
Vapor Deposition Process for Engineering of Dispersed Polymer Electrolyte Membrane Fuel Cell Oxygen Reduction Reaction 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

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 (MEA).

Fiscal Year (FY) 2018 Objectives

- Execute subcontracts.
- Demonstrate that oxygen reduction reaction (ORR) catalyst powders from PVD process achieve mass activity (MA) of more than 300 A/g_{Pt}.

- Clarify the interaction between platinum (Pt), niobium oxide (NbO_x), and carbon (C) in PVD Pt/NbO_x/C catalyst powder.

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:

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

Technical Targets

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

FY 2018 Accomplishments

- PVD-processed ORR catalyst powders at Oak Ridge National Laboratory (ORNL), Exothermics, and Ford Motor Company (Ford) were able to produce carbon-supported, NbO_x-templated Pt catalyst (Pt/NbO_x/C) with in-cell mass activities surpassing 300 A/g_{Pt}.
- X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM) analysis confirmed the interactions: Pt for the most part physically sits on NbO_x, which distributes homogeneously on nano-size carbon powders. There is no electronic interaction between NbO_x and carbon support, although the electronic interaction between Pt and NbO_x is very sensitive to the morphology of Pt relative to that of NbO_x.

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

INTRODUCTION

DOE has set targets (shown in Table 1) 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 applying vapor deposition processes to fabricate catalyst powders and incorporating amorphous NbOx as a secondary support in the powders. The project aims to produce powders—as opposed to a structured catalyst layer—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 as 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 thus 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 must be considered. Specifically, with regard to NbOx, vapor deposition processes yield an amorphous NbOx, which has not been shown to convert to the electrically insulating, crystalline Nb₂O₅ phase. The NbOx also should provide benefits; numerous studies have shown that the presence of NbOx can enhance either mass-normalized or area-normalized activity by two to three times [1–3]. This project explores whether depositions of NbOx 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 Pt/NbO_x/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 Pt/NbO_x/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 then will 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. A rotating disk electrode (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 also will be conducted using the Pt/NbO_x/C catalyst powders according to the protocols and metrics outlined by DOE. 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 results expected are that the use of NbOx will prompt adjustments in ink formulations and reveal performance losses at high current density that must be improved. To address these concerns, the project will use 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 also will be used in testing.

RESULTS

Project work has focused on fabricating new catalyst powders using PVD systems at Exothermics and ORNL. The carbon supports are high-surface-area carbons Ketjen black or acetylene black (AB). The MA of the processed powders is derived from 50-cm² cell results obtained at EWII and from 5-cm² cell at Ford (as shown in Table 1, together with DOE targets for 2020).

Table 1. Progress Toward Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

MYRDD Table 3.4.5 Technical Targets: MEAs for Transportation Applications			
Characteristic	Units	2020 Target	Project Status
Performance at rated power	mW/cm ² at 150 kPa (abs)	1000	750 ¹ , 720 ²

MYRDD Table 3.4.7 Technical Targets: Electrocatalysts for Transportation Applications			
Characteristic	Units	2020 Target	Project Status
PGM content at rated power	g _{PGM} /kW _{gross} at 150 kPa (abs)	0.125	0.200 ¹ , 0.208 ²
PGM loading	mg _{PGM} /cm ² total	0.125	0.150 ^{1,2}
Mass activity	A/mgPGM at 900 mV _{IR-free}	0.44	0.352 ¹ , 0.335 ²
Electrocatalyst stability (0.6 ↔ 0.95 V)	% mass activity loss after 30K cycles	<40	TBD
Loss at 0.8 A/cm ² (0.6 ↔ 0.95 V)	mV loss after 30K cycles	<30	TBD
Support stability (1.0 ↔ 1.5 V)	% mass activity loss after 5K cycles	<40	TBD
Loss at 1.5 A/cm ² (1.0 ↔ 1.5 V)	mV after 5K cycles	<30	TBD

¹ Measured using Exothermics 180308 (PtCo/NbOx/Ketjen black). High current measurements at 0.6 V, 80 °C (Q/DT=2.44), fully humidified.

² Measured using ORNL-L-013 (Pt/NbOx/acetylene black). High current measurements at 0.6 V, 80 °C (Q/DT=2.44), fully humidified.

Table 2 lists the details of the samples made by ORNL and Exothermics (EXO) that exhibit an MA of more than 300 A/g_{Pt}. It can be seen that in-cell MA of more than 300 A/g_{Pt} has been achieved on NbOx-templated Pt-coated ORR catalysts on both AB and Ketjen black carbons.

Table 2. Sample Details with Mass Activity Greater Than 300 A/g_{Pt}

Sample	Composition (AB = acetylene black) (KB = Ketjen black)	Mass Activity (A/g _{Pt})	Test at:	Cell Size (cm ²)	I/C	Cathode / Anode Loadings (mg/cm ²)
ORNL-L-013	35.8% Pt, 0.61% NbOx, AB	335	Ford	5	0.6	0.1/0.05
Exothermics 180109	19.9% Pt, 1.75% NbOx, KB	328	EWII	50	0.8	0.1/0.05
Exothermics 180302	21.5% Pt, 0.23% NbOx, 1.10% Co, KB	309	EWII	50	0.5	0.1/0.05
Exothermics 180308	28.8% Pt, 0.50% NbOx, 1.54% Co, KB	352	Ford	5	0.6	0.1/0.05

The effects of NbOx in the project has been investigated using TEM and XAS analyses. The high-angle annular dark field and elemental mapping of the ORNL-L-013 sample are shown in Figure 1. It can be seen that NbOx is more dispersed on the surface of carbon (AB); the Pt is more clustered but physically laying on top of the NbOx for the most part, forming the desired morphology for enhanced durability and activity.

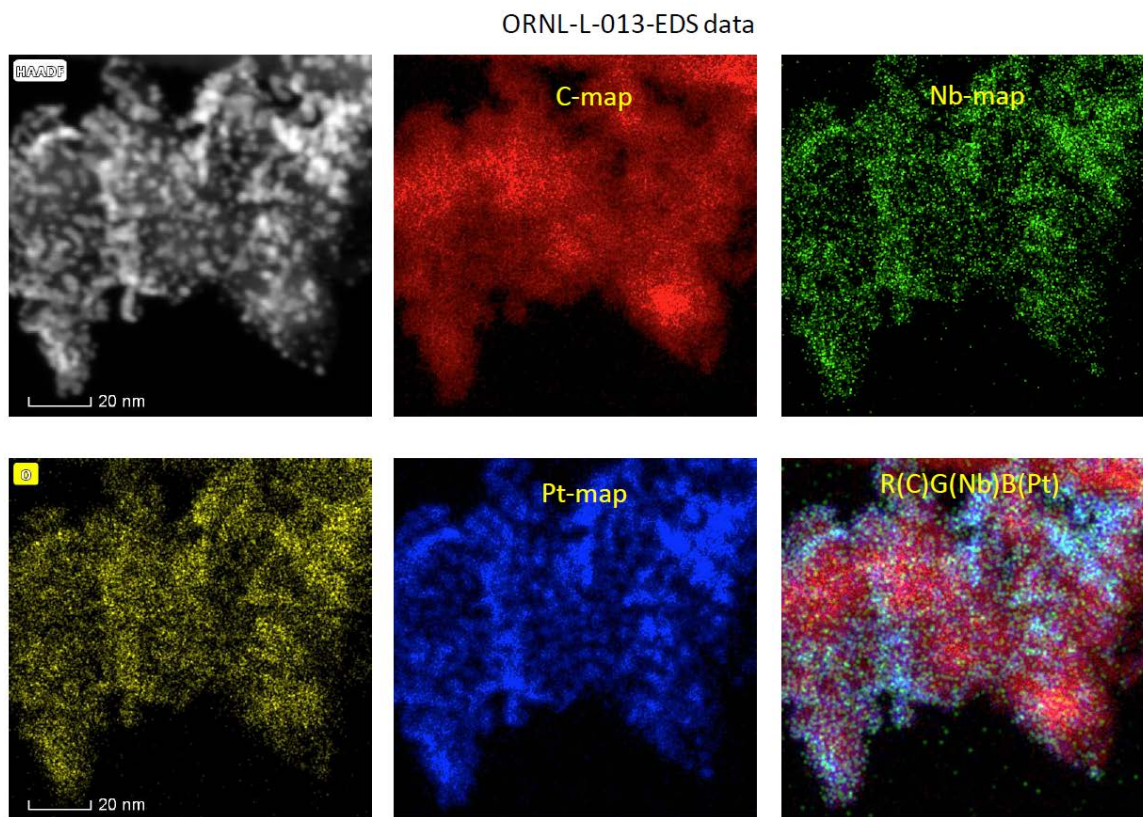


Figure 1. The high-angle annular dark field and elemental mapping in ORNL-L-013 sample

XAS analyses can distinguish the interactions between Pt-C, NbOx-C, and the NbOx and Pt supported on carbon. As a baseline analysis, the XAS is shown in Figure 2a for Tanaka Kikinzoku Kogyo (TKK) Pt (wet-chemical TKK50E) and EXO180209 (26.8 wt% Pt on Ketjen black carbon). The data (Figure 2b) shows that the EXO180209 has slightly shorter Pt-Pt distance than that of commercial TKK 50E but displays very similar numbers of near-neighbor Pt-Pt atoms. The change in Pt-Pt bond distance is not significant, indicating that the type of carbon and the preparation method cannot significantly change the Pt activities as long as the Pt morphology is not significantly altered.

When incorporating NbOx into the catalyst, the first thing that must be determined is whether there is any electronic interaction between NbOx and C. For this purpose, we measured the XAS of vapor processed NbOx on AB carbon (ORNL-L-008, 4.42 wt% NbOx on AB carbon), Pt on NbOx on AB carbon (ORNL-L-013, 0.61 wt% NbOx and 35.8 wt% Pt), and wet-chemically synthesized PtNb/NbOx/AB carbon (5 wt% Nb, 10.6 wt% O, 20.4 wt% Pt, and 64 wt% C).

The Nb X-ray absorption near edge structure (XANES) results are shown in Figure 3, where (a) and (b) are the Nb-XANES analysis, (c) is the derived Nb valence state, and (d) is the Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) analysis. The results show that the NbOx in ORNL-L-008 is slightly more disordered than Nb₂O₅, but no interaction with C was observed by XAS. The XANES and FT-EXAFS of ORNL-L-013 Pt/NbOx/C is close to that of ORNL-L-008 NbOx/C, and also close to that of Nb₂O₅, but the oxidation state of the Nb in ORNL-L-013 Pt/NbOx/C is 4.6, whereas that in ORNL-L-008 NbOx/C is close to 5. Furthermore, there is no Pt-Nb alloying in the sequentially vapor-deposited Pt/NbOx/C samples, unlike those wet-chemically co-deposited Pt-Nb on carbon [4], where significant Pt-Nb alloying can be observed, as shown on Figure 3(d), which is what is expected based on the processing methods.

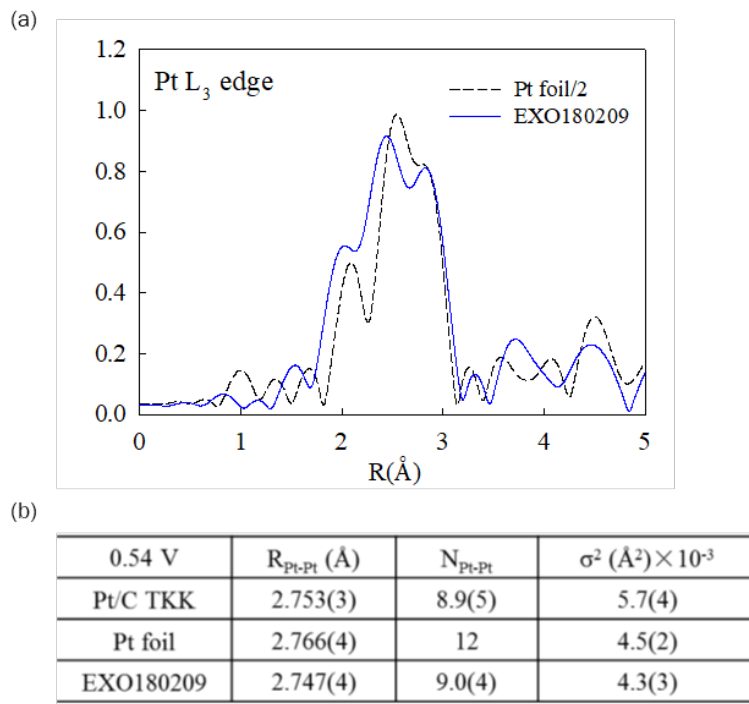


Figure 2. The Pt L3 edge FT-EXAFS comparison at 0.54 V (reversible hydrogen electrode [RHE]) for Pt/C TKK (EA50), Pt foil, and Exothermics 180209 (26.8 wt% Pt on AB carbon)

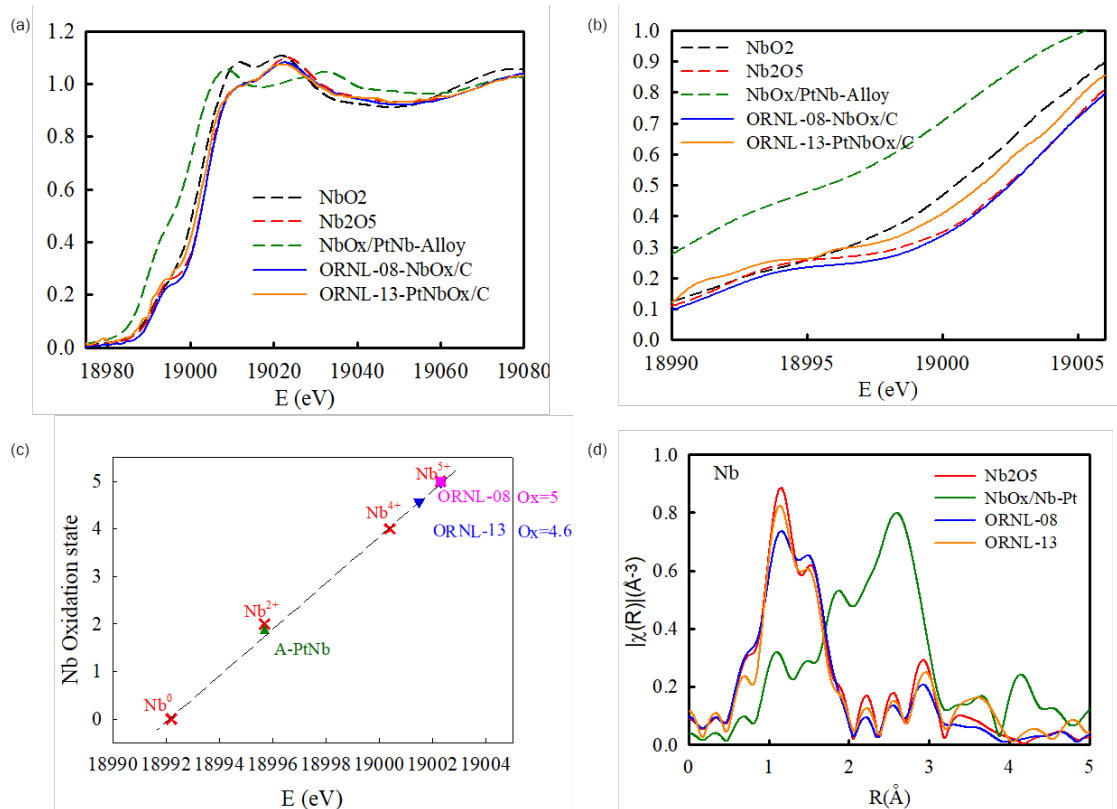


Figure 3. Nb XAS analysis: (a) Nb-XANES analysis, (b) expanded portion for E between 18990 and 19006 eV, (c) quantitative identification of Nb oxidation state from XANES position, and (d) Nb FT-EXAFS comparison

Results of Pt L3-edge XAS analyses on ORNL-L-013 Pt/NbO_x/AB carbon are shown in Figure 4. The presence of Pt-O at 0.54 V and 0.90 V on ORNL-L-013 (Figure 4(a)) indicates the interactions between Pt and the O from the NbO_x rather than from O₂ or H₂O. The presence of Pt-O at 0.54 V in ORNL-13 was further confirmed by XANES (Figure 4(b)), which manifests the charge transfer from Pt to O (ligand effect). As to the Pt-Nb, the data shows that there is no strong interaction between Pt-Nb at 0.54 V (versus RHE, Figure 4(c)), but some interaction between the Pt-Nb at 0.9 V (versus RHE, Figure 4(d)), indicating that the O in NbO_x actively participated in the ORR process. The interaction between Pt and O in the NbO_x could contribute to the ORR activity either positively or negatively depending on the strength of the bonding. If the interaction is weak, then the O in NbO_x acts as a reservoir, facilitating the ORR activity. If the interaction is too strong, then the O from NbO_x holds onto the Pt, preventing the Pt from being actively involved in the ORR reaction, which negatively impacts ORR.

The EXAFS fit results are shown in Table 3 for ORNL-L-013, ORNL-L-019, and EXO180109. The Pt-Pt bond distance in ORNL-L-013 is slightly shortened, probably because of the strong metal-support interaction–induced strain effect as previously shown experimentally by our team and theoretically by other researchers. This could be further improved by engineering the morphology of NbO_x and Pt, the composition of NbO_x, and the extent of disorder on a selected type of carbon support. The templating effects of amorphous NbO_x is one of the main factors that could tremendously enhance ORR activity, as well as durability.

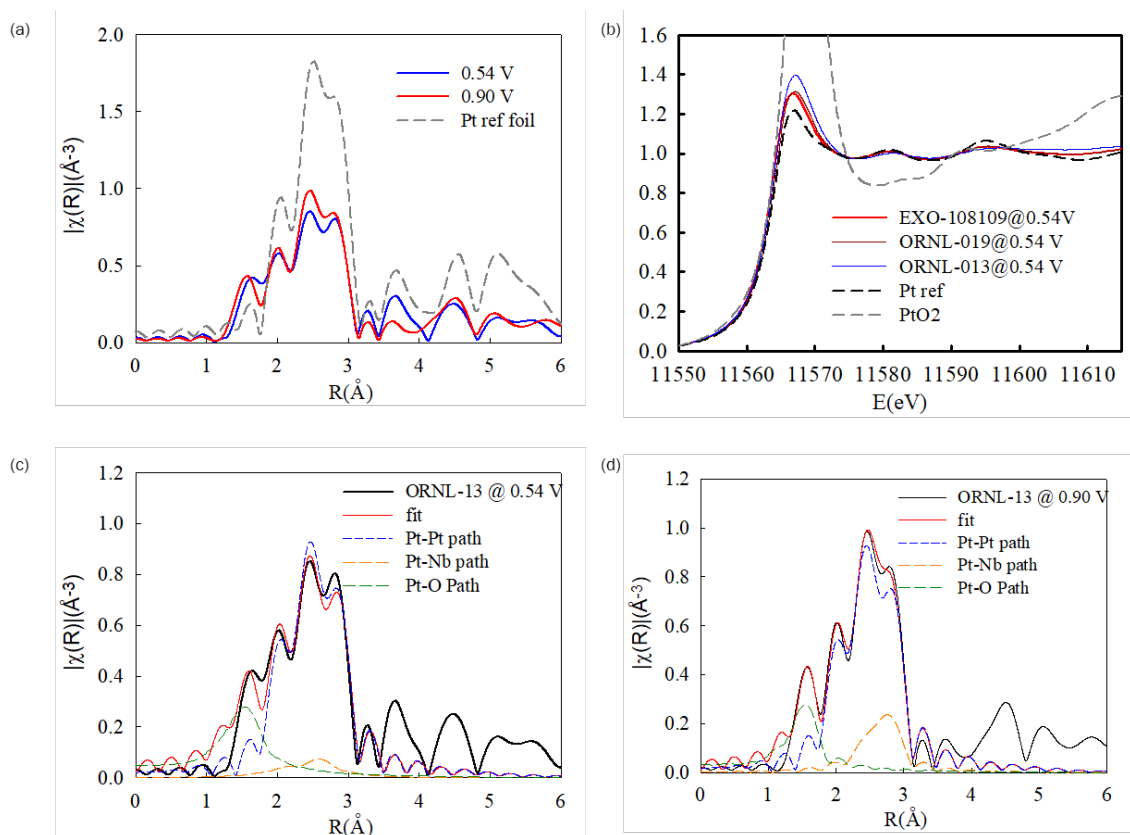


Figure 4. Pt L3-edge XAS; (a) ORNL-L-13 at 0.54 V and 0.9 V (vs. RHE), (b) EXO180109, ORNL-L-019 (37.5 wt% on AB carbon) and ORNL-L-13 at 0.54 V (vs. RHE), (c) EXAFS for ORNL-L-013 at 0.54 V, and (d) at 0.9 V

Table 3. EXAFS Fit Results at 0.9 V Versus RHE

EXAFS 0.9V	Pt-Pt		Pt-Nb		Pt-O	
	N	R (Å)	N	R (Å)	N	R (Å)
Pt foil	12	2.766±0.005	-	-	-	-
ORNL-13	7.8±1.1	2.74±0.01	1.3±0.7	2.86±0.04	0.7±0.5	1.97±0.02
ORNL-19	8.3±0.7	2.75±0.01	-	-	0.6±0.5	1.98±0.02
EXO-108109	9.3±0.7	2.75±0.01	-	-	0.3±0.3	1.99±0.02

CONCLUSIONS AND UPCOMING ACTIVITIES

During FY 2018, ORNL, Exothermics, and Ford have successfully used PVD in processing carbon-supported, NbOx-templated Pt catalyst (Pt/NbOx/C) powders with in-cell mass activities surpassing 300A/g_{Pt}. XAS and TEM analysis confirmed the interactions: Pt for the most part physically sitting on NbOx, which distributes homogeneously on nano-size carbon powders. There is no electronic interaction between NbOx and carbon support, but the electronic interaction between Pt and NbOx is very sensitive to the morphology of Pt relative to that of NbOx. The next step of the project will focus on durability and the ease of incorporation of the catalysts in single cells.

PUBLICATIONS/PRESENTATIONS

1. Shabroni Ghoshal, Qingying Jia, Michael K. Bates, Jingkun Li, Chunchuan Xu, Kerrie Gath, Jun Yang, James Waldecker, Haiying Che, Wentao Liang, Guangnan Meng, Zi-Feng Ma, and Sanjeev Mukerjee, "Tuning Nb–Pt Interactions to Facilitate Fuel Cell Electrocatalysis," *ACS Catal.* 7, no. 8 (2017): 4936–4946.
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3. James Waldecker, "Vapor Deposition Process for Engineering of Dispersed PEMFC ORR Pt/NbOx/C Catalysts," Presented at the 2018 Department of Energy Annual Review. Washington, D.C. June 14, 2018.

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1. K. Sasaki, L. Zhang, and R.R. Adzic, "Niobium Oxide-Supported Platinum Ultra-Low Amount Electrocatalysts for Oxygen Reduction," *Phys. Chem. Chem. Phys.* 10 (2008): 159–167.
2. T. Trefz, N. Kremliaikova, D. Susac, and J. Jankovic, "Sol-Gel Syntheses of Durable Metal-Oxide Hybrid Platinum Catalysts for PEFC," 224th ECS Meeting, Abstract 1501 (2013).
3. L. Zhang, L. Wang, C.M.B. Holt, T. Navessin, K. Malek, M.H. Eikerling, and D. Mitlin, "Oxygen Reduction Reaction Activity and Electrochemical Stability of Thin-Film Bilayer Systems of Platinum on Niobium Oxide," *J. Phys. Chem. C* 114 (2010): 16463–16474.
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