

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

Anusorn Kongkanand
 General Motors Company
 850 Glenwood Ave.
 Pontiac, MI 48340-2920
 Phone: (585) 953-5538
 Email: anusorn.kongkanand@gm.com

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

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Subcontractors

- Andrew Haug, 3M Company, St. Paul, MN
- Joshua Snyder, Drexel University, Philadelphia, PA
- David Muller and Héctor Abruña, Cornell University, Ithaca, NY
- Shawn Litster, Carnegie Mellon University, Pittsburgh, PA
- K.C. Neyerlin, National Renewable Energy Lab, Golden, CO

Project Start Date: April 1, 2016

Project End Date: June 30, 2019

- Mitigate catalyst degradation by using supports with more corrosion resistance than the current high-surface-area carbon (HSC).

Fiscal Year (FY) 2016 Objectives

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

- (B) Cost
- (C) Performance
- (A) Durability

Overall Objectives

- Reduce overall stack cost by improving high-current-density (HCD) performance in H₂-air fuel cells adequate to meet DOE heat rejection and Pt-loading targets.
- Maintain high kinetic mass activities.

Technical Targets

See Table 1.

FY 2016 Accomplishments

- Identified and quantified the primary source of HCD performance limitation on low-Pt loaded fuel cell, then

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

Metric	Units	2016 Status	End of Project Target	DOE 2020 Target
Power per PGM content (150 kPa)	kW _{rated} /g _{PGM}	6.9	[7.5]	>8
Power per PGM content (250 kPa)	kW _{rated} /g _{PGM}	7.7	8.8	-
PGM total loading	mg/cm ²	0.125	<0.125	<0.125
Loss in catalytic mass activity	% loss	0–40%	<40%	<40%
Catalyst cycling (0.6–1.0 V, 30,000 cycles)	mV loss at 0.8 A/cm ²	30	<30	<30
Support cycling (1.0–1.5 V, 5,000 cycles)	mV loss at 1.5 A/cm ²	Not tested	<30	<30
Mass activity @ 900 mV _{IR-free}	A/mg _{PGM}	0.6–0.7	>0.6	>0.44
Performance at rated power (150 kPa)	W/cm ²	0.86	[0.94]	>1.0
Performance at rated power (250 kPa)	W/cm ²	1.01	>1.1	-

PGM – Precious group metal; iR – Internal resistance

generated a catalyst technology roadmap for future catalyst development.

- Developed test criteria for carbon support selection.



INTRODUCTION

The amount of expensive platinum used as the oxygen reduction catalyst in fuel cells must be reduced at least 4-fold to make proton exchange membrane fuel cells cost-competitive with other power sources. In our previous DOE-funded project, we have demonstrated that carbon-supported Pt-alloy catalysts (PtNi/HSC and PtCo/HSC) could show very high oxygen catalytic activity and impressive durability, exceeding the DOE targets [1]. However, their high-power performance fell short of the target.

As the Pt content is reduced in the cathode approaching $<0.1 \text{ mg}_{\text{Pt}}/\text{cm}^2$, large amount of oxygen and proton must be delivered 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 transition metal, such as Ni and Co in the catalyst, can dissolve and migrate into the ionomer phase replacing proton, consequently, reducing ionomer proton conductivity and causing hydrodynamic performance loss. As a result, although these newly developed Pt-alloy catalysts show excellent durable high activity at low power, the target performance at high power has not been realized.

APPROACH

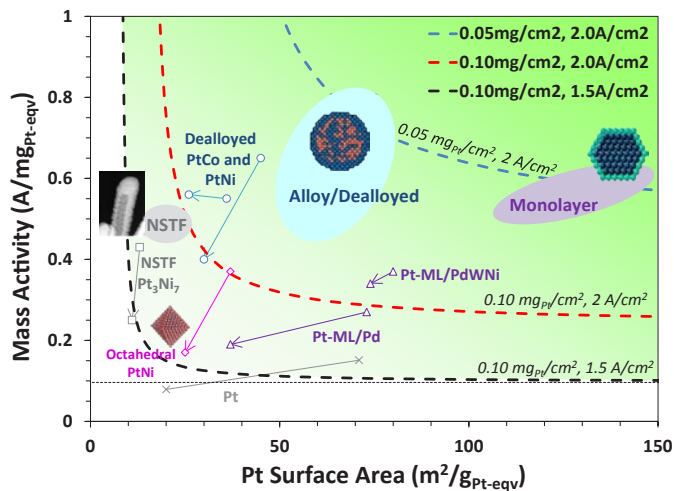
The general approach for this project is to select a carbon support and an electrolyte that have favorable transport properties, then develop a high performance Pt-alloy electrode using these subcomponents. The efforts can be divided into four thrusts: (1) development of carbon support, (2) selection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

RESULTS

As Pt loading and the available Pt area for oxygen reduction reaction (ORR) is reduced, higher oxygen and proton fluxes must be delivered to the Pt surface which leads to noticeable performance losses. The detailed analysis has shown that this performance loss was predominantly oxygen transport resistance, and the resistance showed a strong dependency on available Pt area, also known as the Pt roughness factor [2]. This parameter is the product of Pt loading ($\text{mg}_{\text{Pt}}/\text{cm}^2_{\text{MEA}}$) and Pt-mass-specific electrochemical surface area ($\text{m}^2_{\text{Pt}}/\text{g}_{\text{Pt}}$). As a result, particularly on low-Pt electrode, Pt surface area becomes a very important factor in determining the performance at high power.

Here, we have performed an analysis to reflect the fuel cell requirement for transportation application. Figure 1 provides boundaries (constant voltage lines) for catalyst developers showing material-characteristic regions that meet vehicle power requirements at the end-of-life for a given Pt loading and rated current density. The catalyst ORR mass activity and Pt surface area must be higher than the corresponding dashed parabolic lines to meet the high-power performance requirement. Clearly, materials positioned toward the upper right part of the plot are most desirable and effective in reducing the stack area requirement and thus cost. The electrode reaches end-of-life due to power limitation once the values drop below the dashed line. In the figure, we also include the status (open symbols) and estimates of achievable targets (shaded areas) for some representative catalysts. This analysis will serve as a roadmap for future catalyst development.

The PtCo/HSC developed in the previous project shows a relatively high local oxygen resistance of 25 s/cm. According to the above analysis, we can achieve the DOE target if the resistance can be reduced to 10 s/cm. The project target hence is to search for a carbon support and ionomer that achieves such resistance. During the first year of the project, we have chosen to focus on investigating Pt/C system in order to avoid complication due to the dissolved Co. Figure 2 shows the ORR mass activity and local oxygen resistance of Pt on three types of carbon supports. Although HSC shows the highest



NSTF – Nanostructured thin film

FIGURE 1. ORR mass activity and Pt electrochemical surface area targets which enable the cathode to meet vehicle requirements (0.58 V) at the indicated current density and cathode catalyst loadings. Local resistance of 12 s/cm was used in the analysis. Dashed lines and dotted lines show the minimum values to meet the requirement with and without local resistance, respectively. Catalysts that are above and to the right of a given boundary are sufficient to meet or exceed the voltage requirement. Data points from MEAs at beginning of life (arrow start) and end of life (arrow end) are shown for various catalyst systems, and shaded areas indicate estimate of achievable targets.

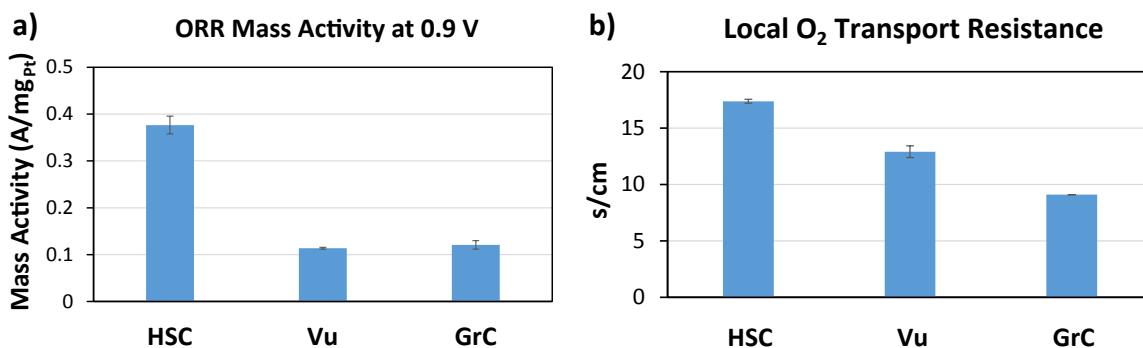


FIGURE 2. ORR mass activity at 0.9 V (a) and local-Pt O₂ transport resistance (b) of Pt catalysts on three different carbon supports

ORR activity, it also shows the largest oxygen resistance. On the other hand, some solid carbons, particularly GrC, show relatively low local oxygen resistance (~10 s/cm). Note that the target is expected to be met if high activity Pt alloy catalyst is successfully developed using this carbon.

Detailed tomographic analysis at Cornell was done to quantify the location of Pt in relation to the carbon for two types of carbon. As shown in Figure 3, porous carbon such as HSC contains a large number of Pt particles inside its carbon particles. These internal Pt may have restricted access to oxygen and proton, resulting in poor HCD performance. Solid carbon such as medium-surface-area carbon, on the other hand, contains mostly surface Pt. This transmission electron microscopy capability will be very powerful in developing new catalysts as well as understanding the structure-function correlation of the electrodes.

To understand the effects of leached transition metal on fuel cell performance, we intentionally introduced known amount of cobalt ions into the MEAs. Electrochemical diagnostic revealed that the local oxygen transport resistance increases with Co²⁺ concentration (Figure 4). This is concerning because it suggests that the HCD performance fall off will be more severe as the catalyst ages. More study is needed to understand how to mitigate these effects.

CONCLUSIONS AND FUTURE DIRECTIONS

Although the project is still in an early stage, several conclusion can be drawn:

- In developing low-Pt fuel cell, Pt surface area and local oxygen transport resistance must be carefully considered.
- Solid carbon tends to show lower local oxygen transport resistance which may make it a preferred choice for a support.

Future work includes:

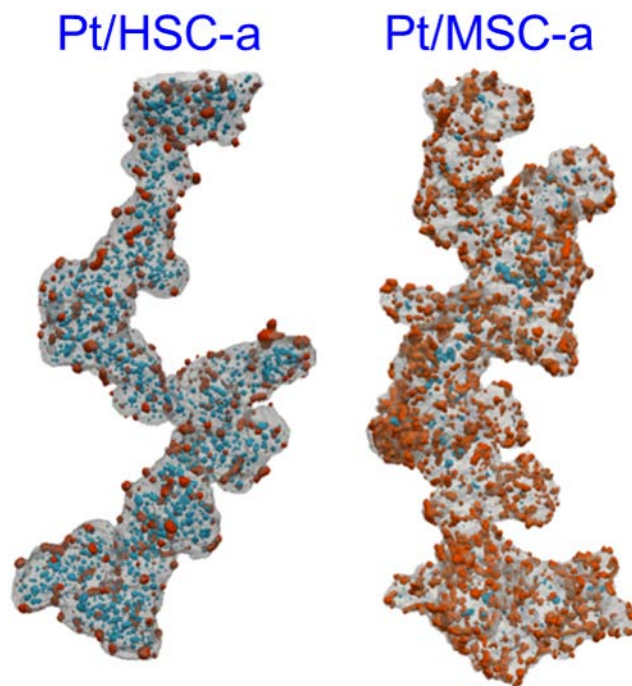


FIGURE 3. Scanning transmission electron microscopic tomographs of Pt/HSC and Pt/Vu showing Pt locating inside (blue dots) and on the surface (red dots) of carbon

- Select preferred carbon support and ionomer and develop Pt catalyst with improved transport property.
- Develop PtCo catalyst with improved dispersion and stability.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. "The Priority and Challenge of High-Power Performance of Low-Platinum Proton-Exchange Membrane Fuel Cells," Anusorn Kongkanand, Mark F. Mathias. *J. Phys. Chem. Lett.* (2016) 7, 1127 [Perspective].

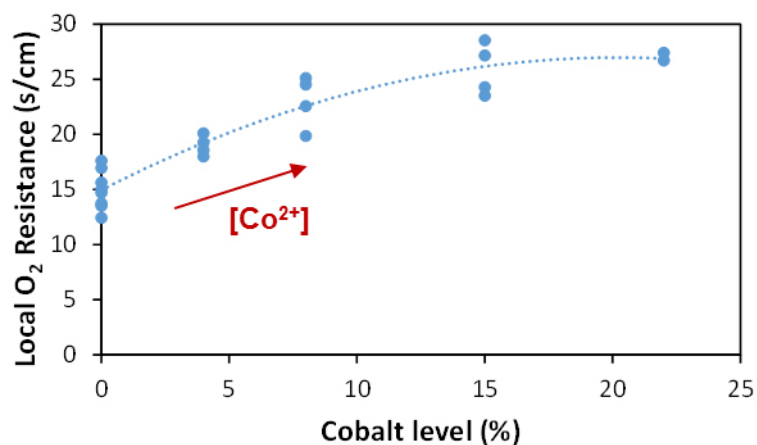


FIGURE 4. Local oxygen resistances measured by limiting current test of MEAs with different levels of Co^{2+} concentration

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1. B. Han, et al., *Record Activity and Stability of Dealloyed Bimetallic Catalysts for Proton Exchange Membrane Fuel Cells*. *Energy Environ. Sci.* 2015, 8(1): p. 258–266.
2. A. Kongkanand and M. Mathias, *The Priority and Challenge of High-Power Performance of Low-Platinum Proton-Exchange Membrane Fuel Cells*. *J. Phys. Chem. Lett.* 2016, 7: p. 1127–1137.

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

3. (Invited) “Characterizing the Pt-Electrolyte Interface in PEM Fuel Cells,” The 14th International Conference on Electrified Interfaces, Changi, Singapore, July 3–8, 2016.