V.A.3 Innovative Non-PGM Catalysts for High-Temperature PEMFCs

Sanjeev Mukerjee
Department of Chemistry and Chemical Biology
Northeastern University (NEU)
360 Huntington Ave., HT 102
Boston, MA 02115
Phone: (617) 373-2382
Email: s.mukerjee@neu.edu

DOE Manager: David Peterson
Phone: (240) 562-1747
Email: David.Peterson@ee.doe.gov

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Subcontractors:
- University of New Mexico (UNM), Albuquerque, NM (Plamen Atanassov)
- Fuel Cell Energy (FCE), Danbury, CT (Ludwig Lipp)
- Pajarito Powder, LLC, Albuquerque, NM (Barr Halevi)

Project Start Date: October 1, 2015
Project End Date: August 31, 2017

Overall Objectives

The objective of this project is to revolutionize high-temperature proton exchange membrane fuel cell (PEMFC) technology based on polymer membranes imbibed with phosphoric acid through development of stable, high-performance precious metal free (PGM-free) cathode catalysts. High-temperature PEMFCs operate in a range of 150–220°C, making them ideal candidates for combined heat and power (CHP) applications. This incubator effort is however, exclusively focused on catalyst development for H_3PO_4-imbibed PEMFCs.

Fiscal Year (FY) 2016 Objectives

The principle objectives of this effort are:

- Develop PGM-free catalysts based on a metal-organic framework (MOF) with unique iron-nitrogen-carbon active sites that are immune to anion poisoning. Elimination of Pt from the cathode would lower total Pt loading from the current state of the art of 3 mg/cm^2 to less than 1.5 mg/cm^2, thereby halving the cost of the catalyst in the membrane electrode assembly (MEA). These catalysts will be scaled up from the ~1 g laboratory level to 100 g batch size.
- Develop unique corrosion resistant support structures for enhanced corrosion resistance as compared to conventional carbon-based supports.
- Provide enhanced mass transport within the reaction layer and gas diffusion layer using a combination of modeling and experiments for obtaining mass transport parameters designed to enable systematic formulation of the gas diffusion and reaction layers.
- Prepare MEAs and perform fuel cell testing using test conditions designed to experimentally obtain mass transport parameters. Perform durability testing relevant to stationary fuel cells. This project aims to meet and exceed the current PGM-based high-temperature polymer electrolyte membrane MEA metrics of 200 mA/cm^2 in H_2/air at 0.65 V with 2.5 bar total pressure at 180°C.
- Perform economic analysis of the fuel cell system to determine market segments for deployment.

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

(B) Cost

Cost is the primary barrier preventing membrane imbibed phosphoric acid (PA) fuel cells and similar systems from reaching commercial reality, with noble metal loading representing a significant cost component. Cost of noble metals in current state of the art membrane-based PA systems is approximately $800–$1,000/kW. Our goal is to bring this cost to below $500/kW. Durability limitations due to carbon corrosion also represent a major barrier to commercialization. This project will address both of these issues, thereby enabling commercialization of membrane imbibed PA fuel cells on an accelerated schedule.

Technical Targets

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

Status at end of the fourth quarter (Q4):

- First quarter (Q1) target, catalyst preparation and scale up, to batch size of 5 g. Test of both inter- and intra-batch reproducibility in terms of anion ($H_2PO_4^-$) tolerance tested in 0.1 M $HClO_4$ with varying amounts of H_3PO_4 (up to 100 mM) successfully met.

TABLE 1. Milestone Summary

Recipient Name		Northeastern University, Sanjeev Mukerjee (Principal Investigator)			
Project Title		Innovative Non-PGM Catalysts for CHP Relevant Proton Conducting Fuel Cells			
Task Number	Task or Subtask Title	Milestone Description (Go/No-go Decision Criteria)	Milestone Verification Process	Anticipated Quarter	
				Date	Quarter
1.1	Catalyst Preparation and Scale Up with MOF Chemistry	Develop scale up chemistry based on reactive ball milling for achieving 5 g batch of MOF-based PGM-free cathode catalyst material	Less than 5% inter- and intra-batch variation in RDE performance using 0.1 M $HClO_4$ with up to 100 mM H_3PO_4	3 mo	Q1
1.1	Catalyst Preparation and Scale Up with MOF Chemistry	Demonstrate initial MEA activity of PGM-free cathode catalyst with PA-imbibed membrane	Polarization measurements demonstrating 100 mA/cm^2 at 0.7 V using H_2/O_2 at 180°C 1.5 bar total pressure	6 mo	Q2
2.1	Improving Mass Transport Characteristics	MEA testing of SSM-templated PGM-free catalyst	MEA performance of 200 mA/cm^2 at 0.65 V, H_2/air, 180°C, 2.5 bar total pressure	9 mo	Q3
Go/No-Go Decision		Fuel cell measurements and validation	To meet/exceed 200 mA/cm^2 at 0.60 V with 2.5 bar total pressure, H_2/air, 180°C. Total PGM catalyst loading on the PA-imbibed membrane-based MEA to be lower than 1.5 mg/cm^2 Pt exclusive to the anode electrode with a PGM-free cathode	12 mo	End of Q4
2.3	Durability Studies	Corrosion testing of SSM-based materials	Open circuit test on SSM-based materials at 180°C, H_2/air	21 mo	Q6
3.2	Fuel Cell Test Validation	Fuel cell test validation at OEM partner facility with 100 cm^2 MEA using PA-imbibed membrane and PGM-free cathode catalyst	Achieving H_2/air performance target of 200 mA/cm^2 at 0.65 V, 180°C, 2.5 bar total pressure	24 mo	Q8

RDE – Rotating disk electrode; OEM – Original equipment manufacturer ; SSM - Sacrificial support method; Q6 - Sixth quarter; Q8 - Eighth quarter

- Second quarter (Q2) target, polarization measurements demonstrating 100 mA/cm^2 at 0.7 V using H_2/O_2 at 180°C 1.5 bar total pressure.
  - NEU MOF: tests conducted at NEU with a polybenzimidazole (PBI) membrane at 200°C in O_2 show performance at 100 mA/cm^2 of 690+ mV (within instrumentation error of 700 mV), therefore successfully meeting the stated target.
  - UNM IMID (blended catalyst from UNM): tests conducted by Brian Benicewicz at the University of South Carolina (USC) with PBI membrane at 180°C in O_2 show performance at 100 mA/cm^2 of 700 mV, therefore successfully meeting the stated target.
- Third quarter (Q3) target, polarization measurements demonstration of 200 mA/cm^2 at 0.6 V using H_2/air at 180°C 2.5 bar total pressure.
  - NEU MOF: tests conducted at NEU with PBI membrane at 200°C show performance at 200 mA/cm^2 of 545 mV, 55 mV shy of the stated target.
  - UNM IMID: tests conducted at USC with PBI membrane at 180°C show performance at 200 mA/cm^2 of 600 mV, therefore successfully meeting the stated target.
- Q4 target, demonstration of replication of stated air performance target from Q3.
  - Given that the required testing was done with different catalysts at different testing facilities, and that performance at each facility was at or near both performance testing, this can be taken as a sign of validation of the required testing systems.

INTRODUCTION

Some initial testing examined hybrid catalysts which consisted of a combination of the PGM-free catalysts materials with a low loading of Pt. Testing switched to pure PGM-free cathodes in high-temperature a PEMFC. Early testing had been done in the absence of poly-tetrafluoroethylene (PTFE). However, durability was very poor due to flooding in the electrode. Therefore, introduction of PTFE to alleviate these issues was dealt with subsequently. Additionally, a full redesign of the electrode and MEA fabrication is underway, and the results have been very encouraging thus far.

APPROACH

For the data shown in this report there are two catalysts in question. First is the solid state reaction scale up MOF provided by Pajarito Powder (MOF Lot #104) , hereon referred to as the NEU MOF. Secondly, another blended catalyst from UNM (UNM IMID), was tested by Brian Benicewicz at USC.

In order to introduce an additional level of morphology control, the UNM team modified the SSM to utilize relatively large (~250 nm) monodispersed silica particles. The second modification in SSM was usage of two imidazole-based precursors, methyl imidazole and imidazolidinyl urea. The combination of two precursors results in an increase of the nitrogen content and graphitization level, which is crucial for durability of PGM-free catalysts. In general, materials were prepared as follows: 5 g methyl imidazole and 5 g imidazolidinyl urea mixed with 2 g of EH5 and 4 g of monodispersed silica. The mixture was dry ball-milled for 20 min and heat treated in N_2 atmosphere for 45 min at T = 925°C. The silica was removed by washing with 25 wt% of HF. The powder was then washed with deionized water until pH ~6 and dried. Dry powder was heat treated in NH_3 atmosphere for 30 min at T = 945°C. The materials are under evaluation by scanning electron microscopy, X-ray photon spectroscopy, and transmission electron microscopy methods. MEA performance was tested at USC using a PBI membrane at 180°C. This MEA is also slated tobe tested at NEU.

A new technique for electrode fabrication has been developed with help from Advent Technologies. An aqueous ink including catalyst, PTFE, as well as stabilization additives, was made and mixed using the Advent Technologies commercial protocol. Using Advent's draw-down method, the ink was deposited onto a commercial gas diffusion layer (GDL) (ELAT HT1200W). Unlike earlier preparatory methods, no heat treatment of the electrode was done following application of the catalyst. Traditionally, heat treatments are used to "activate" the PTFE, and create higher hydrophobicity. However, it was eventually determined that these heat treatments were in fact altering the chemistry of the catalyst, rendering them far less active.

RESULTS

BASF A1100W Pt electrodes (1 mg_{Pt}/cm^2) were used as standard anodes (provided by Advent Technologies), together with commercial PBI membranes. Cathode, anode, membrane, and the requisite sub-gaskets were hot pressed under conditions provided by Advent Technologies. MEAs using the PBI membrane were then placed in an oven at 160°C for 30 min before testing.

Testing of the NEU MOF was done at 200°C (for time purposes, no break-in procedure was done at 180°C as is customary with Advent MEAs). Performance was measured as a function of applied backpressure in both oxygen and air.

Figures 1 and 2 show the oxygen performance of the NEU MOF catalyst, acquired at NEU (Figure 1), as well as the oxygen performance of the UNM IMID catalyst, acquired at USC (Figure 2). Both catalysts met the required oxygen performance targets. Recent studies were done at NEU in order to optimize the PTFE content, the catalyst loading, and the operating temperature. Additionally, newer generation Pt anodes and thinner GDLs were introduced. These changes yielded large increases in performance in both oxygen in air, as will be evident later in this report.

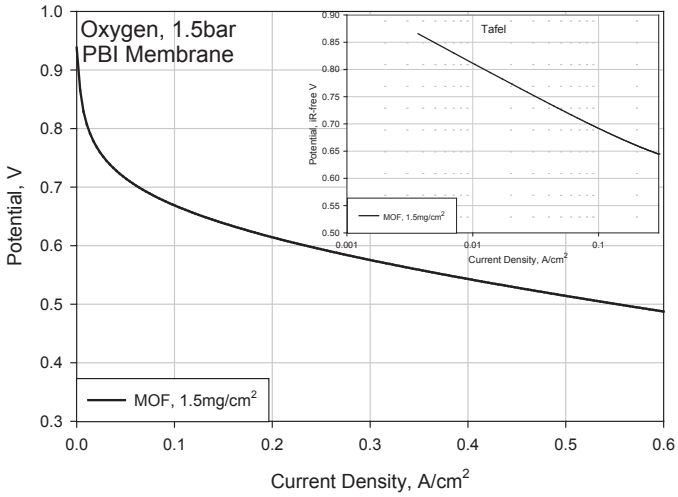


FIGURE 1. Performance in oxygen of the NEU MOF catalyst, tested at NEU. Inset: associated Tafel plot.

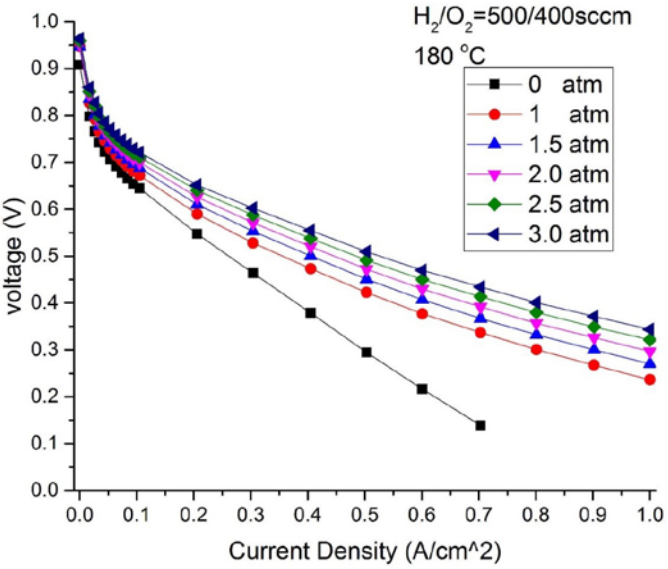


FIGURE 2. Performance in oxygen of the UNM IMID catalyst, tested at USC

The performance in air at NEU (Figure 3) and USC (Figure 4) is presented.

The aforementioned changes to the MEA and testing protocols allowed the NEU performance to get within 55 mV of the stated target, while the USC performance on the UNM IMID catalyst achieved the designated target. Figure 5 shows the rapid progress towards meeting these two performance targets over the recent months.

As is apparent, the changes made at NEU to the fabrication process of the MEAs over the past few months have yielded great progress in terms of performance, both in oxygen as well as in air. The oxygen performance has increased by 150 mV, while the air performance has increased by more than 250 mV (at 200 mA/cm^2, 2.5 bar total pressure). Given that the performance increase in air exceeded that of oxygen, it subsequently reduced the oxygen gain. This is evidence of improved gas transport throughout the catalyst layer. However, the oxygen gain is still nearly double that of a Pt cell, indicating that there is more optimization to be done on fabrication of the cathodes. Nevertheless, this upward trend in performance is very promising towards the development of high-performing, high-temperature PEMFCs using a pure non-PGM cathode catalyst.

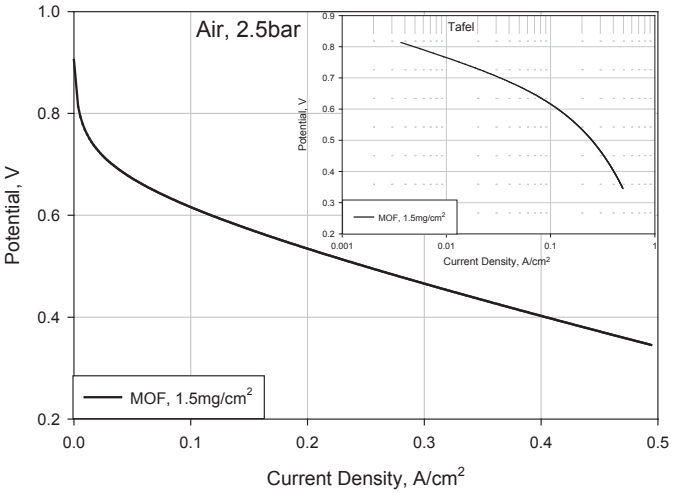


FIGURE 3. Performance in air of the NEU MOF catalyst, tested at NEU. Inset: associated Tafel Plot.

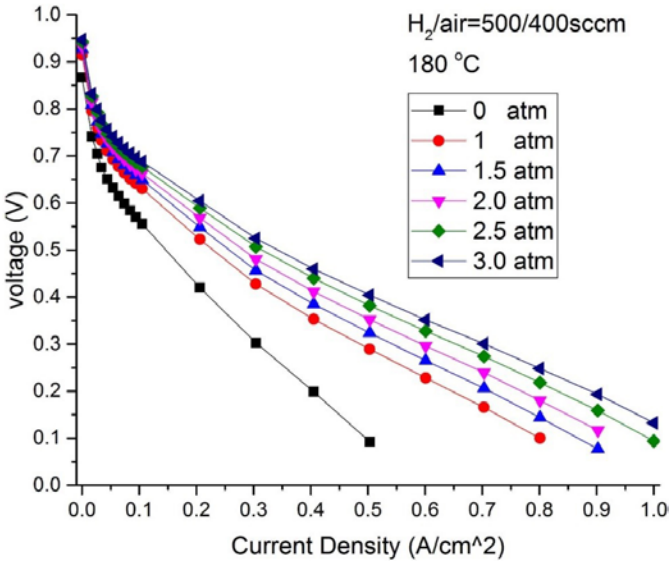
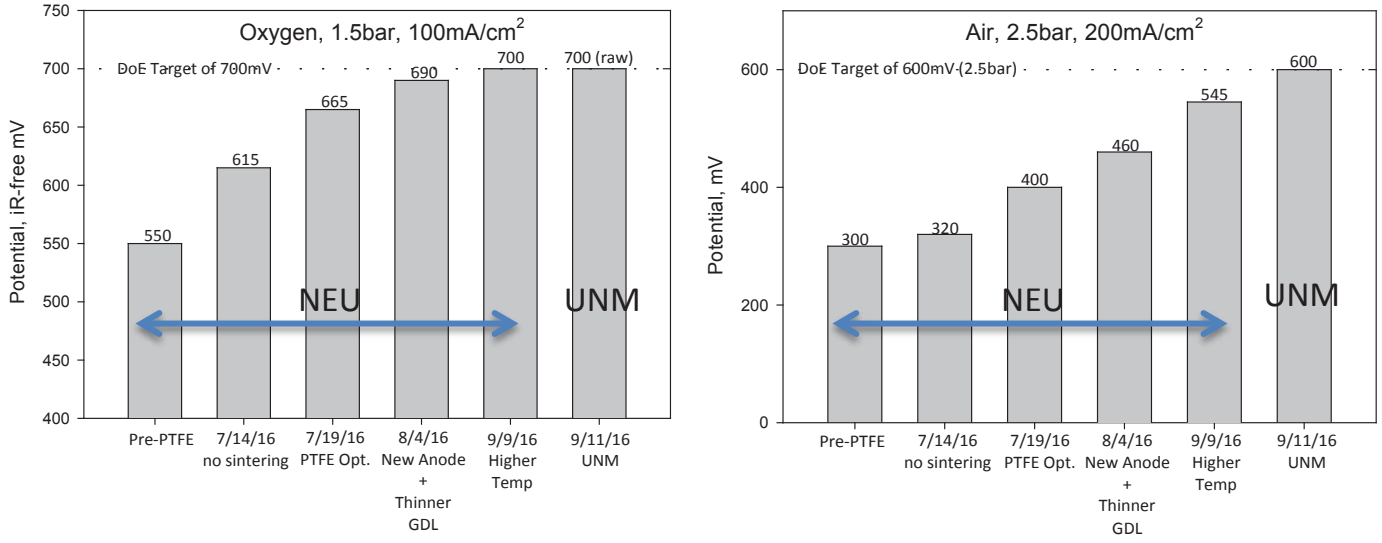


FIGURE 4. Performance in air of the UNM IMID catalyst, tested at USC.



iR - Internal resistance

FIGURE 5. Increase in oxygen and air performance throughout the course of the MEA redesign undertaken at NEU.

CONCLUSIONS AND FUTURE DIRECTIONS

The most recent work was primarily invested in completing a full redesign of our electrode and MEA preparation techniques. The redesign was clearly a success given the performance increases in both oxygen and air.

While there are still more studies to be done to further increase the performance through technological advances in the electrode fabrication, the project will additionally switch gears in an effort to test additional materials beyond the two catalysts specifically referenced in this report. These catalysts will include variants of the MOF, synthesized both at NEU as well as at Pajarito Powder. Additionally, UNM will continue to synthesize new catalysts for testing.

As is directed in the statement of work, experiments will begin in an effort to study the durability of these fuel cells. This will be done through several methods, including chronoamperometric measurements, corrosion testing, and temperature cycling. These protocols should give increased information regarding any potential degradation mechanisms of these catalysts.

Finally, FCE will participate in an effort to scale up to larger MEAs that would be more indicative of commercial utilization, rather than the standard 5 cm^2 electrodes used for testing at NEU. Validation of the FCE testing facilities has already been completed using Pt MEAs fabricated at both Advent Technologies as well as at NEU. Once preliminary catalyst testing has been done at NEU, larger MEAs (45 cm^2 and up), will be manufactured at NEU and shipped to FCE for validation.

FY 2016 PRESENTATIONS

1. "Use of Hybrid Cathodes to Reduce Platinum Content in High Temperature PEMFCs," Ryan Pavlicek. Kara Strickland, Sanjeev Mukerjee, Presentation at the 229th Meeting of the Electrochemical Society, June 1, 2016; San Diego, CA.