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


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Ford Motor Company


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FC162

# Overview

## Timeline

- Project Start Date: 1/1/2017
- Project End Date: 3/31/2020
- Percent complete: 60%

## Barriers

A. Durability
B. Cost
C. Performance

## Budget

- Total project budget: $2,594,412
  - Total recipient share: $518,883
  - Total federal share: $2,075,529
  - Total DOE funds spent*: $1,073,311

* As of 1/31/2019

## 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
- EWii (IRD) Fuel Cells LLC
  - CCM fabrication, fuel cell testing
- Other contributions: NREL (mass transport resistances)

# 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/NbOx/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.**

# 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 | **410**[1a] |

| **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 | **0.366**[1a] |
| PGM loading | $mg_{PGM}/cm^2$ total | 0.125 | 0.150[1-5] |
| Mass activity | $A/mg_{PGM}$ at 900 $mV_{iR\text{-}free}$ | 0.44 | **0.389**[1], 0.335[2] |
| Electrocatalyst stability (0.6 ↔ 0.95 V) | % mass activity loss after 30K cycles | <40 | **14%**[1], **9%**[3], **10%**[4], **1%**[5] |
| Loss at 0.8 $A/cm^2$ (0.6 ↔ 0.95 V) | mV loss after 30K cycles | <30 | **70 mV**[1], **71 mV**[3], **40 mV**[4] |
| 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 180920 (20/2.5% Pt/NbOx on acetylene black) [a] At 250 kPa. [2] Measured using ORNL-L-013 (36/0.6% Pt/NbOx on acetylene black). High current measurements at 0.6 V, 80°C (Q/ΔT=2.44), fully humidified.

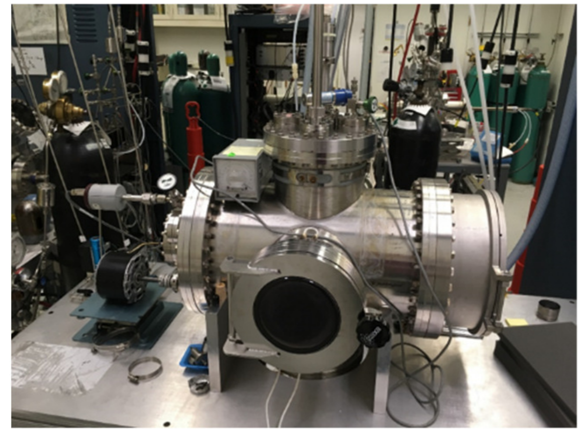
[3,4,5] Measured using ORNL-L-034 (18/8.0% Pt/NbOx), ORNL-L-030 (18/6.3% Pt/NbOx), ORNL-L-032 (31/3.8% Pt/NbOx) respectively. All supported on acetylene black; anode loading 0.05 $mg_{PGM}/cm^2$

**Budget Period 2 focus was on greater durability with increased NbOx**

# Approach: Tasks and Schedule

| | | 2017 | | | | 2018 | | | | 2019 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Quarter | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| **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, 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 | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |

The approach has been to use small batch sampling at ORNL (Task 1.2) to direct large batch production at Exothermics (Tasks 1.5, 1.7). Material characterization (Tasks 1.3, 1.6) and fuel cell testing (Task 2) provide feedback data on understanding activity and durability.



**ORNL**

Small batch: 0.5-2.5 gram batches from ORNL

Large batch: 35-40 gram batches at Exothermics

**EXOTHERMICS**

**Small catalyst batches at ORNL, along with characterization at UM, Northeastern, and EWII, have influenced desired production parameters at Exothermics**

# Approach: Budget Period 1 Showed High, Repeatable Activity

| 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/NbOx/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:<br>ORNL-L-013 (Pt/$NbO_x$/C): 335 A/$g_{Pt}$<br>Exothermics 180109 (Pt/$NbO_x$/C): 328 A/$g_{Pt}$<br>Exothermics 180302 (PtCo/$NbO_x$/C): 309 A/$g_{Pt}$<br>Exothermics 180308 (PtCo/$NbO_x$/C): 352 A/$g_{Pt}$ |

**Project has passed budget period 1 milestones.**

# Approach: Budget Period 2 Milestones Revised to Focus on Material Characterization and Durability

| Budget Period 2 Milestones: 4/1/2018 – 3/31/2019 | |
|---|---|
| ***Revised:*** **Milestone #4 (Q5):** Determine Pt, NbOx, C interactions in PVD Pt/NbOx/C catalysts using elemental mapping, TEM, XAS, XPS; provide comparisons between PVD Pt/NbOx/C and Pt/C | Pt adjacent to or on top of deposited NbOx (amorphous, electronically conducting), enhancing ORR activity and 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 and 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 $mW/cm^2$ for Pt/C; 410 $mW/cm^2$ for Pt/NbOx/C (0.15 $mg/cm^2$, 250 kPa) |
| **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) | **Mass activity % loss goal and <100 mV loss @ 0.8 $A/cm^2$ in electrocatalyst cycle have been shown. (Q7-8)**<br><br>Support corrosion test on going. (Q7-8) |
| **<u>Go/No-go Decision Point for Budget Period 2 (end of Year 2)</u>:** 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 0.15 $mg_{PGM}/cm^2$**; testing at lower loading is on-going. |

**Milestones 4 met with line-of-sight to meeting other milestones and GNG**

# Approach: Budget Period 3 Milestones Conform to Target Tables

| Budget Period 3 Milestones: 4/1/2019 – 3/31/2020 | |
|---|---|
| **Milestone #10 (Q9):** 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 (Q10):** Large batch PVD catalyst, ≤ 0.125 $mg_{PGM}/cm^2$ – BOL mass activity of ≥ 0.44 $A/mg_{PGM}$ | Exothermics, EWII |
| **Milestone #12-14 (Q11):** 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 (Q12):** 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. | EWII |

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

# Collaborations

| Partner | Project Roles |
|---|---|
| | **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). |
| | **FFRDC partner.** Responsible for production of small batch $Pt/NbO_x/C$ and for transferring lessons learned small batch catalyst optimization to Exothermics for large batch production. Support role for XRF measurements. (Task 1) |
| | **Sub-contractor, Industry.** Responsible for production of large batch $Pt/NbO_x/C$. Can support with BET, PSD characterization. (Task 1) |
| | **Sub-contractor, University.** Responsible for TEM and particle size measurements. Can also support with SEM, XPS, and other characterization techniques. (Task 1) |
| | **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). |
| | **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*

# Accomplishments and Progress: Experimental Design

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

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

EXPERIMENTAL DESIGN WITH NOMINAL WT%

| | 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 |

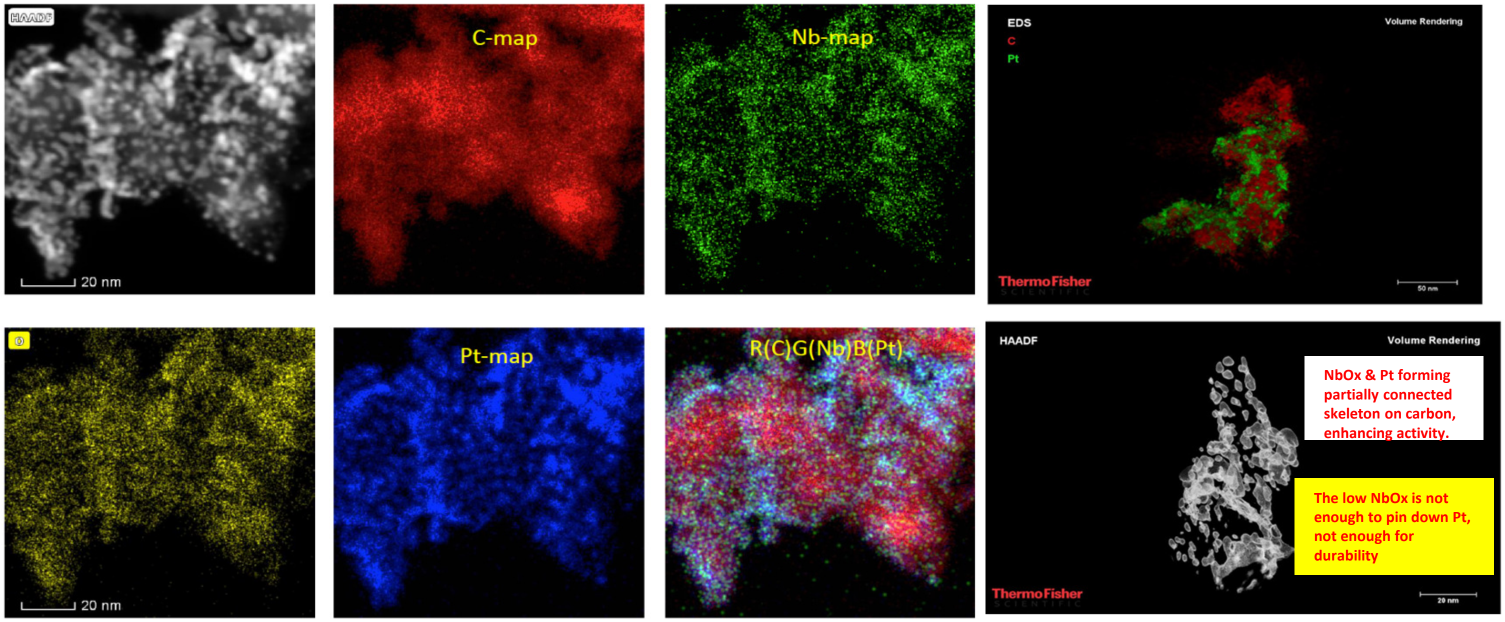
| Sample Name | Temperature | Nb Deposition: Ar/O2 Ratio | Nb Deposition: Time (hours) | Nb Deposition: Power (W) | Pt Deposition: Time (hours) | Pt Deposition: Power (W) | Pt Loading from XRF (wt.%) | NbOx Loading from XRF (wt.%) |
|---|---|---|---|---|---|---|---|---|
| ORNL-L-030 | Room (off-gassed 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** |
| Umicore$ | wet chemical commercial | NA | NA | NA | NA | NA | **28.3** | **NA** |

* Ketjen black carbon
$ high surface area carbon
All other samples are supported on acetylene black

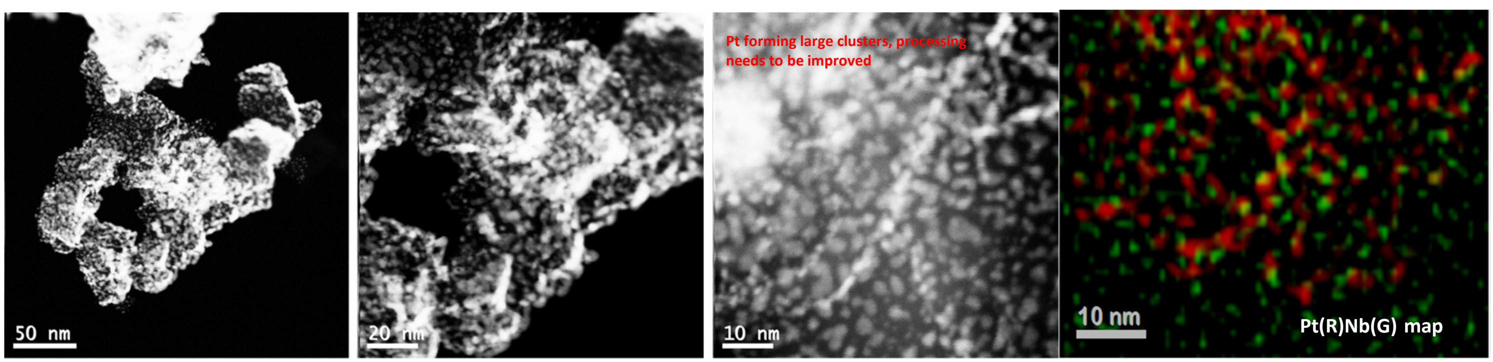
**Small batch experimental design was used to point toward better Pt, NbOx composition for large batch samples**

# Milestone #4: Microstructural Analysis with TEM & XPS - understanding the morphology of NbOx and Pt

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



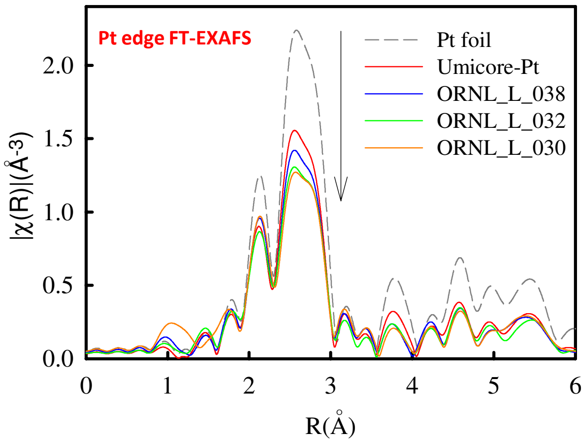

Exothermics 180920 (20.0% Pt, **2.5% NbOx**, AB, MA=389 A/cm2, MA drop =25%, 0.8 A/cm$^2$ voltage drop = 70 mV)

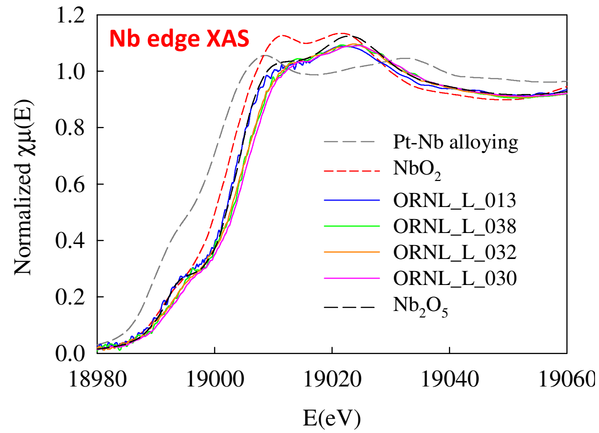


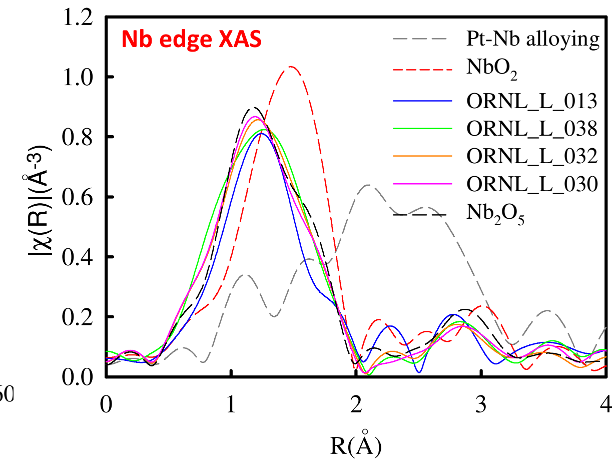

**Greater NbOx → uniform distribution of NbOx. Pt forms partially connected network on top & adjacent to NbOx, enhancing ORR activity & durability.**

# Milestone #4: Electronic Interaction through XAS

NbOx wt%: ORNL-L-013 (0.61%) < ORNL-L-038 (1.34%) < ORNL-L-032 (3.82%) < ORNL-L-030 (6.3%)




- With increasing NbOx 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.

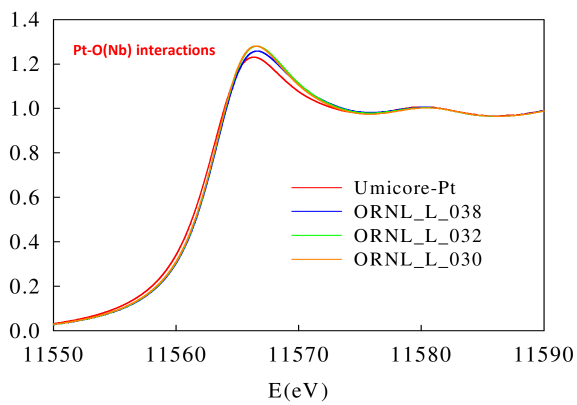
- The Nb XAS signal does not change with Nb content.
- No Nb-Pt interactions are detectable.
- The bulk oxidation state of Nb is nearly saturated close to +5 (x=4.6)

**There are no Pt-NbOx interactions**

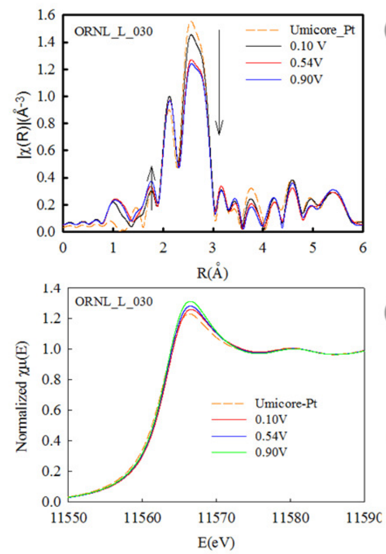
Northeastern University
Center for Renewable Energy Technology

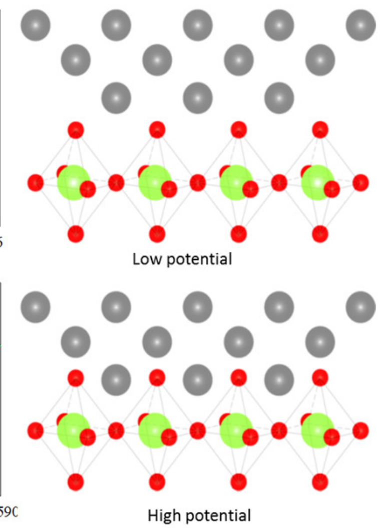
# Milestone #4: Electronic Interaction through XAS

NbOx wt%: ORNL-L-013 (0.61%) < ORNL-L-038 (1.34%) < ORNL-L-032 (3.82%) < ORNL-L-030 (6.3%)




With increasing NbOx 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 transfers 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 onto $NbO_x$ 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 may account partly for degradation.

Northeastern University
Center for Renewable Energy Technology

**$NbO_x$-induced durability improvement may come from interaction between Pt and O from NbOx**

# Milestones #5, 7: Durability Comparison

EWii

Electrocatalyst AST (MYRDD P.1) run at EWii with 100 ugPt/cm² on cathode using 50 cm² FCT single cell. Fuel cell mass activities at 0.9 $V_{iR\text{-}free}$ and corrected for $H_2$ x-over.

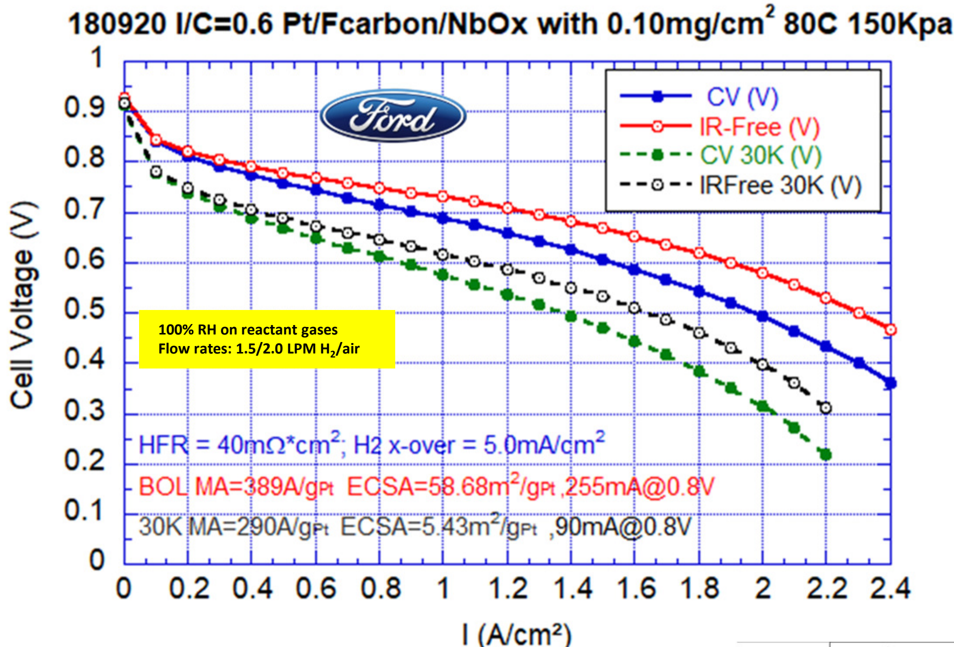
| Sample | Carbon | % Pt | % NbOx | I/C | Anode Loading (ug/cm²) | RDE BOL Mass Activity (A/gPt)* | FC Mass Activity Loss (%) | FC ECA Loss (%) | Voltage Loss at 0.8 A/cm² (mV) |
|---|---|---|---|---|---|---|---|---|---|
| Commercial reference | HSA | 28.3 | 0 | 0.5 | 50 | 560 | 35 | 40 | 59 |
| | | | | 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 |
| Exothermics 180109 | Ketjen | 19.9 | 1.75 | 0.5 | 50 | 455 | 39 | 67 | 224 |
| Exothermics 180209 | Ketjen | 26.8 | 0 | 0.8 | 50 | 440 | 35 | 65 | 180 |
| Exothermics 180920 | 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 |

* same ink as FC test
AB = acetylene black

Green: Aligned with final project target
Yellow: Aligned with Milestone #7

**Most Pt/NbOx/C show <40% mass activity loss. Lower V loss shown with ↑ NbOx.**

# G/NG for Budget Period 2: Electrocatalyst AST

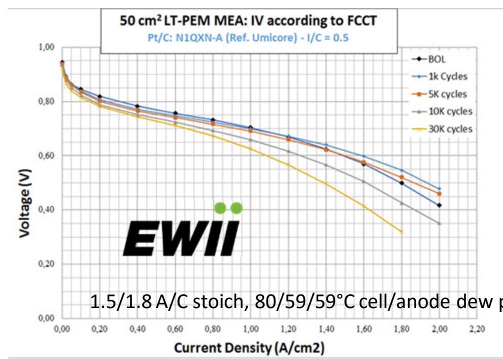


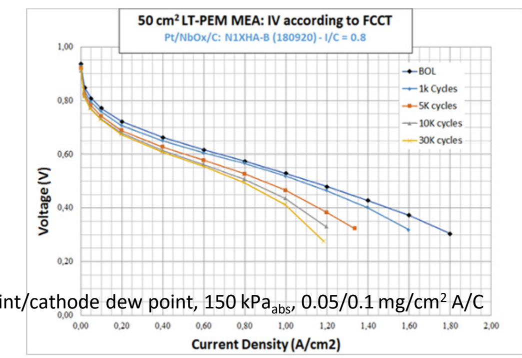

Ford testing: 5 $cm^2$ single cell test with Exothermics 180920 at anode / cathode Pt loadings of 0.05/0.1 $mg_{Pt}/cm^2$ show samples can meet 2nd go/no-go mass activity target

- **BOL mass activity of 389 $A/g_{Pt}$ and EOT mass activity of 290 $A/g_{Pt}$**
- Need to repeat with 0.025 $mg_{Pt}/cm^2$ anode loading

EWii testing:

- During ASTs, mass activity measurements were not performed with proper electrode conditioning – ASTs to be redone
- Lower performance also observed for Pt/NbOx/C polarizations using MYRDD Table P.6 (a.k.a. FCTT method)




1.5/1.8 A/C stoich, 80/59/59°C cell/anode dew point/cathode dew point, 150 $kPa_{abs}$, 0.05/0.1 $mg/cm^2$ A/C

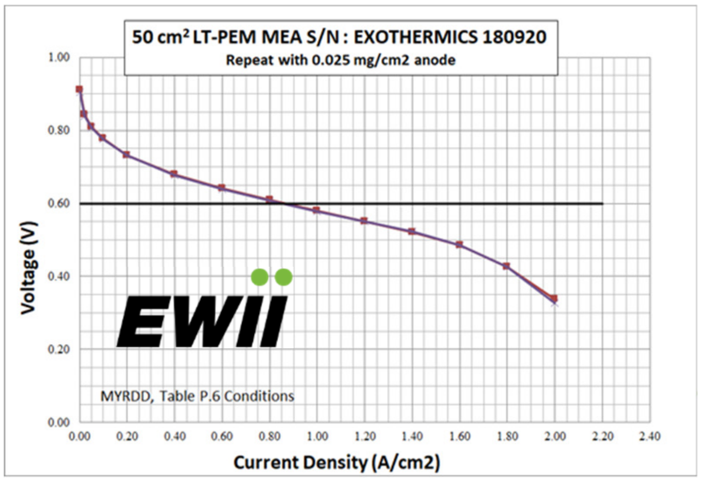
| number of cycles | Voltage at 0.8 A/cm2 | Voltage loss (mV) |
|---|---|---|
| 0 | 0,73 | 0 |
| 1000 | 0,72 | 8,46 |
| 5000 | 0,72 | 15,56 |
| 10000 | 0,69 | 38,66 |
| 30000 | 0,67 | 58,66 |

| number of cycles | Voltage at 0.8 A/cm2 | Voltage loss (mV) |
|---|---|---|
| 0 | 0,570 | 0 |
| 1000 | 0,570 | 0,00 |
| 5000 | 0,530 | 40,00 |
| 10000 | 0,510 | 60,00 |
| 30000 | 0,500 | 70,00 |

**Ford fuel cell tests show mass activities that align with Budget Period 2 Go/No-Go**

# Milestone #6: Power Density

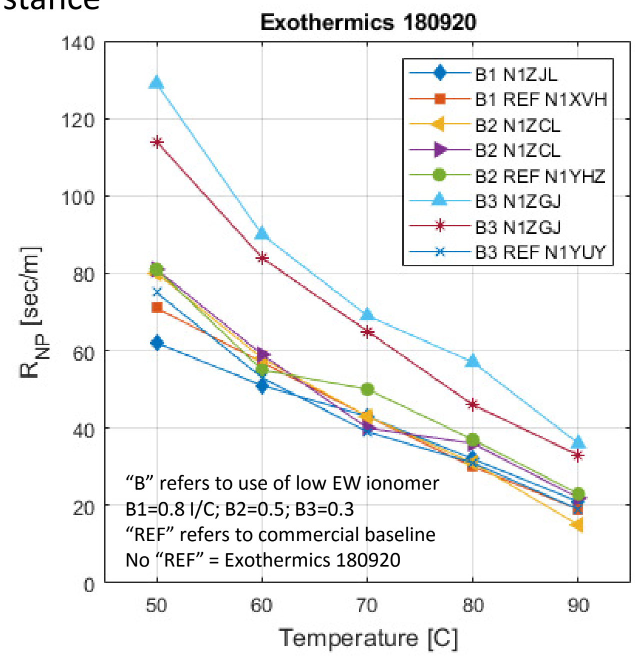
Exothermics 180920 (Pt/NbOx/C):
From Ford test (prior slide, differential, 100% RH):
**930 mW/cm²** at 0.6 V, 80°C (Q/ΔT=2.44 kW/K)
From EWii test (below, MYRDD Table P.6):
**538 mW/cm²** at 0.6 V, 80°C (Q/ΔT=2.44 kW/K)
From NREL test (MYRDD Table P.6 with 90°C, 250 $kPa_{abs}$):
**410 mW/cm²** at 0.692 V (Q/ΔT=1.45 kW/K)




EWii has been focusing on the durability of the catalyst under electrocatalyst AST conditions, did not optimize the initial cell performance.

Exothermics 180209 (Pt/C):
From EWii test (MYRDD Table P.6 with 94°C, 250 $kPa_{abs}$):
**608 mW/cm²** at 0.668 V (Q/ΔT=1.45 kW/K)

NREL performed limiting current testing on 3 cm² cell. $R_{NP}$ = non-pressure dependent mass transport resistance




- 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

**PVD Pt/C sample tested at Q/ΔT=1.45 kW/K showed >500 mW/cm². Limiting current measurements do not show added resistances from PVD catalyst.**

# Select Reviewer Comments

- “The effect of Nb on the catalysts is not very clearly illustrated, nor is the parameter space. It is unclear what the catalyst parameters to be varied are.” “More science is necessary; it is important to understand the NbOx 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 NbOx and on carbon, respectively. The Pt bonding interactions should be measured, and durability measurements should be taken.”
  - Response: The effects of NbOx and Pt concentration are being systematically studied through an experimental design with the small batch preparation system at ORNL. Microstructural analysis by TEM indicates larger Pt sitting adjacent to or on top of pre-deposited NbOx. XPS and XAS confirmed that the Nb valence state is around 4.6 in the NbOx phase, and XAS also confirmed there is a Pt-O interaction between Pt and the O in NbOx, which contributes to the enhanced durability. Electrocatalyst cycling shows enhancement in durability with increased NbOx. Exothermics is making a larger batch of samples following EWii test results on activity and durability.
- “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”
  - Response: Performance stability under load cycling has been performed for electrocatalyst cycling at EWii. Other issues will be addressed in budget period 3 or may be outside the scope of this project.

# Future Work

- **<u>Go/No-Go Decision Point for Budget Period 2 (end of Year 2)</u>:**

  Validation of PVD deposited catalyst powders via MEA BOL Testing with 40-50 $cm^2$ single cell having a cathode loading of ≤ 0.125 $mg_{PGM}/cm^2$ giving a **BOL mass activity of ≥ 0.30 $A/mg_{PGM}$** at 900 $mV_{iR\text{-}free}$ and MA drop of less than 30% after electrocatalyst cycling of 30K cycles, following the protocols given in Table 3.4.7 of FCTO's MYRDD Plan.

- Actions related to Go/No-Go:
  - EWii: Ink processing & fuel cell testing on candidate samples to obtain mass activity values and AST durability (both <u>support corrosion</u> and electrocatalyst) for both the catalyst & substrate.
    - Mass activity measurements to be done with conditioning same as for measurements prior to GNG1 in 2018.
    - Full examination of voltage losses in kinetic region, and at 0.8 $A/cm^2$, including proton conductivity.
  - ORNL: Produce samples at higher batch size in Big Chamber so that fuel cell testing can be done.
  - Exothermics: Improving deposition conditions to make large batch of catalysts based on ORNL experimental design results.
  - Northeastern U: Help test MEAs made by EWii for ORR activity and durability.
- Beyond Go/No-Go
  - Continue XAS studies to understand source of activity for newer samples
    - Use XAS as function of potential to understand Pt-NbOx interactions
    - Use XAS to observe Nb oxidation state after fuel cell testing
  - Work with Strategic Analysis to refine cost estimates on a scaled up Exothermics PVD process
  - Work to characterize performance stability for PVD processed catalysts under start/stop 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, SU/SD AST, and OCV AST for high performing materials after go/no-go.
  - 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

- Go/No-Go still to be confirmed as of early March 2019
  - Best mass activity and durability after electrocatalyst AST has been achieved in cell testing at Ford with anode Pt loading of 0.05 $mg_{Pt}/cm^2$. EWII is working to confirm on 50 $cm^2$ cell at anode loading of 0.025 $mg_{Pt}/cm^2$.
- Milestone #1-4 has been met, #5, 7-8 mostly met, #6 is being tested.
- Northeastern has shown almost no Pt-Nb interactions (no alloying), but a Pt-O interaction between the Pt and the O in NbOx, and the interaction increases as NbOx concentration increase from 1.5 wt.% to 6 wt.%, contributing to the enhanced durability of the PVD Pt/NbOx/C catalysts. TEM microstructural analysis shows physical evidence that NbOx is homogeneously deposited on top of the carbon powers, and Pt is adjacent to or on top of the pre-deposited NbOx. However, the Pt is prone to clustering during large batch deposition and modification is being made to change the catalyst processing.
- Actions are being taken to address cost analyses (Strategic Analysis), as well as performance stability under start/stop cycling, and structural stability of the catalyst under the ink-making process.

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# TECHNICAL BACKUP SLIDES

FC-162

# Accomplishments and Progress: GNG 1

- Go/No-Go Decision Point for Budget Period 1 has been passed
  - Four catalysts showed > 300 $A/g_{PGM}$ mass activity

| 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 |

Fabrication conditions:

- ORNL-L-013: AB carbon off-gassed at 400°C for 12 hours, followed by Nb sputtering in 10:1 $Ar:O_2$ environment for 1.5 hours at 150 W. Pt sputtering followed in Ar for 1.5 hours at 140 W.
- Exothermics samples were off-gassed at >200°C, and sputtered at >100°C. Nb sputtering was done in 3% $O_2$/Ar for 180109 and 180302 (2% for 180308) for 8 hours at 100 W. Pt or PtCo sputtering followed in Ar for 5 hours at 300 W.

**Both small and large batch samples have passed the go/no-go criteria**

# Fuel Cell Testing Results: AST

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

- 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)

| | | | | | FC TEST | FC TEST | FC TEST | RDE | FC TEST | FC TEST | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample** | **Carbon Support** | **% Pt** | **% NbOx** | I/C | BOL $ECA_{Avg}$ ($m^2/g_{Pt}$) | EoL $ECA_{Avg}$ ($m^2/g_{Pt}$) | BoL ECA @ RT | **BOL Mass Activity (A/gPt)** | BOL Mass Activity (A/gPt) | 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** |