batch Size Intra and Inter Batch Variability	g %	50 g & trajectory to 100 g 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

University) show great promise for an alternative approach. Preliminary measurements indicate that this material has the potential to meet both the low and high current density areal activity targets in air. Our initial report (the last annual report) showed this data using small batch synthesis (a batch size of less than 1 g). Current efforts include developing approaches for scaling up the synthesis using low cost precursors, and these have achieved 30 g batch size levels. While the low current density performance is well in excess of 30 mA/cm^2 (100 mA/cm^2 at 0.8 $V_{non\ IR\text{-}corrected}$), the high current density target is still a challenge with the current state-of-the-art exhibiting 750 mA/cm^2 at 0.4 $V_{non\ IR\text{-}corrected}$) short of the targeted 1 A/cm^2.

Our current efforts towards scale-up performed by PPC 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 successfully demonstrated less than 5% variability in performance in the low current density target potential (0.8 V) and approximately 5% variability at the higher current density (0.6 V). These variabilities reflect both inter and intra batch measurements. These data are based exclusively on areal activity measurements made 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 (Fe-organic charge transfer salt based on nicarbazin) catalysts shows excellent tolerance to catalysts stability tests (based on Nissan protocol, similar to DOE protocol). Carbon corrosion testing that involved load cycling to 1.5 V vs. the reference hydrogen electrode, however, indicated significant losses; these results were similar to losses seen with a PGM cathode.

The understanding of the nature of the active site was significantly advanced in this reporting period with the 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 by a second cascade step of further reduction of the peroxide in surrounding Fe-N_2 sites. This description of the mechanism was supported with in situ X-ray absorption spectroscopy (XAS) and targeted electrochemical probe measurements.

✧ ✧ ✧ ✧ ✧

INTRODUCTION

Recent reports [1–3] have clearly demonstrated the significant advancements made in enabling good oxygen reduction activity with iron-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 [1,4]. This report provides for the first time a comprehensive view of (a) the gains in oxygen reduction reaction (ORR) activity derived from materials prepared using current state-of-the-art materials developed by two different university groups (NEU and UNM) and the successful scale-up of these by a startup company, PPC; (b) the successful transition from previous operations in oxygen to air (MSU, NEU, and PPC); (c) excellent durability in terms of catalyst stability (*vide* DOE and Nissan protocols) (UNM and NTCNA); and (d) a detailed understanding of the nature of active sites and electrocatalytic pathways as distinct from the parallel pathway in alkaline electrolytes (UNM and NEU).

APPROACH

The approach adopted in this reporting period involved blends of materials derived using two separate approaches: a UNM group's silica templating methodology referred to as UNM-CTS and a UNM-CBDZ approach. The former (UNM-CTS) was derived using the 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, and both were supported on

silica followed by several pyrolysis and etching steps. Typical blends comprised of a 1:1 mixture. The Northeastern University approach involved a one pot synthesis of an MOF material referred to as ZIF-8 that encapsulated a chelated metal salt.

These materials were tested in single cells (5 cm^2) using a commercial anode electrode (Alfa Aesar) with a 0.1 mg/cm^2 Pt loading. The typical cathode loading was 3 mg/cm^2 and the membrane used was a 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. In this annual report all reported tests were conducted at PPC, using scaled-up batches of 50 g and above for the UNM-CTS approach and 30 g for the NEU-MOF approach. Common test protocols were replicated at NTCNA and NEU. Durability measurements were performed using two well-established protocols (catalyst durability) and carbon corrosion tests (both are DOE protocols). Investigation of the nature of active sites and ORR electrocatalysis steps as measured using in situ synchrotron spectroscopy at the Fe-K edge were performed under actual cell operando conditions.

RESULTS

PPC has scaled up formulations of both the UNM sample and the NEU-developed approach and also modified the UNM catalyst for improved performance. Brief descriptions of the approaches employed for both catalysts are given in the approach section. The UMN catalyst was reformulated to (a) improve mass transport to meet the areal activity target in hydrogen/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 g batch [1], with the goal that the methods developed could be applied for synthesizing between 30 g and 50 g, with a long-term goal of 100 g batches.

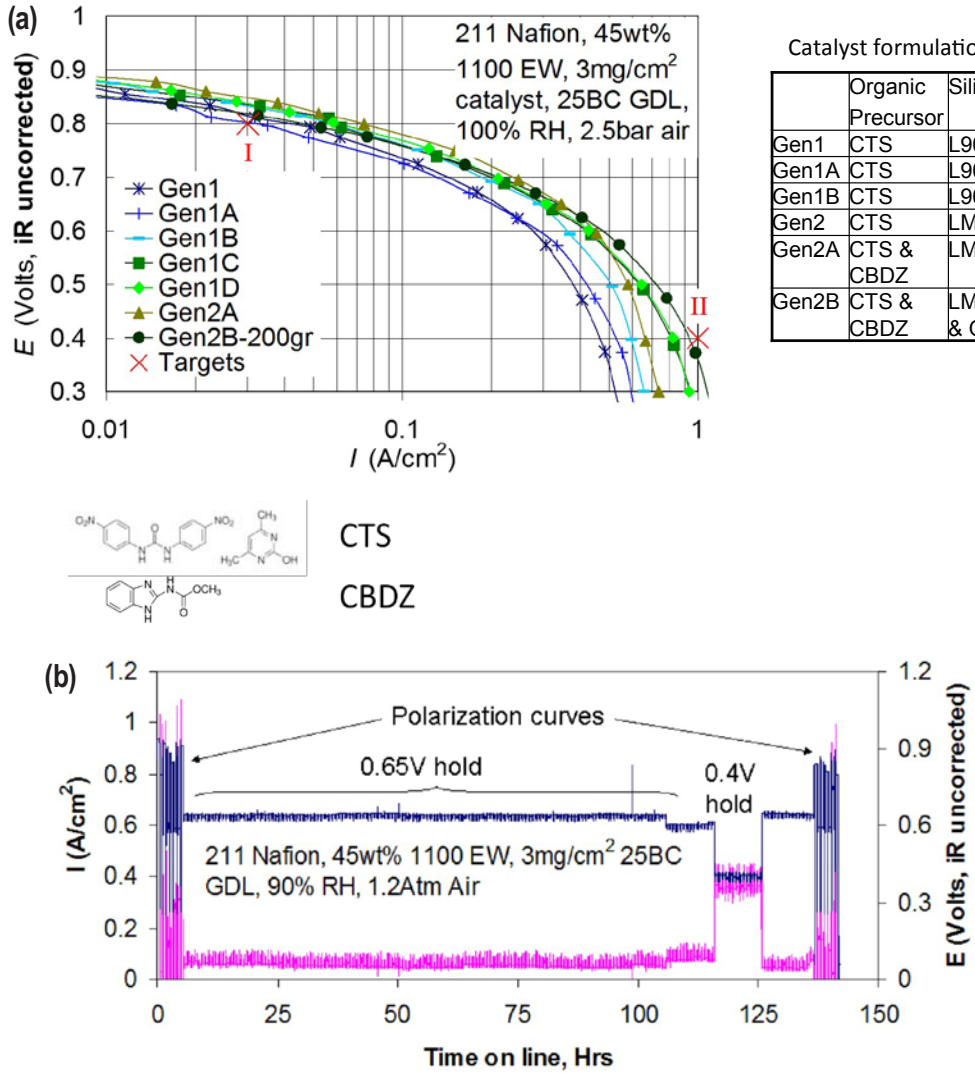
Demonstration of progress towards 100 g per batch synthesis of the original Fe-CTS catalyst involved pre-treatment of precursors to reduce and eliminate residual precursor and batch consistency effects on manufacturing. As mentioned above the milestone is to meet the hydrogen/air areal performance target of 30 mA/cm^2 at 0.8 V and 1,000 mA/cm^2 at 0.4 V in 2.5 bar air and 80°C at 100% humidification.

Progress towards 100 g 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. In this way, 200 g batches have been prepared.

A brief summary illustrating these developments is presented showing a nearly 80% improvement in performance in air (compared to previous reporting period) with 70 mA/cm^2 at 0.8 V and 1,000 mA/cm^2 at 0.8 V achieved using 3 mg/cm^2 loading gas diffusion electrodes. Figure 1a shows two separate blend formulations, Gen 1 and Gen 2, made using variations in silica templates. Comparison of Gen 2 (100% CTS batch) and Gen 2A (CTS/CBDZ blend with variation of silica template show remarkable inter batch reproducibility in hydrogen/air performance in accordance to this project's targeted operating conditions. 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 performance at 70 mA/cm^2 current density. The higher current density target of 1 A/cm^2 at 0.4 V (infrared [IR]-corrected) (second quarter, FY 2015) has nearly been met with current activity at 0.92 A/cm^2 (uncorrected) and 1.05 A/cm^2 (IR-corrected). These performance figures are better delineated in the corresponding Tafel (semi-log plot) shown in Figure 1a. Both of these results are reported without any IR correction.

A brief introduction to the NEU catalyst synthesis methodology is reported in Figure 2a, wherein an iron-based non-PGM ORR electrocatalyst utilizes an 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, key variables known to improve the catalytic activity and mass transport. A one pot encapsulation procedure developed by NEU uses a zinc MOF (ZIF-8 MOF) synthesized in the presence of chelated iron (or Co) precursors. The final product was dried in a vacuum oven for four hours at 70°C and then further treated by either one or two heat treatments in argon at 1,050°C and ammonia at 950°C, respectively. Preliminary rotating disc electrode (RDE) analysis shown in Figure 2b shows performance exceeding that of platinum in alkaline electrolyte (0.1 M KOH) and a half wave potential difference of 70 mV compared to platinum in acidic pH (0.1 M $HClO_4$). Non-iron-containing MOF shows, in comparison, 400 mV over-voltage indicating predominant peroxide generation. Preliminary fuel cell measurements made using hydrogen/oxygen (1.5 bar total pressure), 80°C, and 100% humidification indicated performance in excess of 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 hydrogen/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).

After a lengthy analysis, PPC identified unique processing equipment and supplies needed for the technology transfer and scale-up. Once in place, lengthy visits by PPC personnel to NEU led to creation of standard operating procedures, and critical points of manufacturing were



Catalyst formulations

	Organic Precursor	Silica
Gen1	CTS	L90
Gen1A	CTS	L90
Gen1B	CTS	L90
Gen2	CTS	LM150
Gen2A	CTS & CBDZ	LM150
Gen2B	CTS & CBDZ	LM150 & OX50

FIGURE 1. Areal activity measured using 5 cm^2 single cells using H_2/air (2.5 bar total pressure), 80°C, 100% humidity using 3 mg/cm^2 non-PGM catalyst loading at the cathode and anode comprising of a commercially obtained Pt/C catalyst (JM Hispec 2000, 0.1 mg/cm^2 Pt loading on SGL substrate). The non-PGM catalyst depicted was comprised of both a pure UNM-CTS (Gen 1) and a formulation (1:1) of UNM-CTS and UNM-CBDZ using different formulations of silica support (resultant pore formation). Here, the batch sizes used were in excess of 50 g. (a) Tafel slope exhibiting performance meeting this project's milestones for both low and high current density operation, including a 200 g batch. (b) 0.65 V potentiostatic hold test for the 200 g batch, exhibiting excellent stability over 100 h.

determined to be (1) making the MOF, (2) mixing the MOF and precursors, and (3) pyrolysis both in inert and reactive atmospheres. To establish calibration points of processing equipment a series of materials at the different stages of manufacturing identified have been sent to project partners (NEU and NTCNA) and are being characterized to determine points of congruency in the processing. This procedure allowed baseline levels and sensitivity of processing variables for the key processing steps to be established and used during scale-up.

Scale-up required modification of the both the recipe and procedure used in the key MOF-forming step. First, switching from a small shaker-type mill to a larger planetary ball mill lead to a tendency for powder clumping that is inherent with powder milling. When simply applying NEU's procedure with a planetary ball mill, the resulting MOF powder included clumps, and the resultant material had a lower surface area than what is required for producing good catalysts. Clumping increased with 10, 20, and 50x batch sizes. Numerous iterations of precursor pretreatments, sequence of addition, and even material ratios were attempted unsuccessfully. Methods were found in the literature and with NEU's assistance, a formulation that decreased clump formation was successfully achieved even when applied at 50x scale, producing good quality MOF as determined by X-ray diffraction (XRD), Brunauer-Emmett-

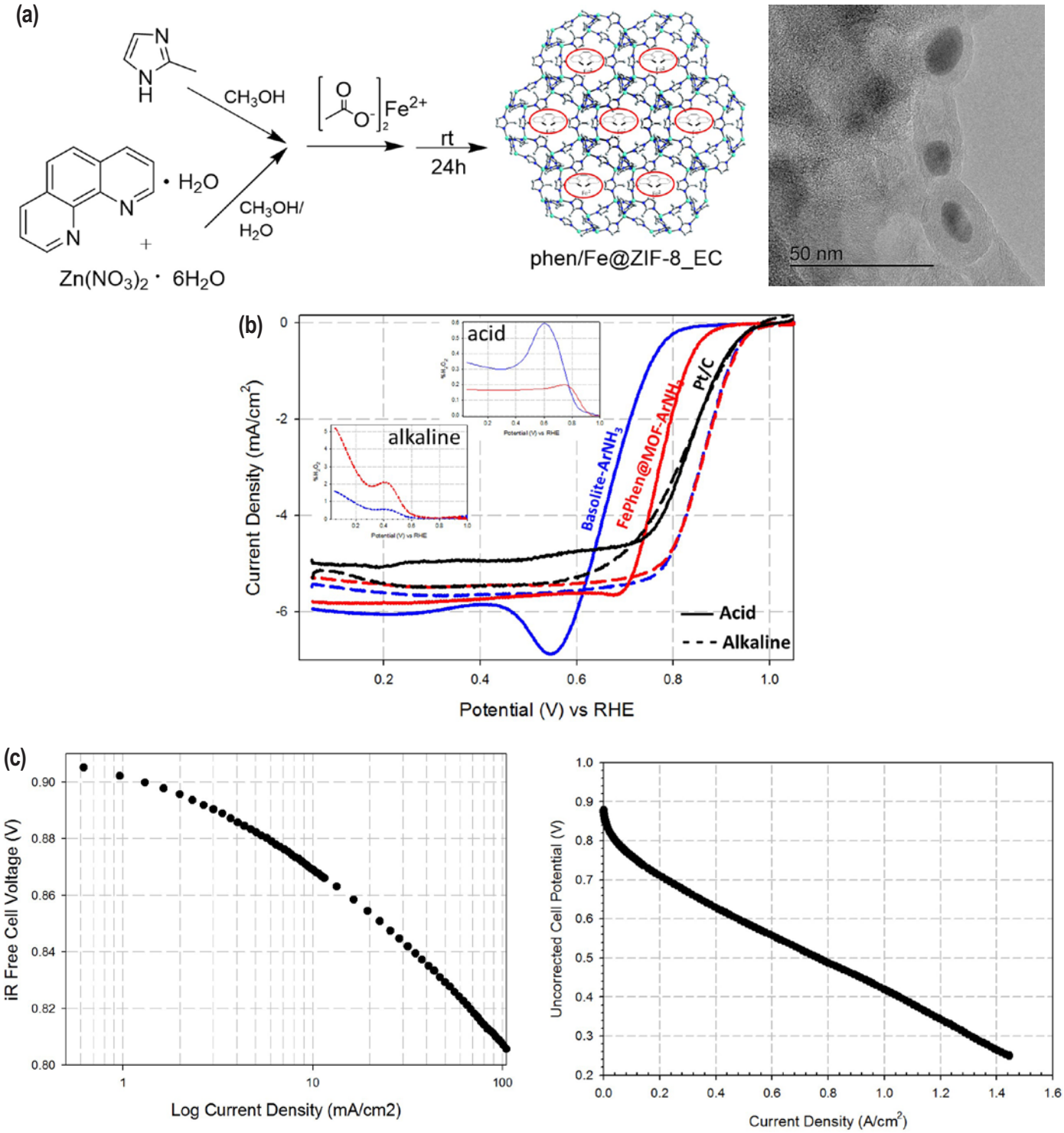


FIGURE 2. (a) Schematic showing the one pot synthetic approach for NEU MOF-based iron encapsulated catalysts. Scanning electron microscope micrograph shows encapsulation and carbon fiber formation. (b) RDE comparison with Pt/C (Tanaka 30% Pt/C) in both acid and alkaline pH (0.1 M KOH and $HClO_4$). Also plotted is a non-iron-containing catalyst referred to as Basolite. (c) Tafel plot for single cell data (5 cm^2) in H_2/O_2 with 1.5 bar total pressure, 100% RH, 80°C. Also shown is the corresponding linear polarization data (IR-uncorrected) in H_2/air showing the concomitant low and high current density performances under 2.5 bar total pressure.

Teller surface areas at different processing steps, and final catalyst performance. Figure 3a shows the XRD patterns of commercial ZIF-8 MOF, as well as the time trajectory of MOF phase evolution at various milling times, and the final 50x batches used for making the excellent performance MOF-based catalyst shown in Figure 3b. Figure 3b shows the performance of scaled-MOF based catalysts, and improvement in both performance and scale to a final catalyst made at 50x scale (30+ g per batch) with performance after being on-line for more than two hours of more than 100 mA/cm^2 at 0.8 V, and 800 mA at 0.4 V in 2.5 bar air.

Iron speciation in the Fe-CTS and Fe8AA catalysts was characterized with Fe Mössbauer spectroscopy [5,6] together with in situ XAS (Figure 4). Two iron species (D1 and D2) were identified in the Fe8AA catalyst that resulted in the appearance of two doublets (Figure 1a). D1 and D2 can be assigned to a four-fold nitrogen or nitrogen–carbon coordination of Fe^{II} in low-spin (LS) and medium-spin state (MS), respectively [5,7]. Consistently, the Fourier transform of the sole extended X-ray absorption fine structure (EXAFS) peak around 1.5 Å (without phase-correction) is assigned to the Fe-N_4 moieties based on EXAFS fitting results. D1 and D2 are the subject of ongoing research related to the exact site structure and to the integration of FeN_4 or FeN_2C_2 moieties that can be viewed either as defect sites within a graphene layer (edge defects) or as a structure bridging two graphene zigzag-or armchair-edges [5,6]. The observed ORR activity has been widely linked to either or both of the D1 and D2 species. In addition to the two doublets (D1 and D2), three more iron species were identified in the Fe-CTS catalyst resulting in a singlet, and two sextets (Figure 1c). The singlet is assigned to either γ-Fe or super paramagnetic iron nanoparticles [5] while the sextet's parameters match those of α-Fe and iron carbide [5,7]. The coexistence of the Fe-N species and metallic iron nanoparticles (NPs) under reactive conditions in acid are in good agreement with in situ XAS results, the two FT-EXAFS peaks around 1.5 and 2.1 Å are ascribed to the Fe-N scattering and Fe-Fe scattering within pure iron NPs and/or iron carbides, respectively. The long-term existence of metallic iron species in an acidic environment strongly suggests that they are fully wrapped in graphitic layers. These metallic iron species were previously believed to be inactive due to their lack of exposure to the electrochemical environment. However, recently published research by various groups has shown that the nitrogen-doped carbon encapsulating these metallic iron species are highly ORR active [1,8,9]. Therefore, the control over the content in the final products after high-temperature treatment as shown here has enormous consequences on elucidating the fundamental synthesis/morphology/activity correlations for non-PGM catalysts.

CONCLUSIONS

- Catalyst blends (1:1) prepared by PPC using 50+ g batch sizes with University of New Mexico 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 hydrogen/air (2.5 bar total pressure, 80°C, 100% RH). High current density is currently at 920 mA/cm^2 at 0.4 V. 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. This approach has been scaled up to 30 g batches.
- 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

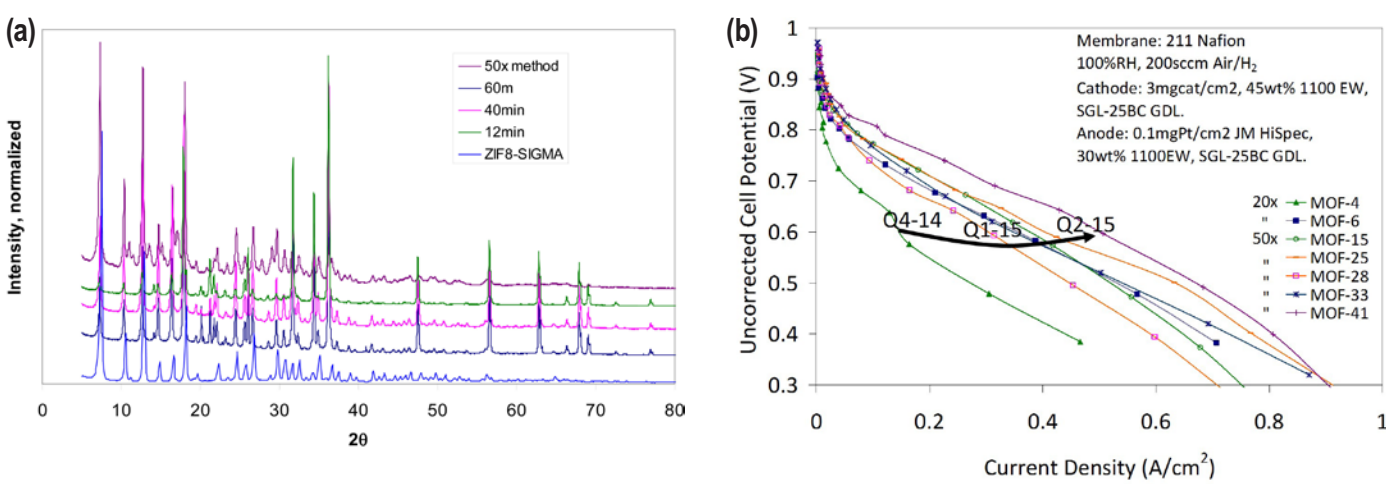


FIGURE 3. (a) Time evolution of XRD patterns measured at different time intervals of precursor ball milling of MOF Fe-chelates exhibiting the evolution of MOF structure as a result of reactive ball milling. (b) Evolution of areal activity as a function of scale-up efforts measured in H_2/air, 80°C, 100% RH, 2.5 bar pressure using 3 mg/cm^2 cathode MOF derived catalyst and standard 0.1 mg/cm^2 Pt/C anode.

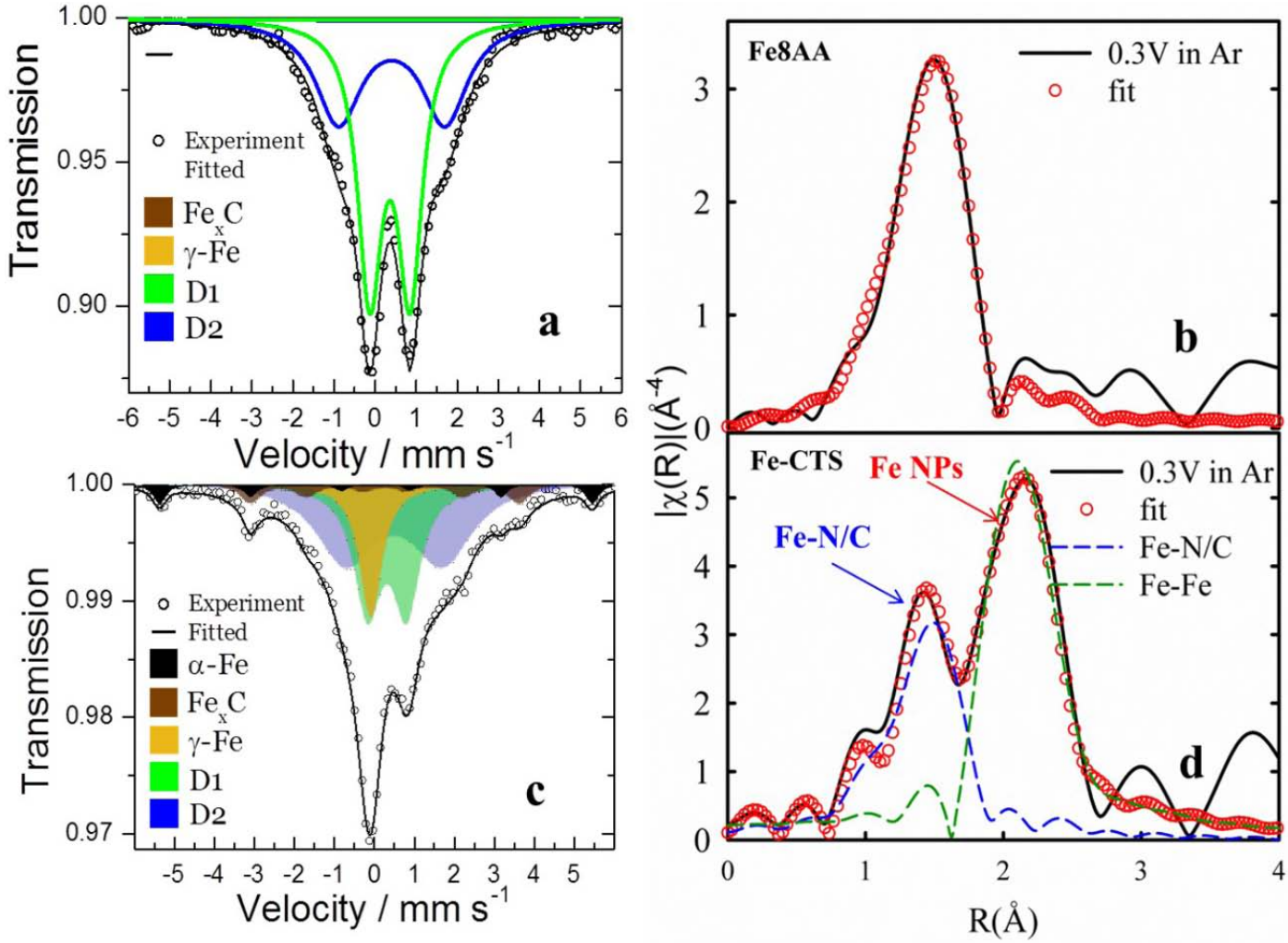


FIGURE 4 (a-d). Mossbauer spectra collected [5,7] for UNM catalysts, FeAA8Pyr (Fe-Amino-antipyrene) and Fe-CTS (Fe-organic charge transfer salt based on nicarbazin) in consonance with in situ synchrotron XAS in terms of Fe K edge Fourier transform of the EXAFS showing remarkable congruence on identification of the relative presence of Fe-N and Fe-NPS moieties.

latter, however, is on par with those observed for PGM catalysts.

- Switching behavior involving the transition metal as identified using Mossbuer spectroscopy [5,6], and in situ XAS indicates the central role it plays in determining the activity of ORR.

FUTURE DIRECTIONS

- The principle focus of the group will be to meet the high current density areal activity target at 0.4 V (IR-uncorrected) using both UNM and NEU blend formulations.
- We will optimize scale-up and MEA fabrication for MOF based catalysts from NEU.
- NTCNA will perform testing to validate durability under DOE protocols.
- We will further test the validity of the proposed mechanism using the final set of in situ and operando synchrotron XAS data in conjunction with density functional theory calculations. In addition, we will use the in situ spectroscopy to probe degradation pathways.

FY 2014-2015 PUBLICATIONS/REFERENCES

1. Ganesan, S., Leonard, N., and Barton, S.C. Impact of transition metal on nitrogen retention and activity of iron–nitrogen–carbon oxygen reduction catalysts. *Physical Chemistry Chemical Physics* 16, 4576–4585 (2014).

2. Leonard, N.D., and Barton, S.C. Analysis of Adsorption Effects on a Metal-Nitrogen-Carbon Catalyst Using a Rotating Ring-Disk Study. *Journal of The Electrochemical Society* 161, H3100–H3105 (2015).

3. Robson, M.H., Artyushkova, K., Patterson, W., Atanassov, P., and Hibbs, M.R. Non-platinum Carbon-Supported Oxygen Reduction Catalyst Ink Evaluation Based on Poly (sulfone) and Poly (phenylene)-Derived Ionomers in Alkaline Media. *Electrocatalysis* 5, 148–158 (2014).

4. Serov, A., Artyushkova, K., Andersen, N.I., Stariha, S., and Atanassov, P. Original Mechanochemical Synthesis of Non-Platinum Group Metals Oxygen Reduction Reaction Catalysts Assisted by Sacrificial Support Method. *Electrochimica Acta* (2015).

5. Serov, A., Artyushkova, K., and Atanassov, P. Fe-N-C Oxygen Reduction Fuel Cell Catalyst Derived from Carbendazim: Synthesis, Structure, and Reactivity. *Advanced Energy Materials* 4 (2014).

6. Tylus, U. *et al.* Elucidating Oxygen Reduction Active Sites in Pyrolyzed Metal–Nitrogen Coordinated Non-Precious-Metal Electrocatalyst Systems. *The Journal of Physical Chemistry C* 118, 8999–9008 (2014).

7. Serov, A., Tylus, U., Artyushkova, K., Mukerjee, S., and Atanassov, P. Mechanistic studies of oxygen reduction on Fe-PEI derived non-PGM electrocatalysts. *Applied Catalysis B: Environmental* 150, 179–186 (2014).

8. Strickland, K., Miner, E., Jia, Q., Tylus, U., Ramaswamy, N., Liang, W., Sougrati, M.T., Jouen, F., and Mukerjee, S., 'Metal Nx Free Electrocatalyst with High Activity for Oxygen Reduction Reaction,' Nature Comm., 6, 7343 (2015).

9. Nano-strcutured non-platinum catalysts for automotive fuel cell applications, A. Serov, K. Artyushkova, E. Niangar, C. Wang, N. Dale, F. Jaouen, M-T. Sougrati, Q. Jia, S. Mukerjee, and P. Atanassov, Nano-Energy, 16, 293 (2015).

REFERENCES

1. Strickland, K. *et al.* Highly active oxygen reduction non-platinum group metal electrocatalyst without direct metal-nitrogen coordination. *Nat. Commun.,* **6,** 7343 (2015).

2. Wu, G., More, K.L., Johnston, C.M., and Zelenay, P. High-performance electrocatalysts for oxygen reduction derived from polyaniline, iron, and cobalt. *Science* **332,** 443–447 (2011).

3. Jaouen, F. *et al.* Recent advances in non-precious metal catalysis for oxygen-reduction reaction in polymer electrolyte fuel cells. *Energy Environ. Sci.* **4,** 114–130 (2011).

4. Chung, H.T., Won, J.H., and Zelenay, P. Active and stable carbon nanotube/nanoparticle composite electrocatalyst for oxygen reduction. *Nat. Commun.* **4,** 1922 (2013).

5. Kramm, U.I., Lefèvre, M., Larouche, N., Schmeißer, D., and Dodelet, J.-P. Correlations between mass activity and physicochemical properties of Fe/N/C catalysts for the ORR in PEM fuel cell via 57Fe Mößbauer spectroscopy and other techniques. *J. Am. Chem. Soc.* (2013).

6. Kramm, U.I. *et al.* Structure of the catalytic sites in Fe/N/C-catalysts for O_2-reduction in PEM fuel cells. *Phys. Chem. Chem. Phys.* **14,** 11673–11688 (2012).

7. Ramaswamy, N., Tylus, U., Jia, Q., and Mukerjee, S. Activity descriptor identification for oxygen reduction on nonprecious electrocatalysts: Linking surface science to coordination chemistry. *J. Am. Chem. Soc.* **135,** 15443–15449 (2013).

8. Deng, D. *et al.* Iron Encapsulated within Pod-like Carbon Nanotubes for Oxygen Reduction Reaction. *Angew. Chem. Int. Ed.* **52,** 371–375 (2013).

9. Hu, Y. *et al.* Hollow Spheres of Iron Carbide Nanoparticles Encased in Graphitic Layers as Oxygen Reduction Catalysts. *Angew. Chem. Int. Ed.* **53,** 3675–3679 (2014).