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: 3/31/2020
- Percent complete: 0%

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*: $18,489

* As of 3/31/2017

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

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.

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

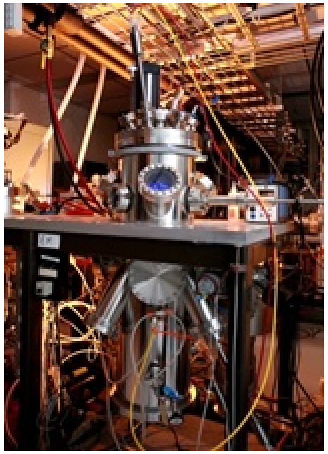
In addition to activity, this project will also focus on high current density.

Approach: Advantages of PVD

- Physical vapor deposition (PVD) for the production of an oxygen reduction catalyst has many advantages:
  - Elimination of a large number of production variables for solution prepared materials
    - Eliminated variables include humidity, mixing time and speed, and competitive adsorption of solubilized species
    - Should significantly improve reproducibility and lower costs
  - With nearly pure metal targets, reagent costs are lower and there are no impurities from precursors or solvents
    - Reduced material costs
    - Better performance
  - In principle, no drying or post-synthesis annealing is needed
    - Reduction of manufacturing steps
  - PVD process eliminates the need to treat aqueous or solvent waste (environmental benefit)

- Despite the use of PVD, a powder catalyst is still desired
  - Powder catalyst can be directly fabricated into inks and cast using conventional MEA fabrication technology

Can PVD be used to generate a powder catalyst for oxygen reduction?



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

Sputter system at Exothermics

Approach: PVD on Powders

- PVD can be done on powders:
  - Arc plasma deposition (350°C) downwards into a rotating chamber
  - Magnetron sputtering onto powder agitated by tumbling (similar to a front-loaded clothes dryer)
- PVD processing onto powders provides this project a unique position in the DOE catalyst portfolio

Schematic of ORNL system (batch size: 1-2 grams)

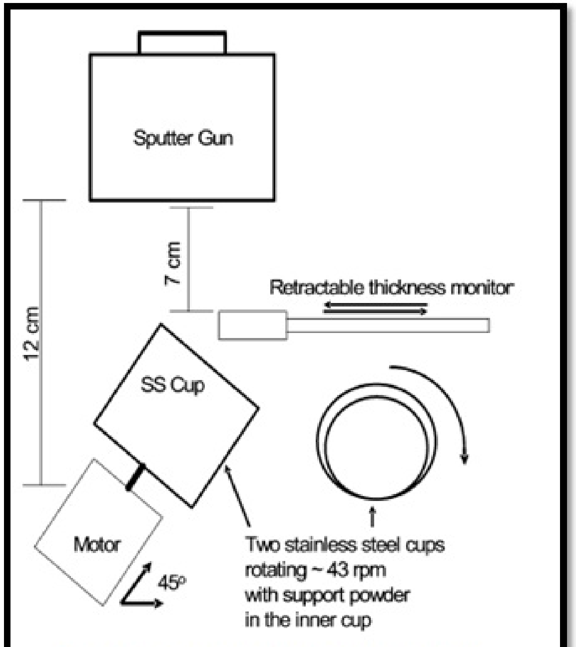


Fig. 1. Schematic representation of deposition chamber.

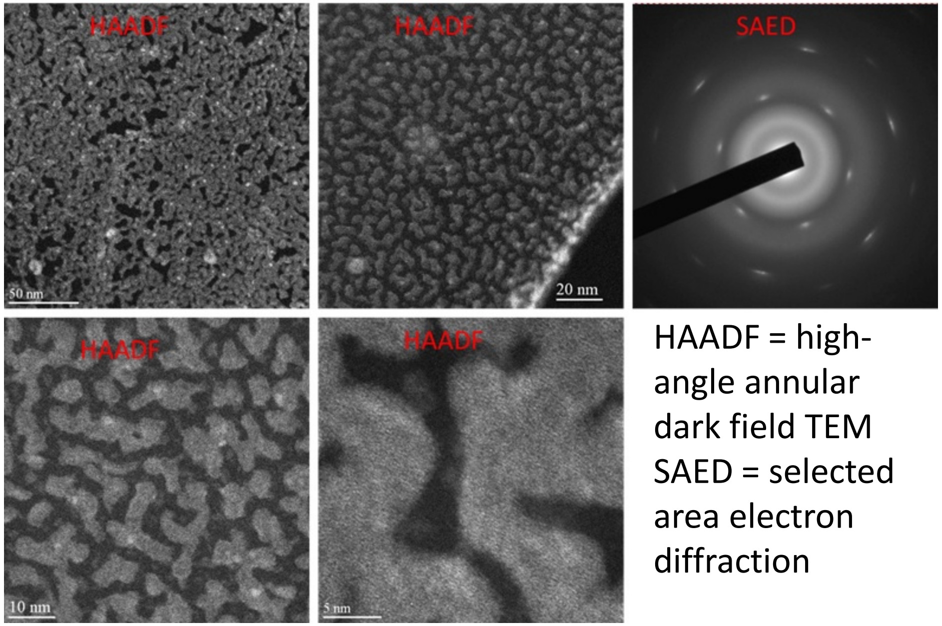
- Exothermics can perform magnetron sputtering onto powders at scales equivalent to 100K fuel cell systems per year with existing capacity
- Labor and energy costs do not exceed 1.5% of precious metal costs
- Reclaim costs per run need to be minimized
  - Target efficiency and utilization can be enhanced with novel geometries

- **PVD processing on powders to be pursued with magnetron sputtering**
- **Reclaim costs will be important to quantify and can be reduced with novel targets**
- **Labor and energy costs are small compared to precious metals**

Approach: Advantages of Niobia

Niobium oxide presents numerous advantages:

- Chemical stability in acid solutions
- Pt/NbO_x or NbO_2/C catalysts have been described to have 2-3X mass or specific activity versus Pt/C
  - Sasaki, Zhang, and Adzic, *Phys. Chem. Chem. Phys.* **10** (2008) 159–167
  - Trefz, Kremliakova, Susac, and Jankovic, 224th ECS Meeting, Abstract 1501 (2013)
  - Zhang et al., *J. Phys. Chem. C* **114** (2010) 16463-16474
  - Most NbO_2 or NbO_x was from ball-milling or sol-gel
- However, electrically insulating Nb_2O_5 can be a problem
  - Low activity shown in Senevirathnea, Huia, Campbell, Yec, and Zhang, *Electrochimica Acta* **59** (2012) 538– 547



HAADF = high-angle annular dark field TEM
SAED = selected area electron diffraction

Using sputtering, Ford discovered that 30 Å thick NbO_x grows into amorphous, isolated, worm-shaped islands on graphene (U.S. 9,468,909)

Niobium oxides are stable and can increase ORR activity, but electrically insulating Nb_2O_5 must be avoided. Ford found that PVD deposition of niobium oxide creates electronically conductive amorphous phases.

Approach: Proof of Principle Experiments

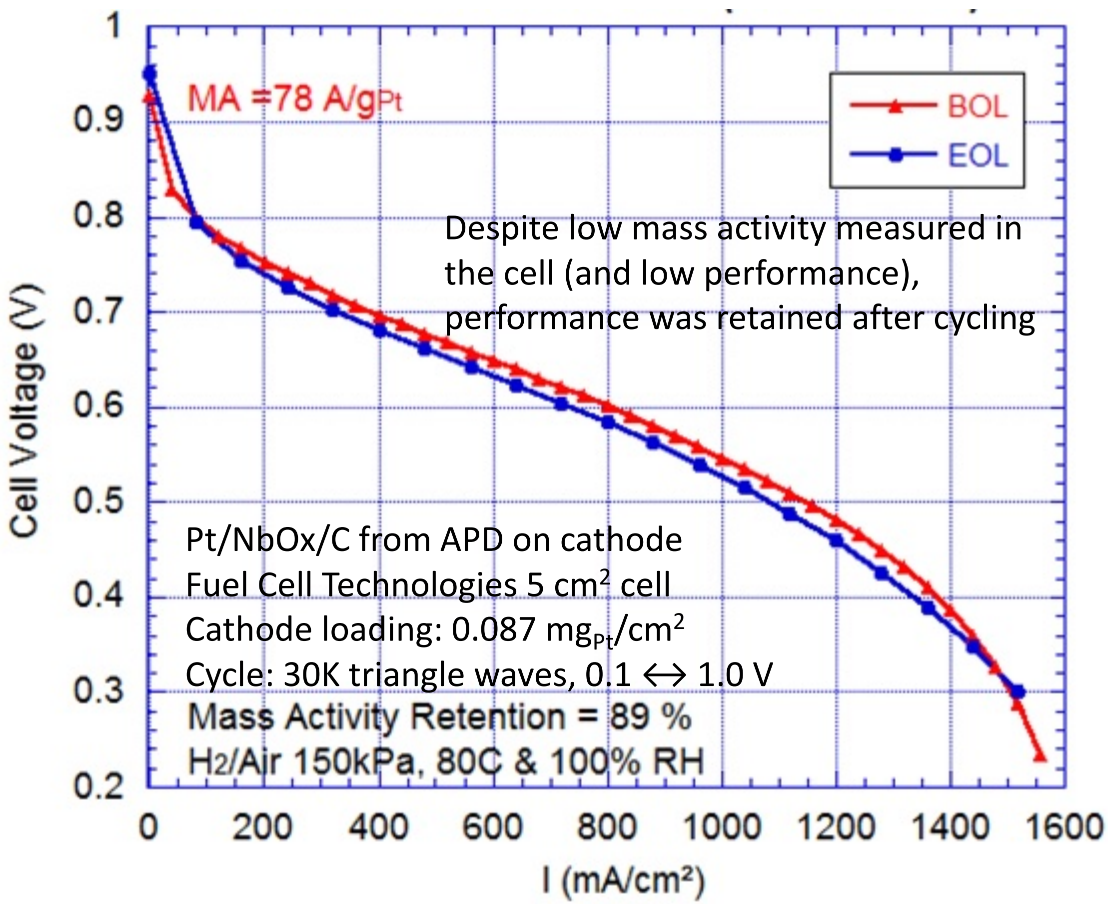
Cycle used in RDE: square wave, 0.1 ↔ 1.05 V, 25K cycles, O_2 bubbled

Catalyst	Pt wt%	Nb wt%	BMA (A/g_{PGM})	BSA (uA/cm^2)	BESCA (m^2/g)	RMA (%)
Pt/HSAC (commercial)	52	-	172	276	62	88
Pt/graphene (APD)	10	-	164	762	22	64
Pt/NbOx/graphene (APD)	10	2	309	800	39	85
Pt/NbOx/graphitized carbon (APD)	8	9	400	531	76	100
Pt/NbOx/graphitized carbon (APD)	23	20	224	409	55	72
Pt/NbOx/graphitized carbon (wet chem)	8	4	512	575	89	85
Pt/NbOx/HSAC (wet chem)	12	3	630	528	119	76
Pt/NbOx/HSAC (wet chem)	35	9	321	374	86	85

HSAC = high surface area carbon; BMA= beginning of life mass activity; RMA = retention of mass activity; BSA = beginning of life specific activity; BESCA = beginning of life ECSA; APD = arc plasma deposition

Ford testing on small batch Pt/NbOx/C samples from APD or wet chemistry confirmed that high activity is shown with incorporation of NbOx. NbOx helps to maintain activity during cycling with graphitized supports. Increasing Pt wt% with PVD is a challenge, and often coincides with decreased mass activity.

Approach: Addressing MT Resistances, Durability



Wire-wound bar method used for making cathode; Ford has since developed an ultrasonic spray method

Project plans to address low power density by 1) diagnosing mass transport resistances with a limiting current protocol, 2) iterating with electrode fabrication parameters to eliminate MT resistances

Limiting current protocol is >80 "mini-polarizations" using varying O_2 concentration, T, P to reveal P-dependent, and non-Fickian (Knudsen, ionomer film) MT resistances

Even with less advanced electrode fabricating processes that led to poor performance, cycling of the catalyst did not significantly reduce performance

Approach: Tasks and Schedule

- Project will begin with small batch (1 g) Pt/NbOx/C production at ORNL
  - Control factors in Tasks 1.1-1.2 include carbons, chamber dosing, P, T
  - Characterization (UM, NEU - Tasks 1.3, 1.6) and testing in RDE (Ford - Task 1.3) and fuel cells (EWII – Task 2)
  - Wet chemistry Pt/NbOx/C for baseline comparison (Task 1.4)

	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	■	■	■	■	■	■	■	■	■	■	■	■	■

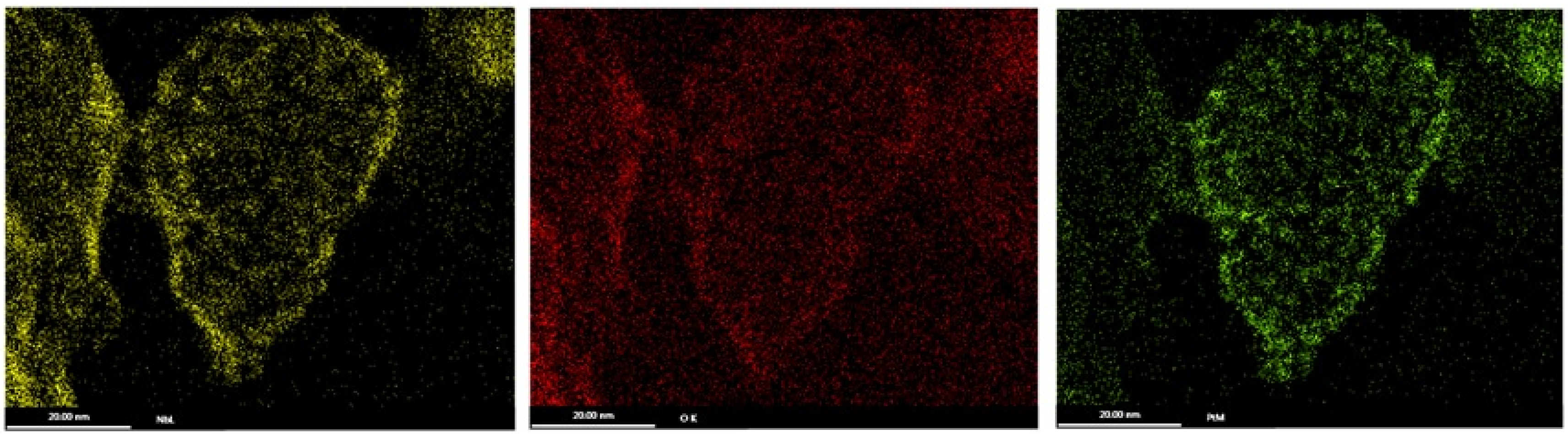
  - Preferred deposition parameters will be determined and used in scaleup at Exothermics (20-40 grams)
- Tasks 1.5 and 1.7 refer to chamber preparation at Exothermics, and catalyst processing respectively

Project will progress from understanding new PVD methodology at small scale, establishing preferred processing parameters, and then applying the learning on larger scale at Exothermics

Approach: Experienced Partners

- ORNL and Exothermics have already deposited Pt/NbOx/C powders (a few batches in 1Q 2016)
- UM has been able to distinguish Pt, Nb, O in TEM images for Pt/NbOx/C samples
- NEU has worked extensively on arc plasma deposited samples in XAS

TEM characterization showing that Pt, Nb, and O are well-dispersed through samples:



Niobium Oxygen Platinum

Catalyst synthesis and characterization partners are already familiar with Pt/NbOx/C system from prior work. Experience processing Pt/NbOx/C into MEAs at Ford will be used to help EWII get started.

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	Oak Ridge National Laboratory; University of Michigan
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.	Ford; Oak Ridge National Laboratory
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}	Ford; Oak Ridge National Laboratory
<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.	Oak Ridge National Laboratory; EWII

Special note: Although no specific milestones are assigned to Northeastern University, its XAS characterization will be used throughout the project to understand the causes of activity and durability, or lack thereof

Northeastern University
Center for Renewable Energy Technology

First budget period will focus on small batch catalyst synthesis at ORNL. Go/no-go based on achieving mass activity in a fuel cell.

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

Milestone #4 (Q5): Large batch PVD catalyst - Pt, Nb loadings at <10% variation (XRF)

Milestone #5 (Q6): Large batch PVD catalyst - 2-10 nm Pt particle sizes (TEM)

Milestone #6 (Q7): Large batch PVD catalyst - mass activity @ 0.9 V > 0.4 A/mg_{PGM} (RDE)

Milestones #7-9 (Q8): 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; < 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)

<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 ≥ 0.35 A/mg_{PGM}. Mass activity following electrocatalyst and support cycling > 0.21 A/mg_{PGM}** (60% of 0.35 A/mg_{PGM}).

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)

Milestone #11 (Q10): Large batch PVD catalyst, ≤ 0.125 mg_{PGM}/cm^2 – BOL mass activity of ≥ 0.44 A/mg_{PGM}

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.

Second and third budget periods will focus on Exothermics catalyst scaleup, as well as showing high power density and durability.

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. 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).
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

Accomplishments and Progress: Small Batch Sputtering

Research is focusing on ways to defeat funicular bonding from water, which keeps the support carbon aggregated together and prevents uniform coating

Preliminary work focused on optimizing deposition conditions to obtain optimized Pt/NbO_x dispersion.

- Identifying carbon source
- Mixing protocols
- Deposition conditions (pressure, rates, O_2/Ar ratio, time, etc.)

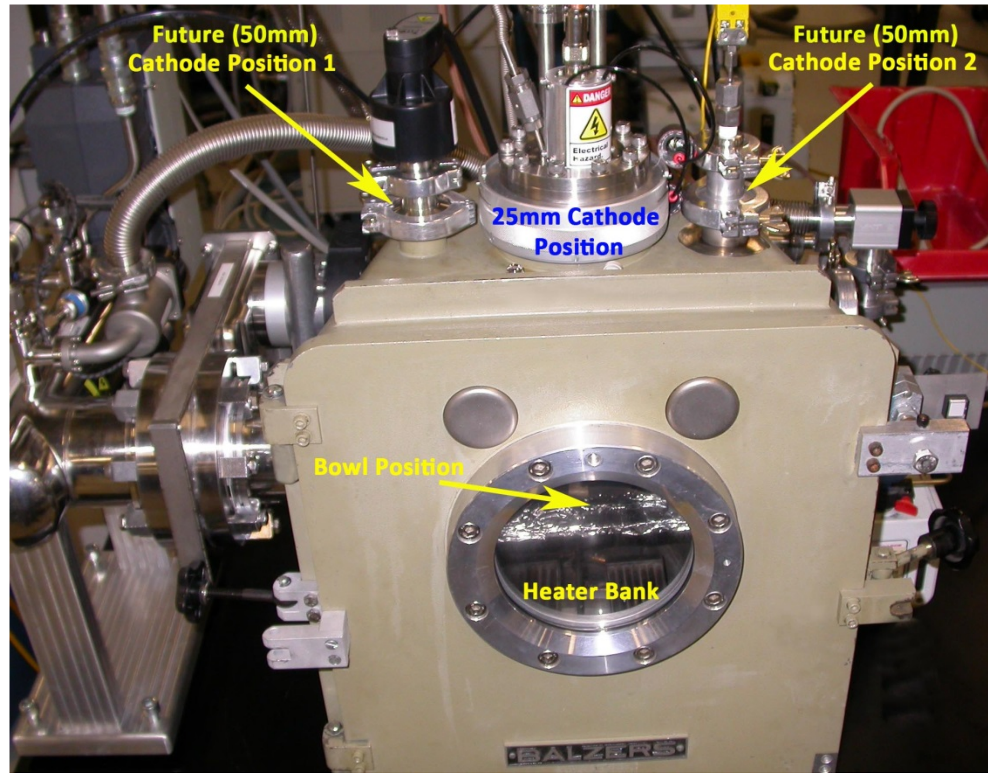
These variables will control catalyst particle size, weight loading and uniformity which will determine performance

OAK RIDGE National Laboratory

Goal is to maximize Pt in "egg-shell" configuration before getting to mass transport limitation in fuel cell.

Accomplishments and Progress: Large Batch Sputtering System Upgrades

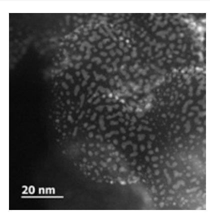
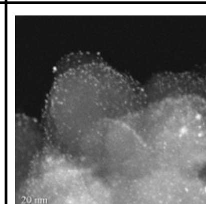
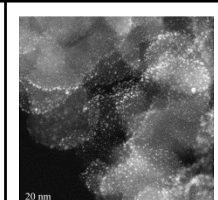
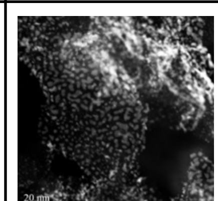
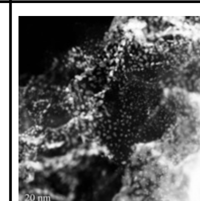
- Upgrading from one (25mm or 75mm) cathode to two 50mm cathodes
- Metallic or reactive deposition (oxides, nitrides, etc.,) possible via bipolar pulsed DC sputtering.
- Radiant heat and RF etch added for substrate de-gassing and functionalization.
- Improved deposition efficiency via use of new cathode and bowl positioning.



EXOTHERMICS INC

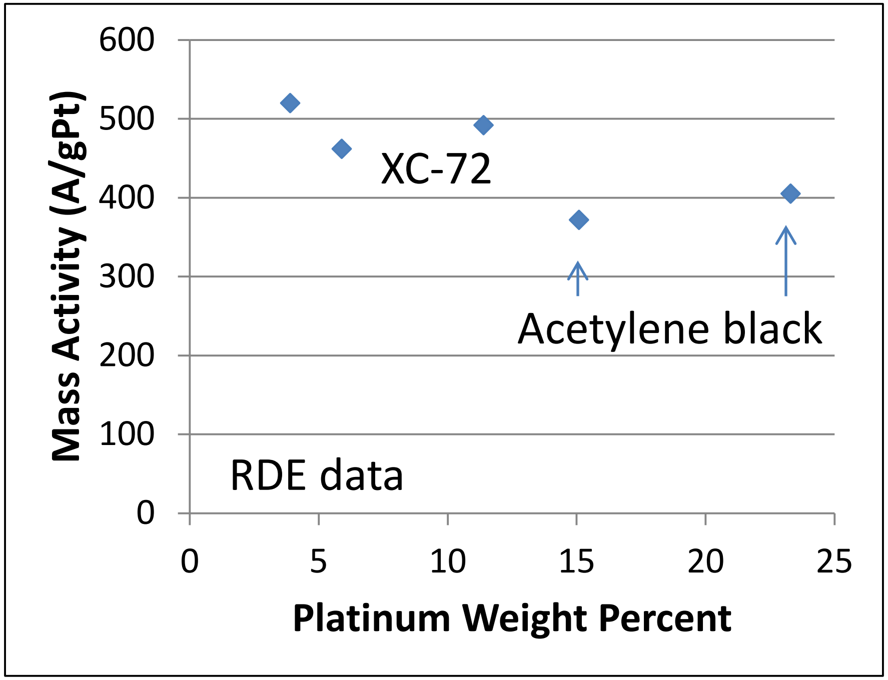
Accomplishments and Progress

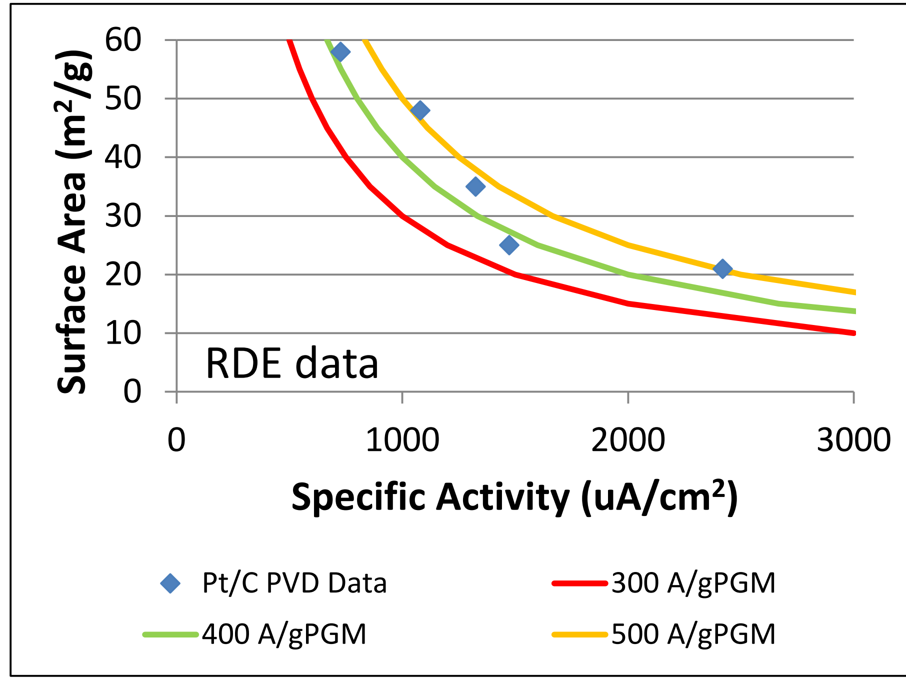
Tasks 1.1-1.3 have begun with deposition of Pt/C through PVD at ORNL. XRF, RDE performed at Ford. TEM, XPS at U Michigan.

Sample:	gmv-080	gmv-081	gmv-082	gmv-084	gmv-085
Carbon	XC-72	XC-72	XC-72	acetylene black	acetylene black
Deposition temperature	room	room	room	room	room
Deposition time (h:mm)	1:00	2:16	2:55	3:00	2:28
Deposition pressure (mtorr)	10	20	10	10	10
Use of stir bar?	No	Yes	Yes	No	Yes
Pt wt% (XRF)	11.4	3.9	5.9	15.1	23.3
Pt^0 percent (XPS, 4f region)	33	13	20	22	28
Pt^{2+} percent (XPS, 4f region)	37	39	42	47	33
Pt^{4+} percent (XPS, 4f region)	30	48	38	31	39
Pt^0 + Pt^{2+} percent (XPS, 4f region)	70	52	62	69	61
Average mass activity (A/gPt, RDE)	492	520	462	372	405
Average specific activity (uA/cm^2, RDE)	2418	1079	1325	1473	726
Average surface area (m^2/g, RDE)	21	48	35	25	58
TEM image					

PVD Pt/C from ORNL yields very small Pt particle size, yet very high mass and specific activities. Stir bar linked to higher surface area.

Accomplishments and Progress





- Higher Pt weight percent is still a challenge with PVD, but the project has achieved some line-of-sight toward higher Pt wt% with acetylene black carbon and stirring. Process could be improved with elevated temperature.
- RDE mass activities are already on the order of 300-500 A/g_{Pt}, although durability of Pt/C from PVD would not be expected to be good (small particles).
- For Pt/NbOx/C, oxygen % in plasma and water dosing are other parameters to explore.

Project has line-of-sight toward maintaining high activity at higher Pt weight percent. For Pt/NbOx/C synthesis, there will be additional parameters to explore.

Future Work

- Almost all of project still to come
- Catalyst synthesis
  - Selection of processing parameters, carbon
  - Small batch experimental designs at ORNL
  - Transfer of small batch understanding to Exothermics
  - Preparation of Exothermics chamber
  - Large batch experimental design at Exothermics
  - Refined cost analysis based on large batch sample parameters
- Catalyst characterization
  - TEM, XPS characterization at UM: particle size, compositional analysis, oxidation states
  - XAS characterization through Northeastern U.
  - XRF and RDE characterization at Ford: Pt, Nb wt%, mass activity
- Fuel cell testing
  - Selection of balance-of-MEA components and cell formats for testing
  - Polarizations to determine power density
  - Electrocatalyst cycling
  - Support corrosion cycling
  - Limiting current measurements to diagnose MT resistances
  - EIS characterization (HFR, proton conductivity) to diagnose ohmic losses

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 activity and durability opportunities offered by use of niobium oxide as a secondary support
- Amorphous niobium oxide is electrically conductive and appears to remain stable during both RDE and fuel cell cycling
- Project will focus on small batch (1 g) processing in the first budget period and then scale up to larger batches (20-40 grams) in the 2nd and 3rd budget periods.
- Project has milestones that address mass activity, durability, and power density. Go/no-go decisions are all premised on fuel cell performance.
- Most project partners have prior experience processing or characterizing Pt/NbOx/C catalysts.
- Pt/NbOx/C catalysts have shown higher activity and durability versus commercial Pt/C. However, increasing Pt wt% while maintaining activity will be a challenge.
- Recent work with Pt/C PVD samples show interestingly high mass activity and line-of-sight toward higher Pt wt%

TECHNICAL BACKUP SLIDES

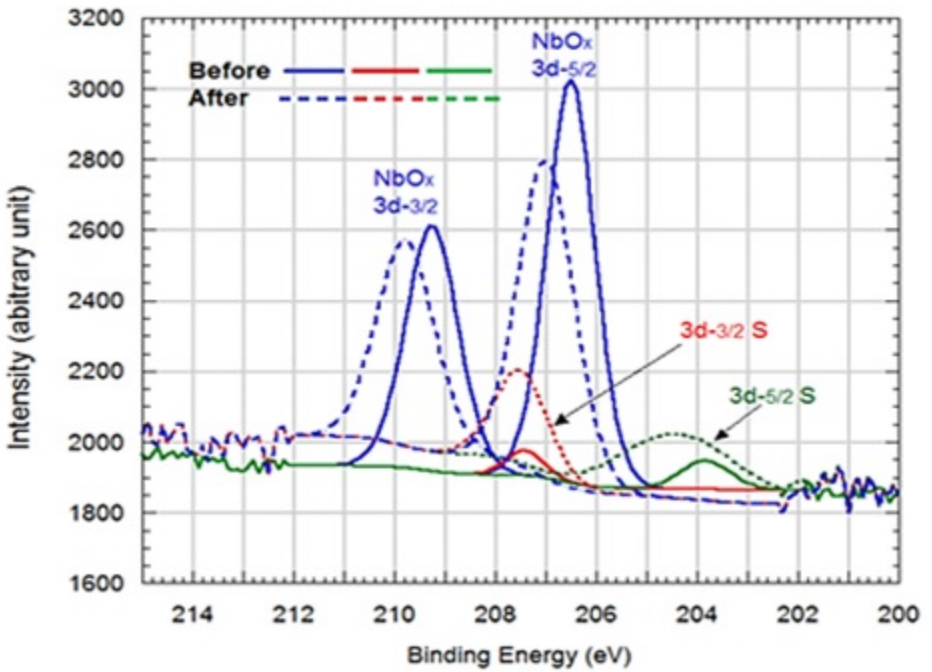
FC-162

Acknowledgments

- Ford
  - Jun Yang
  - Chunmei Wang
  - Owen Lu
  - Chunchuan Xu
- 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

Is Nb_2O_5 Formed During Cycling?

XPS of 13wt.% Pt / 10.wt% a-NbO_x / graphitized carbon as made and after 25K 0.1 ↔ 1.0 V cycles in oxygen (RDE)



Solid line shows the as-made sample, while the dotted line shows the sample after 25K cycles

The peak at 203.7 eV marked 3d-5/2S corresponds to +2, the peak at 206.6 eV marked as 3d-5/2 corresponds to +4

While there was some peak shift to a higher binding energy, a greater percentage of surface Nb was at lower binding energy (growth of low binding energy peaks)

Budget

Task	Budget Period 1 (1/1/17-3/31/18)	Budget Period 2 (4/1/18-3/31/19)	Budget Period 3 (4/1/19-3/31/20)	TOTAL
1 - Development, Characterization, and Validation of Catalyst Material and Development and Implementation of PVD process parameters	**$580,278**	**$570,318**	**$535,717**	**$1,686,313 (65%)**
Exothermics	*$190,062*	*$170,638*	*$194,570*	*$555,270*
Oak Ridge NL	*$89,000*	*$85,000*	*$54,000*	*$228,000*
Northeastern U.	*$147,700*	*$156,100*	*$156,100*	*$459,900*
U. Michigan	*$49,973*	*$54,349*	*$55,678*	*$160,000*
Ford	*$103,543*	*$104,231*	*$75,369*	*$283,143*
2 - Catalyst Layer Development and MEA Validation	**$217,429**	**$299,660**	**$286,058**	**$803,147 (31%)**
EWII	*$137,219*	*$239,540*	*$232,223*	*$608,982*
Ford	*$80,210*	*$60,120*	*$53,835*	*$194,165*
3 – Project Management and Reporting (Ford)	**$20,188**	**$41,696**	**$43,068**	**$104,952 (4%)**
TOTAL	**$817,895**	**$911,674**	**$864,843**	**$2,594,412**