

V.A.17 Vapor Deposition Process for Engineering of Dispersed PEMFC ORR Pt/NbO_x/C Catalysts

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Subcontractors:

- Exothermics, Inc., Amherst, NH
- EWII Fuel Cells, LLC, Albuquerque, NM
- Northeastern University, Boston, MA
- University of Michigan, Ann Arbor, MI

Project Start Date: January 1, 2017

Project End Date: March 31, 2020

- Demonstrate metal particle distribution from PVD process between 2 nm and 10 nm.
- Demonstrate consistency of Pt and NbO_x loadings from PVD processes.

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

The project seeks to develop an electrocatalyst for oxygen reduction, as well as membrane electrode assemblies (MEAs) containing the electrocatalyst, that meet targets relating to the durability, cost, and performance technical barriers. Targets associated with reducing platinum group metal (PGM) content relate to cost.

Most project work so far has focused on fabricating new catalyst powders using PVD systems at Oak Ridge National Laboratory (ORNL). The 5 cm² cell status shown in Table 1 is from samples produced with arc plasma deposition prior to the project award.

FY 2017 Accomplishments

- PVD processes at ORNL were able to produce carbon-supported platinum catalyst (Pt/C) with mass activities measured by rotating disk electrode (RDE) that ranged from 0.3 A/mg_{PGM} to 0.5 A/mg_{PGM}.

Overall Objectives

- Develop a new cathode catalyst powder.
- Improve the catalyst powder manufacturing process.
- Demonstrate the physical vapor deposition (PVD) process is scalable in a cost effective manner.
- Show ease of integration of catalyst into a membrane electrode assembly.

Fiscal Year (FY) 2017 Objectives

- Execute subcontracts.

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

Characteristic	Units	DOE 2020 Electrocatalyst and MEA Targets	Project Status (5 cm ² cell)
Mass activity	A/mg _{PGM} @ 0.9 mV _{IR-free}	≥0.44	0.078
PGM total loading	mg _{PGM} /cm ² _{geo}	≤0.125	0.087, cathode
PGM content at rated power	g _{PGM} /kW _{gross}	≤0.125	0.620, cathode
MEA performance	mW/cm ² _{geo} @ V, T where Q/ΔT = 1.45 kW/K	≥1.000	140
Electrocatalyst stability (0.6 V ↔ 0.95 V)	% mass activity loss after 30,000 cycles	<40	N/A
Loss at 0.8 A/cm ² (0.6 V ↔ 0.95 V)	mV loss after 30,000 cycles	<30	N/A
Support stability (1.0 V ↔ 1.5 V)	% mass activity loss after 5,000 cycles	<40	N/A
Loss at 1.5 A/cm ² (1.0 V ↔ 1.5 V)	mV after 5,000 cycles	<30	N/A

N/A – not available

- PVD process Pt/C samples from ORNL showed platinum particle sizes that ranged from 2 nm to 11 nm.



INTRODUCTION

The Department of Energy has set targets for higher performing catalysts that will address the two major vehicle-related barriers to the commercialization of automotive fuel cell systems: cost and durability. This project seeks to generate new catalysts that meet these targets by (1) applying vapor deposition processes to fabricate catalyst powders and (2) incorporating amorphous niobium oxide as a secondary support in the powders. The project aims to produce powders, as opposed to a structured catalyst layer, in order to enhance roughness factor and allow ease of integration into established ink processes at catalyst coated membrane suppliers.

Vapor deposition provides numerous advantages. With a well-controlled, high volume sputtering process, reproducibility of the catalyst powders should be enhanced compared to the conventional wet chemistry process. Targets made for vapor deposition are very pure, limiting the possibility of impurities (e.g., chlorides, iron) being incorporated into the final powder and compromising performance or durability. Furthermore, a vapor deposition process may be able to limit the amount of aqueous or solvent waste generated in catalyst powder fabrication, although some estimation of precious metal reclamation processes still needs to be considered. Specifically, with regard to niobium oxide, vapor deposition processes yield an amorphous niobium oxide, which has not been shown to convert to the electrically insulating, crystalline Nb_2O_5 phase. The niobium oxide should also provide benefit; numerous studies have shown that the presence of niobium oxide can enhance either mass-normalized or area-normalized activity by 2–3X [1–3]. Furthermore, this project will explore whether depositions of niobium oxide on the surface of porous carbon have the capability to eliminate routes toward platinum surface coalescence.

APPROACH

The project approach centers on two sources for the production of $\text{Pt}/\text{NbO}_x/\text{C}$ catalysts, beginning with small batch (1–2 g) production at ORNL and scaling up to much larger batch (20–40 g) production at Exothermics. ORNL will establish the procedure needed to make $\text{Pt}/\text{NbO}_x/\text{C}$ catalysts by varying parameters such as carbon type, deposition time, pressure, power applied to the metal targets, and, in the case of reactive sputtering, inert/oxidant ratio in the chamber. Samples will then be evaluated for repeatability in terms of platinum and niobium weight percentages by

X-ray fluorescence (XRF), as well as for particle size by transmission electron microscopy (TEM). RDE will be used to screen which catalyst samples are most active, and X-ray absorption spectroscopy will be used to understand why catalysts are active or durable in the contexts of adsorbates, Pt-Pt and Pt-Nb interatomic distances, and Pt-Pt and Pt-Nb coordination numbers.

Fuel cell testing will also be conducted using the $\text{Pt}/\text{NbO}_x/\text{C}$ catalyst powders according to the protocols and metrics outlined by the Department of Energy. Tests will include polarization curves, performance checks at rated power conditions, electrocatalyst cycling at voltages between 0.6 V and 0.95 V, and catalyst support cycling between 1.0 V and 1.5 V. The project team expects that the use of niobium oxide will prompt adjustments in ink formulations, and will reveal performance losses at high current density that will need to be improved. To address these concerns, the project will make use of limiting current techniques to diagnose non-Fickian mass transport resistances, as well as pressure-dependent mass transport resistances. Other diagnostics covering gas crossover, roughness factor, proton conductivity in the catalyst layer, and catalyst activity will also be used in testing.

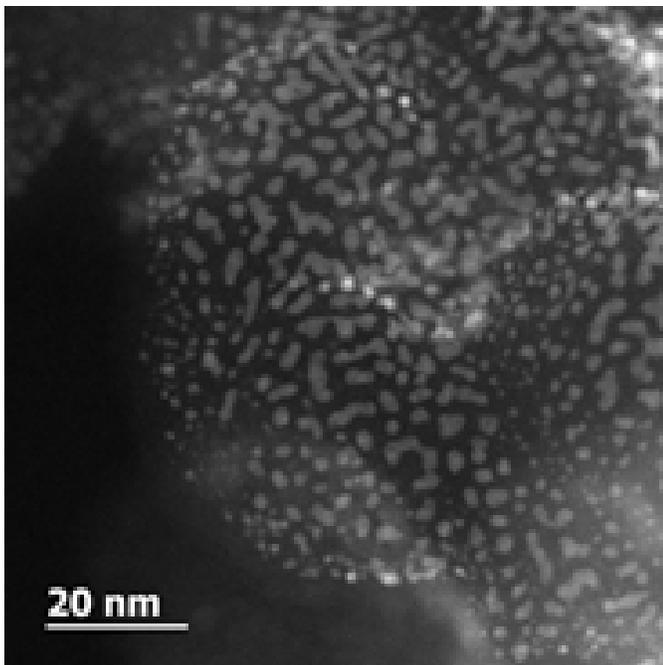
RESULTS

The project has begun with preparation of samples at ORNL. Before depositing niobium oxide, ORNL prepared Pt/C samples using PVD. The PVD process involved the rotation of a carbon powder—either XC-72 or an acetylene black—upon which platinum was sputtered from a pure platinum metal target at room temperature. Table 2 summarizes the results. Sample gmV-080 showed an amazingly high specific activity ($2,418 \mu\text{A}/\text{cm}^2$), which more closely resembled the activity of platinum bulk phase, as opposed to platinum nanoparticles. However, the surface area measurement of $21 \text{ m}^2/\text{g}$ indicated that nanoparticles were in existence, and the TEM image generated at the University of Michigan confirmed the presence of nanoparticles (Figure 1).

While the high activity of the gmV-080 sample was impressive, the lower platinum weight percent measured by XRF (11.4%) was indication that a catalyst layer made from this catalyst would be relatively thick, even at lower mg/cm^2 loading. Therefore, other samples were made in hopes of increasing platinum weight percent. Samples gmV-081, -082, and -083 showed low platinum weight percent, although high specific activities were still seen for gmV-081 and gmV-082. Samples gmV-084 and gmV-085 showed that higher platinum weight percent could be achieved using acetylene black carbon. Like with gmV-084 and gmV-085, higher specific activities were obtained than expected. Given the relatively conventional surface areas, the higher specific activities also translated into higher mass activities. Figure 2 shows that while mass activity might be expected to decrease at

TABLE 2. Results of Pt/C Fabrication at ORNL

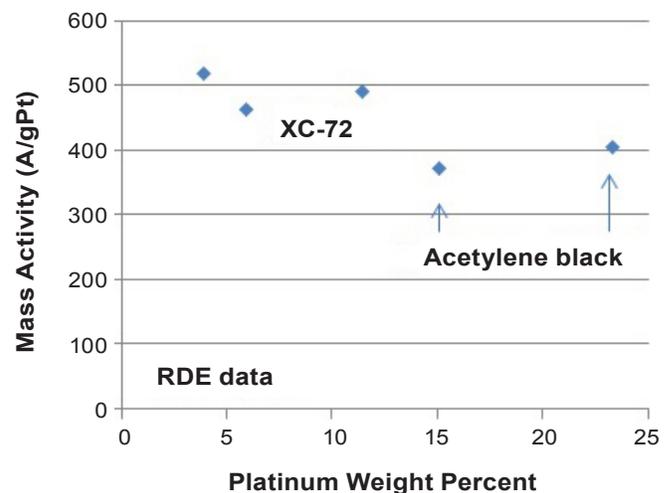
Sample:	gmv-080	gmv-081	gmv-082	gmv-083	gmv-084	gmv-085
Carbon	XC-72	XC-72	XC-72	XC-72	acetylene black	acetylene black
Pt wt% (XRF at Ford)	11.4	3.9	5.9	0.5	15.1	23.3
Deposition time (h:mm)	1:00	2:16	2:55	3:00	3:00	2:28
Pressure (mtorr)	10	20	10	10	10	10
Stir bars?	No	Yes	Yes	No	No	Yes
Temperature	Room	Room	Room	Room	Room	Room
Average mass activity (A/g _{Pt} , RDE)	492	520	462		372	405
Average specific activity (μA/cm ² , RDE)	2,418	1,079	1,325		1,473	726
Average surface area (m ² /g, RDE)	21	48	35		25	58
Calculated Pt particle size (nm)	13	6	8		11	5

**FIGURE 1.** TEM image of sample gmv-080: Pt deposited on XC-72 carbon

higher and more desirable Pt weight percentages, the higher Pt weight percentage samples still show high mass activity. Figure 3 shows that based on RDE data, most samples are between 0.3 A/mg_{Pt} and 0.5 A/mg_{Pt} mass activity, although in some cases higher surface area compensates for lower specific activity.

CONCLUSIONS AND UPCOMING ACTIVITIES

The project has demonstrated particularly high mass activity Pt/C samples made from PVD, at Pt weight percentages up to 23%. In the immediate future, efforts

**FIGURE 2.** Mass activity versus Pt weight percent for ORNL PVD Pt/C samples

will be undertaken with X-ray absorption spectroscopy to understand why the activity is high. At the very least, X-ray absorption spectroscopy should be able to show whether coordination, Pt-Pt interatomic distances and oxygen-containing adsorbates are similar to Pt bulk phase. ORNL PVD deposition will move on to making Pt/NbO_x/C samples after having achieved high activity with Pt/C. Characterization such as TEM and XRF will be used to iterate ORNL deposition conditions toward targeted weight percentages of Pt and Nb, and toward high activity and durability of the catalysts.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. James Waldecker, “Vapor Deposition Process for Engineering of Dispersed PEMFC ORR Pt/NbO_x/C Catalysts,” presented at the 2017 Department of Energy New Project Kick-Off Meeting, Washington, D.C., February 2017.

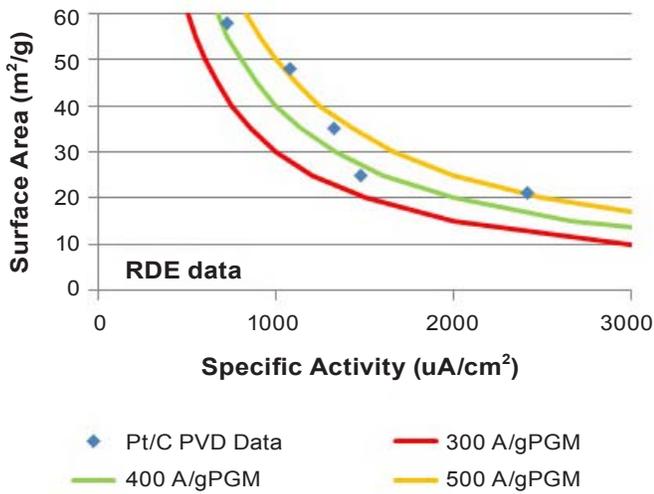


FIGURE 3. Surface area versus specific activity plots with constant mass activity curves for ORNL PVD Pt/C samples

2. James Waldecker, "Vapor Deposition Process for Engineering of Dispersed PEMFC ORR Pt/NbO_x/C Catalysts," presented at the 2017 Department of Energy Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 2017.

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