Vapor Deposition Process for Engineering of Dispersed PEMFC ORR Pt/NbO_x/C Catalysts

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FC162

Overview

Timeline

- Project Start Date: 1/1/2017
- Project End Date: 9/30/2020
- Percent complete: 85%

Barriers

A. Durability

B. Cost

C. Performance

Budget

- Total project budget: $2,366,412
  - Total recipient share: $518,883
  - Total federal share: $1,847,529
  - Total DOE funds spent*: $1,387,243

* As of 3/31/2020

Partners

- Oak Ridge National Laboratory
  - Small batch catalyst production
- Exothermics, Inc.
  - Large batch catalyst production
- University of Michigan
  - TEM, XPS, other characterization
- Northeastern University
  - X-ray absorption spectroscopy
- IRD (EWII) Fuel Cells LLC
  - CCM fabrication, fuel cell testing

Relevance

OBJECTIVE: Develop, integrate, and validate a new cathode catalyst material by developing and optimizing a vacuum powder coating physical vapor deposition (PVD) process

- Develop a New Cathode Catalyst Powder
  - $Pt/NbO_x/C$ for high durability, power density, mass activity
- Improve the Catalyst Powder Manufacturing Process
  - PVD with superior reproducibility over solution based methods
- Demonstrate the PVD Process is Scalable in a Cost Effective Manner
  - Scale up from small batch (~ 1-2 g) to large batch (20-40 g)
- Show Ease of Integration
  - Powders amenable to already established CCM/MEA manufacturing processes (ink processes)

This project focuses not just on a higher performing and more durable novel catalyst, but also on making the catalyst with a reproducible, scalable process.

Relevant Targets

The targets below are specified as part of quarterly milestones or go/no-go decisions:

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

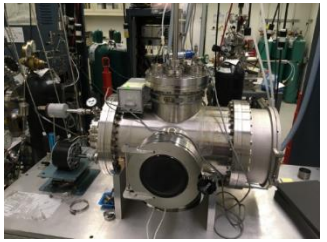
MYRDD Table 3.4.7 Technical Targets: Electrocatalysts for Transportation Applications		
Characteristic	Units	2020 Target
PGM content at rated power	g_{PGM}/kW_{gross} at 150 kPa (abs)	0.125
PGM loading	mg_{PGM}/cm^2 total	0.125
Mass activity	A/mgPGM at 900 $mV_{iR\text{-}free}$	0.44
Electrocatalyst stability (0.6 ↔ 0.95 V)	% mass activity loss after 30K cycles	<40
Loss at 0.8 A/cm^2 (0.6 ↔ 0.95 V)	mV loss after 30K cycles	<30
Support stability (1.0 ↔ 1.5 V)	% mass activity loss after 5K cycles	<40
Loss at 1.5 A/cm^2 (1.0 ↔ 1.5 V)	mV after 5K cycles	<30

In addition to activity, this project will also focus on high current density.

Approach: Tasks and Schedule

		2017			2018				2019				2020			
	Quarter	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
TASK 1:	**Development, Characterization, and Validation of Catalyst Material and Development and Implementation of PVD process parameters**															
1.1	Develop the Catalyst Matrix															
1.2	Small Batch Catalyst Synthesis and Carbon Fluidization															
1.3	Catalyst Powders Materials Characterization															
1.4	Synthesis of Catalytic Material with Solution Based Method															
1.5	Target Processing, Chamber Conversion, and Large Batch Carbon Nanoparticle Vacuum Fluidization															
1.6	XAS Evaluation of BOL and Cycled Catalyst Powders															
1.7	Processing of Large Batch Sputter Deposition on Powder															
TASK 2:	**Catalyst Layer Development and MEA Validation**															
2.1	Baseline Materials Specification and Testing Protocol Development for DOE MEA Validation Cycling															
2.2	Catalyst Layer and MEA Development with Process Optimization															
2.3	MEA BOL Validation															
2.4	MEA Cycling Validation															
TASK 3:	**Project Management and Reporting**															
3.1	Project Management															
3.2	Documentation and Reporting															

ORNL



EXOTHERMICS

Small batch: 0.5-2.5 gram batches from ORNL

Large batch: 35-40 gram batches at Exothermics

Budget Period 1 Milestones: 1/1/2017 – 3/31/2018

Milestone #1 (Q1): Demonstrate that small batch PVD catalyst synthesis has a narrow metal particle size distribution (2-10nm) on the carbon powder via TEM	Line-of-sight sputtering yields wide Pt particle size distributions. Narrow distribution may not be necessary for performance, durability. Future particle size distribution milestones removed.
Milestone #2 (Q2): Demonstrate that small batch PVD catalyst synthesis is able to reliably reproduce Pt and Nb loadings (with <10% variation) on the carbon powder by XRF measurement.	Repeatability shown for Pt within +/- 10% of average. Nb within +/- 40% at very low average weight percent (0.9%).
Milestone #3 (Q3): RDE testing of PVD Pt/NbO_x/HSAC catalysts demonstrates a BOL mass activity (at 0.9 V) above 0.40 A/mg_{PGM}	Project has shown 23 samples to have met this milestone: 10 from ORNL, 8 from Ford APD (small batch), and 5 from Exothermics (large batch). 14 non-alloyed, 9 alloyed. Pt wt% from 13-71% (22 with 17% or higher).
<u>Go/No-Go Decision Point for Budget Period 1 (end of Year 1)</u>: Validation of PVD deposited catalyst powders via MEA BOL Testing with 40-50 cm^2 single cell having a cathode loading of ≤ 0.150 mg_{PGM}/cm^2 giving a **BOL mass activity of ≥ 0.30 A/mg_{PGM}** at 900 $mV_{iR\text{-}free}$ following the protocols given in Table 3.4.7 of FCTO's MYRDD Plan.	Project has shown 4 samples to have met this milestone: 1 from ORNL (small batch), 3 from Exothermics (large batch). 2 non-alloyed, 2 alloyed.

Project has passed all budget period 1 milestones.

Budget Period 2 Milestones: 4/1/2018 – 3/31/2019

Revised: **Milestone #4 (Q5):** Determine Pt, NbO_x, C interactions in PVD Pt/NbO_x/C catalysts using elemental mapping, TEM, XAS, XPS; provide comparisons between PVD Pt/NbO_x/C and Pt/C	Pt adjacent to or on top of deposited NbOx (amorphous, electronically conducting) enhancing ORR activity & durability.
Revised: **Milestone #5 (Q6):** Durability comparison between PVD Pt/NbOx/C, PVD Pt/C, and Pt/C	Partially crystallized nano-carbon particle with proper amount of NbOx & Pt necessary
Milestone #6 (Q7): Large batch PVD catalyst - > 500 mW/cm^2 at $Q/\Delta T_i$ < 1.45 kW/˚C, 0.125 mg_{PGM}/cm^2, $P_{air,in} \leq$ 150 kPa	608 mW/cm2 achieved at $Q/\Delta T$=1.45 at 94ºC (MYRDD Table P6 conditions)
Milestones #7-8 (Q8): < 40% mass activity loss and < 100 mV loss at 0.8 A/cm^2 in electrocatalyst cycle (0.6-0.95 V); < 40% mass activity loss and < 200 mV loss at 1.5 A/cm^2 in support corrosion cycle (1-1.5 V)	MA goal & <100 mv loss @ 0.8 A/cm^2 in elecrocatalyst cycle met. (Q7-8) Support corrosion cycle met. (Q7-8)
Go/No-go Decision Point for Budget Period 2 (end of Year 2): Large batch PVD catalyst, total loading of ≤ 0.125 mg_{PGM}/cm^2: **BOL mass activity of ≥ 0.30 A/mg_{PGM}. Mass activity following electrocatalyst and support cycling > 0.21 A/mg_{PGM}** (70% of 0.30 A/mg_{PGM}).	Go/No-go decision point met for total loading 0.125 mg_{PGM}/cm^2 on 5 cm^2 single cell.

Budget Period 3 Milestones: 4/1/2019 – 9/30/2020

(no activity from 4/1/2019 to 9/30/2019, no-cost extension 4/1/20 - 9/30/2020)

Milestone #10 (Q14): Large batch PVD catalyst - 1) mass activity > 0.40 A/mg_{PGM} and 2) electrocatalyst AST (30K cycles) with < 40% loss in mass activity (RDE)	Ford, Exothermics
Milestone #11 (Q14): Large batch PVD catalyst, ≤ 0.125 mg_{PGM}/cm^2 – BOL mass activity of ≥ 0.44 A/mg_{PGM}	IRD, Exothermics
Milestone #12-14 (Q14): Large batch PVD catalyst - > 1,000 mW/cm^2 at $Q/\Delta T_i$ < 1.45 kW/˚C, for 0.125 mg_{PGM}/cm^2, $P_{air,in} \leq$ 150 kPa; < 40% mass activity loss and < 30 mV loss at 0.8 A/cm^2 in electrocatalyst cycle (0.6-0.95 V); < 40% mass activity loss and < 30 mV loss at 1.5 A/cm^2 in support corrosion cycle (1-1.5 V)	
Milestone #15 (Q14): A set of MEAs (6 or more, each with active area ≥ 50 cm^2) is made available for independent testing at a DOE-approved location.	IRD

Budget Period 2 milestones revised to focus on material characterization and durability. Milestones 4 & 5 met, 6 met MYRDD Table p6 conditions, 7&8 MA loss after AST test met, initial in-cell test at 0.125 mg_{PGM}/cm^2 met

Collaborations

Partner	Project Roles
Ford	**Prime, Industry.** Responsible for project management (Task 3), XRF measurements for Pt, Nb wt%, RDE testing (Task 1). Support role for MEA fabrication and fuel cell testing (Task 2).
OAK RIDGE National Laboratory	**FFRDC partner.** Responsible for production of small batch Pt/NbO_x/C and for transferring lessons learned from small batch catalyst optimization to Exothermics for large batch production. Support role for XRF measurements. (Task 1)
EXOTHERMICS INC	**Sub-contractor, Industry.** Responsible for production of large batch Pt/NbO_x/C. Can support with BET, PSD characterization. (Task 1)
UNIVERSITY OF MICHIGAN	**Sub-contractor, University.** Responsible for TEM and particle size measurements. Can also support with SEM, XPS, and other characterization techniques. (Task 1)
Northeastern University Center for Renewable Energy Technology	**Sub-contractor, University.** Role is to help understand by XAS whether coordination numbers, interatomic distances, and the presence of adsorbates (e.g. –OH) influence performance and durability (Task 1).
IRD Fuel Cells (EWII)	**Sub-contractor, Industry.** Responsible for MEA fabrication using Pt/NbOx/C catalysts on the cathode, and for fuel testing (Task 2).

All collaborations are within the DOE Hydrogen and Fuel Cells Program

Relevance: Targets and Status

The targets below are specified as part of quarterly milestones or go/no-go decisions:

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 $mV_{iR\text{-}free}$	0.44	**0.352[1], 0.335[2],0.389[3]**
Electrocatalyst stability (0.6 ↔ 0.95 V)	% mass activity loss after 30K cycles	<40	**14%[3],9%[4], 10%[5] & 1%[6]**
Loss at 0.8 A/cm^2 (0.6 ↔ 0.95 V)	mV loss after 30K cycles	<30	**70 mV[3],71 mV[4] & 40 mV[5]**
Support stability (1.0 ↔ 1.5 V)	% mass activity loss after 5K cycles	<40	**7.1%[7]**
Loss at 1.5 A/cm^2 (1.0 ↔ 1.5 V)	mV after 5K cycles	<30	**25 mV[7] @ 0.4 A/cm^2**

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

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

[3,4,5,6] Measure using EXO180920, ORNL-L-034 and ORNL-L-030, ORNL-L-032 respectively, anode loading 0.05 mg_{PGM}/cm^2.

[7] Measured using EXO180920, anode loading 0.025 mg_{PGM}/cm^2 on a 5 cm^2 single cell.

Durability was the focus, high current testing still to come.

Accomplishments and Progress: GNG 2

Strategy: optimize the concentration and morphology of NbO_x and Pt on acetylene black (AB) carbon nano-particles:

- ORNL made 6 samples with 1.5, 3 and 6 wt.% NbO_x and 20, 30 wt.% Pt.
- Exothermics two large batch samples with and without NbO_x.
- Umicore wet-chemical synthesized sample with comparable PVD Pt.

	1.5% NbOx	3% NbOx	6% NbOx
20% Pt	ORNL-L-037	ORNL-L-035	ORNL-L-034
30% Pt	ORNL-L-038	ORNL-L-032	ORNL-L-030

Sample Name	Temperature	Nb Deposition: Ar/O2 Ratio	Nb Deposition: Time (hours)	Nb Deposition: Power (W)	Pt Deposition: Time (hours)	Pt Deposition: Power (W)	**Pt Loading from XRF (wt.%)**	**NbOx Loading from XRF (wt.%)**
ORNL-L-013	Room (off-gassed to 400C for 12 hours)	10	1.5	150	1.5	140	**35.8**	**0.61**
ORNL-L-030	Room (off-gassed to 400C for 12 hours)	10	18.7	150	0.97	140	**27.7**	**6.3**
ORNL-L-032	Room (off-gassed to 400C for 12 hours)	10	9.3	150	1	140	**30.6**	**3.82**
ORNL-L-034	Room (off-gassed to 400C for 12 hours)	10	18.7	150	0.67	140	**18.1**	**8.0**
ORNL-L-035	Room (off-gassed to 400C for 12 hours)	10	5.6	150	0.58	140	**21.5**	**2.72**
ORNL-L-037	Room (off-gassed to 400C for 12 hours)	10	3.9	150	0.63	140	**21.3**	**1.77**
ORNL-L-038	Room (off-gassed to 400C for 12 hours)	10	3.7	150	1	140	**28.2**	**1.34**
EXO 180109*	off-gassed to >200C; sputter at >100C	32.3	8	100	5	300	**19.9**	**1.75**
EXO 180920	off-gassed to >200C; sputter at >100C	32.3	8	100	4.5	300	**20.0**	**2.5**
EXO 181114	off-gassed to >200C; sputter at >100C	NA	NA	NA	4.5	300	**30.2**	**NA**
Commercial Reference$	wet chemical commercial	NA	NA	NA	NA	NA	**28.3**	**NA**

* Ketjen black carbon
$ high surface area carbon (Umicore Pt catalyst)
All other samples are supported on acetylene black

Fuel Cell Testing Results – AST: GNG2

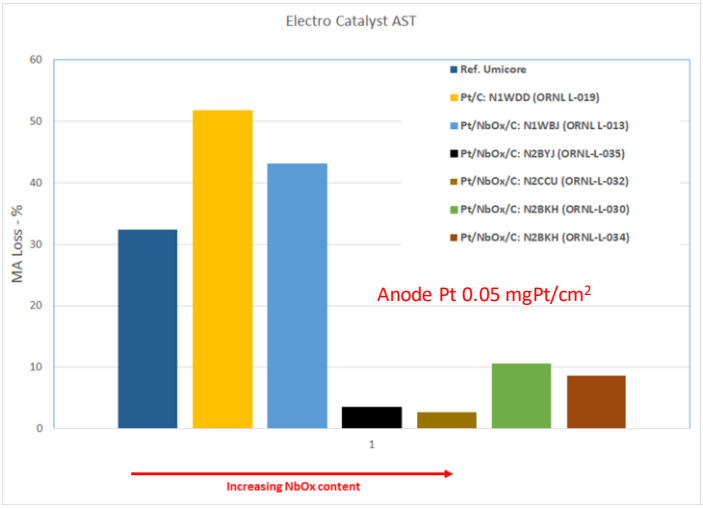
IRD

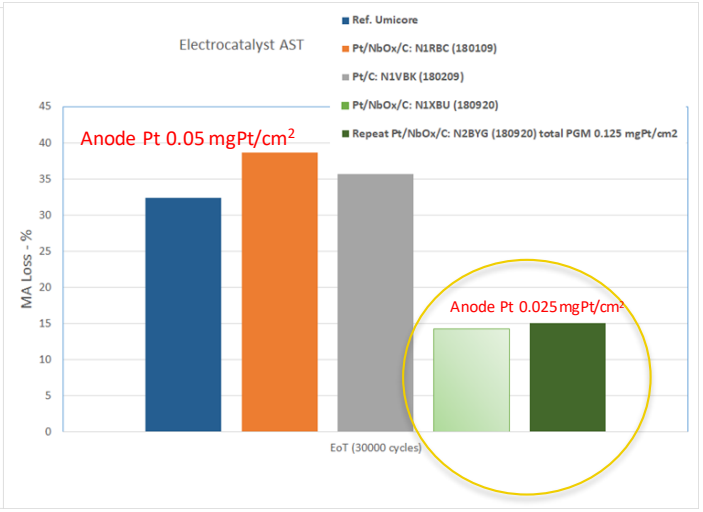
All anodes comprising 0.05 or 0.025 mg Pt/cm^2 and all cathodes comprising 0.10 mg Pt/cm^2

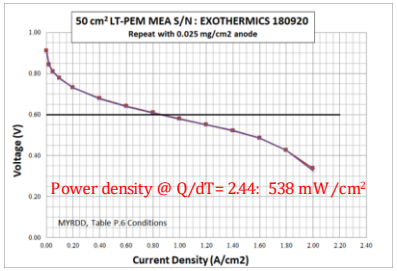
- BOL MA measured using RDE protocols and settings according to MYRDD table P1
- MA % loss (A/g Pt) are at 0.9 V iR free and corrected for H_2 x-over
- All AST measured in 50 cm^2 single-cell hardware (FCT hardware)

After GNG1, has issue with in-cell MA test, RDE MA valid

Sample	Carbon Support	% Pt	% NbOx	I/C	FC TEST BOL ECA_{Avg} (m^2/g_{pt})	FC TEST EoL ECA_{Avg} (m^2/g_{pt})	FC TEST BoL ECA @ RT	RDE BOL Mass Activity (A/gPt)	FC TEST BOL Mass Activity (A/gPt)	FC TEST EOL Mass Activity (A/gPt)	ECA (% Loss)	MA (% Loss)	Voltage Loss at 0.8 A/cm^2 after 30 K Cycles (pre-ECA, mV)
Exothermics 180109	Ketjen	19.9	1.75	0.5	20.4	6.7		455	107	65	67	39	224
Exothermics 180209	Ketjen	26.8	0	0.8	23.2	8.1		440	93	60	65	35	180
Exothermics 180920	Acetylene black	20.0	2.5	0.5	23.6	9.4		525	109	94	60	14	190
Exothermics 180920	Acetylene black	20.0	2.5	0.8	33.2	7.3		476	73	49	78	33	70
Exothermics 180920 repeat low PGM	Acetylene black			0.8	27.0	19.7		490	95	81	27	15	65
Exothermics 181114	Acetylene black	20.0	0	0.5	12.5	-		430	111	-			
Exothermics 181114	Acetylene black	20.0	0	0.8		-		422					
Commercial reference	High surface area	28.3	0	0.5	25.1	15.0		560	300	196	40	35	59
Commercial reference	High surface area	28.3	0	0.8	33.0	9.9		574	375	202	70	46	70
ORNL-L-013	Acetylene black	35.8	0.61	0.5	26.8	10.2		409	113	64	62	43	120
ORNL-L-019	Acetylene black	37.5	0	0.5	25.1	11.4		385	260	125	55	52	180
ORNL-L-034	Acetylene black	18.1	8.0	0.5	30.9	15.4		144	58	53	50	9	71
ORNL-L-030	Acetylene black	27.7	6.3	0.5	12.9	12.5		231	92	83	3	10	40
ORNL-L-032	Acetylene black	30.6	3.82	0.5	19.1	10.0	38.3	355	74	73	48	1	130
ORNL-L-035	Acetylene black	21.5	2.72	0.5	19.5	17.5	54.8	287	57	55	10	4	160



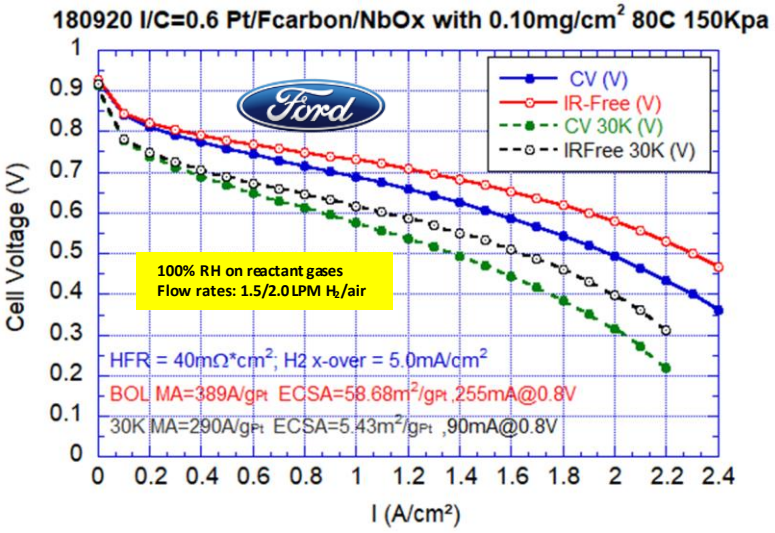


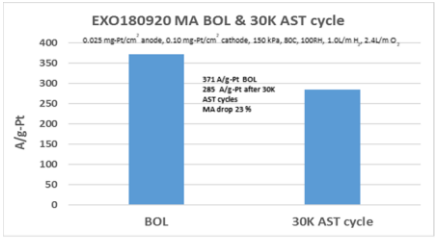


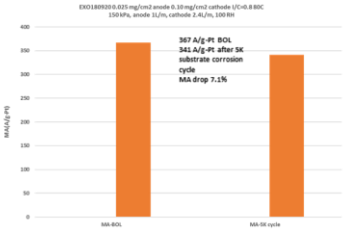
- **MA** drop of below 30% has been achieved in samples made on both small batch ORNL-L-030, 032, 034 & 035 as well as large batch EXO180920 with anode Pt loading of 0.05 mgPt/cm^2, and also on EXO180920 with 0.025 mgPt/cm^2 anode loading
- **Best durability combination obtained on EXO180920 with MA drop of 15% and voltage loss of 65 mV at 0.8 A/cm^2 with a power density of 538 mW/cm2 at Q/dT of 2.44**

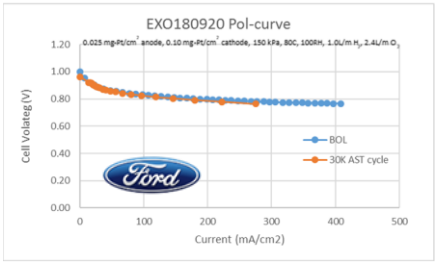
In-Cell Characterization& Transport Resistance:GNG2

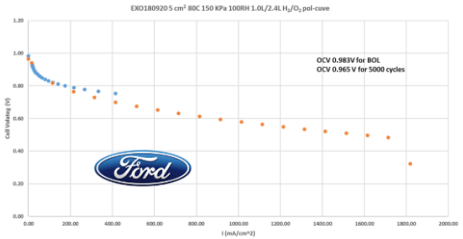
- 5 cm^2 single cell test at anode Pt loading of 0.05 $mgPt/cm^2$ show samples meet 2nd go/no-go MA target towards electrocatalyst AST







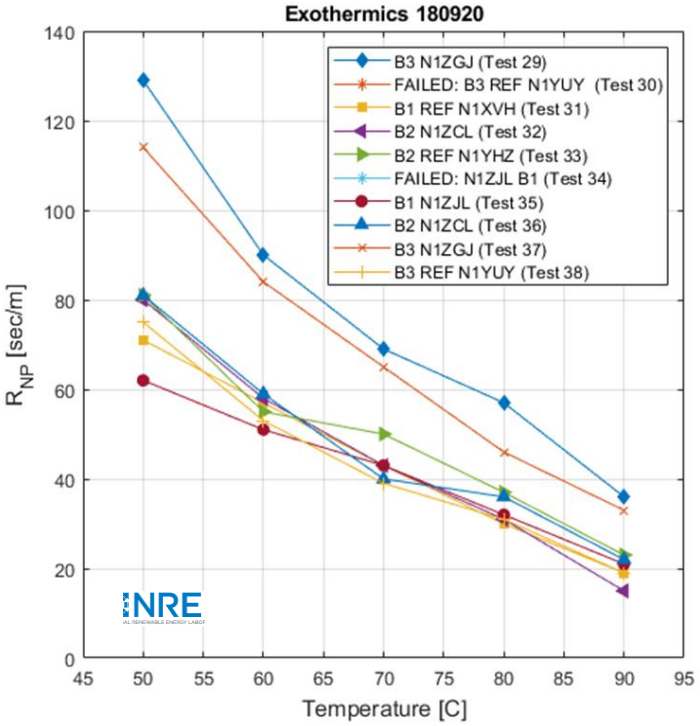




- 5 cm^2 single cell test at anode Pt loading of 0.025 $mgPt/cm^2$ show samples meet 2nd go/no-go MA target towards electrocatalyst AST & carbon corrosion cycling.

Exo 180920 meets 2nd Go/No-go MA targets

Mass Transport Resistance measurements to clarify the effects of novel catalysts on cell performance



NREL performed limiting current testing on 3 cm^2 cell

- "B" refers to use of low EW ionomer
- B1=0.8 I/C; B2=0.5; B3=0.3
- "REF" refers to commercial baseline
- No "REF" = Exothermics 180920
- At higher I/C (0.5 and 0.8), non-pressure dependent mass transport resistance (R_{NP}) is roughly the same for Exothermics 180920 and the commercial standard
- Low I/C catalyst layers: increase in R_{NP} for Exothermics 180920 versus commercial baseline

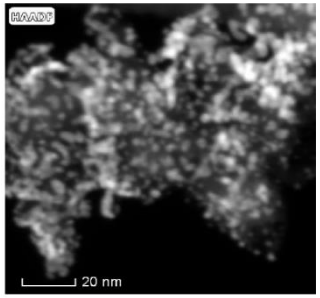
NbO_x incorporation into the catalyst does not increase non-pressure dependent mass transport resistance (RNP)

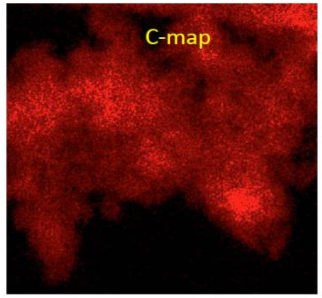
Microstructural Analysis with TEM & XPS:GNG2

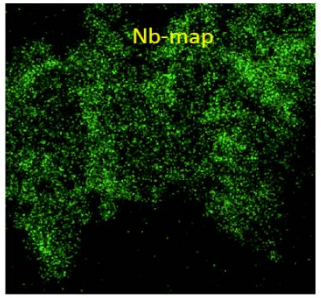
--- understanding the morphology of NbO_x and Pt

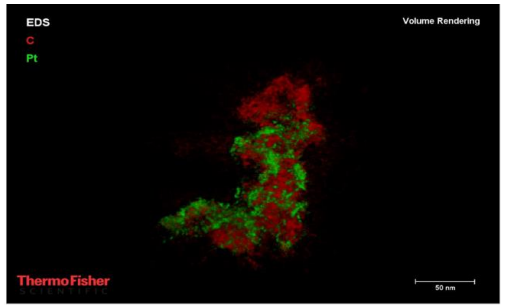
ORNL-L-013 (35.8% Pt, 0.61% NbO_x, AB, MA=335 A/cm^2, MA drop =43%, 0.8 A/cm^2 voltage drop = 120 mV)

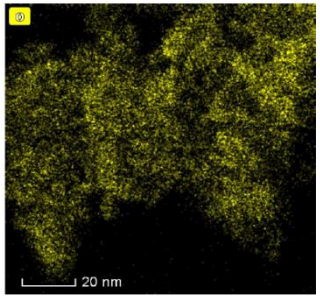
ORNL-L-013-EDS data

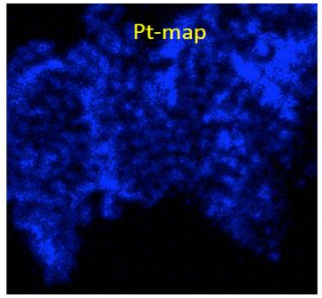


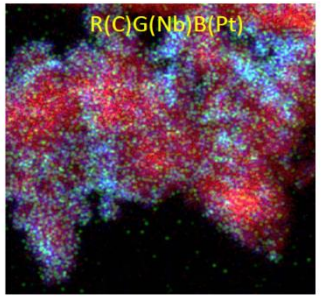


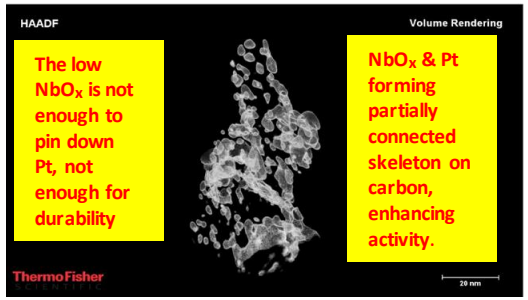




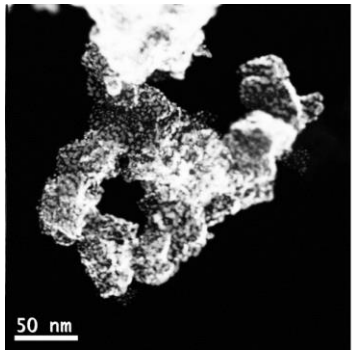


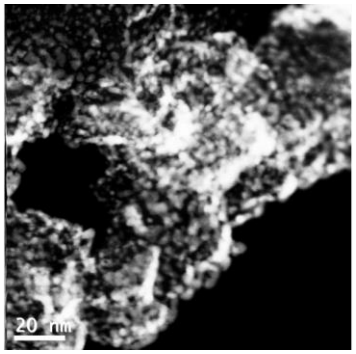


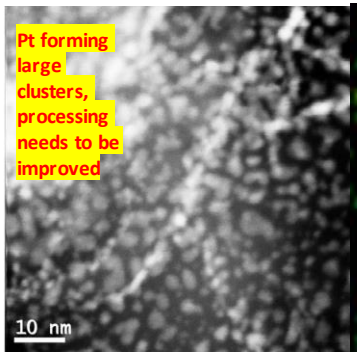


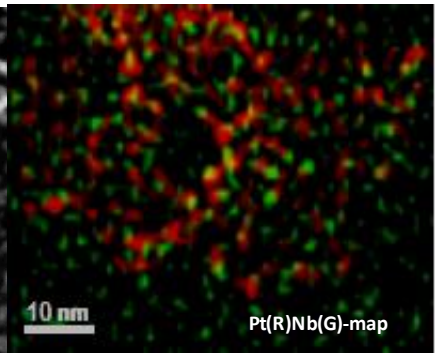


Exo180920 (20.0% Pt, 2.5% NbO_x, AB, MA=389 A/cm2, MA drop =25%, 0.8A/cm2 voltage drop = 70 mV)



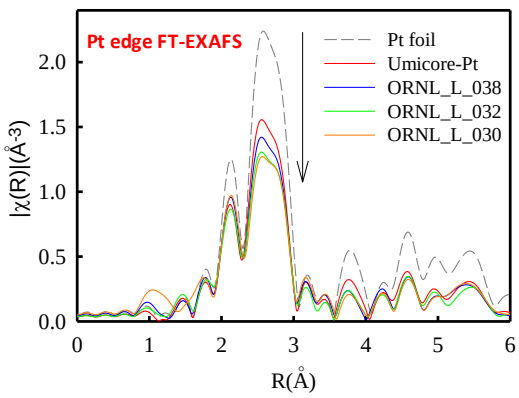


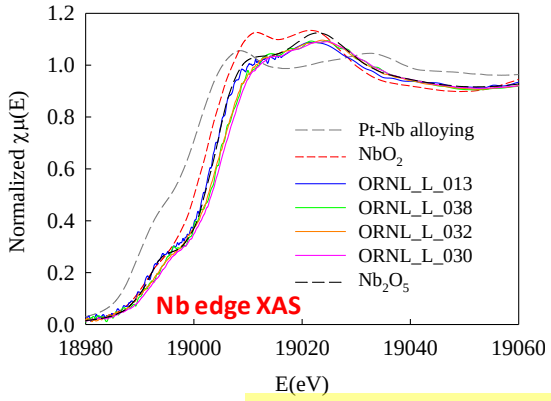


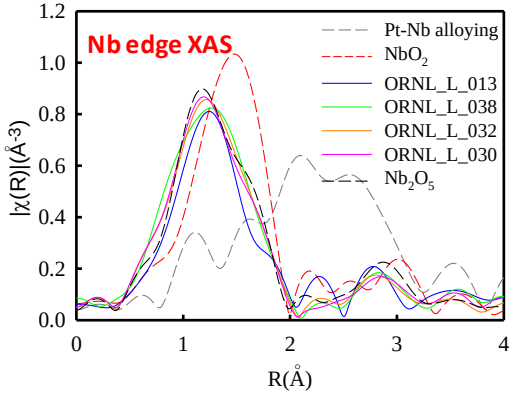


- More NbO_x forming a uniform distribution of NbO_x, Pt forming partially connected network on top & adjacent to NbO_x, enhancing ORR activity & durability

Electronic Interaction through XAS:GNG2



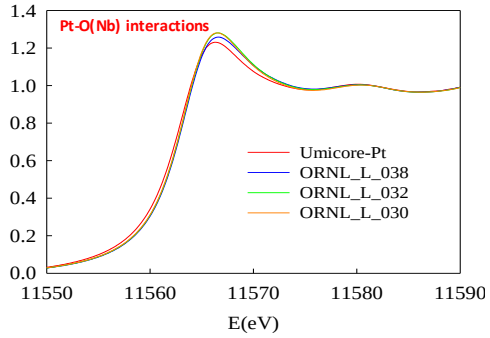




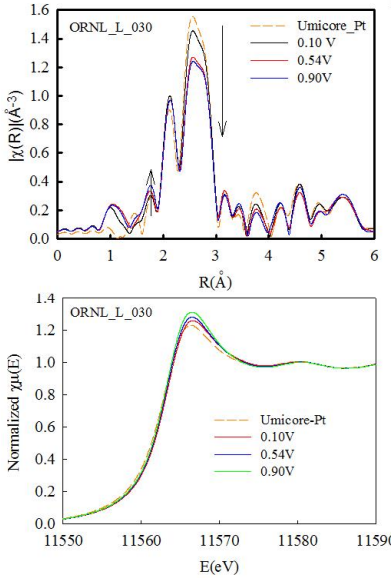
- With increasing NbO_x content, the intensity of the FT-EXAFS peak decreases.
- The shape of the FT-EXAFS peak does not change much with increasing Nb content, indicating the lack of significant Pt-Nb interactions.

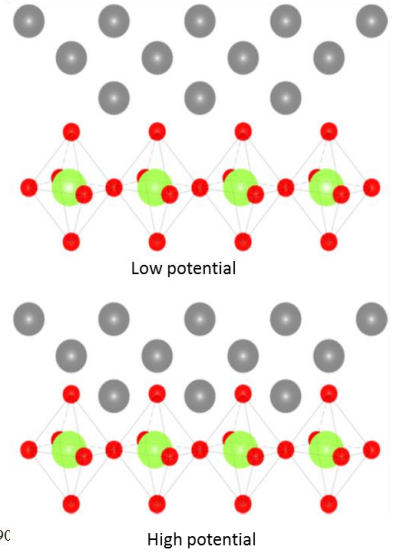
- The Nb XAS signal does not change with Nb content.
- No Nb-Pt interactions are detectable.
- The oxidation state of Nb is nearly saturated close to +5 (x=4.6)

So no Pt-NbOx interactions



With increasing NbO_x content, the white line intensity of the Pt XANES increases, indicating less number of electrons in the Pt 5d orbitals. This suggest the interaction between Pt and O that comes from NbOx wherein charge transfer from Pt to O.





- The *in-situ* data suggest the Pt-O interaction throughout the whole potential region, which indicates that Pt is tightly anchored into NbO_x in contact with O.
- The increase in the FT-EXAFS intensity or the coordination number at low potentials indicates that the Pt clusters move away from the substrate at low potentials, which could cause some degradation.

NbO_x-induced durability improvement

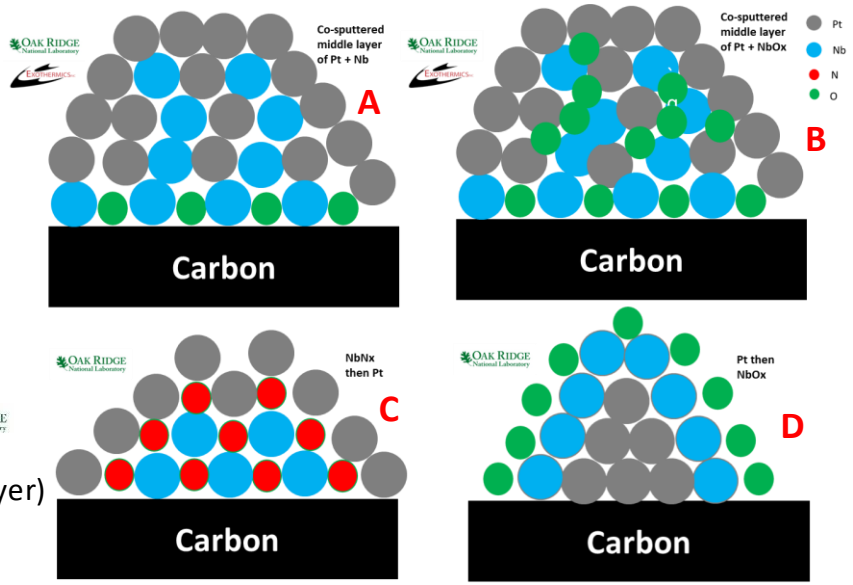
Lessons Learned & Strategy into Budget Period 3

Lessons Learned through GNG 2

- By controlling the amount and morphology of NbO_x and Pt, both Exothermics & ORNL samples have generated samples that passed 2nd GNG criteria.
- Increasing the NbO_x concentration in general will reduce the loss in MA & voltage drop at 0.8 A/cm^2.
- Pt sitting on top & around amorphous NbO_x necessary for both high activity & durability, partially connected Pt thin Pt 3-D network is preferred.

Strategy into budget period 3

- Strategy
  - Refining the developed morphology: on the AB nano carbon substrate sequentially sputter NbO_x then Pt for in-cell tests against all milestones.
  - Enhancing the electronic interactions between the base niobium species and the platinum electrocatalyst:
    - Co-sputtering a middle layer of NbO_x +Pt (**B**) or Nb + Pt (**A**) on top of the NbO_x (and a Pt top layer)
    - NbN_x instead of NbO_x (**C**)
    - First Pt on carbon then NbO_x thin layer (**D**)



Accomplishments and Progress in Budget Period 3

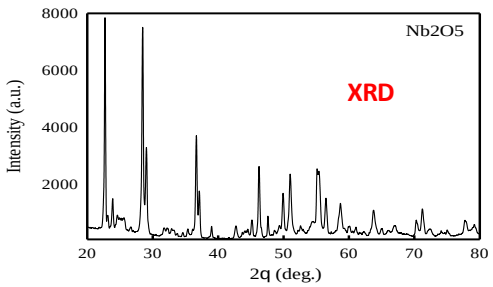
- ORNL made 7 samples: similar composition with Umicore (**044**), similar Pt deposition then NbO_x (**046**), Pt+Nb co-deposition in O_2 (**047**), Nb nitride + Pt (**048**), similar composition to ORNL-L-013 (**049**), NbO_x then Pt+Nb co-deposition (**050**), & Pt+Nb co-deposition in N_2 (**051**).
- Exothermics made 4 large batch (30 to 50 grams) samples with NbOx (3 to 8 wt.%) & Pt (25 to 35 wt.%) in various layouts: NbO_x then Pt (**Exo191112 & Exo191121**), repeat run of Exo180920 (**Exo200115**), NbO_x & ($Pt+NbO_x$) co-deposition (**Exo200218**), NbO_x & (Pt+Nb) co-deposition (**Exo200228**).
- Umicore wet-chemical synthesized sample (reference) with comparable PVD Pt.

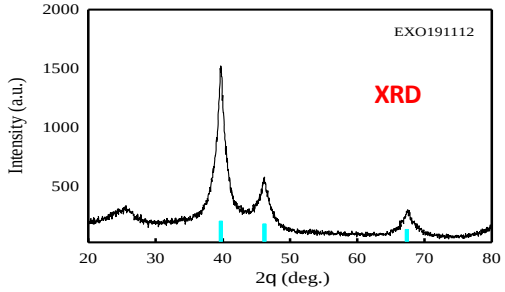
Sample Name	Purpose	Carbon Support	Pt Loading from XRF (%)	NbOx Loading from XRF (%)	Average Particle Size from TEM (nm)	Pt/Nb Atomic Ratio from XPS	Nb 3d 5/2 Peak Location (eV)
Umicore	reference		28.3	N/A	4.1, 3.6	N/A	N/A
ORNL-L-044	Pure Pt, comparing with Umicore ref	AB	28.0	0.00	2.0	N/A	N/A
ORNL-L-046	Pt first then NbOx on top (D)	AB	30.3	1.56	1.9	11.82	206.40
ORNL-L-047	Pt and Nb co-sputtered in O_2	AB	39.5	5.39	1.9	3.65	206.37
ORNL-L-048	Nb deposited in N_2 then Pt in Ar (C)	AB	12.5	2.03	1.9	4.18	206.74
ORNL-L-049	NbOx then Pt on top	AB	32.4	1.95	2.0	15.06	206.52
ORNL-L-050	NbOx first then co-sputter Nb/Pt	AB	45.1	6.09	2.3	4.09	206.38
ORNL-L-051	Pt and Nb co-sputtered in N_2	AB	39.8	6.87	1.9	3.25	206.69
Exo 191112	NbOx then Pt on top	AB	35.0	7.18	1.8	3.07	206.95
Exo 191121	NbOx then Pt on top	AB	29.9	6.39	2.1	3.40	206.95
Exo 200115	NbOx then Pt , repeat run for Exo 180920	AB	31.8	3.52	2.0	5.51	206.90
Exo 200218	NbOx then (Pt +NbOx) co-sputtering on top + Pt (B)	AB	29.3	4.49	1.8	4.70	206.79
Exo 200228	NbOx then (Pt + Nb) co-sputtering on top + Pt (A)	AB	34.1	6.37	1.9	4.08	206.98

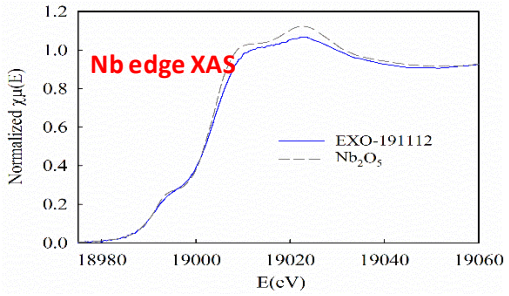
- **ORNL samples made in small batch of about 1 gram, in general, can control the oxidation state of Nb less than 5 (Nb 3d 5/2 peak closer to 206 eV than 207 eV).**
- **Exothermics samples (larger batch of 30 to 50 grams) have higher Nb oxidation state closer to 5 (Nb 3d 5/2 peak closer to 207 eV), but both are less than insulating Nb_2O_5. The difference in Nb valence state may affect the electronic conductivity of the deposited NbO_x.**
- **The Pt particle size is usually smaller (about 2 nm) than wet-chemical processed Umicore sample with similar composition (about 4 nm).**

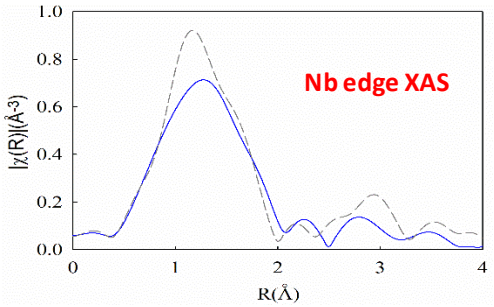
Accomplishments and Progress in Budget Period 3

- RDE analysis indicates that Exo191112 shows high mass activity (1127 A/g-Pt), a promising candidate for in-cell test against milestones 10-15 in Q14 (work delayed due to coronavirus shutdown).

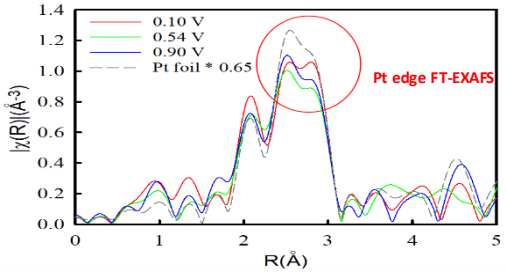


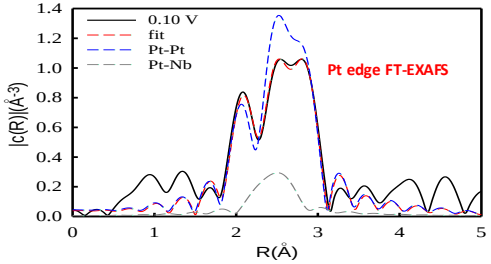


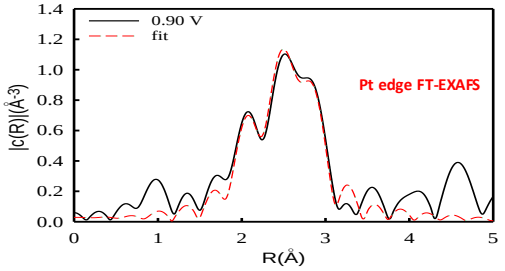




Nb in Exo 191112 is Nb_2O_5-like, but amorphous.
Pt has very small crystal size.
AB carbon mostly disordered.
No Nb-Pt interactions observed as-prepared.







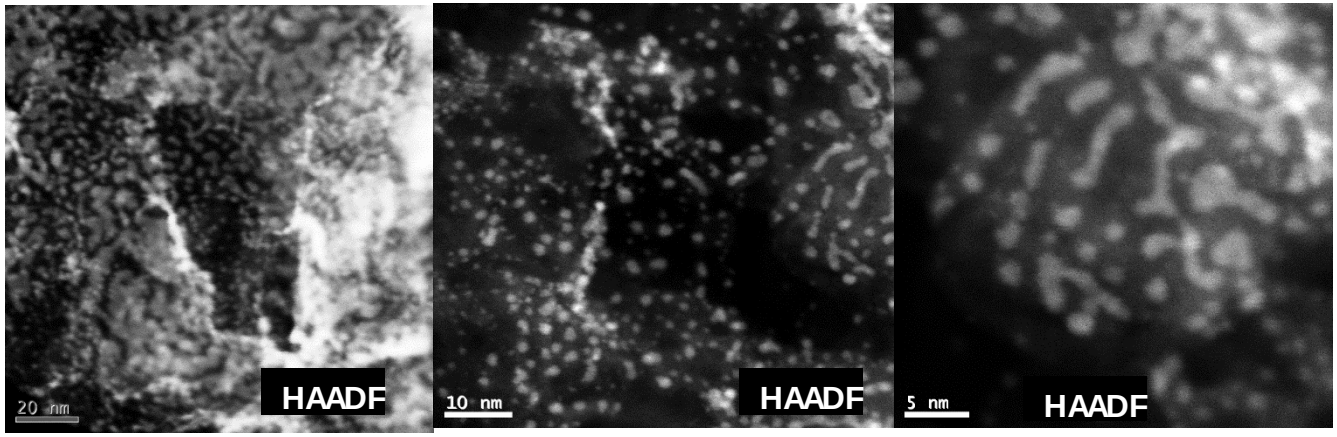
Pt side	R_{Pt-Pt} (Å)	N_{Pt-Pt}	R_{Pt-Nb} (Å)	N_{Pt-Nb}
Pt foil	2.767±0.003	12 (fixed)	-	-
0.10 V	2.750±0.005	8.6±1.0	2.76±0.02	0.4±0.3
0.54 V	2.752±0.003	9.6±0.8	2.75±0.02	0.2±0.2
0.90 V	2.754±0.004	10±0.8	-	-

Significant Pt-Nb interactions seen at low potentials 0.1 V, due likely to the presence of O vacancies in NbO_x allowing for direct Pt-Nb interactions.
Compressive strain not significant.

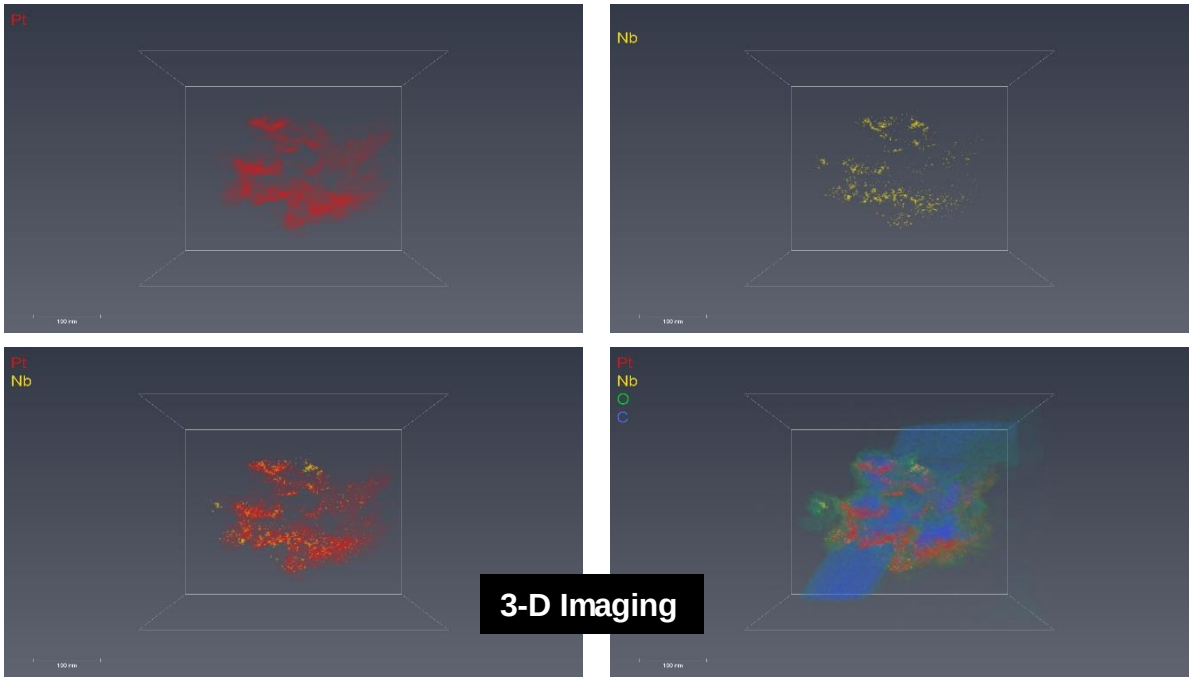
NbO_x-induced ORR activity improvement due to the NbO_x-induced electronic effect that suppresses the electron transfer from Pt to the ORR intermediates, weakening the Pt-O bonding energy.

Accomplishments and Progress in Budget Period 3

--- understanding the morphology of NbO_x and Pt in Exo 191112



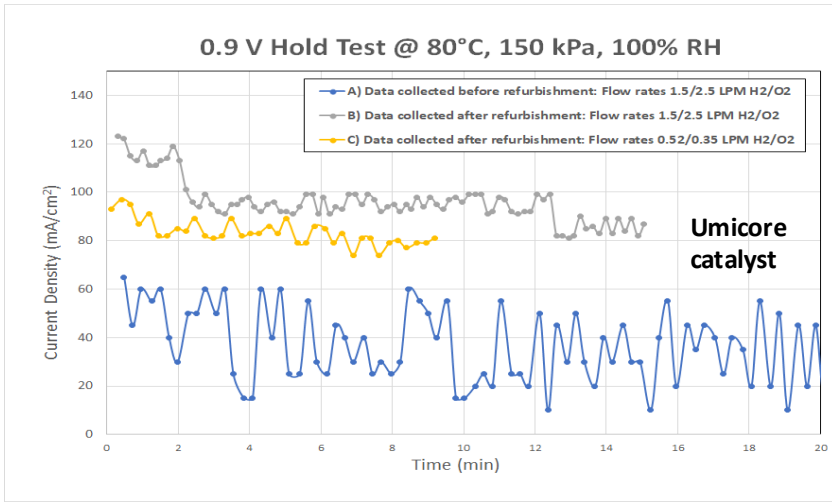
Enlongated Pt rod and connected 2-D Pt network form on top of a homogeneously distributed amorphous NbO_x layer

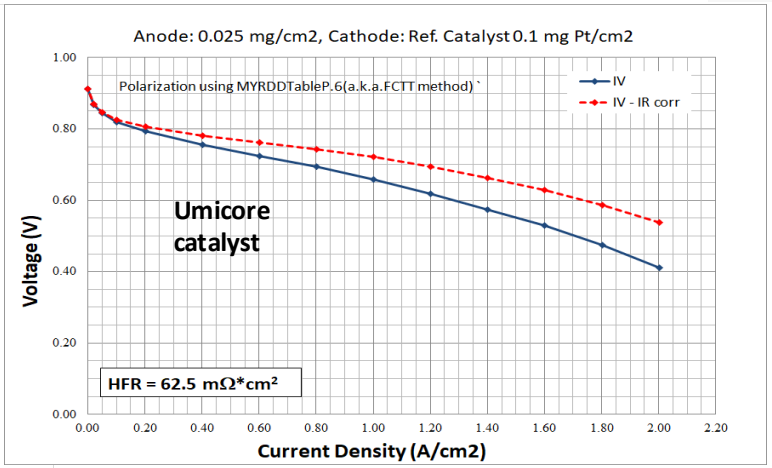


Pt connected 3-D network forms on top of clustered amorphous NbO_x cluster. **NbO_x morphology & distribution to be refined**

Progress in Budget Period 3

- IRD ready for in-cell tests against milestones 6, 11-15 after refurbishing test stations

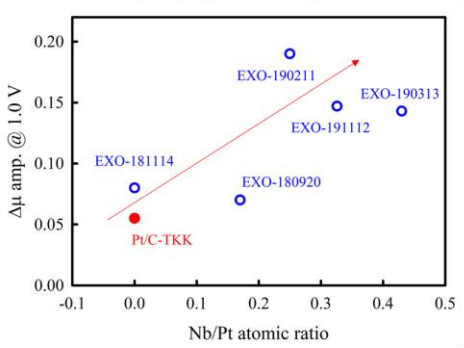




- Northeastern observed Δμ & Nb/Pt relation, needs to clarify its relevance to MA

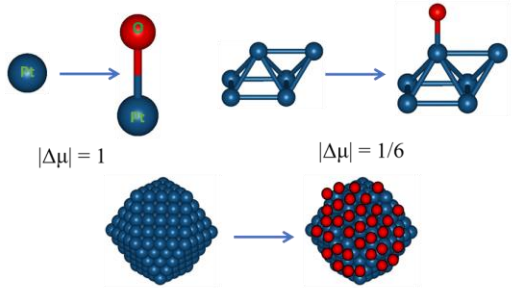
Northeastern University
Center for Renewable Energy Technology

|Δμ| analysis



Sample	Pt (wt.%)	NbOx (wt.%)
Exo 190211	27.9	5.94
Exo 190313	20.4	8.02
Exo 181114	30.2	NA

Understanding |Δμ|



For nanoparticles with dispersion of D (D = N_{surf}/N_{total} decreasing with increasing particle size), assuming the Pt surface is fully covered by O, |Δμ| = D, and thus decreases with increasing particle size.
If the surface O(H) coverage, which is directly related to the specific ORR activity, is denoted as C_s, then:

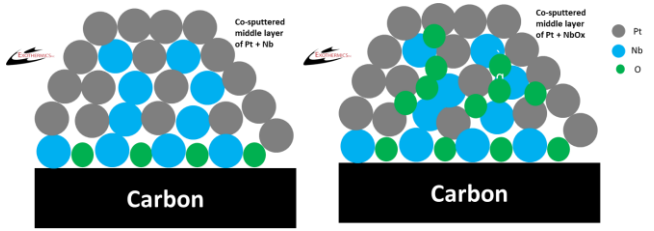
$$|\Delta\mu| = D \times C_s = \frac{N_{surf}}{N_{total}} \times C_s$$

Note N_{surf}/N_{total} is not only related to particle size, but also particle shape.

- In general the |Δμ| increases with Nb content, indicating higher Pt utilization (or higher dispersion (D)), that is, more Pt is covered by OH_{ad} at elevated potentials.

- Ford & Exothermics preparing & testing 6 samples with mixed Pt+Nb or Pt+ NbO_x intermediate layer in larger batch.

SAMPLE	bottom	intermediate mixture			top
	NbOx (wt.%)	Pt (wt%)	Nb(wt.%	NbOx (wt.%)	Pt (wt.%)
1	3	24	1		5
2	3	22	3		5
3	3	20	5		5
4	3	24		1	5
5	3	22		3	5
6	3	20		5	5



Further enhance electronic interaction, MA & durability

Select Reviewer Comments

- "The project team is working on simplifying a PVD process for improved reproducibility. However, to date, the PVD process appears to have issues with "line of sight," and getting uniform niobia does not appear to have happened. There are issues with reproducibility between the two systems in use; either this needs to be fixed, or one of the systems needs to be discontinued. At least from the discussion, it seems the tumbling of the carbon is not yet as reproducible as it needs to be. The team has shown various loadings of niobia on carbons; however, the weight percent of NbO_x has been relatively low—samples range from 0.5% to 13.3% (on slide 12), and slide 5 shows a 17.6 wt.% NbO_x sample. However, it seems unreasonable that a full coverage on the acetylene black can be obtained at any of these weight percentages. Noting that, of course NbO_2 is six times heavier than carbon, and these carbon materials are rather porous."
  - Response: The chamber size does affect the homogeneity of NbOx on nano-carbon as well the control of the valence state. The laboratory scale ORNL sputtering chamber can control the valence state of the Nb better, usually more toward 2, while the larger Exothermics chamber produce x close to 2.5. ORNL chamber is more suitable for composition & morphology engineering. Exothermics can reproduce reliably in term of composition and morphology, it is working on the powder stirring system to achieve homogeneity. On the other hand, the goal of the current project does not need to cover the nano-carbon with NbO_x, it needs the NbO_x to help the Pt forming 2-D connected network of several atomic layers to realize the improvement of MA through electronic interaction, strain control & crystal orientation. The physical pinning as well as the electronic interaction can also enhance its durability.
- More science is necessary; it is important to understand the NbO_x coverage and bonding on carbon and how this affects the carbon porosity. The team needs to understand the Pt bonding and how much is on NbO_x and on carbon, respectively. The Pt bonding interactions should be measured, and durability measurements should be taken (as planned in the future work).
- The following additions will help the project understand the quality of PVD-made catalysts better:
  - Performance stability under load cycling and start/stop cycling
  - Structural stability of the catalyst under the ink-making process
  - Understanding of the shelf life of PVD catalysts
- Work to narrow the particle size distribution could be beneficial.
- The use of state-of-the-art carbon supports is recommended.
  - Response: More In-situ XAS analysis will address the issues related to science at Northwestern University, at IRD the stability issues related to cell performance, and at Exothermics on particle size distribution control.

Future Work

- To the End of Budget Period 3
  - Continue XAS studies to understand source of activity for newer samples that show RDE mass activity > 0.44 A/mg_{Pt}
  - Work to characterize in-cell performance stability for PVD processed catalysts under cycling, as well as structural stability of the catalyst under ink-making
  - Modifying and refining synthesis procedures to achieve homogeneous Pt distribution in Exothermics processed large batch samples.
  - Durability: Run support corrosion AST, electrocatalyst cycle AST, for high performing materials.
  - Robustness tests
  - Continued measurements on all samples using TEM, XRF, XPS, XAS, RDE

Any proposed future work is subject to change based on funding levels

Summary

- 2nd Go/No-Go passed
  - Best mass activity & durability after electrocatalyst AST & substrate corrosion cycle has been achieved in cell testing at Ford with anode Pt loading of 0.025 mg_{Pt}/cm^2. EWII is working to confirm on 50 cm^2 cell at anode loading of 0.025 mg_{Pt}/cm^2.
- Milestones #1-5 and 7-8 have been met, 6 is being tested.
- High MA (>1000 A/g-Pt) catalyst powders have been prepared in large batch by Exothermics.
- Northeastern has further confirmed almost no Pt-Nb interactions (no alloying) in as prepared state, but a Pt-O interaction between the Pt and the O in NbO_x. Pt–Nb interaction could be induced by applied voltage, its origin and sample dependence being studied by in-situ XAS.
- TEM microstructural analysis (3-D Elemental Mapping) shows that the homogeneity of NbO_x deposited on top of the carbon powders greatly affect the Pt, which is adjacent to or on top of the pre-deposited NbO_x. However, the Pt is prone to clustering during large batch deposition and modification is being refined to control the catalyst morphology & Nb valence state during processing.
- IRD & Ford ready for in-cell testing against milestones 6 (IRD) & 10-15.

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