V.A.13 Development of Durable Active Supports for Low Platinum Group Metal Catalysts (SBIR I)

Barr Zulevi (Primary Contact), Alexey Serov
Pajarito Powder, LLC (PPC)
3600 Osuna Road NE, Suite 309
Albuquerque, NM 87109-4427
Phone: (215) 687-2290
Email: bhalevi@pajaritopowder.com

DOE Manager: Gregory Kleen
Phone: (240) 562-1672
Email: Gregory.Kleen@ee.doe.gov

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Overall Objectives

To develop novel active carbon supports (cathode side of membrane electrode assembly [MEA]) with engineered morphology which allows platinum to be uniformly dispersed in 3-dimensional mesoporous structure and increase the graphitization of the engineered carbon support (ECS) in order to improve durability of Pt/ECS.

- Synthesize engineered active carbon-based supports.
- Optimize supports characteristics to improve platinum dispersion, platinum-carbon interaction, and level of ECS graphitization.
- Demonstrate durability of electrocatalysts in accelerated stress protocol.

Fiscal Year (FY) 2017 Objectives

- Synthesize active ECS with controlled morphology and high graphitization level.
- Optimize platinum dispersion on ECS.
- Demonstrate improved durability of optimized Pt/ECS in accelerated stress protocol.

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: Low durability of carbon supported commercial Pt/C catalysts

(B) Cost: High cost of commercial Pt/C catalysts

(C) Performance: Low performance of low Pt content MEA

Technical Targets

The project main target is engineering an active carbon support with controlled morphology and chemical speciation to allow platinum to be dispersed inside of three-dimensional matrix. The final Pt/ECS catalyst will approach DOE 2020 design point in catalyst activity and durability (Table 1).

FY 2017 Accomplishments

Pajarito Powder synthesized several active ECS materials with variation of pore former agents, organic precursors, and transition metals. The main accomplishments of the project up to this date can be summarized as follows:

- Preliminary data on screening of different transition metals for formation of active ECS showed that cobalt produced highly graphitized carbon supports with high surface area and well dispersed Pt.
- A proprietary method of platinum deposition was optimized to deposit platinum on active ECS controlling Pt particle size in the range of 2.1–7 nm.
- Methods of integration of novel Pt/ECS into the MEA was developed and several MEAs were evaluated by fuel cell tests.

TABLE 1. MEAs for Transportation Applications

Characteristic	Units	DOE 2020 Electrocatalyst and MEA Targets	Project Status (5 cm^2 cell, differential conditions)
Mass activity	A/mg_{PGM} @ 0.9 $mV_{iR\text{-}free}$	≥0.44	0.29
PGM total loading	$mg\text{-}PGM/cm^2_{geo}$	≤0.125	0.100 cathode
Support cycling (1.0–1.5 V, 5,000 cycles)	Support cycling (1.0–1.5 V, 5,000 cycles)	mV loss at 1.5 A cm^{-2}	NA

PGM – platinum group metal

- Initial data shows that the developed Pt/ECS has a lower degradation rate in start-stop protocol compared to commercial Pt/C catalyst (Figure 1).

INTRODUCTION

Commercially available carbon materials are designed for multiple applications, such as conductive additives, solar cells, and supercapacitors [1]. Some of these generic carbon materials were adopted for development projects optimizing the synthesis of supported PGM catalysts and MEAs in fuel cell applications [2]. Research groups are evaluating several classes of carbon-based materials to be used as PGM supports in low temperature fuel cells [3]. However, these materials are either not commercially available or are cost prohibitive to be utilized by PGM catalysts manufacturers.

The main degradation routes in MEA performance are platinum poisoning (anode), platinum dissolution (cathode), and carbon corrosion (cathode). In this proposal, PPC will develop durable, carbon-based supports based on the concept of active co-catalysis in oxygen reduction reaction (ORR). The PGM nano-particles will be loaded on the support which consists of (1) atomically dispersed electrocatalytically active centers with intrinsic ORR activity, (2) optimized morphology for PGM deposition and triple phase interface, and (3) an increased level of graphitization.

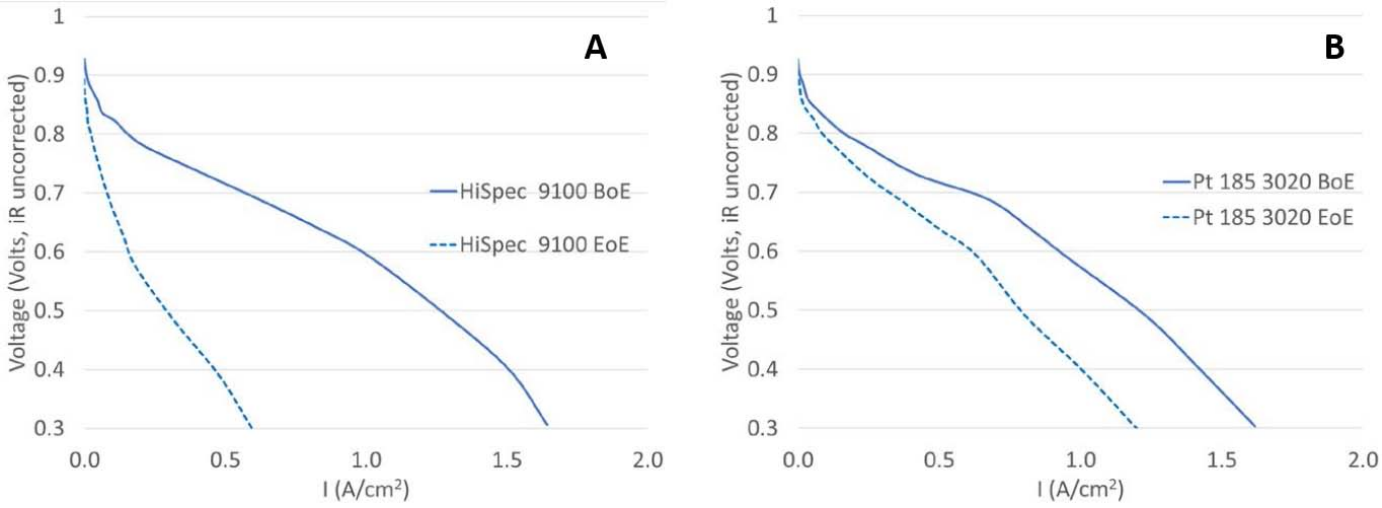
APPROACH

The synthetic approach on making active ORR carbon-based catalyst is based on University of New Mexico technology licensed by PPC. Pajarito Powder modified and improved this method, which is trademarked as VariPore™ (Figure 2). The synthesis of active support includes formation of 3-dimensional porous structure by using pore forming agents. Hard templates (MgO, Al_2O_3 and SiO_2) are used in the synthesis and support characteristics will be optimized. The support characteristics to be controlled include pore size, pore modality, and surface area.

In order to create active carbon supports such structure as Fe-N-C will be formed by high temperature treatment of mixture of transition metal (Fe, Co, Mn, and Cr), organic precursor, and pore forming engines. After synthesis catalysts will be extensively washed with $HNO_{3(diluted)}$ to remove unreacted transition metals and then both evaluated on their own in fuel cell tests and once Pt is added.

UPCOMING ACTIVITIES

Additional experiments with active support derived from cobalt are needed. We will optimize them by tuning the amount and type of pore formers, heat treatment temperature, and duration of heat treatment. Platinum will be deposited by PPC in order to evaluate the activity of Pt/ECS by MEA tests and the best candidate will be down-selected for evaluation by team member Advent.



BoE – beginning of everything; EoE – end of everything; iR – internal resistance

FIGURE 1. MEA performance of (A) commercial Pt/C cathode and (B) PPC developed Pt/ECS catalyst in beginning of life (BoE) and after accelerated stress protocol support corrosion test. Conditions: (A) Anode Pt/C (0.05 mg cm^{-2}), Cathode: Pt/C (0.1 mg cm^{-2}); (B) Anode: Pt/C (0.05 mg cm^{-2}), Cathode: Pt/ECS (0.1 mg cm^{-2}). T_{cell} = 80ºC, 100% relative humidity, 26 psig back pressure.

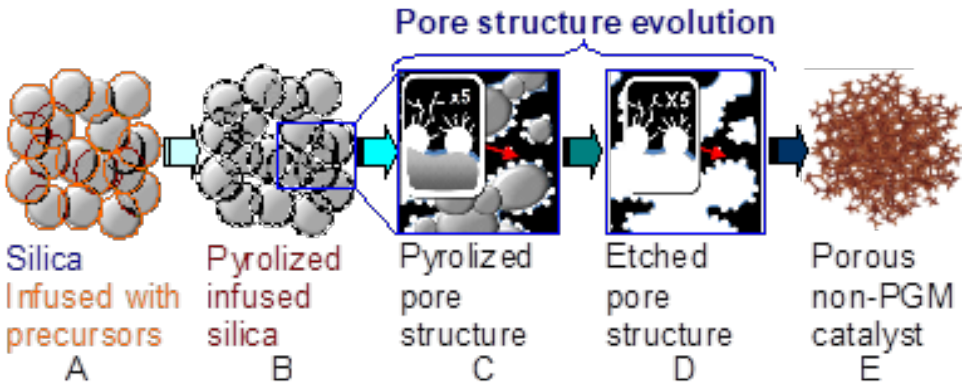


FIGURE 2. The approach on making durable active support

FY 2017 PUBLICATIONS/PRESENTATIONS

1. B. Halevi, A. Lubers, G. McCool, S. McKinney, and H. Romero, *"Durable Engineered Carbon Supports*," 231st ECS Meeting, New Orleans, 2017.

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2. S. Sharma, B.G. Pollet, *Support materials for PEMFC and DMFC electrocatalysts—a review*, J. of Power Sources 208 (2012) 96–119.

3. E. Antolini, *Carbon supports for low-temperature fuel cell catalysts*, Appl. Catal. B: Environmental (88) (2009) 1–24.