
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
- IRD Fuel Cells, LLC, Albuquerque, NM
- Northeastern University, Boston, MA
- University of Michigan, Ann Arbor, MI

Project Start Date: January 1, 2017
Project End Date: September 30, 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) 2019 Objectives

- Execute subcontracts.
- Demonstrate oxygen reduction reaction (ORR) catalyst powders from PVD process achieve mass activity of above 300 A/g_{Pt} as well as durability against accelerated electrocatalyst tests.

- Clarify the interaction between Pt, NbO_x, and C in PVD Pt/NbO_x/C catalyst powders.

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 (MYRDD) 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 (PGM) content relate to cost. Progress toward these targets is listed in Table 1, together with DOE targets for 2020.

FY 2019 Accomplishments

- Experimental design at ORNL identified the desired composition range for NbO_x and Pt.
- A large batch of samples with desired compositions was produced at Exothermics.
- In-cell performance meets DOE durability targets for catalyst mass activity loss. X-ray adsorption spectroscopy (XAS) and transmission electron microscopy (TEM) analyses clarify the relative distribution of NbO_x and Pt. These techniques also show an electronic interaction between the O from NbO_x and Pt that exists for a wide range of potential.

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

Table 1. Progress toward Meeting Technical Targets for Vapor Deposition Process for Engineering of Dispersed Polymer Electrolyte Membrane Fuel Cell ORR Pt/NbOx/C Catalysts

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)	1,000	930, ^a 720 ^b
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	0.161, ^a 0.208 ^b
PGM loading	mg _{PGM} /cm ² total	0.125	0.150 ^{a-e}
Mass activity	A/mg _{PGM} at 900 mV _{IR-free}	0.44	0.389, ^a 0.335 ^b
Electrocatalyst stability (0.6 ↔ 0.95 V)	% mass activity loss after 30,000 cycles	<40	14%, ^a 9%, ^c 10%, ^d 1% ^e
Loss at 0.8 A/cm ² (0.6 ↔ 0.95 V)	mV loss after 30,000 cycles	<30	70 mV, ^a 71 mV, ^c 40 mV ^d
Support stability (1.0 ↔ 1.5 V)	% mass activity loss after 5,000 cycles	<40	TBD
Loss at 1.5 A/cm ² (1.0 ↔ 1.5 V)	mV after 5,000 cycles	<30	TBD

^a Measured using Exothermics 180920 (20/2.5 wt % Pt/NbOx on acetylene black).

^b Measured using ORNL-L-013 (36/0.6 wt % Pt/NbOx on acetylene black). High current measurements at 0.6 V, 80°C (Q/DT=2.44), fully humidified.

^{c, d, e} Measured using ORNL-L-034 (18/8.0 wt % Pt/NbOx), ORNL-L-030 (18/6.3 wt % Pt/NbOx), ORNL-L-032 (31/3.8 wt % Pt/NbOx), respectively. All supported on acetylene black; anode loading 0.05 mg_{PGM}/cm².

INTRODUCTION

DOE has set targets as 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 (1) applying vapor deposition processes to fabricate catalyst powders, and (2) incorporating amorphous niobium oxide as a secondary support in the powders. The project's aim is 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 Nb₂O₅ phase. The niobium oxide should also provide benefits; 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 Pt/NbO_x/C catalysts, beginning with small batch (1–2 g) production at Oak Ridge National Laboratory (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 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 TEM. A rotating disk electrode (RDE) will be used to screen which catalyst samples are most active, and XAS 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 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 and 0.95 V, and catalyst support cycling between 1.0 and 1.5 V. The project 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 composition and morphology of the catalyst powders has been found critical to its ORR activities and durability. Previous experiments have identified the composition range as 1.5 to 6 wt % for NbO_x and 20 to 30 wt % for Pt, respectively. ORNL successfully produced six samples based on a design of experiment of 1.5 wt %, 3 wt % and 6 wt % NbO_x and 20 wt % and 30 wt % Pt, providing the catalyst for accelerated stress tests (ASTs) to optimize the NbO_x and Pt weight percentages. The compositions of the six samples are shown in Table 2. ORNL reproduced ORNL-L-030 with ORNL-L-039 with comparable compositions.

Exothermics has produced large batches of samples, including EXO180920, with composition similar to ORNL-L-035. Exothermics also produced two large batches of samples EXO190211 and EXO190313 with higher NbO_x concentration. The composition of EXO190211 is similar to ORNL-L-030 and ORNL-L-039, while that of EXO190313 is similar to that of ORNL-L-034, as shown in Table 2 and Table 3.

Table 2. ORNL Big Chamber DOE Samples for AST Durability and Mass Activity with NbOx and Pt

Sample Name	Temperature	Nb Deposition: Ar/O ₂ Ratio	Nb Deposition: Time (h)	Nb Deposition: Power (W)	Pt Deposition: Time (h)	Pt Deposition: Power (W)	Pt Loading from XRF (wt %)	NbOx Loading from XRF (wt %)
ORNL-L-030	Room (off-gassed to 400 °C for 12 h)	10	18.7	150	0.97	140	27.7	6.3
ORNL-L-032	Room (off-gassed to 400 °C for 12 h)	10	9.3	150	1	140	30.6	3.82
ORNL-L-034	Room (off-gassed to 400 °C for 12 h)	10	18.7	150	0.67	140	18.1	8.0
ORNL-L-035	Room (off-gassed to 400 °C for 12 h)	10	5.6	150	0.58	140	21.5	2.72
ORNL-L-037	Room (off-gassed to 400 °C for 12 h)	10	3.9	150	0.63	140	21.3	1.77
ORNL-L-038	Room (off-gassed to 400 °C for 12 h)	10	3.7	150	1	140	28.5	1.34
ORNL-L-039	Room (off-gassed to 400 °C for 12 h)	10	18.7	140	0.97	150	26.7	6.58
EX0180109	Off-gassed to >200 °C; sputter at >100 °C	32.3	8	100	5	300	19.9	1.75
EX0180920	Off-gassed to >200 °C; sputter at >100 °C	32.3	8	100	4.5	300	20.0	2.5
EX0181114	Off-gassed to >200 °C; sputter at >100 °C	NA	NA	NA	4.5	300	30.2	NA
Umicore	Wet chemical commercial	NA	NA	NA	NA	NA	28.3	NA

Table 3. XPS Nb 3d_{5/2} Binding Energies for PVD Processed Pt/NbO_x/C and NbO_x/C

Sample	Pt wt %	NbOx wt %	Carbon Support	Nb 3d _{5/2} Binding Energy (eV)
Nb ₂ O ₅ standard	0	100	N/A	207.89
ORNL-L-015	20.7	0.92	Acetylene black	207.07
ORNL-L-008	0	4.42	Acetylene black	207.69
EX0180109	19.9	1.75	Ketjen black	207.49
EX0180606	0	0.62	Ketjen black	207.54
EX0180920	20.0	2.50	Acetylene black	207.05
EX0190211	27.9	5.94	Acetylene black	206.91
EX0190313	20.4	8.00	Acetylene black	207.50

Figure 1 shows the high-angle annular dark-field and composition mapping of samples ORNL-L-013 (0.61 wt % NbO_x and 35.8 wt % Pt) and EX0180920 (2.5 wt % NbO_x and 20 wt % Pt). It can be seen that the NbO_x and Pt form a partially connected skeleton on carbon, but the lower NbO_x concentration in ORNL-L-013 is not enough to pin down platinum during the electrocatalyst AST. When increasing the NbO_x concentration, the NbO_x distribution is more uniform. Pt forms a partially connected network on top and adjacent to NbO_x, enhancing ORR activity and durability.

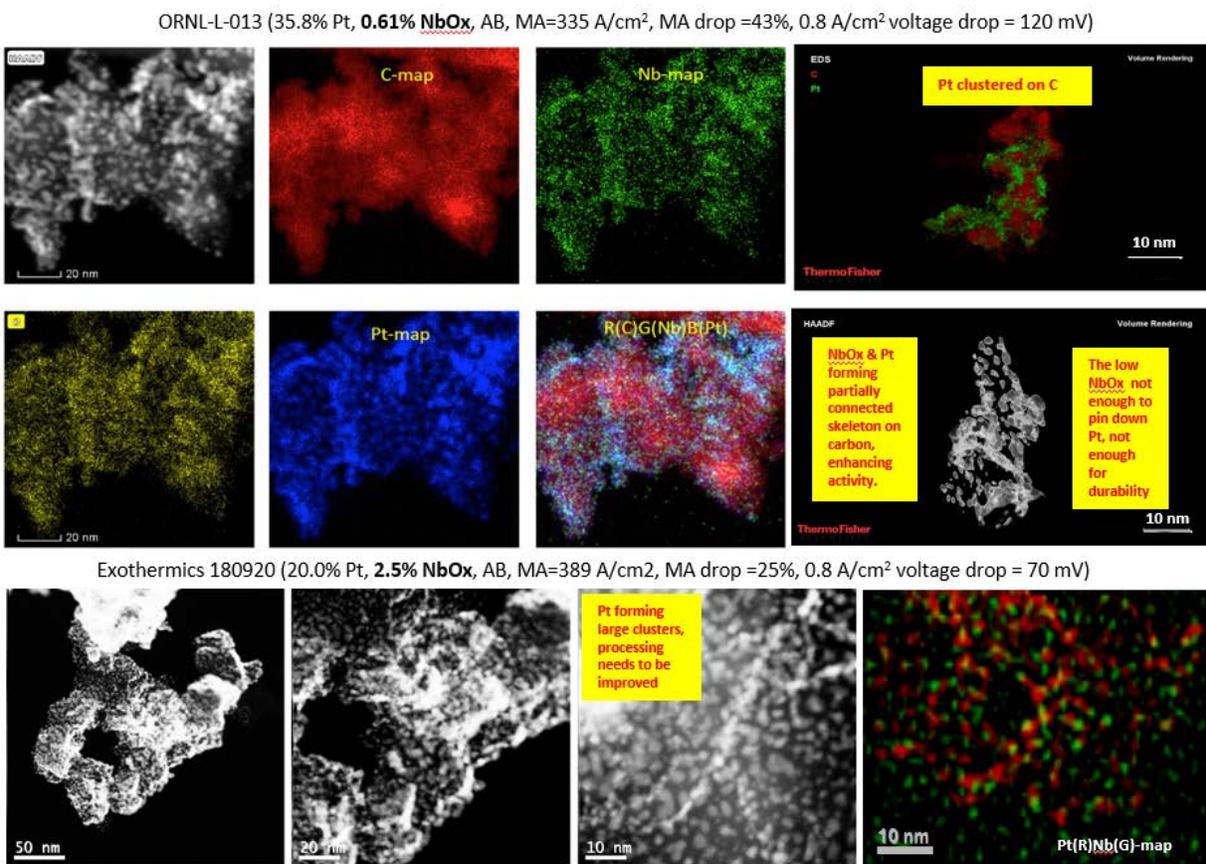


Figure 1. The morphology of NbO_x and Pt in ORNL-L-013 and EXO180920 through microstructural analysis with TEM

XAS was performed to clarify the electronic interactions on four samples with different NbO_x concentrations: ORNL-L-013 (0.61 wt % NbO_x), ORNL-L-038 (1.34 wt %), ORNL-L-032 (3.82 wt %) and ORNL-L-030 (6.3 wt %). Figure 2 shows the XAS analysis results. Figure 2a shows the Pt edge Fourier transform–extended X-ray absorption fine structure (FT-EXAFS) results for the four samples together with Umicore reference sample and Pt foil. It can be seen that increasing NbO_x content decreases the intensity of the FT-EXAFS peak. However, the shape of the FT-EXAFS peak does not change much with increasing Nb content, indicating the lack of significant Pt-Nb interactions, as shown in Figure 2b. Similarly, the Nb XAS signal does not change significantly with Nb content either, further confirming no detectable Nb-Pt interactions. The Nb edge FT-EXAFS show the bulk oxidation state of Nb as $x = 4.6$ in NbO_x, which suggests the sputtered NbO_x has oxygen vacancies that preserve electronic conductivity.

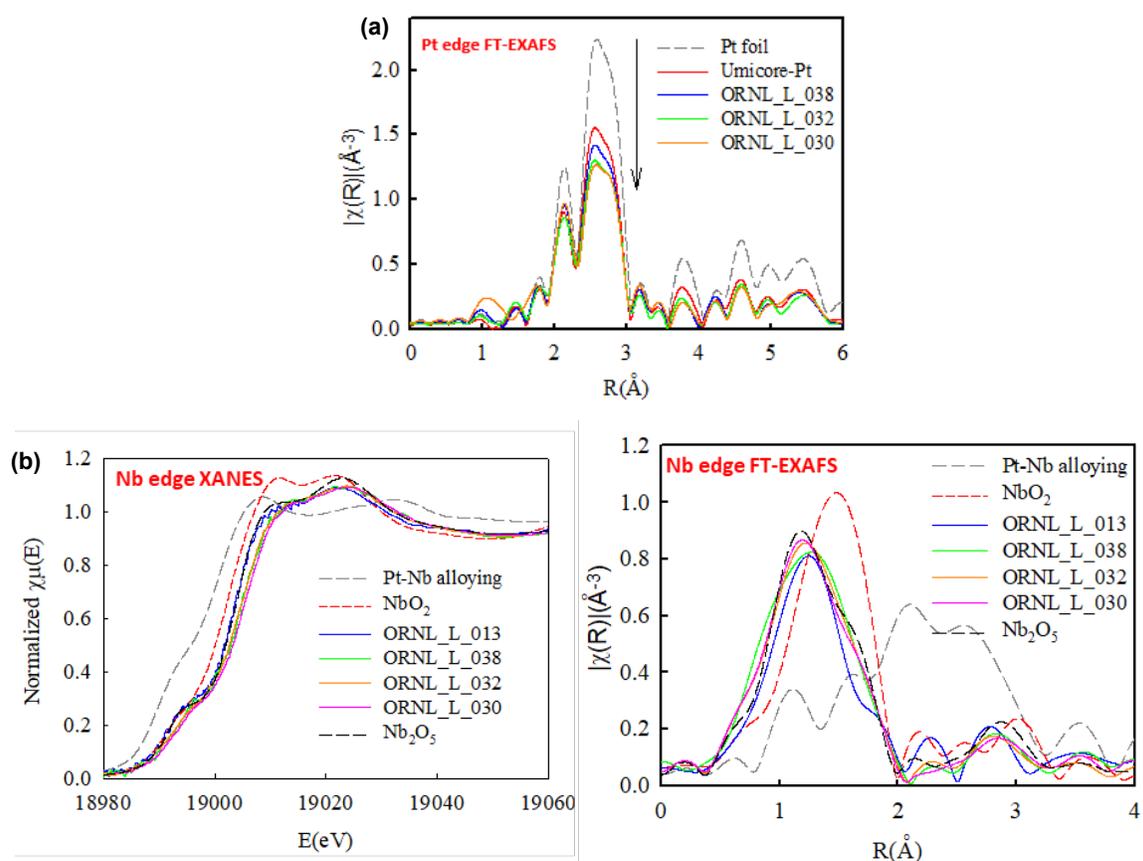


Figure 2. The XAS of four ORR catalysts with different NbOx concentrations: ORNL-L-013 (0.61 wt % NbOx), ORNL-L-038 (1.34 wt %), ORNL-L-032 (3.82 wt %) and ORNL-L-030 (6.3 wt %). (a) Pt edge FT-EXAFS and (b) Nb edge XANES and Nb-edge FT-EXAFS.

XAS analyses for the interaction between the O in NbOx and Pt are shown in Figure 3, which shows that increasing the NbOx content enhances the white line intensity of the Pt X-ray absorption near edge structure (XANES), reducing the number of electrons in the Pt 5d orbitals. This suggests that there is an interaction between Pt and O that comes from NbOx due to the charge transfer from Pt to the O from NbOx.

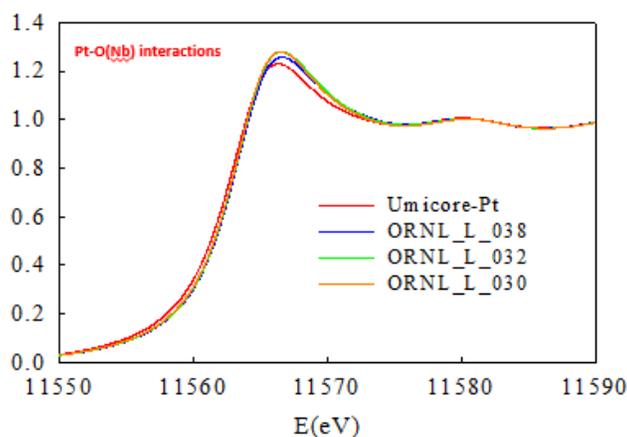


Figure 3. The FT-EXAFS analysis of the Pt-O(Nb) interaction in Umicore reference sample, ORNL-L-038, ORNL-L-032, and ORNL-L-030.

The in situ XAS of ORNL-L-030 (6.3 wt % NbOx and 27.7 wt % Pt) and reference Umicore sample are shown in Figure 4, where the XAS is collected at a cathode voltage of 0.10 V, 0.54 V, and 0.90 V versus the hydrogen reference electrode. The in situ data suggest there is a Pt-O interaction throughout the whole potential region, which indicates that Pt is tightly anchored onto NbOx in contact with O. The increases in the FT-EXAFS intensity (reflecting the Pt-Pt coordination number) at low potentials indicate that the Pt clusters move away from the substrate at low potentials. The model proposed on the right side of Figure 4 could explain why the interaction between Pt and O from NbOx can induce the durability improvement in NbOx containing ORR catalysts.

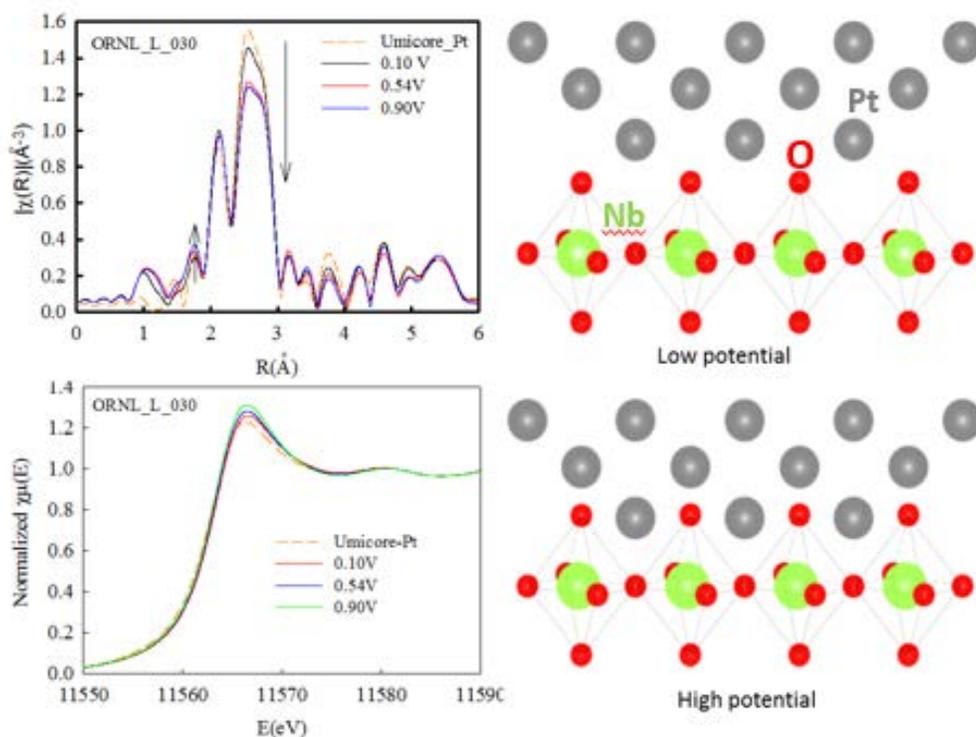


Figure 4. The in situ analysis of ORNL-L-030 and proposed Pt-O interaction

Table 4 shows the durability of the developed and commercial catalysts in electrocatalyst AST (MYRDD P.1) run at IRD Fuel Cells with 0.1 mg-Pt/cm² cathode loading using a 50 cm² FCT single cell, measured at 0.9 V_{IR-free} and corrected for hydrogen cross over. The results show that for most of the developed Pt/NbOx/C catalysts, the mass activity loss is less than 40%. On the other hand, the voltage loss at 0.8 A/cm² current density is sensitive to both the catalyst and the ionomer-to-carbon (I/C) ratio of the ink. In general, the higher the concentration of NbOx in the catalyst, the lower the voltage loss at 0.8 A/cm² current density at the same I/C ratio, as can be seen when comparing sample ORNL-L-035 (Pt 21.5 wt %) and ORNL-L-034 (Pt 18.1 wt %) with NbOx loadings of 2.72 wt % and 8.0 wt %, respectively. The corresponding voltage losses at 0.8 A/cm² are 160 mV for ORNL-L-035 and 71 mV for ORNL-L-034. Furthermore, the voltage loss is very sensitive to the I/C ratio, as shown for sample EXO180920, with NbOx 2.5 wt % and Pt 20 wt %. A voltage drop of 65 to 70 mV is achieved with I/C = 0.8, which is much lower loss than the 190 mV obtained with I/C = 0.5.

Table 4. Durability Comparison of ORR Catalyst with Various NbOx and Pt Combinations under Electrocatalyst AST

Sample	Carbon	% Pt	% NbOx	I/C	Anode Loading ($\mu\text{g}/\text{cm}^2$)	RDE BOL Mass Activity (A/g-Pt)	Fuel Cell Mass Activity Loss (%)	Fuel Cell ECA Loss (%)	Voltage Loss at 0.8 A/cm ² (mV)
Commercial reference	HSA	28.3	0	0.5	50	560	35	40	59
				0.8	50	574	46	70	70
ORNL-L-013	AB	35.8	0.61	0.5	50	409	43	62	120
ORNL-L-019	AB	37.5	0	0.5	50	385	52	55	180
ORNL-L-035	AB	21.5	2.72	0.5	50	287	4	10	160
ORNL-L-032	AB	30.6	3.82	0.5	50	355	1	48	130
ORNL-L-030	AB	27.7	6.3	0.5	50	231	10	3	40
ORNL-L-034	AB	18.1	8.0	0.5	50	144	9	50	71
EXO180109	Ketjen	19.9	1.75	0.5	50	455	39	67	224
EXO180209	Ketjen	26.8	0	0.8	50	440	35	65	180
EXO180920	AB	20.0	2.5	0.5	50	525	14	60	190
				0.8	50	476	33	78	70
				0.8	25	490	15	27	65

BOL – beginning of life

ECA – electrochemical active area

HSA – high surface area

AB – acetylene black

Figure 5 shows the polarization curve of a 5 cm² single cell test with EXO180920 at anode/cathode Pt loading of 0.05/0.1 mg-Pt/cm² showing a beginning of life (BOL) mass activity of 389 A/g-Pt and 290 A/g-Pt before and after a 30,000 cycle electrocatalyst AST, meeting the project's second DOE go/no-go targets. The power density was measured to be 930 mW/cm² at 0.6 V, 80°C, and Q/ ΔT = 2.44 kW/K. IRD has installed a new test station, and the air and fuel exhaust needs to be modified to properly maintain the proper cell working conditions. IRD will work on the 50-cm² single cell activity and durability measurements in terms of electrocatalyst and substrate corrosion AST.

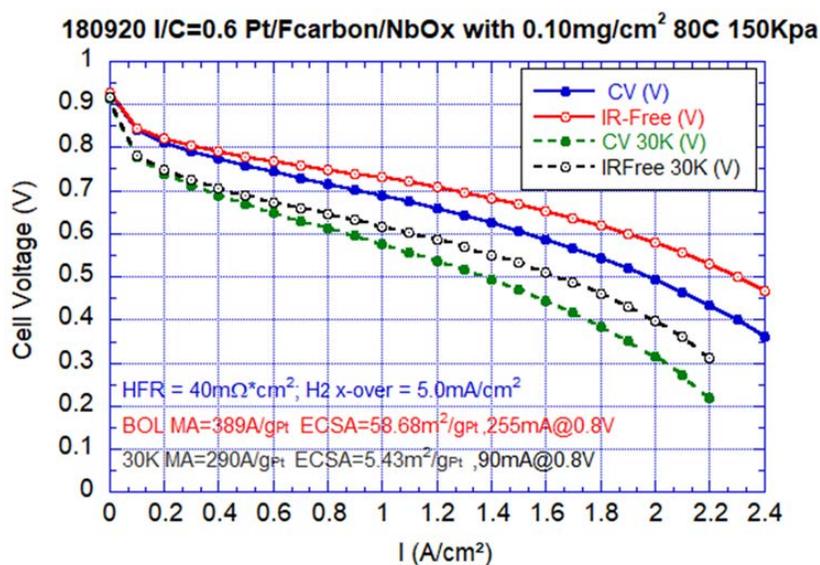


Figure 5. Polarization curve of 5-cm² single cell at BOL and after 30,000 cycles in the electrocatalyst AST

Figure 6 shows the non-pressure-dependent mass transport resistance for cells made of reference Umicore (REF) and EXO180920 catalysts. The National Renewable Energy Laboratory (NREL) performed limiting

current testing on a 3-cm² cell. The results show that the non-pressure-dependent mass transport resistance (R_{NP}) is roughly the same for EXO180920 and the reference Umicore catalyst, indicating the PVD method does not induce added resistance in association with the PVD catalyst. Figure 6 also shows that in lower I/C catalyst layers, EXO180920 samples show higher non-pressure-dependent mass transport resistances than commercial baseline Umicore catalysts.

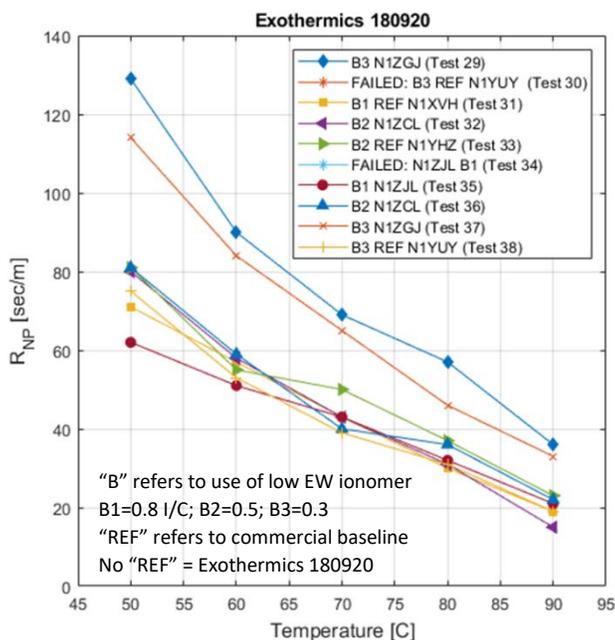


Figure 6. Non-pressure-dependent mass transport resistance as a function of temperature for Umicore and EXO180920 at I/C = 0.8 (B1), 0.5 (B2), and 0.3 (B3)

CONCLUSIONS AND UPCOMING ACTIVITIES

During FY 2019, ORNL, Exothermics, and Ford have successfully narrowed down the desired catalyst composition as 1.5 to 6 wt % NbOx and 20 to 30 wt % Pt, and used PVD in processing carbon-supported, NbOx-templated platinum catalyst (Pt/NbOx/C) powders with in-cell mass activities surpassing 390 A/g_{Pt} at BOL and 290 A/g_{Pt} after 30,000 cycles of the electrocatalyst AST. Non-pressure-dependent mass transport resistance measurements indicate that the PVD method will not induce additional resistance at I/C ratios equal to or above 0.5. TEM analysis confirmed the interactions: Pt for the most part is physically sitting on or adjacent to NbOx, which distributes homogeneously on nano-size carbon powders, forming partially connected networks. There is an electronic interaction between Pt and the O in NbOx, enhancing both the ORR activity and durability.

The next step of the project will focus on the optimization of the composition and morphology to maximize the mass activity and its durability, as well as the fundamental understanding of the role played by amorphous NbOx in the developed ORR catalysts.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. James Waldecker, “Vapor Deposition Process for Engineering of Dispersed PEMFC ORR Pt/NbOx/C Catalysts,” presented at the DOE Hydrogen and Fuel Cells Program 2019 Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., May 1, 2019.

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