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


P.I. – Jim Waldecker

Ford Motor Company


June 14, 2018

FC162

# Overview

## Timeline

- Project Start Date: 1/1/2017
- Project End Date: 3/31/2020
- Percent complete: 30%

## Budget

- Total project budget: $2,594,412
  - Total recipient share: $518,883
  - Total federal share: $2,075,529
  - Total DOE funds spent*: $527,629

* As of 3/31/2018

## Barriers

A. Durability
B. Cost
C. Performance

## 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 Fuel Cells LLC
  - CCM fabrication, fuel cell testing

Other contributions: Strategic Analysis (cost analysis), FC-PAD (catalyst layer microscopy), 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 | 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] |
| 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 |

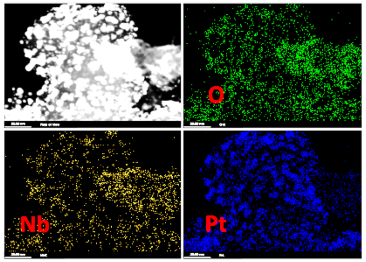
[1] Measured using Exothermics 180308 (PtCo/NbOx/Ketjen black). High current measurements at 0.6 V, 80°C (Q/ΔT=2.44), fully humidified.
[2] Measured using ORNL-L-013 (Pt/NbOx/acetylene black). High current measurements at 0.6 V, 80°C (Q/ΔT=2.44), fully humidified.

**Go/no-go drove early focus on activity. Durability, high current testing still to come.**

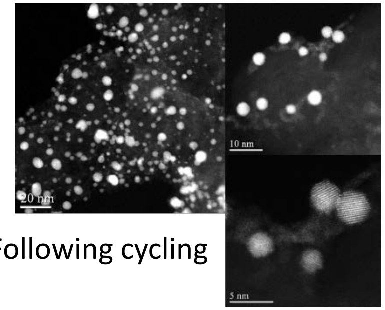
# Approach: PVD to Simplify Processing, Niobia for Stability

- Physical vapor deposition (PVD) for the production of an oxygen reduction catalyst has many advantages:
  - Improved reproducibility from elimination of a large number of production variables
  - No impurities from precursors or solvents
  - In principle, no drying or post-synthesis annealing is needed
  - Deposition of controlled stoichiometry $Nb_xO_{1-x}$ suboxide phases
    - Nb/O ratios controlled by metering molar ratio of reactive and non-reactive gaseous species via reactive magnetron sputtering.
- Sputtering onto a powder support to generate a powder catalyst allows use of conventional MEA fabrication technology
- PVD processing onto powders provides this project a unique position in the DOE catalyst portfolio

- Niobium oxide has been cited for enhancing ORR activity, but in this project, durability is the motivation.
- Prior work suggested NbOx networks may help to pin Pt particles.



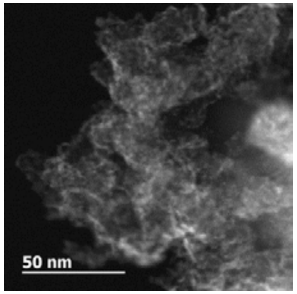
As prepared



Following cycling

Arc plasma deposition Pt/NbOx/C sample showed well-dispersed Pt, Nb. Following 25K 0.1-1.0 V cycles, Pt particles grew, but NbOx network appeared to “pin” Pt particles.

Connected network of 17.6 wt% NbOx deposited on acetylene black using magnetron sputtering at ORNL




**PVD can be used to generate a carbon-supported Pt powder. NbOx can be used to help anchor Pt on carbon.**

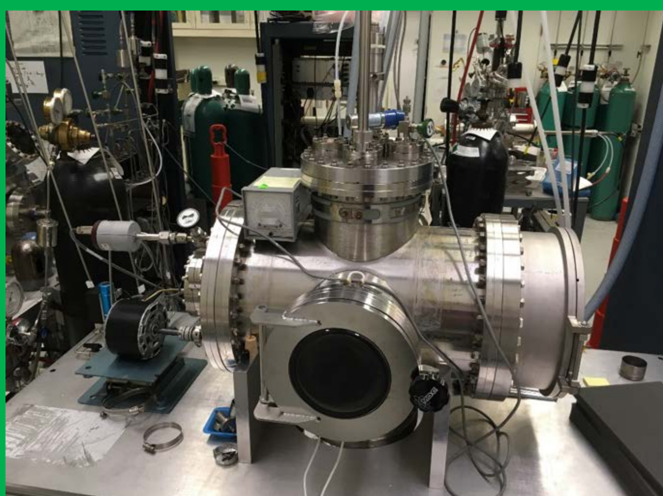
# Approach: PVD Methods

Ford arc plasma deposition (small batch)

PVD can be done on powders:

- Arc plasma deposition (350°C) downwards into a rotating chamber
  - Low batch size; useful for surveying new powder compositions
- Magnetron sputtering onto powder agitated by tumbling
  - Scalable to large batch size

DC magnetron sputtering chamber at Oak Ridge National Laboratory (small batch)



Magnetron sputter system at Exothermics (large batch)

**ORNL and Ford were able to provide a high number of small batch sample to determine trends with composition. Exothermics is providing large batch samples.**

# Approach: PVD Cost Estimation

Strategic Analysis study included:

- Dual barrel system design
- Capital equipment sizing
- PVD operating assumptions
  - 70 kg batches, 63/year/chamber
  - 95.9 hour cycle time (each cycle with 31 labor hours)
- Bill of materials and summation of total capital costs for system: $1.37M
- Operational costs including sputtering and recycle
  - 37.5% target metal utilization
  - Recovery every 10 cycles
  - 95% Pt, Nb recovery

| | Units | Baseline PtCo/HSC | Alternative PVD PtNbOx/C |
|---|---|---|---|
| **Catalyst Usage (mass to inking station)** | gCatalyst/system | 30.25 | 34.56 |
| **Pt mass fraction** | gPt/gCatalyst | 28.56% | 25% |
| **Pt Usage (mass to inking station)** | gPt/system | 8.639 | 8.639 |
| **Cathode Loading** | mgPt/cm2 | 0.1 | 0.1 |
| **Catalyst yield (on total process)** | Net / Gross | 95% | 100% |
| **Cost Summary** | | | |
| **Pt Cost (net)** | $/system | $442.33 | $425.54 |
| **Processing Cost** | $/system | $34.40 | $13.80 |
| **QC** | $/system | $4.59 | $4.59 |
| **Packaging** | $/system | $0.23 | $0.23 |
| **Total** | $/system | $481.55 | $444.16 |
| **Total** | $/kW | $6.02 | $5.55 |
| **Delta to Baseline** | $/system | NA | -$37.39 |
| **Delta to Baseline** | $/kW | NA | -$0.47 |

Exothermics provisionally agrees with the SA cost analysis. However, Exothermics does recommend a sensitivity study be done on capital cost and amortization time.

- Labor is accurate
- Inputs well accounted for
- May be opportunities to reduce cost associated with making Pt, Nb targets

**PVD process can result in processing cost savings versus baseline catalyst**

# Approach: Tasks and Schedule

| | 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 | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |

- Small batch and large batch catalyst synthesis are ongoing, as well as characterization, MEA development, and BOL validation
- MEA cycling is still forthcoming (Q6 until end of project)

**Catalyst synthesis and characterization, and MEA BOL validation are proceeding. Durability testing is scheduled to begin in Q6 (Jul-Sep 2018).**

# 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. High pressure sputtering could help, but experimental scope may be large. 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: 1 from ORNL (small batch), 3 from Exothermics (large batch). 2 non-alloyed, 2 alloyed. |

**Project has passed go/no-go and RDE activity milestone.**
**Repeatability milestone is pending.**
**Particle size distribution milestone may not align with reality of catalyst characteristics.**

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

| Milestone | |
|---|---|
| ***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 | University of Michigan; Northeastern University Center for Renewable Energy Technology |
| ***Revised:*** **Milestone #5 (Q6):** Durability comparison between PVD Pt/NbOx/C, PVD Pt/C, and Pt/C | EWII |
| **Milestone #6 (Q7):** Large batch PVD catalyst - > 500 mW/cm² at $Q/\Delta T_i$ < 1.45 kW/˚C, 0.125 $mg_{PGM}/cm^2$, $P_{air,in}$ ≤ 150 kPa | EWII; Exothermics |
| **Milestones #7-8 (Q8):** < 40% mass activity loss and < 100 mV loss at 0.8 A/cm² in electrocatalyst cycle (0.6-0.95 V); < 40% mass activity loss and < 200 mV loss at 1.5 A/cm² in support corrosion cycle (1-1.5 V) | EWII; Exothermics |
| **<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 $A/mg_{PGM}$). | |

# Budget Period 3 Milestones: 4/1/2019 – 3/31/2020

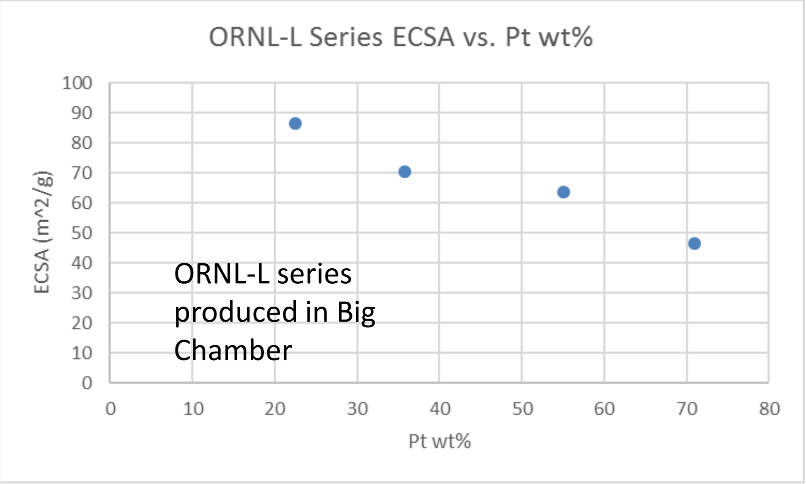
| Milestone | |
|---|---|
| **Milestone #10 (Q9):** Large batch PVD catalyst - 1) mass activity > 0.40 $A/mg_{PGM}$ and 2) electrocatalyst AST (30K cycles) with < 40% loss in mass activity (RDE) | Ford; Exothermics |
| **Milestone #11 (Q10):** Large batch PVD catalyst, ≤ 0.125 $mg_{PGM}/cm^2$ – BOL mass activity of ≥ 0.44 $A/mg_{PGM}$ | EWII; Exothermics |
| **Milestone #12-14 (Q11):** Large batch PVD catalyst - > 1,000 mW/cm² at $Q/\Delta T_i$ < 1.45 kW/˚C, for 0.125 $mg_{PGM}/cm^2$, $P_{air,in}$ ≤ 150 kPa; < 40% mass activity loss and < 30 mV loss at 0.8 A/cm² in electrocatalyst cycle (0.6-0.95 V); < 40% mass activity loss and < 30 mV loss at 1.5 A/cm² in support corrosion cycle (1-1.5 V) | |
| **Milestone #15 (Q12):** A set of MEAs (6 or more, each with active area ≥ 50 cm²) is made available for independent testing at a DOE-approved location. | EWII |

**Budget Period 2 milestones revised to focus on material characterization and durability**

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

# Accomplishments and Progress: ORNL Synthesis

- As of the 2017 AMR, the project had shown high RDE activity for PVD Pt/C made in small batches at ORNL. Concerns existed about low Pt wt%.
- Initial PVD Pt/NbOx/C samples at ORNL had low NbOx wt%
  - Systematic study mapped NbOx wt% to Ar:$O_2$ ratio, Nb target power (0-19 wt% NbOx without Pt)
  - Systematic study mapped Pt wt% to deposition time, Pt target power for both Pt/NbOx/C and Pt/C (23-65 wt% Pt)
  - ➢ Issues with low Pt, Nb wt% were overcome
- Early ORNL samples from "Baby Chamber" could not achieve ECSA > 49 $m^2/g$, despite use of acetylene black (AB) support
  - Switch to "Big Chamber" with two targets
  - Maintained vacuum between Pt and Nb sputtering and increased ECSA




**Chamber environment, target powers and deposition time were adjusted to achieve sufficient Pt, NbOx wt%. Chamber with two targets used to achieve higher ECSA.**

# Accomplishments and Progress: Exothermics Synthesis

Passed GNG

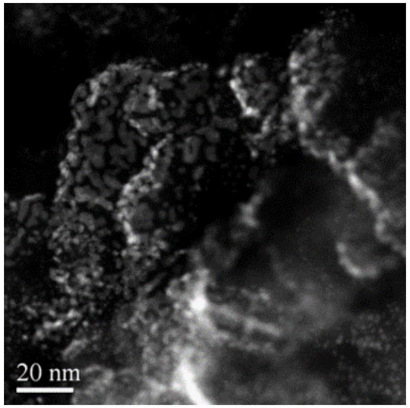
| Sample | Nb Deposition: $Ar/O_2$ Ratio | Nb Deposition Time (hrs) | Nb Deposition Power (W) | Pt Deposition Time (hrs) | Pt Deposition Power (W) | Carbon Support | Pt wt% | Co wt% | NbOx wt% |
|---|---|---|---|---|---|---|---|---|---|
| 170731 | 32.3 | 6 | 400 | N/A | N/A | J32 | 0 | 0 | 13.3 |
| 170822 | 32.3 | 6 | 400 | 2.5 | 400 | J32 | 10.6 | 0 | 6.3 |
| 170915 | N/A | N/A | N/A | 3 | 500 | J32 | 37.5 | 0 | 0 |
| 171106 | 32.3 | 6 | 400 | 5 | 300 | J32 | 23.9 | 0 | 5.14 |
| 171117 | 32.3 | 6 | 400 | 5 | 300 | J32 | 19.7 | 0 | 5.52 |
| 180109 | 32.3 | 8 | 100 | 5 | 300 | Ketjen | 19.9 | 0 | 1.75 |
| 180119 | N/A | N/A | N/A | 5 | 300 | Ketjen | 24.8 | 0 | 0 |
| 180201 | N/A | N/A | N/A | 5 | 300 | Ketjen | 23.2 | 0 | 0 |
| 180209 | N/A | N/A | N/A | 5 | 300 | Ketjen | 26.8 | 0 | 0 |
| 180302 | 32.3 | 8 | 100 | 5 | 300 (PtCo) | Ketjen | 21.5 | 1.10 | 0.23 |
| 180308 | 49 | 8 | 100 | 5 | 300 (PtCo) | Ketjen | 28.8 | 1.54 | 0.50 |

- Exothermics batches showed somewhat predictable changes in Pt, NbOx wt% with changes in synthesis conditions. Pt-only samples within +/- 10%.

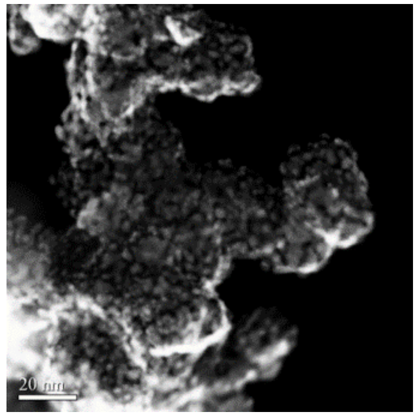
**Exothermics sample weight percents qualitatively showed expected response to synthesis parameters. PtCo sputtering feasibility shown.**

# Accomplishments and Progress: Pt Particle Sizes

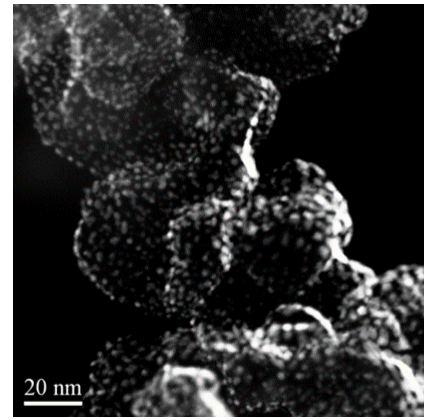
ORNL2-022 (23.1% Pt)



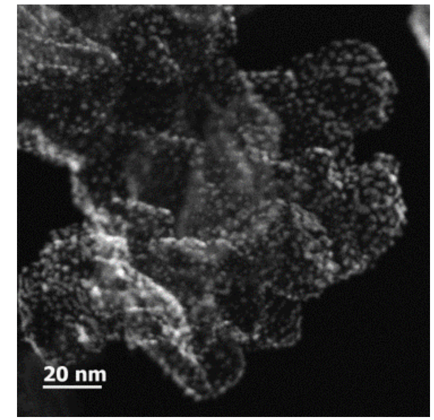

ORNL2-023 (60.8% Pt)



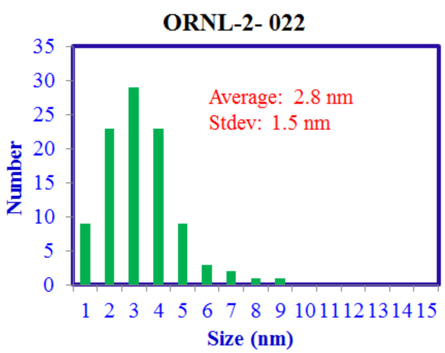

Exothermics 180109 (19.9% Pt)

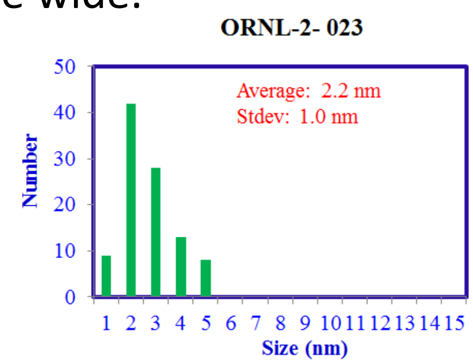


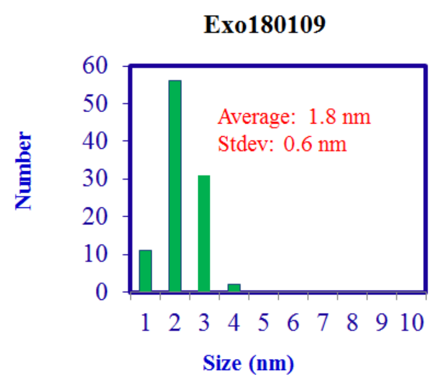

Exothermics 180308 (28.8% Pt)

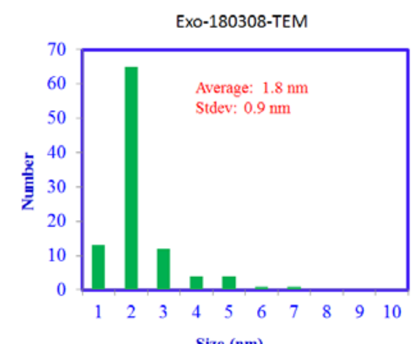



UM TEM showed that line-of-sight sputtering can lead to both areas where particles are heavily clustered, as well as areas where particles are sparse. The result is a wide particle size distribution. Average particle sizes for both ORNL and Exothermics are near 2 nm, but distributions are wide.



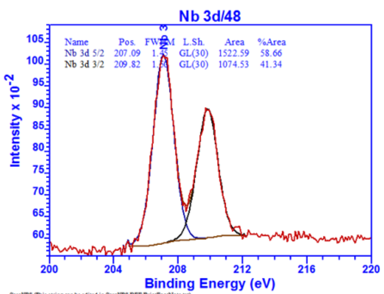




**Milestone #1 will not be passed. Line-of-sight sputtering does not yet lead to narrow particle size distributions.**

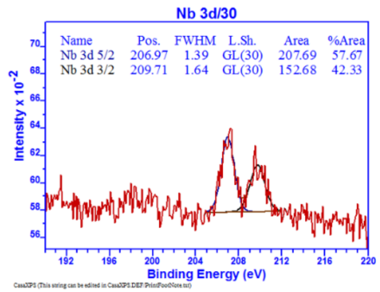
# Accomplishments and Progress: X-Ray Characterization

From standard $Nb_2O_5$, the UM XPS measured 207.89 eV for the Nb $3d_{5/2}$ peak. Average ORNL sample: 207.17 eV. Average Exothermics: 207.42 eV.

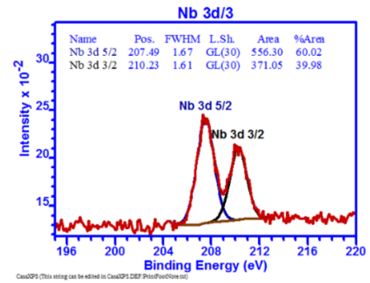
ORNL2-022 (23.1% Pt)



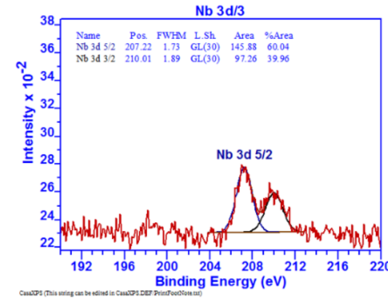

ORNL2-023 (60.8% Pt)



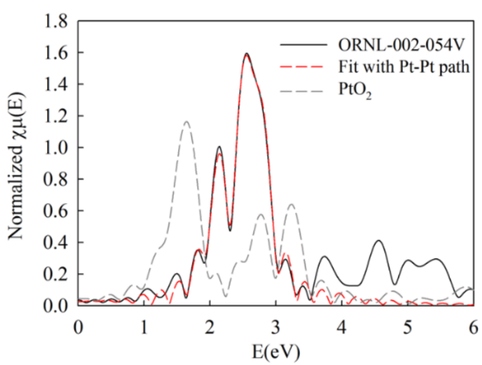

Exothermics 180109 (19.9% Pt)




Exothermics 180308 (28.8% Pt)

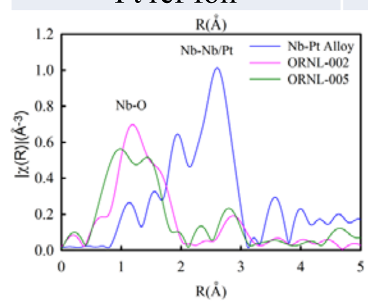



NEU EXAFS data from early ORNL samples shows no strain effect, lack of Pt-Nb interaction.

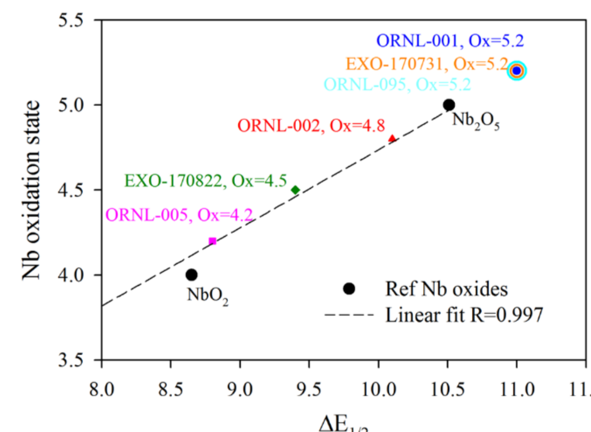



Pt $L_3$ EXAFS: Good fit with only Pt-Pt interactions

| Data at 0.54 V | $R_{PtPt}$ (Å) |
|---|---|
| ORNL2-002 | 2.756±0.001 |
| ORNL2-005 | 2.754±0.001 |
| Pt ref foil | 2.756±0.001 |




Nb K-edge EXAFS: No Pt-Nb alloying




Bulk oxidation states higher than suggested by XPS

**Surface Nb oxidation state shown by XPS to be lower than +5, although EXAFS shows it can be +5 in the bulk. No Pt-Nb alloying has been shown.**

# Accomplishments and Progress: Milestone #2

- Milestone #2: 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.
- ORNL sought to show repeatability on Big Chamber.
  - Acetylene black carbon baked for 12 hours at 400°C
  - Nb reactive sputtering: 10:1 Ar:$O_2$, 150 W, 1.5 hours
  - Pt sputtering: Ar, 140 W, 1 hour
    - **Pt**: A variation of +/- 1 standard deviation (2.4 wt%) is slightly over 10% of the average weight percent for Pt. Milestone is close to being met.
    - **Nb**: +/- 1 standard deviation (0.38 wt%) is 42% of the average weight percent; however, signal/noise is low.

| Sample | Pt wt% | NbOx wt% |
|---|---|---|
| ORNL-L-012 | 22.5 | 1.19 |
| ORNL-L-015 | 20.7 | 0.92 |
| ORNL-L-016 | 21.7 | 0.92 |
| ORNL-L-017 | 19.3 | 0.77 |
| ORNL-L-018 | 21.2 | 0.70 |
| AVERAGE | 21.1 | 0.90 |
| ST. DEV. | 1.2 | 0.19 |

**Milestone is close to being met with improved techniques at ORNL. NbOx weight percent may need to be higher for more meaningful results.**

# Accomplishments and Progress: Milestone #3

- RDE testing of PVD Pt/NbOx/C catalysts demonstrated mass activity > 0.4 $A/mg_{PGM}$ for 23 samples
  - 10 of these samples are small batch samples made at ORNL

| Sample | Composition (AB = acetylene black, KB = Ketjen black, J32 = graphitized) | Mass Activity (A/gPGM) | Specific Activity ($uA/cm^2_{Pt}$) | ECSA ($m^2/g$) |
|---|---|---|---|---|
| ORNL2-010 | 47.3% Pt, 0.50% NbOx, AB | 591 | 1229 | 43 |
| ORNL2-011 | 57.5% Pt, 0.81% NbOx, AB | 436 | 1122 | 39 |
| ORNL2-022 | 23.1% Pt, 1.46% NbOx, AB | 513 | 1047 | 49 |
| ORNL2-023 | 60.8% Pt, 0.94% NbOx, AB | 477 | 1157 | 41 |
| ORNL2-024 | 46.1% Pt, 0.24% NbOx, AB | 529 | 1314 | 40 |
| ORNL2-031 | 62.2% Pt, 0.59% NbOx, AB | 456 | 1086 | 42 |
| ORNL-L-010 | 55.1% Pt, 1.41% NbOx, AB | 452 | 721 | 63 |
| ORNL-L-011 | 71.0% Pt, 0.73% NbOx, AB | 457 | 982 | 47 |
| ORNL-L-012 | 22.5% Pt, 1.19% NbOx, AB | 503 | 584 | 86 |
| ORNL-L-013 | 35.8% Pt, 0.61% NbOx, AB | 490 | 695 | 71 |

"ORNL2-…" series produced on Baby Chamber. "ORNL-L-…" series produced on Big Chamber. Nb deposition for all samples performed with 10:1 $Ar:O_2$ environment for 1.5 hours at 150 W. Pt deposition for all samples in Ar environment. Deposition times range from 1 to 6 hours. Pt deposition power was 140 W for all samples except ORNL2-023 and -031 (70 W).

**Pt/NbOx/C samples with wide range of Pt wt% showed high mass activity**

# Accomplishments and Progress: Milestone #3

- 5 samples from Exothermics (large batch)
- 8 samples from Ford APD (small batch)

| Sample | Composition (AB = acetylene black, KB = Ketjen black, J32 = graphitized) | Mass Activity (A/gPGM) | Specific Activity ($uA/cm^2_{Pt}$) | ECSA ($m^2/g$) |
|---|---|---|---|---|
| Exothermics 171117 | 19.7% Pt, 5.52% NbOx, J32 | 420 | 806 | 50 |
| Exothermics 180109 | 19.9% Pt, 1.75% NbOx, KB | 519 | 730 | 71 |
| Exothermics 180302 | 21.5% Pt, 1.10% Co, 0.23% NbOx, KB | 653 | 926 | 67 |
| Exothermics 180302-HNO3 | 17.3% Pt, 0.49% Co, 0.17% NbOx, KB | 652 | 901 | 72 |
| Exothermics 180308 | 28.8% Pt, 1.54% Co, 0.50% NbOx, KB | 672 | 885 | 76 |
| Ford APD-11062017 | 21.3% Pt, 2.39% NbOx, J32 | 461 | 693 | 67 |
| Ford APD-01102018 | 30.2% Pt, 3.75% NbOx, AB | 429 | 515 | 83 |
| Ford APD-02052018 | 17.7% Pt, 1.58% Ni, 1.07% NbOx, J32 | 539 | 504 | 107 |
| Ford APD-02082018 | 17.5% Pt, 1.36% Co, 1.07% NbOx, J32 | 455 | 480 | 95 |
| Ford APD-02082018-HNO3-1hr | 18.7% Pt, 0.39% Co, 1.21% NbOx, J32 | 538 | 489 | 110 |
| Ford APD-02082018-HNO3-0hr | 19.3% Pt, 0.38% Co, 1.25% NbOx, J32 | 531 | 605 | 88 |
| Ford APD-03022018 | 13.9% Pt, 1.17% Co, 1.43% NbOx, J32 | 449 | 634 | 71 |
| Ford APD-04152018 | 22.5% Pt, 2.15% Co, 2.12% NbOx, AB | 607 | 883 | 69 |
| Ford wet chemistry | 23.4% Pt, 18.4% NbOx, AB | 265 | 359 | 74 |

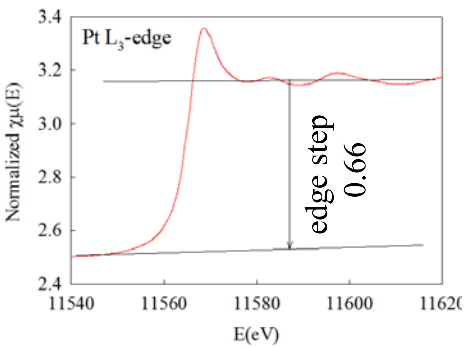
Exothermics samples made as described on previous slide. Ford APD used 150 V for NbOx sputtering and 100 V for Pt/PtNi/PtCo sputtering. 11062017: 2.5K/40K pulses NbOx/Pt at 300°C. 01102018: 3.5K/45K pulses at 370°C. All others: 3K/80K pulses at 300°C. "-HNO3" indicates dealloying through $HNO_3$ acid treatment.

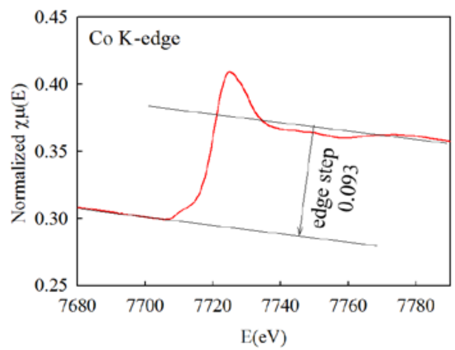
**Use of KB helped to increase Exothermics surface area and activity. Alloying impact more pronounced for Exothermics than Ford APD.**

# Accomplishments and Progress: NEU Study on Exothermics Alloy

Northeastern University
Center for Renewable Energy Technology

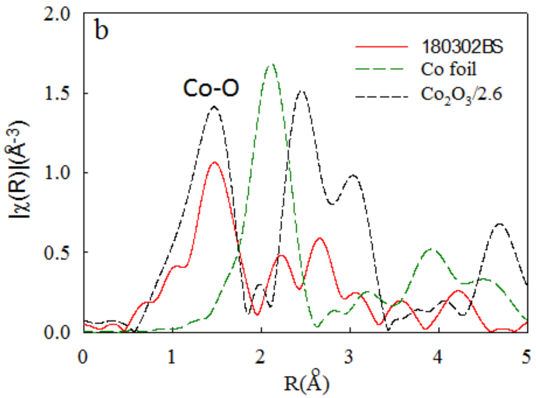
- Good agreement on Pt/Co atomic ratio between XRF and XAS.
  - Atomic ratio from XRF for Exothermics 180302: **5.6**




(0.66*4.5 Pt mol in edge step)/(0.093*5.6 Co mol in edge step) = **5.7**

- Most Co in oxide, not alloy → Some Co gets dissolved.



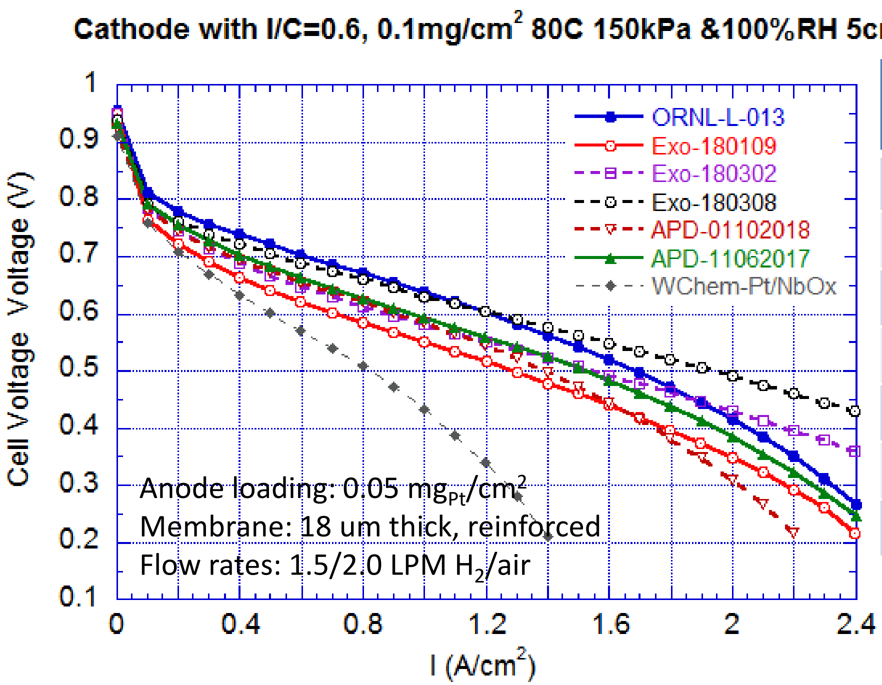

However, despite the lesser alloying, there is still a strain effect:

| 0.54 V | $R_{Pt-Pt}$ (Å) | $N_{Pt-Pt}$ |
|---|---|---|
| 180302BS | 2.740(4) | 8.5(8) |
| Pt/C TKK | 2.753(3) | 8.9(5) |
| Pt foil | 2.766(4) | 12 |

**Alloying in Exothermics PtCo/NbOx/C not as effective as expected, but does exist.**

# Accomplishments and Progress: Ford Cell Testing

- Ford polarization curves measured under differential conditions using SGL 29BC GDL and a supplier half-CCM for anode/membrane.
- Catalyst mixed at low solid percentage in IPA/water solvent and then sonicated. Catalyst ink applied directly to the membrane through ultrasonic spray deposition




| Sample | HFR ($m\Omega*cm^2$) | $H_2$ x-over ($mA/cm^2$) | MA ($A/g_{Pt}$) | ECSA ($m^2/g$) |
|---|---|---|---|---|
| ORNL-L-013 | 44 | 5 | 335 | 23 |
| Exo 180109 [1] | 53 | 5 | 113 | 30 |
| Exo 180302 [1] | 66 | 5 | 208 | 50 |
| Exo 180308 | 49 | 5 | 352 | 36 |
| APD-01102018 | 49 | 5 | 288 | 17 |
| APD-11062017 | 48 | 5 | 270 | 39 |
| Wet chemistry | 46 | 5 | 123 | 10 |

[1] Mass activities for Exothermics 180109 and 180302 were later measured at EWII with EWII ink recipes. Values in this table should be taken to represent the Ford ink recipe.

- At 0.6 V, $g/kW_{gross}$ for Exothermics 180308 = ($0.15\ mg_{Pt}/cm^2$)/(0.6 V * 1.25 $A/cm^2$) = 0.2. However, at 80°C and 0.6 V, $Q/\Delta T$=2.44 (> 1.45). There is still more work to do on mass transport or proton transport losses.

**Fuel cell testing demonstrated achievement of activity targets, but also showed more progress needs to be made on high current performance.**

# Accomplishments and Progress: EWII Cell Testing

EWII

- Fuel cell mass activity on Exothermics 180302:

| MEA S/N | Cathode Catalyst [Exothermics] | Cathode Loading ($mg/cm^2$) | I/C | OCV | HFR ($m\Omega*cm^2$) | ECA ($m^2/g$) | MA (A/g Pt) |
|---|---|---|---|---|---|---|---|
| 1st trial – Standard recipe | | | | | | | |
| N1PFB-A | PtCo/NbOx/C -180302 | 0.15 | 0.80 | 944 | 54 | 11 | 53 |
| N1QGV-A | PtCo/NbOx/C -180302 | 0.10 | 0.80 | 940 | 48 | 28 | 99 |
| 2nd trial – Standard recipe | | | | | | | |
| N1PFB-B | PtCo/NbOx/C -180302 | 0.15 | 0.80 | 960 | 42 | 19 | 160 |
| 3rd trial – "Ketjenblack" recipe | | | | | | | |
| N1QMS-A | PtCo/NbOx/C -180302 | 0.10 | 0.30 | 970 | 63 | 17 | 246 |
| N1QOF-A | PtCo/NbOx/C -180302 | 0.10 | 0.50 | 980 | 51 | 17 | 309 |
| N1QTM-A | PtCo/NbOx/C -180302 | 0.10 | 0.80 | 970 | 54 | 15 | 168 |

- Fuel cell mass activity on Exothermics 180109:

| MEA S/N | Cathode Catalyst [Exothermics] | Cathode Loading ($mg/cm^2$) | I/C | OCV | HFR ($m\Omega*cm^2$) | ECA ($m^2/g$) | MA (A/g Pt) |
|---|---|---|---|---|---|---|---|
| 1st trial – Standard recipe | | | | | | | |
| N1PBD-A | Pt/NbOx/C -180109 | 0.15 | 0.80 | 930 | 88 | 8.3 | 94 |
| N1PGX-A | Pt/NbOx/C -180109 | 0.10 | 0.80 | 910 | 43 | 12.7 | 270 |
| 2nd trial – "Ketjenblack" recipe | | | | | | | |
| N1QUX-A | Pt/NbOx/C -180109 | 0.10 | 0.30 | 960 | 60 | 18.1 | 260 |
| N1RBC-A | Pt/NbOx/C -180109 | 0.10 | 0.50 | 940 | 57 | 19.2 | 317 |
| N1RGN-A | Pt/NbOx/C -180109 | 0.10 | 0.80 | 950 | 54 | 15.1 | 328 |

- Anode: 0.05 $mg_{Pt}/cm^2$
- 50 $cm^2$ FCT cell
- 16-minute holds

Older "Ketjenblack" recipe found to be preferred for higher mass activity

Higher I/C (0.8) lowered mass activity for PtCo, but not for Pt

EWII believes low ECA may be a data analysis issue

**High mass activity achieved at EWII with older ink recipe, 0.15 total loadings.**

# 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**

# Accomplishments and Progress: Reviewer Comments

- "Unfortunately, the PI's team continues in this tradition of having poor RDE results. The PI quotes the project's RDE Pt/C activities at 0.2 A/cm$^2$ —per Gasteiger's 2005 paper. Since then, Garsany et. al. (*Journal of The Electrochemical Society*, 161 (5) F628-F640 [2014]), with improved methodology, moved the benchmark from around 0.2 A/mg Pt at 0.9 V and 1600 rpm in 0.1 M $HClO_4$ to 0.4 A/mg Pt."
  - Response: Other than Milestone #3, project targets are based on fuel cell measurements, not RDE. Project has decided to devote resources to refining fuel cell testing, not RDE. RDE was used for screening and noting trends.
- "There should be cost analysis to account for capital expenditures or operational expenditures of the sputter system at scale."
  - Response: Strategic Analysis prepared the cost analysis shown. Exothermics mostly agrees and will discuss further refinements in estimating capital costs.
- "A go/no-go decision based on the long-term stability of the Pt/NbOx/C catalysts and cost savings versus existing Pt/C catalysts should be made in Budget Period 1, not later. No fundamental science on Pt-niobia or niobia-C interaction is planned, despite the project's having university partners."
  - Response: Budget Period 1 GNG remained focused on mass activity, but milestones and a GNG associated with stability have been prioritized in Budget Period 2. Cost savings versus PtCo/C has been addressed with added cost analysis. Milestone #4 (Q5) will address Pt-niobia and niobia-C interactions, in addition to some of the work already done by Northeastern University.

# 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 small batch catalyst optimization to Exothermics for large batch production. (Task 1) |
| Exothermics Inc | **Sub-contractor, Industry.** Responsible for production of large batch Pt/$NbO_x$/C. Can support with BET, skeletal density characterization. (Task 1) |
| University of Michigan | **Sub-contractor, University.** Responsible for TEM and particle size measurements, as well as 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). |
| EWII | **Sub-contractor, Industry.** Responsible for MEA fabrication using Pt/NbOx/C catalysts on the cathode, and for fuel cell testing (Task 2). |

*All collaborations are within the DOE Hydrogen and Fuel Cells Program*

# Future Work

- Durability and materials characterization are the highest priorities for Budget Period 2
  - Added milestone for comparing PVD Pt/NbOx/C vs. PVD Pt/C vs. conventional Pt/C with the DOE electrocatalyst cycling AST.
  - Materials characterization to understand Pt, niobia, and carbon interactions in high activity catalysts using elemental mapping, TEM, XPS, XAS.
    - Mapping to be conducted for powders and for catalyst layers (FC-PAD).
    - XAS to continue on high activity samples, including Nb EXAFS
- Electrocatalyst and support corrosion ASTs
- Mass transport losses: Technology Service Agreement (TSA) has been signed with NREL as of December 2017. NREL will measure mass transport resistances for high activity catalyst layers as part of the TSA.
- Wet chemistry Pt/NbOx/C: sample needed with lower NbOx to provide more direct comparison with PVD samples
- Further refinements needed for ORNL repeatability, as well as for capital cost estimations from Strategic Analysis
- Continued sample synthesis at Exothermics

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

# Summary

- Project motivated by reproducibility and processing simplifications offered by PVD, as well as by durability opportunities offered by use of niobium oxide as a secondary support.
- Strategic Analysis cost analysis costs the possibility of a lower cost fuel cell system with use of PVD catalysts.
- Budget Period 1 go/no-go target of 300 $A/g_{PGM}$ has been met with both small and large batch PVD Pt/NbOx/C materials.
- ORNL demonstrated that high Pt wt% is achievable. Low ECSA in early ORNL samples addressed by switch to larger two-target system.
- Exothermics has been able to consistently produce large catalyst batches with weight percentages roughly consistent with changes in synthesis controls.
- Materials characterization has shown wide particle size distributions related to line-of-sight sputtering for both small and large batch samples.
- XPS shows lower surface oxidation states for Nb versus those observed in the bulk by EXAFS.
- EXAFS indicated no Pt-Nb alloying, as well as a small alloying effect for between Pt and Co in samples made from the Exothermics PtCo target.
- ORNL is close to repeatability for Pt and Nb weight percentages in small batch samples
- 23 PVD Pt(or Pt alloy)/NbOx/C samples exceeded 400 $A/g_{PGM}$ in RDE. Exothermics samples did appear to show some activity gain with increased surface area and alloying.
- Collaborators have all made substantial contributions, including catalyst synthesis at ORNL and Exothermics, TEM/XPS at UM, XAS at NEU, and fuel cell testing at EWII
- Future work is focused on durability, materials characterization, and high current performance, with continued efforts on catalyst synthesis and repeatability.

# TECHNICAL BACKUP SLIDES

FC-162

# Acknowledgments

- Ford
  - Jun Yang
  - Chunmei Wang
  - Owen Lu
  - Chunchuan Xu
  - Mark Sulek
- Exothermics
  - Stephen DiPietro
- Oak Ridge National Lab
  - Gabriel Veith
- University of Michigan
  - Kai Sun
- Northeastern University
  - Sanjeev Mukerjee
  - Qingying Jia
  - Serge Pann
- EWII
  - Madeleine Odgaard
  - Debbie Schlueter

# Iso-Mass Activity Plot (RDE)