
FY18 SBIR Phase II Release 1: Multi-Functional Catalyst Support

Minette Ocampo (Primary Contact), Paul Matter, Christopher Holt, Alex Beutel, Andrew Gluntz
pH Matter LLC
6655 Singletree Dr
Columbus, Ohio 43229
Phone: 614-396-7820
Email: mcocampo@phmatter.com

DOE Manager: Donna Ho
Phone: 202-586-8000
Email: Donna.Ho@ee.doe.gov

Contract No: DE- SC0017144 (FY18 SBIR Phase II Release 1)

Subcontractors:

- Giner Inc., Newton, MA
- National Renewable Energy Laboratory, Golden, CO

Project Start Date: May 21, 2018

Project End Date: May 20, 2020

Overall Objectives

- Optimize the properties of the support and catalyst synthesis process for improved durability and high-current-density operation.
- Demonstrate the performance of membrane electrode assemblies (MEAs) that meet 2020 DOE targets for automotive proton exchange membrane (PEM) fuel cells at low platinum group metal (PGM) loadings.
- Establish pH Matter's platinum/multi-functional carbon support (Pt/MFCS) material as a commercial low-PGM catalyst.

Fiscal Year (FY) 2019 Objectives

- Optimize Pt/MFCS catalyst properties for improved performance and durability.
- Optimize the MEA fabrication process using commercially relevant MEA production equipment for improved high-current-density performance.

- Demonstrate scalable synthesis of down-selected MFCS and establish quality control procedures.
- Demonstrate DOE targets for catalyst activity and durability in a 25-cm² MEA.

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 Plan¹:

- Cost: Enhance the Pt catalyst activity to reduce its loading levels.
- Durability: Optimize the interaction between the catalyst and the support material to improve chemical and thermal stability.
- Performance: Demonstrate improved performance in an MEA.

Technical Targets

This Phase II Small Business Innovation Research (SBIR) project is focused on developing new catalyst materials to achieve DOE targets for electrocatalyst performance and durability at low PGM loading for a PEM fuel cell.

The DOE 2020 technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

- Optimized Pt/MFCS catalyst properties and demonstrated significantly improved high-current-density performance from the Phase I baseline catalyst.
- Optimized MEA fabrication and testing procedures to improve overall performance.
- Achieved DOE 2020 targets for catalyst activity and durability with a 30% Pt-alloy/MFCS catalyst.
- Demonstrated 1 kg/h synthesis process for down-selected MFCS supports.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- Assembled a pilot-scale reactor that enabled up to 100-g batch synthesis of Pt/MFCS catalyst.

Table 1. Progress toward Meeting Technical Targets for Electrocatalysts and MEAs for Automotive Applications

Characteristic	Units	DOE 2020 Electrocatalyst and MEA Targets	Project Status (25 cm ² cell)
PGM loading	mg-PGM/cm ² _{geo}	≤0.125	0.1 ^a
Mass activity	A/mg _{PGM} @ 900 mV _{IR-free}	≥0.44	0.90
MEA performance	mA/cm ² _{geo} @ 800 mV	≥300	380
Loss in initial catalytic activity	% mass activity loss	≤40	24
Loss in performance at 0.8 A/cm ² _{geo}	mV	≤30	0
Loss in electrochemical surface area (m ² /g _{Pt})	% ECSA loss	≤40	17

^a Cathode loading

ECSA – electrochemical surface area

INTRODUCTION

PEM fuel cells offer a clean and efficient means of energy conversion for numerous applications, including automotive power. Unfortunately, wide-scale PEM fuel cell adoption for automotive application is partially limited by the high cost of the fuel cell stacks. The main issues are the high cost of the PGM electrode materials and the relatively fast degradation of the electrodes (namely the cathode in both cases). Low-PGM catalysts have faced challenges with durability for vehicle applications [1]. During cell operation, platinum (and other metals) can leach from the electrode and move into the electrolyte membrane, causing loss of catalyst activity [2]. Further, the mass transfer rate of the water product out of the cathode ultimately limits the fuel cell current density. To lower PEM fuel cell cathode costs, enhancement of the Pt catalyst activity is needed to reduce its loading levels. To enhance the activity and durability of Pt catalysts, numerous approaches are being pursued, including: optimizing the size and shape of the Pt particles, alloying the Pt with other metals, and/or forming core-shell structures with a thin layer of the Pt on a stable supportive core [3]. Other approaches include optimizing and boosting the interaction between the catalyst particle and the support material.

Work in Phase I demonstrated the feasibility of CN_xP_y supports to improve the durability of low-PGM catalysts without the need for significant alloying. The next steps for this project in Phase II are further optimization of the multi-functional carbon supports and MEA synthesis; testing to demonstrate catalyst durability and other DOE 2020 targets in 25-cm² MEAs; and achieving commercial adoption.

APPROACH

The overall objective of the project is to develop MFCS that are engineered to perform better than conventional PEM fuel cell carbon supports. The approach is based on synthetic nitrogen- and phosphorus-doped carbon, CN_xP_y. The doping of the carbon improves metal-support adhesion and reduces mobility of the platinum during voltage cycling.

To achieve high-current-density operation, the properties of the support and the platinum deposition process will be optimized. These properties include hydrophobicity, graphiticity, and pore size of the support. Platinum loading, platinum location, and extent of alloying will be examined for the platinization process. To combat cathode flooding, selected support materials will undergo novel hydrophobic surface treatments prior to metal deposition. These surface treatments have been shown to drastically increase hydrophobicity of CN_xP_y materials without adverse effects on catalyst activity. To demonstrate improved performance in an MEA, pH Matter will partner with Giner Labs to optimize the performance of the down-selected catalysts in an MEA

using Giner’s capabilities in ink formulations and MEA development. Giner will lead development of inks and scalable state-of-the-art MEA fabrication as well as MEA testing.

To achieve commercial adoption of the developed low-PGM catalyst, methodologies will be developed to synthesize the catalyst with a scalable process to be able to fulfill commercial-quantity orders. MEAs will then be sent to the National Renewable Energy Laboratory (NREL) and potential customers/partners for independent third-party validation and to establish pH Matter’s Pt/MFCS catalyst as a commercial high-performing low-PGM catalyst.

RESULTS

Support and Catalyst Synthesis

Various MFCS were synthesized and different variables were examined to optimize performance of the support. For each sample, typically 50 grams of support was prepared using a pilot-scale reactor. Several different non-metal CN_xP_y compositions were synthesized and examined with various treatment conditions. Different pore structures from the Phase I baseline material were examined in order to increase platinum loading into more accessible pores. A support was also synthesized at higher processing temperatures to examine the effects of processing temperature on the porosity and graphiticity of the support. Repeatability of the synthesis process was confirmed, and sample uniformity and scalability were improved using scalable equipment and a 1-kg/h throughput reactor. Down-selected supports for customer/partner sampling were given names based on the process and pore structure as follows:

- MFCS-A: denotes Phase I baseline support, microporous throughout
- MFCS-B: denotes lower-surface-area mesoporous “accessible pore” support
- MFCS-C: denotes intermediate microporous support.

Pore size distributions for selected samples are shown in Figure 1. The peak at $\sim 50\text{--}100 \text{ \AA}$ (5–10 nm) is observed for MFCS-B accessible pore samples, which is an ideal pore size for a support to stabilize catalysts and maintain high current density (i.e., good accessibility of gases) [4]. MFCS-B prepared with a scalable process exhibited similar pore structure as the qualified small-scale batch. Intermediate microporous MFCS-C samples have a smaller pore size, as seen by the peak at $20\text{--}30 \text{ \AA}$ (2–3 nm) in Figure 1 for BJH (Barrett, Joyner, and Halenda) adsorption, but they have much higher surface area than MFCS-B samples.

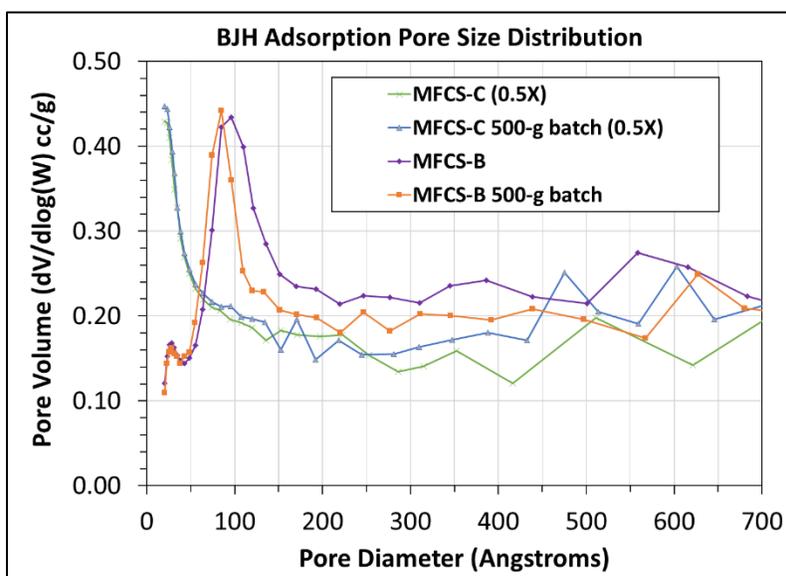


Figure 1. Pore size distribution of selected synthesized MFCS samples

Different variables were examined to optimize the platinum deposition process. Catalysts were prepared with different platinum loadings to achieve the optimal thickness in an electrode. Pt alloys (1:1 mole ratio) also were prepared to improve activity, and different reduction temperatures were examined to achieve optimal particle size and durability. A total of more than 200 experiments were run to optimize the catalyst synthesis process. Through these experiments, it was determined that the optimal reduction conditions were dependent on the platinum loading, the type of support used, and other process history. Different batch syntheses also confirmed the repeatability and scalability of the catalyst synthesis process.

Rotating disk electrode testing was performed on all synthesized catalysts to determine electrochemical surface area (ECSA) and gauge oxygen reduction reaction activity. Transmission electron microscopy imaging was also performed on some down-selected catalysts to determine platinum distribution and location. For the “accessible pore” MFCS-B support, however, it is difficult to determine the location of the platinum particles with conventional transmission electron microscopy alone. To confirm the accessibility and/or location of the platinum particles, carbon monoxide (CO) stripping at variable relative humidity (RH) in an MEA was performed for a down-selected MFCS-B catalyst. Figure 2 shows the platinum utilization of the accessible pore catalyst at different RH compared to Pt/Vulcan carbon (VC) and Pt/Ketjenblack taken from literature [5]. VC is denser and has very little internal porosity with most Pt particles found on the exterior of the carbon, thus the Pt particles are accessible even at low RH. Ketjenblack has a microporous structure where Pt particles are found mostly in the interior micropores of the support. Pt on Ketjenblack support then is mostly accessible at high RH. The accessibility of Pt particles on MFCS-B support is between that of the VC and Ketjenblack. The CO stripping result confirms the presence of platinum in the accessible pores with the ideal pore geometry to yield both good transport and activity.

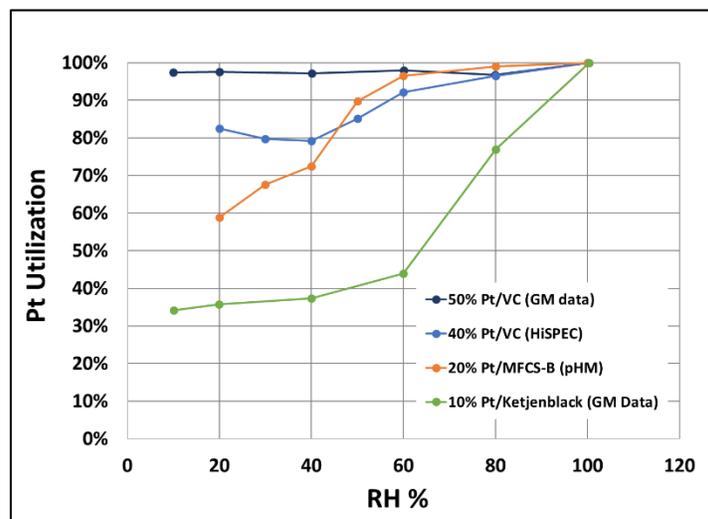


Figure 2. Pt utilization on MFCS-B measured by CO stripping in an MEA at 80 °C with varying RH and compared with different commercial supports

For the first year of the project, a rotating pilot-scale reactor was assembled that enabled up to 100-g batch synthesis. Two 20-g batches of Pt/MFCS-B catalysts were synthesized and delivered to prospective partners. The oxygen reduction reaction activity of the large-scale batch matched the activity of the qualified small-batch synthesis of the same catalyst.

MEA Testing

Down-selected catalysts that performed well in rotating disk electrode testing were sent to Giner for further MEA optimization. The 25-cm² MEAs were prepared and tested at Giner for initial performance and catalyst durability. With continuous optimization of the catalyst synthesis and MEA fabrication processes, DOE targets for catalyst activity and durability were achieved with 30% Pt-alloy/MFCS-C (catalyst 58-159) as shown in Figure 3 and Table 2. A repeat synthesis batch of the same type of catalyst was also tested in an MEA twice,

and both tests showed similar performance and durability as catalyst 58-159, which verifies repeatability of results.

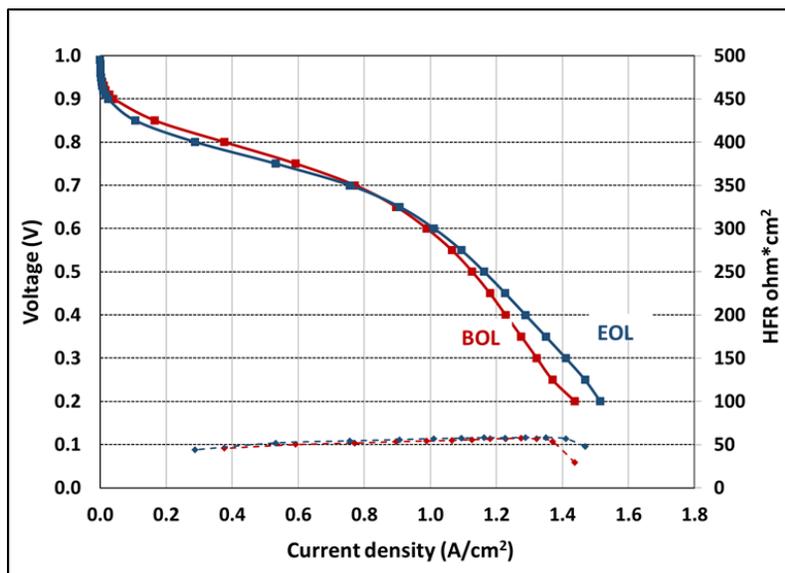


Figure 3. Polarization curves for catalyst 58-159 (30% Pt-Co/MFCS-C) MEA fabricated and tested at Giner in H₂/air; 25-cm² active area, 80 °C, 100% RH, 150 kPa. Cathode loading of 0.1 mg_{PGM}/cm² before (beginning of life, BOL) and after (end of life, EOL) catalyst durability cycling

Table 2. Summary of Results for Catalyst Durability Cycling of 58-159 Relative to DOE 2020 Targets

	Loading (mg/cm ²)	BOL Mass Activity (A/mg _{Pt})	BOL Current at 0.8 V	% Mass Activity Loss	ECSA Loss	ΔV @ 0.8 A/cm ²
DOE 2020 Targets	0.125	>0.44	>0.3 A/cm ²	<40%	<40%	<30 mV
58-159: 30% Pt-Co/MFCS-C	0.1	0.90	0.38 A/cm ²	24%	17%	0

A 25-cm² replicate of the 58-159 MEA fabricated by Giner was delivered to NREL for third-party validation. Above-target initial mass activity of 0.5 A/mg_{Pt} was measured by NREL with no apparent degradation in mass activity @ 0.9 V and ECSA degradation of 39% after durability cycling, meeting the target. The catalyst itself proved to be very durable based on third-party testing.

CONCLUSIONS AND UPCOMING ACTIVITIES

pH Matter’s Pt-Co/MFCS-C catalyst has achieved DOE 2020 automotive targets for catalyst activity and durability and results have been verified by third-party testing. The catalyst synthesis process also has been optimized to improve uniformity and scalability to be able to fulfill commercial orders and begin the first step of establishing pH Matter’s Pt/MFCS material as a commercial low-PGM catalyst with excellent durability. More accessible pores for the MFCS-B support will continue to be optimized to achieve high power performance with good durability. Higher-current-density performance also will be improved through addition of more hydrophobic materials. Samples will be provided to prospective partners to determine gaps in the technology with regard to customer specifications.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Minette Ocampo, Paul Matter, Christopher Holt, Alex Beutel, and Andrew Gluntz, “Multi-Functional Catalyst Support,” presented at the DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Crystal City, VA, April 29, 2019.

REFERENCES

1. D. Banham et al., DOE Catalyst Working Group Meeting, Argonne, IL, July 2017.
2. K. More, “FC-PAD Components and Characterization,” 2017 DOE Annual Merit Review Proceedings.
3. Adzic et al., US Patent 7,691,780 B2 (2010).
4. A. Kongkanand, “Highly Accessible Catalysts for Durable High-Power Performance,” 2018 DOE Annual Merit Review Proceedings.
5. E. Padgett, N. Andrejevic, Z. Liu, A. Kongkanand, W. Gu, K. Moriyama, Y. Jiang, S. Kumaraguru, T.E. Moylan, R. Kukreja, and D.A. Muller, Tue. “Editors’ Choice—Connecting Fuel Cell Catalyst Nanostructure and Accessibility Using Quantitative Cryo-STEM Tomography,” *J. Electrochem. Soc.* 165 (2018): F173–F180; doi: 10.1149/2.0541803jes.