V.A.9 Development of Novel Non-PGM Electrocatalysts for Proton Exchange Membrane Fuel Cell Applications

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- Pajarito Powder, Albuquerque, NM (Dr. Bar Halevi)
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Project Start Date: August 1, 2010
Project End Date: August 1, 2014

Overall Objectives and Objectives for Fiscal Year (FY) 2013

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 principle target for the reporting fiscal year was to reach the project's Go/No-Go milestone of 100 mA/cm^2 at 0.8 V (internal resistance-free, iR-free) at 80°C, pure H$_2$/O$_2$, with 1.5 bar total pressure. In addition, the project also will demonstrate

scale-up capability for the down-selected catalyst in the range of 10-20 gm.

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.

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

Characteristic	Units	2015 Target	NEU 2012 status
Specific Activity @ 80ºC, 150 kPa, H$_2$/O$_2$, 100% relative humidity (RH)	A/cm^3 A/cm^2	300 A/cm^3 (iR-free) 100 mA/cm^2 (iR-free)	130 A/cm^3 85 mA/cm^2
Durability at 80ºC Cycling: Catalyst Durability	% loss of activity	5%	<1%
Durability at 80ºC Cycling: Carbon Corrosion Durability	% loss of activity	10%	<50% Partially recoverable

FY 2013 Accomplishments

1. Cross-laboratory rotating disk electrode (RDE) measurement of a wide variety of samples emanating from diverse choice of polymer precursors at MSU, NEU, a UNM indicates a confluence in terms of performance; measured values are very close (within the errors inherent in these measurements) to those of the current state-of-the-art materials recently reported by our partners at LANL [1]. Two catalysts were down-selected based on these results, the first referred to as UNM-CTS catalyst (from UNM) and the second referred to as NEU-Fe MOF (from NEU).

2. Extrapolation of fuel cell-derived iR corrected data obtained using UNM-Fe-CTS electrocatalysts currently

indicates volumetric performance in the range of 150-400 A/cm^3. This performance is beyond the DOE 2015 target of 300 A/cm^3. All measurements and conducted with pure H$_2$/O$_2$, 1.5 bar total pressure, 100% humidification using a 212 Nafion$^®$ membrane. Geometric area activity measurement conducted on the same electrocatalyst under the conditions mentioned above show 100 mA/cm^2 at 0.8 V (iR-free). These measurements were conducted independently at NEU as well as at the NTCNA using three separate membrane electrode assemblies (MEAs) from two different electrocatalyst batches (iR-free is currently 105 mA/cm^2).

3. Durability measurements conducted on the down-selected UNM-Fe-CTS catalysts show excellent tolerance to catalyst stability tests (based on Nissan protocol, similar to DOE). Carbon corrosion tests, which involve load cycling to 1.5 V vs. the reference hydrogen electrode, however, indicated significant losses, which followed along similar lines to the losses with a PGM cathode.

4. 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 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 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) excellent durability in terms of catalyst stability (*vide* DOE and Nissan protocols) and recovery of losses incurred during carbon corrosion measurement when placed under load, and (c) detailed understanding of the nature of active site and electrocatalytic pathways as distinct from the parallel pathway in alkaline electrolytes.

APPROACH

The approach adopted in this reporting period involved (a) material preparation using a wide variety of precursor materials in conjunction with Fe-containing salts pyrolyzed at temperatures of 700-800°C under inert atmosphere followed with repeated steps (up to three) of etching (in acid) and repyrolysis, (b) rotating ring disc electrode and fuel cell tests using well-established protocols for cross-laboratory performance comparison and extrapolation of volumetric activity (from iR-corrected fuel cell data), (c) durability measurements using two well-established protocols (catalyst durability) and carbon corrosion tests (both DOE protocols), and (d) investigation of the nature of active site and ORR electrocatalysis steps as measured using in situ synchrotron spectroscopy at the Fe-K edge under actual cell *operando* conditions.

RESULTS

Following intensive work aiming to develop an alternative to precious metal-based catalysts for ORR cathodes, the most promising catalysts are materials synthesized using the sacrificial support method (SSM) originating at UNM. Based on consistent studies, a few SSM-based catalysts (Fe-AAPyr [Fe-amino-antipyrene], Fe-CTS [Fe-charge transfer salt], and Fe-CBDZ [Fe-carbandazim]) were selected for further testing to validate activity and stability in a fuel cell environment. As shown in the later sections, the catalysts based on a CTS precursor have shown the most promising results. Fe-CTS catalysts were prepared by modified SSM (Figure 1). The detailed synthesis approach is delineated in the July 2013 interim report. Briefly, the precursor material was a CTS (nicarbazin, NCB - Nicarbazin, Sigma-Aldrich), and the Fe salt chosen was iron nitrate (Fe(NO$_3$)$_3$*9H$_2$O, Sigma-Aldrich); this was in conjunction with the UNM silica templating approach to fabricating electrocatalysts. Figure 2 shows the ORR-iV curves of catalysts at 1,600 RPM in O$_2$-saturated 0.5 M H$_2$SO$_4$ solution measured at the NTCNA. Table 2 lists the E$_{1/2}$, the kinetic currents at 0.8 V, and the Tafel slope of catalysts. The iV curves and ORR activities were compared with those of a TKK 20% Pt on a high surface area carbon catalyst. Fe-CTS presented the highest kinetic current density of 4.6 mA cm^{-2} with a Tafel slope of 52 mV/decade. This kinetic current density achieved 50% of the kinetic current of 20% Pt-based catalyst. In the iV curves, Fe-CTS showed an active reduction peak around 0.75 V, which might be associated with the active site of the catalyst. Based on the results summarized in Table 2 and shown in Figure 2, Fe-CTS showed the highest activity among the tested catalysts, so Fe-CTS was chosen for MEA tests and further optimization.

Figures 3a and 3b represent linear polarization results with pure H$_2$/O$_2$, fully humidified at 80°C with 1.5 bar total
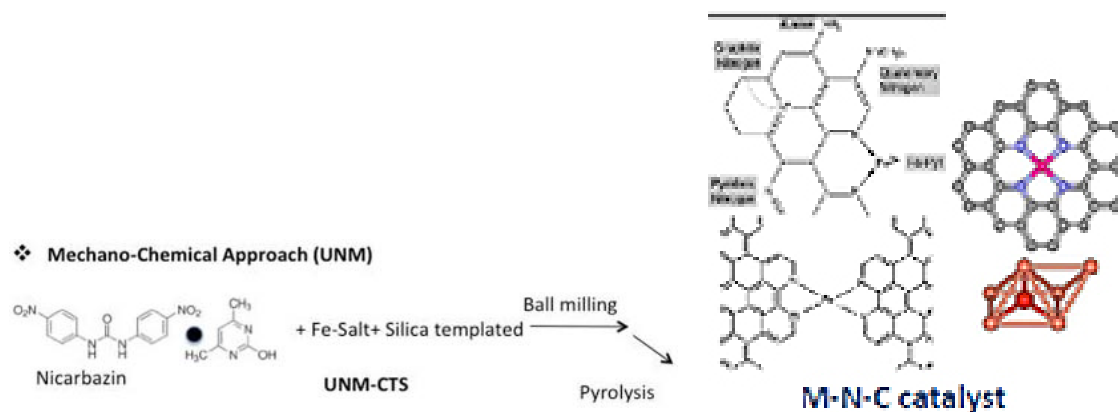
FIGURE 1. Representation of chemistry and pyrolysis conditions used for the down-selected electrocatalysts by cross-laboratory partners, UNM and NEU.
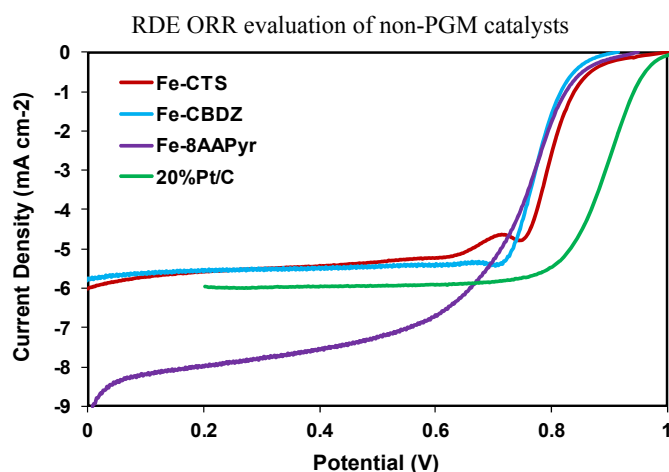
FIGURE 2. Cross-laboratory comparison of ORR activity measured using rotating ring disk electrode technique, performance comparison shown at 900 rpm. Electrolyte is 0.1 M $HClO_4$, room temperature with standard catalyst loading of ~600 µg/cm².

TABLE 2.

Catalyst	$E_{1/2}$ mV	Kinetic Current* mA cm^{-2}	Tafel Slope mV/decade
Fe-CTS	796	4.6	52
Fe-CBDZ	776	2.31	50
Fe-8AAPyr	747	2.32	90
20%Pt/C	894	8.3	57

pressure. The membrane used in these tests at NEU was Nafion® (212), with cathode catalyst loading at 2 mg/cm² and the choice of anode reference electrode as Pt/C, 0.4 mg/cm² (common electrode used as reference by NTCNA and NEU, sourced from Johnson Mathey Fuel Cells, Inc.) The substrate used on the cathode side for spray addition of non-PGM catalysts was from SGL Carbon (25 BCH). Linear polarization measurements were conducted using 18 MEAs prepared from three separate batches of UNM-CTS catalysts with groups containing variations of relative ratios of Nafion® (between 35% and 50% based on total carbon content of the catalyst layer). The best results (Figure 3a) were obtained with total Nafion® content of 50% with a group of three separate MEAs prepared using catalysts from two separate batches. Since a standard conventional anode electrode is used with pure H_2, the fuel cell polarization measurements amount to a quasi half-cell measurement of the cathode polarization losses.

Corrections for iR were conducted according to the methodology described in detail earlier [3-5], with the aid of a non-linear regression analysis of the overall polarization behavior which can be described using the equation $E = E°_{OCV} - (\eta_{act,a} + \eta_{act,c}) - \eta_{ohmic} - (\eta_{conc,a} + \eta_{conc,c})$. Experimental fitting results gave reproducible values of η_{ohmic}, which was used for iR correction of the polarization data shown in Figure 3b. All three MEAs based on two separate batches of UNM-CTS catalysts passed the metrics. The iR correction conducted using the regression method was independently verified using electrochemical impedance measurements conducted as a function of current density.

In addition volumetric projection of the data of the areal activity was calculated using the procedure described earlier [6]. In order to use the fuel cell data in the context of volumetric activity, the well-known relationship:

$$I_{vol}(E) = \frac{I_{areal}(E) \times \rho}{loading}$$

was used with projection conducted from a range of current densities measured close to the ORR onset potential (0.1 to 10 mA/cm^2) to 0.8 $V_{iR-free}$ (reported in this case for a total pressure of 1.5 bar) and a catalyst layer density of 0.4 g/cm^3. Such a projection over decades of current density was designed to obtain volumetric activity values without the concomitant effects of ohmic and mass transport losses and has been reported as standard practice in earlier references [1,2]. Figure 3c shows the results of our projection and the resultant volumetric activity, and we used the exact procedures reported earlier [1,2] for this projection. It is important to note that the data obtained for this projection was acquired using a more sensitive potentiostat with higher current resolution (nano-amps) as compared to those reported in Figures 3a and 3b where a standard electronic load box was employed for its higher current range. The iR-corrected Tafel plot shown in terms of area activity in 3b clearly meets the project's Go/No-Go criterion. The plot in Figure 3b is an average of the performance from the three best MEAs with concomitant error bars showing variation in the data. In each

volumetric projection (Figure 3c) more than 15 points were used within a current range of 0.1 to 10 mA/cm^2. In two of the MEAs reported for their areal activity (Figures 3a-b) the concurrent volumetric activity (measured separately, Figure 3c) exceeded 400 A/cm^3 at 0.8 $V_{iR-free}$, pure H$_2$/O$_2$ with 1.5 bar total pressure, a value above the DOE target for 2017. However, it is important to note that this volumetric activity should be used with great caution as it is a projected number.

Validation of the fuel cell results measured at NEU was independently conducted at NTCNA. Measurements conducted at the NTCNA are shown in Figure 4. The UNM Fe-CTS down-selected catalysts were made into MEAs using an NRE211 membrane. In making the ink, the Fe-CTS catalyst was mixed with deionized water, ethanol, and 20% Nafion® dispersion (Ion Power DE2020). We aimed to optimize the ionomer-to-catalyst (I/C) ratio in the catalyst ink recipe. Three I/C ratios of 0.54, 0.82, and 1.2, corresponding to 35, 45, and 55 wt% Nafion®, respectively, were investigated. The amount of Nafion® was adjusted to make the catalyst ink corresponding to the three I/C ratios.

Sample	mV @ 200 A/cm³	A/cm³ @ 0.8 V (iR free)
MEA 2	809	400
MEA 10	796	150
MEA 14	810	400
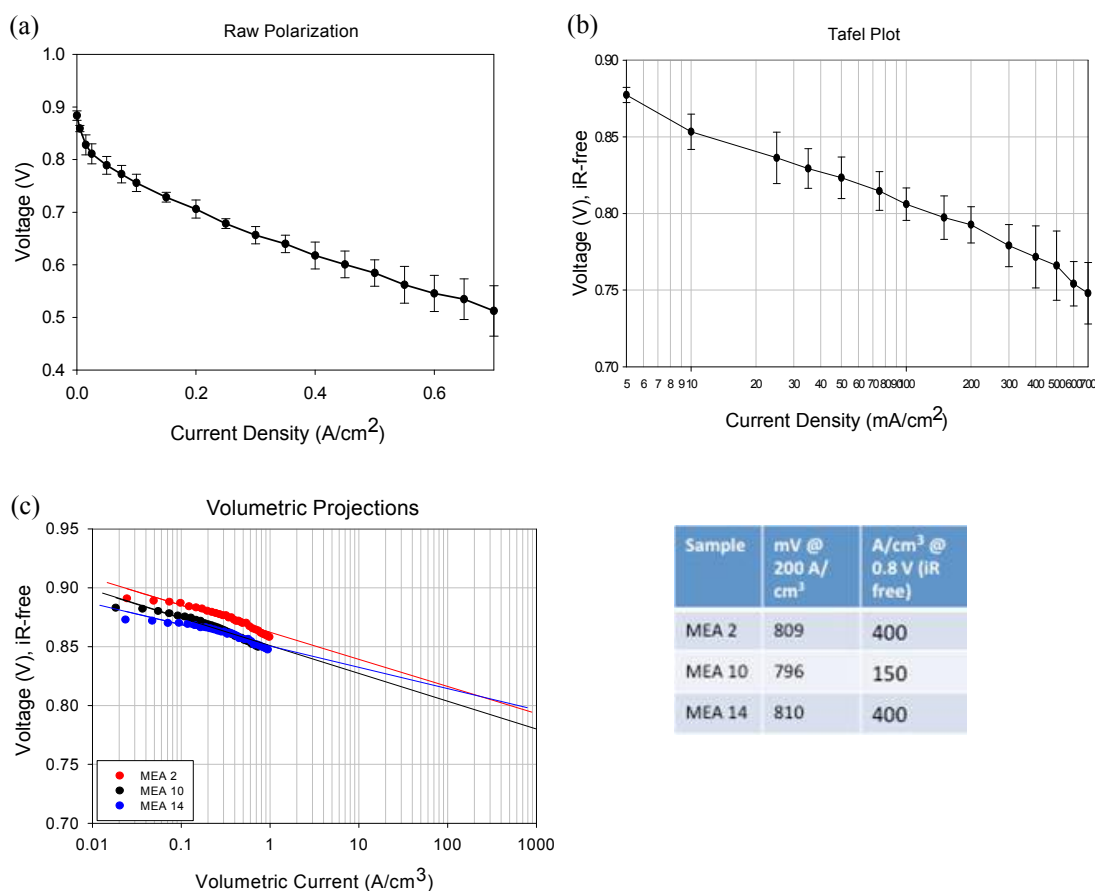
FIGURE 3. Fuel cell polarization results from UNM-Fe-CTS catalysts measured using a 5-cm^2 single cell conducted at NEU using DOE-recommended operating conditions of 80°C, 100% humidification, pure H$_2$/O$_2$, 1.5 bar total pressure. Error bars in the fuel cell data indicate average of results from three different MEAs sourced from two separate batches of electrocatalysts. Cathode loading used was 2 mg/cm^2, 50% Nafion®. (a) Raw polarization results, (b) iR-corrected Tafel plot showing the results meeting the DOE Go/No-Go metrics, and (c) volumetric projection of the data measured at low current densities projected to 0.8 V (iR-free).
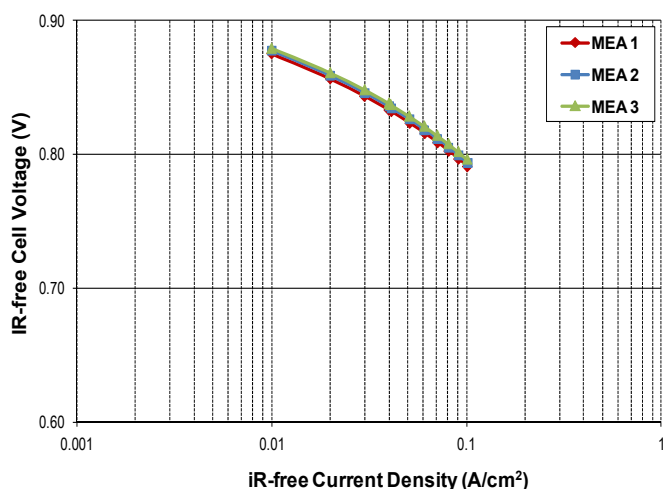
FIGURE 4. Fuel cell polarization results from UNM-Fe-CTS catalysts measured using a 25-cm^2 single cell conducted at NTCNA using DOE-recommended operating conditions of 80°C, 100% humidification, pure H$_2$/O$_2$, 1.5 bar total pressure. Results from three different MEAs sourced from two separate batches of electrocatalysts are shown. Cathode loading used was 4 mg/cm^2, 55% Nafion®.

The homogenized catalyst ink was sprayed onto SGL 25BCH gas diffusion layers (GDLs) using the in-house spray system at NTCNA. The system is an automated spray deposition machine capable of preparing reproducible, uniformly-sprayed gas diffusion electrodes (GDEs) with accurate loading. For each GDE, the catalyst loading was kept constant at 4 mg/cm^2, regardless of the Nafion® content of the ink (35, 45, or 55 wt%).

MEAs (25 cm^2) were assembled by hot-pressing a JMFC GDE (0.4 mg Pt/cm^2) anode, an NRE211 membrane, and an UNM Fe-CTS-based GDE cathode (4 mg$_{catalyst}$/cm^2). The MEAs were tested using custom-designed 25-cm^2 cell hardware on a Hydrogenics fuel cell test station. In order to verify the absence of Pt contamination on the non-PGM catalyst cathode, cyclic voltammograms (CVs) of all the MEAs tested at different Nafion® loadings were obtained. The CV profiles of all the MEAs did not exhibit any peaks that could be attributed to Pt contamination.

As shown in Figure 4, the MEA containing the Fe-CTS catalyst with 55% Nafion® gave 100 mA cm^{-2} at 0.8 V$_{iR-free}$, the first report of fuel cell performance that meets the current DOE design target for non-PGM cathode proton exchange membrane fuel cell catalysts for potential future automotive applications. This result was reproduced using three MEAs from two different catalyst batches. The reproducibility of the high current densities obtained with this catalyst is confirmed by the overlapping Tafel plots.

Durability measurements of the UNM-Fe-CTS catalyst were also independently conducted at NTCNA. The
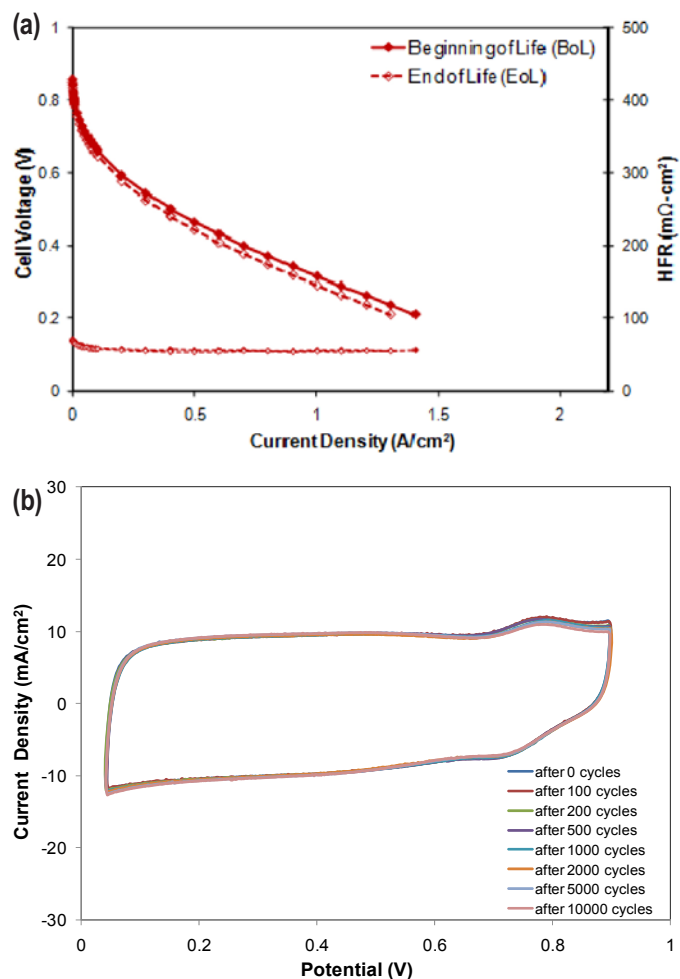
FIGURE 5. Durability measurements conducted at the NTCNA using DOE protocols for catalyst stability are shown for the UNM-Fe-CTS catalyst. As shown, this sample showed excellent durability for catalyst stability test.

durability evaluation used automotive accelerated stress tests, which simulate the actual stack conditions under fuel cell electric vehicle operating conditions. The catalyst showed excellent durability under the Nissan load cycling protocol (Table 2), with polarization performance undergoing minimal change after 10,000 potential cycles (shown in Figure 5a for the Nafion® 45% sample). All MEAs that were tested under the load cycling protocol showed the same durability regardless of Nafion® content.

The corresponding CV profile, as shown in Figure 5b, also did not change significantly after 10,000 potential cycles. The beginning-of-life CV shows a clean profile with no peaks that can be attributed to Pt contamination, and the end-of-life CV (CV after 10,000 potential cycles) also does not show any peaks due to Pt. This is good evidence that no Pt particles migrated from the anode to the cathode during the potential cycling durability test.

Scale-Up Efforts at Pajarito Powders

Pajarito Powder has begun an initial scale-up of the CTS catalyst developed by UNM in anticipation of a successful continuation of the DOE contract. Pajarito Powder's initial statement of work included scaling up the best-performing catalyst at the time, which was the MSU Fe-Melamine catalyst that was the previous best-performing catalyst. Pajarito successfully scaled the Fe-Melamine catalyst according to the statement of work by the time of the Go/No-Go decision in late June. However, by this time the newly developed UNM-Fe-CTS catalyst had emerged as the leading catalyst, meeting the Go/No-Go criteria. It was far too late to change catalysts for scale-up by the time the CTS had been initially tested.

Nevertheless, Pajarito Powder began initial scale-up investigations of UNM-Fe-CTS catalyst in anticipation of Phase 2 of the DOE project. The results of the initial scale-up efforts for the Fe-CTS catalysts are reported here. This was conducted as an additional effort funded internally by Pajarito to assist in initial phase of the DOE project.

The Fe-CTS catalyst is made using an SSM developed at UNM where C/N precursors are mixed with iron metal salts and silica. The mixture is then pyrolized at ambient pressure, the silica and excess iron are etched and leached, and the compound is then pyrolyzed again to achieve better performance and stability. This chemically intensive approach has several key steps requiring optimization in the scale-up effort. The initial scale-up effort is focused on a 10-20 gram batch, with the goal that the methods developed can be applied towards 30-50 gram batches immediately, and 100-200 gram batches in the near future, while further demonstrating a technology trajectory to 1-kg batches.

The synthesis process is readily divided into five major steps: a) mixing of precursors and silica, b) first pyrolysis, c) etching of silica and leaching of excess iron, d) washing catalyst after etch/leach, and e) second pyrolysis. Each of these steps was analyzed for ease of scale-up, and appropriate scale-up equipment was purchased and installed. For example, the mixing of dry precursors was done at UNM in 100 mL planetary mill jars. This can be readily scaled up using a ball-mill with 4x1 L jars, so that 4x200+ grams of precursor mixture can be made in a single processing step, yielding 4x50 grams of catalyst. Other methods of mixing, such as dry and wet shear mixers as well as continuous slurry homogenizers, are also being examined.

The pyrolysis step was initially scaled from 15-ml alumina boats used at UNM to 150-mL alumina boats, where each 150-mL boat yields ~7 grams of finished catalyst. 25 grams of finished catalyst therefore requires 500 mL of precursor mix, so that four 150-mL alumina boats yield 30-gram batches. Pyrolysis of multiple 150-mL boats in parallel in a 3-inch inside diameter tube furnace with

30-inch heated zone therefore allows 25-gram+ batches to be made. Further, custom-made shallow pans with 2,000-mL+ precursor capacity will allow for 200+ gram-per-batch pyrolysis in the same system, and installation of a 6-inch pyrolysis processing tube will allow for 400+ gram-per-batch pyrolysis. The pyrolysis conditions, including sweep rate, temperature ramp and dwell, and oxygen scrubbing, had to be adjusted to account for the increase in scale of processing tube.

The etching step has been scaled up as well with 25+ grams of finished catalyst etched in a single batch. Etching scale-up required proportional increases in etchant and processing vessel volumes, as well as several modifications to the procedure, since the larger batch sizes create slower diffusion of etchants and etching products in the larger volume slurry of the catalyst/silica mix for a 25-gram batch. The increase in hydrofluorhydric acid (HF) use also required installation of an HF vapor-scrubbing hood. Post-etching washing done in the lab scale using repeated centrifugation/decanting cycles was streamlined to culminate in filtration using HF-compatible washing and filtration equipment. Powder drying using vacuum heating allows for quick drying and reduction in processing time.

The second pyrolysis conditions had to be similarly adjusted; sweep rate, temperature ramp and dwell, and oxygen scrubbing had to be adjusted to account for the increase in scale of processing tube.

As expected, the lab-scale synthesis for Fe-CTS had to be modified in several stages, with steady improvements made in the very brief three months that the Fe-CTS formulation has existed and been available for scale-up. The performance of the 30+ gram batches produced at Pajarito Powder is approaching the performance of the UNM-Fe-CTS catalyst measured at both NEU and NTCNA. The performance data show that Pajarito Powder has demonstrated the ability to produce 30+ gram batches of the UNM-Fe-CTS catalyst, and therefore also demonstrate the scalability of the UNM-Fe-CTS catalyst (Figure 6).

CONCLUSIONS

1. Cross-laboratory studies of materials emanating from the pyrolysis of diverse polymer precursors in conjunction with Fe and Co salts indicate a common evolution of active sites for ORR reduction. Down-selected catalysts referred to as UNM-Fe-CTS have successfully met the Go/No-Go milestones with independent measurements at NEU and NTCNA with a statistically significant number of MEAs and batches of catalysts.

2. Detailed durability studies indicate excellent tolerance to catalyst stability tests, and relatively poor resistance to carbon corrosion test protocols; the latter, however, is at par with those observed for PGM catalysts.

Pyrolysis profile optimization for 30+ grams Fe-CTS catalyst
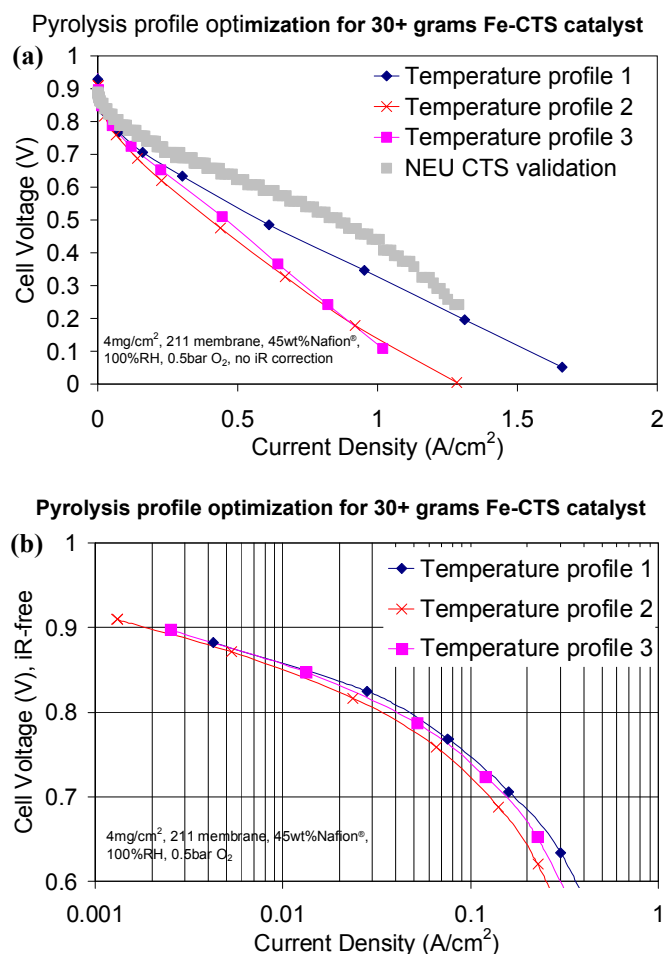
FIGURE 6. (a) Pyrolysis thermal profile effects on 30+ grams batch-scale Fe-CTS performance. Performance validation from NEU is shown for comparison measured under similar conditions. (b) Corresponding Tafel plots for the 30+ gm scaled-up samples.

3. Scale-up of 30+ gms batch size has been demonstrated using the down-selected electrocatalyst.

FUTURE DIRECTIONS

1. The principle focus of the group will be to transition the team to Phase II of this effort, where the focus will be to significantly improve the mass transport in the GDL for enabling transition from operation in pure O_2 to air.

2. Optimize scale-up and MEA fabrication for meeting DOE Phase 1 metrics with the scaled-up batches in a consistent way.

3. Further test the validity of the proposed mechanism using a final set of in situ and *operando* synchrotron XAS data in conjunction with density functional theory calculations. In addition, use the in situ spectroscopy to probe degradation pathways.

FY 2013 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).

2. 'Structure of the catalytic sites in Fe/N/C-catalysts for O_2-reduction in PEM fuel cells', Ulrike I. Kramm, Juan Herranz, Nicholas Larouche, Thomas M. Arruda, Michel Lefèvre, Frédéric Jaouen, Peter Bogdanoff, Sebastian Fiechter, Irmgard Abs-Wurmbach, Sanjeev Mukerjee, and Jean-Pol Dodelet, *Phys. Chem. Chem. Phys.*, 2012, **14**, 11673–11688.

3. 'Highly active and durable templated non-PGM cathode catalysts derived from iron and aminoantipyrine', A. Serov, M. H. Robson, B. Halevi, K. Artyushkova, and P. Atanassov, *Electrochimica Acta,* Volume 22, August 2012, Pages 53–56.

4. 'Templated non-PGM cathode catalysts derived from iron and poly(ethyleneimine) precursors', A. Serov, M. H. Robson, K. Artyushkova, and P. Atanassov, Applied Catalysis B: Environmental, Volume 127, 30 October 2012, Pages 300–306.

5. 'Density functional theory calculations of XPS binding energy shift for nitrogen-containing graphene-like structures', K. Artyushkova, B. Kiefer, B. Halevi, A. Knop-Gericke, R. Schlogl, and P. Atanassov, *Chem. Commun.*, 2013, 49, 2539.

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