

V.A.8 Highly Accessible Catalysts for Durable High-Power Performance

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- Identify pathways to improve the fuel cell performance toward DOE targets.
- Evaluate effects of carbon supports on fuel cell performance.

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
- (C) Performance

Technical Targets

See Table 1 on next page.

FY 2017 Accomplishments

- Met DOE high-power target by developing a carbon support with low transport resistance while maintaining high oxygen reduction reaction (ORR) activity.
- Obtained early promising results with intermetallic PtCo electrocatalysts and ionic liquids.
- Improved understanding of the degradation of PtCo electrocatalysts and its impact.



Overall Objectives

- Lower overall stack cost by improving high current density (HCD) performance in H₂/air fuel cells appropriate to meet DOE heat rejection and Pt-loading targets.
- Maintain long term high electrocatalytic mass activities.
- Mitigate catalyst HCD degradation.

Fiscal Year (FY) 2017 Objectives

- Identify and quantify performance loss terms observed on state-of-the-art cathode catalyst and membrane-electrode assembly (MEA).

INTRODUCTION

The amount of platinum used in the ORR catalyst in fuel cells must be lowered by at least four-fold to enable proton exchange membrane fuel cells (PEMFCs) cost-competitiveness with other power sources. In our previous DOE-funded project, we demonstrated that carbon-supported Pt-alloy catalysts (PtNi/HSC and PtCo/HSC) exhibited very high ORR electrocatalytic activity and impressive durability, exceeding the DOE targets [1]. However, their high-power performance fell short of the target.

As the Pt content is lowered in the cathode, approaching <math><0.1 \text{ mg}_{\text{Pt}}/\text{cm}^2</math>, large oxygen and proton fluxes must be supplied to the Pt surface, causing a performance loss due to a relatively high local transport resistance in the state-of-the-art electrode. In addition, the non-precious transition metal in the catalyst, such as Ni or Co, can dissolve and migrate

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

Metric	Units	PtCo/HSC-a	PtCo/HSC-e	PtCo/HSC-f	DOE 2020 Target
		2016	2017-1	2017-2	
PGM total loading (both electrodes)	mg/cm ²	0.125	0.125	0.088	<0.125
Mass activity @ 900 mV _{IR-free}	A/mg _{PGM}	0.6-0.7	0.6	0.7	>0.44
Loss in catalytic (mass) activity	% loss	0-40%	40%	TBD	<40%
Performance at 0.8 V (150 kPa, 80°C)	A/cm ²	0.304	0.306	0.382	>0.3
Power at rated power (150 kPa, 94°C)	W/cm ²	0.80	0.89	0.93	>1.0
Power at rated power (250 kPa, 94°C)	W/cm ²	1.01	1.19	1.26	-
PGM utilization (150 kPa, 94°C)	kW/g _{PGM}	6.4	7.1	10.6	>8
PGM utilization (250 kPa, 94°C)	kW/g _{PGM}	8.1	9.5	14.3	-
Catalyst AST (0.6–1.0 V)	mV loss at 0.8A/cm ²	30	20	TBD	<30
Support AST (1.0–1.5 V)	mV loss at 1.5 A/cm ²	>500	>500	TBD	<30

Green: meets target; Red: does not meet target

HSC – high surface area carbon; PGM – platinum group metal; AST – DOE's accelerated stability test; TBD – to be determined

into the ionomer phase, replacing protons and consequently lowering the ionomer proton conductivity and causing hydrodynamic performance loss. As a result, although these Pt-alloy catalysts exhibit excellent durable high-activity at low power, the target performance at high power has not been realized, limiting its cost reduction benefit.

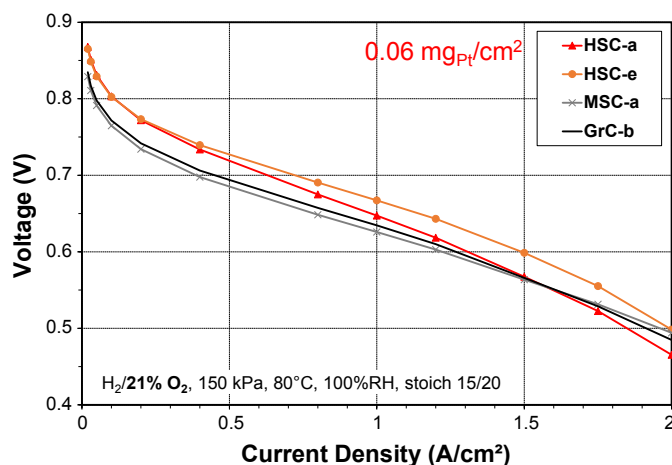
APPROACH

The general approach for this project is to identify and select a carbon support and an electrolyte that have favorable transport properties, and subsequently develop a high performance Pt-alloy electrode using these subcomponents. The efforts can be divided into four thrusts: (1) development of carbon support, (2) selection of electrolyte (ionomer or ionic liquid), (3) development of stable highly-dispersed Pt alloy nanoparticles, and (4) understanding the effects of the transition metal on performance.

RESULTS

As Pt loading and the available Pt area for the ORR are lowered, higher oxygen and proton fluxes must be delivered to the Pt surface, leading to noticeable performance losses. A detailed analysis showed that this performance loss was predominantly attributable to oxygen transport resistance, with the resistance showing a strong dependency on available Pt area and ionomer-Pt interface [2]. As a result, particularly on low-Pt content electrodes, the Pt surface area and the ionomer type become very important factors in determining the performance at high power. Moreover, state-of-the-art Pt alloy catalysts are commonly deposited on HSC, whose particles are porous in nature. A majority of the deposited Pt particles are embedded in the carbon, making it difficult for proton and O₂ to access.

The PtCo/HSC, developed in the previous project, showed a relatively high local oxygen resistance of 25 s/cm. According to previous analysis, we would achieve the DOE target if the resistance could be reduced to 10 s/cm. We found that by changing the carbon support to a non-porous “solid” type carbon, such resistance could be reduced to 10 s/cm. However, the ORR activity also decreased by 2–3 fold. It is believed that the direct contact of the ionomer with the Pt surface poisons the ORR activity of Pt, and that a porous carbon support could help prevent such direct contact for Pt located inside the pores. Figure 1 shows the fuel cell polarization curves of Pt catalysts supported on different carbons. In the low current density region,



MSC – medium surface area carbon; GrC – graphitized carbon

FIGURE 1. Fuel cell polarization curves under differential operating condition with cathode Pt loadings of 0.06 mg_{Pt}/cm². H₂/air, 80°C, 100% relative humidity (RH), 150 kPa_{abs}, stoichiometry of 15/20. 5 cm² active area.

where ORR activity dominates, porous carbons (HSC) show higher voltage. In the HCD region, where transport losses become noticeable, solid carbons (medium surface area carbons and graphitized carbon) perform better. By selecting the appropriate carbon support, we were able to develop a catalyst with both good ORR activity and transport properties (HSC-e).

Further development of the PtCo catalysts on these new carbon supports yielded very high ORR mass activity of about 0.6–0.7 A/mg_{PGM}, comparable to the best PtNi and PtCo developed in the previous project [1]. The fuel cell performance, particularly at HCD, is significantly improved as shown in Figure 2. Under fuel cell operating conditions, relevant to DOE's heat rejection criteria (relatively high temperature and pressure), no noticeable transport-related voltage loss was observed on the new carbon supports operating at HCD. This results in a substantial improvement in high-power performance and PGM utilization as summarized in Table 1. Using the performance of PtCo/HSC-e, our second best electrocatalyst, the DOE-funded cost analysis team estimated that it would reduce the cost of the fuel cell system by about 14% or \$7.5/kW [3,4].

Electrochemical evaluation of the catalyst with various carbon supports after DOE ASTs showed that porous carbons generally better retained Pt surface area and ORR activity under normal fuel cell operation, but did poorly under highly abusive testing. Evaluation of the electrode after the catalyst AST, using a range of advanced characterization techniques at Cornell, Carnegie Mellon University, and Argonne National Laboratory indicated that, regardless of the carbon type employed, the degradation was very similar

at a macroscopic scale (Figure 3). This confirms that Pt dissolution/redeposition and migration dominate degradation. On the other hand, at the microscopic scale, as identified by high-resolution transmission electron microscopy with electron energy loss microscopy, Pt and PtCo nanoparticles in HSC catalysts show a lesser degree of particle coalescence after the stability test. The HSC advantage in mitigating particle coalescence is also manifested in a higher retention of Pt electrochemical surface area and ORR activity. These results illustrate the advantages of using porous carbon support on both initial performance and durability of the catalyst.

At the metal catalyst level, Cornell has been developing high loading (40%) ordered intermetallic Pt₃Co nanoparticle catalysts on HSC supports. A procedure for upscaling and preventing trace halide contamination was developed. Promising ORR activity was observed in rotating disk electrode, and MEA evaluation is underway. On the other hand, previous studies showed that interactions of the electrolyte (ionomer) and the Pt surface poison ORR activity and contribute to the local transport losses [2]. 3M and Drexel have been evaluating alternative ionomers and ionic liquids to mitigate these losses.

Cobalt and platinum dissolution is a major cause of catalyst degradation. National Renewable Energy Laboratory has performed extensive ex situ dissolution tests to determine the rate of Pt and Co dissolution and redeposition under various conditions. A cell level degradation model is being developed to incorporate these findings. Figure 4 presents one example, showing the effects of the potential on the Pt equilibrium concentration in solution and a comparison

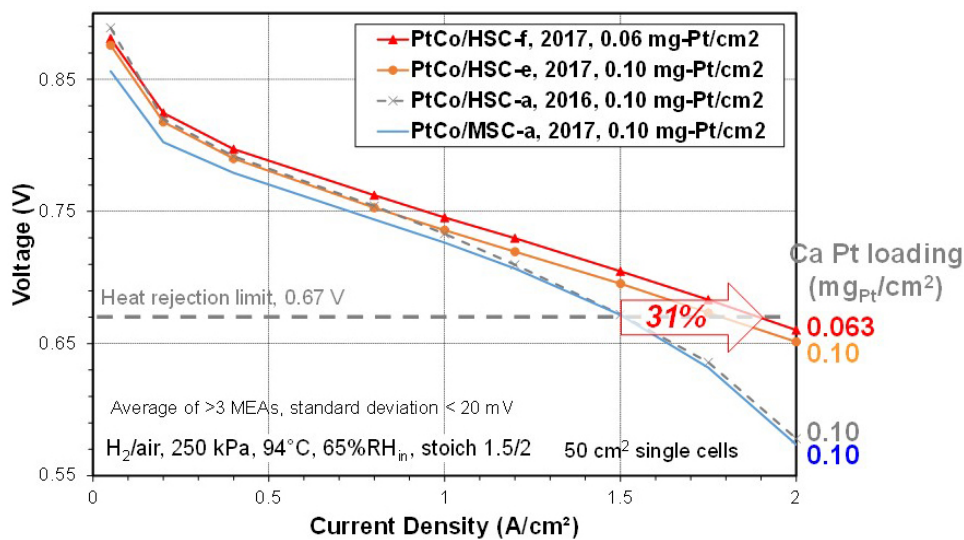


FIGURE 2. 50 cm² fuel cell polarization curves of PtCo catalysts deposited on different carbon supports. Cathode Pt loadings were 0.06 mg_{Pt}/cm² or 0.10 mg_{Pt}/cm² as indicated in the legend. Operating conditions in the order of anode/cathode: H₂/air, 94°C, 65/65% RH, 250/250 kPa_{abs,outlet}, stoichiometries of 1.5/2. Horizontal dash line indicates heat reject target (Q/ΔT of 1.45) recommended by DOE.

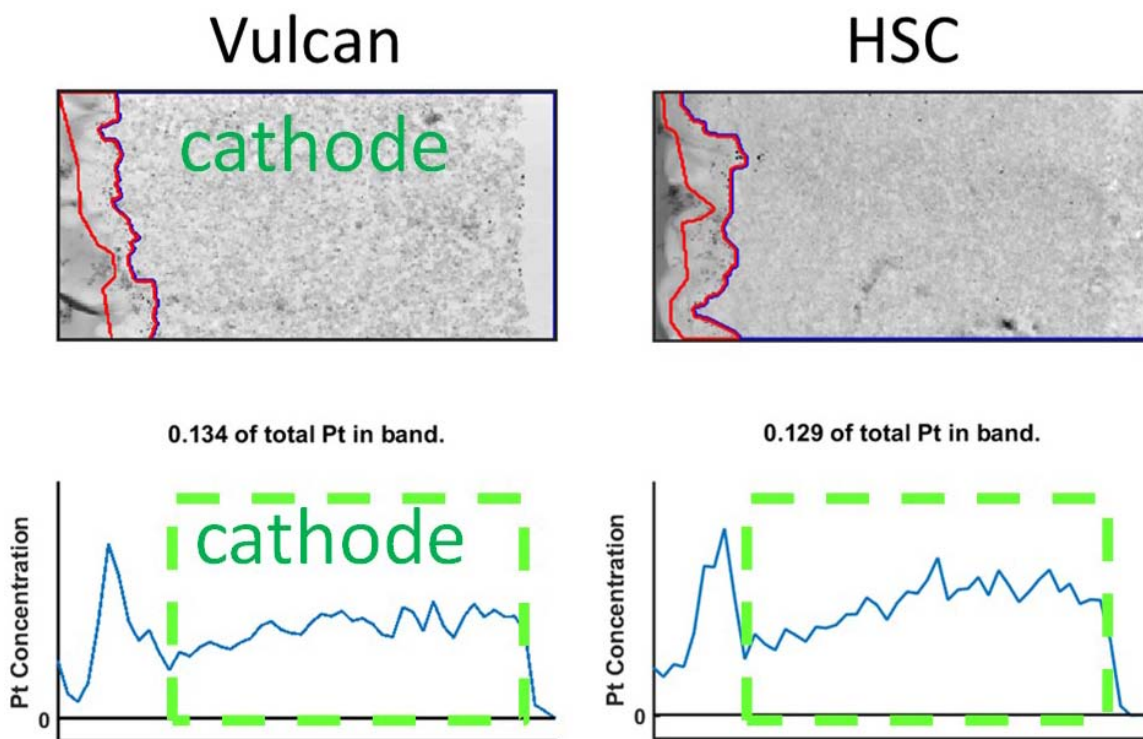


FIGURE 3. Quantification using transmission electron microscopy with energy-dispersive X-ray spectroscopy of Pt distribution in the cathode and cathode/membrane interface after AST (30,000 cycles between 0.6 V and 0.95 V, trapezoidal wave)

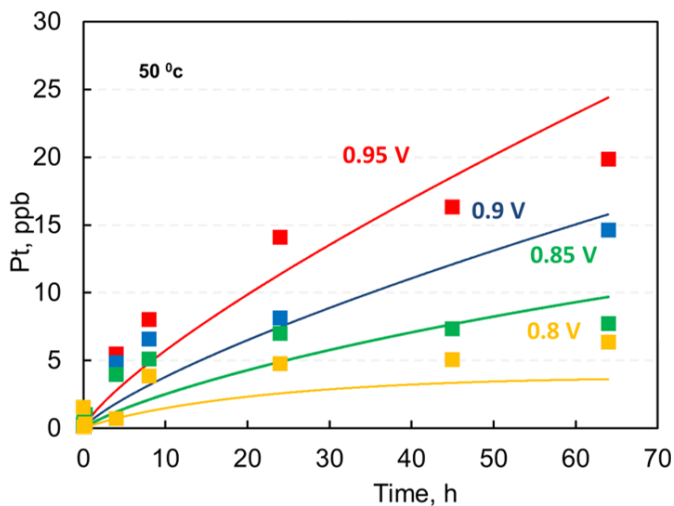


FIGURE 4. Equilibrium concentration of dissolved Pt in the electrolyte solution during a potential hold experiment

between the experiment and model. Experimental and modeling efforts at Carnegie Mellon University and General Motors are focused on understanding the effects of dissolved Co on the proton and oxygen transport properties of the ionomer. These results provide critical information, useful

for determining the operating condition of a fuel cell so as to mitigate catalyst degradation.

Last, several new techniques and capabilities have been developed to accelerate the development of low-PGM electrodes. These include: (1) MEA preparation from small amounts of catalyst powder, (2) CO displacement in an MEA to quantify Pt-ionomer interactions, (3) CO stripping in an MEA to quantify Pt accessibility, (4) mathematical modeling to predict fuel cell performance with dissolved cobalt, and (5) mathematical modeling with nano/meso morphology determined from X-ray computed tomography and transmission electron microscopy tomography.

CONCLUSIONS AND UPCOMING ACTIVITIES

- Exceeded DOE 2020 target on PGM utilization with new carbon supports. This was largely done by lowering the resistance in carbon micropores while maintaining the ORR activity advantage gained in porous carbons.
- Improved the understanding of catalyst degradation due to (a) the effects of the carbon support and (b) Pt and Co dissolution/redeposition.
- Improved understanding of the performance tolerance to dissolved cobalt.

- Several new techniques and capabilities have been developed to accelerate the development of low-PGM electrodes.
- Upcoming activities include:
 - Optimizing PtCo deposition on selected carbons.
 - Continuing development of intermetallic alloys, alternative ionomers, and ionic liquids for improved ORR activity/stability and transport.
 - Experimental and modeling studies to understand the proton and oxygen transport in carbon micropores.
 - Visualization of dissolved cobalt during operation.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. R&D Award by the DOE Hydrogen and Fuel Cells Program. “For outstanding achievements in developing low platinum group metal catalysts for PEMFC.” June 2017.

2. Editors’ Choice recognition by the *J. Electrochem. Soc.* for excellent publication.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. “Electrochemical Diagnostics and Modeling in Developing the PEMFC Cathode,” Anusorn Kongkanand, Venkata Yarlagadda, Taylor Garrick, Thomas E. Moylan, Wenbin Gu, *ECS Transactions* (2016) 75, 25.

2. [Editors’ Choice] “Electrochemically Active Surface Area Measurement of Aged Pt Alloy Catalysts in PEM Fuel Cells by CO Stripping,” Taylor Garrick, Thomas E. Moylan, Michael K. Carpenter, Anusorn Kongkanand, *J. Electrochem. Soc.* (2017) 164, F55.

3. “Characterizing Electrolyte and Platinum Interface in PEM Fuel Cells Using CO Displacement,” Taylor Garrick, Thomas E. Moylan, Venkata Yarlagadda, Anusorn Kongkanand, *J. Electrochem. Soc.* (2017) 164, F60.

4. “Preparation of PEMFC Electrodes from Milligram-Amount Catalyst Powder,” Venkata Yarlagadda, Samuel E. McKinney, Cristin L. Keary, Levi Thompson, Barr Zulevi, and Anusorn Kongkanand, *J. Electrochem. Soc.* (2017) 164, F845.

5. “High-Loading Intermetallic Pt₃Co/C Core-shell Nanoparticles as an Enhanced Catalyst toward the Oxygen Reduction Reaction,” Yin Xiong, Yao Yang, Li Xiao, Héctor D. Abruña. (submitted).

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