WO₃ and HPA based systems for durable Pt catalysts in PEMFC cathodes

2012 DOE Hydrogen and Fuel Cells Program Review

John Turner

May 15th, 2012

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## Overview

### Timeline
- **Start Date:** 05/01/2010
- **End Date:** 04/30/2014
- **Percent Complete:** 40%

### Budget
- **Total project funding:** $2.9M
  - **DOE share:** $2.6M
  - **Cost share**
    - **CSM:** $204,315
    - **CU:** $54,000
- **Funding received in FY10:** $500k
- **Funding received in FY11:** $550k
- **Planned Funding for FY12:** $975k

### Barriers
- **Durability**
- **Cost**
- **Performance**

### Partners
- **S. George:** UC Boulder
- **A. Herring:** CSM
- **S. Hamrock:** 3M
- **K. Adjemian:** NTCNA
- **Tanaka Kikinzoku Kyogo (TKK)**

### Project lead – NREL
(John Turner, Anne Dillon, Katie Hurst, Bryan Pivovar, K.C. Neyerlin, Jason Zack, and Shyam Kocha)
Relevance: Objectives

Improve electrocatalyst, MEA durability, and activity through the use of Pt/WO₃ and HPA modification to approach automotive PEMFC activity (0.44 mA/mgₚt) and durability targets (5000h/10y).

- **Enhance Pt anchoring to support**
  - Suppress loss in Pt ECA under load cycling operations
  - Enhance electrocatalytic activity

- **Lower support corrosion**
  - Increased durability under automotive startup/shutdown operation.
  - Suppress Pt agglomeration/electrode degradation

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Simplify system and lower system cost
**Approach**

**NREL & CSM**
- Synthesize WO$_3$
- Characterize WO$_3$ & Pt/WO$_3$ for:
  - Conductivity
  - BET surface area
  - TEM

**CU – Steve George**
1. Prepare Pt nanoclusters on WO$_3$
2. Analyze the structures formed using FTIR, XPS, SEM, TEM, Raman, etc.,
3. Measure Pt particle size, BET, etc.,
4. Provide samples to CSM & NREL

**CSM – Andy Herring**
1. Synthesize HPA
2. Immobilize HPA to Pt/C
3. Prepare Pt nano/C
4. Immobilize HPA to C
5. Prepare Pt nano/HPA-C
6. Immobilize/Covalently bond HPA to WO$_3$
7. Prepare Pt nano/HPA- WO$_3$
8. Alternative WO$_3$ synthesis

**Electrochemical Characterization**

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NATIONAL RENEWABLE ENERGY LABORATORY
5.7.1 - Establish at least 2 standard test protocols to evaluate and benchmark the durability of alternative Pt supports. 12/11 Completed

5.7.2 - Obtain cyclic voltammograms (CVs) and mass activity for Pt on WO$_3$, HPA, or a combination of the two with electrochemical surface areas greater than 25 m$^2$/g Pt. 4/12 “yes”(ECA)

5.7.3 - Demonstration of controlled nano-structured Pt placement and loading on WO$_3$, HPA, or a combination having mass activity (0.28 A/mg Pt @ 900 mV iR-free) comparable to baseline Pt/C (DOE Status). 9/12 Not yet
Protocols for Electrocatalyst/Support Durability Evaluation

1.0–1.6 V Regime

- Support degradation
- Pt agglomeration

0.60–1.0 V Regime

- Pt dissolution
- Pt agglomeration

Start-up/Shut-down Regime

Normal Operating Regime

Scan Rate: 100 mV/s

Scan Rate: 500 mV/s

Durability Working Group Co-chairs: Debbie Myers & Rod Borup

Team for catalyst supports
Shyam Kocha (NREL)—Lead
KC Neyerlin (NREL), Eric Brosha (LANL), Mahlon Wilson (LANL), Lior Elbaz (LANL), Nilesh Dale (NTCNA), Vijay Ramani (IIT).
Accelerated Stress Test for Support Durability – Protocols tested at Nissan

<table>
<thead>
<tr>
<th></th>
<th>Nissan</th>
<th>NREL</th>
<th>DOE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temp</strong></td>
<td>60°C</td>
<td>Room Temp</td>
<td>Room Temp</td>
</tr>
<tr>
<td><strong>Scan Rate</strong></td>
<td>500 mV/s</td>
<td>100 mV/s</td>
<td>1.2 V Hold</td>
</tr>
<tr>
<td><strong>No of Cycles</strong></td>
<td>5000 Cycles</td>
<td>6000 Cycles</td>
<td>No Cycles</td>
</tr>
<tr>
<td><strong>Total time for test</strong></td>
<td>~ 8 Hrs</td>
<td>~ 24 Hrs</td>
<td>~ 400 Hrs</td>
</tr>
</tbody>
</table>
Nissan and NREL protocols result in comparable losses for ECA, $i_s$ and $i_m$.
Nissan protocol (60°C) takes only 8h due to higher temperature accelerant.
NREL protocol is conducted at RT and takes 24 h using low scan rate accelerant.
Synthesis
HWCVD Production of Tungsten Oxide Nanostructures
Synthesis at 150 Torr 4% $\text{O}_2$ in Ar, filament temperature $\sim$ 2000°C.

- Dramatic change in particle morphology
  - Lower furnace temperature
  - Sequential depositions lead to rod growth

Stoichiometry of $\text{WO}_x$ Controlled by Oxidation in Air

Different oxide stoichiometries are made by annealing in air. Hot-wire grown at RT is $\text{WO}_{1.7}$ (TGA)

NEXAFS data from SLAC to give us oxygen bonding

- 58.7 m$^2$/g$_{\text{WO}_x}$ (No anneal)
- 49.0 m$^2$/g$_{\text{WO}_x}$ (400°C 15 min)
- 47.9 m$^2$/g$_{\text{WO}_x}$ (400°C 60 min)
- 26.0 m$^2$/g$_{\text{WO}_x}$ (700°C 10 min)
Tungsten Oxide Wet Chemistry Synthesis

Pyrolysis of \((\text{C}_4\text{H}_9)_4\text{NW}_{10}\text{O}_{32}\).
(Tetrabutylammoniumdecatungstate)

XRD pattern—as synthesized WO₃ nanorods.

Raman

XRD pattern—as synthesized WO₃ nanorods.

Nanorods

Spindles

Needles

Plates

Porous
HPA Functionalization of Carbon and WO$_3$

- Stabilize nano-metallic particles
- Decompose peroxide
- Alter electrochemistry on Pt surface
- Conduct protons

Wells-Dawson Sandwich Fe$_4^{II}$ (H$_2$O)$_2$(P$_2$W$_{15}$O$_{56}$)$_2^{16-}$

HPA functionalization of Carbon black confirmed by EDX spectra.
A literature recipe* was modified significantly to synthesize size-controlled Pt nanoparticles by:

- Decreasing the temperature to 80°C
- Bubbling dilute CO into solution
- Gradually adding 0.25M NaOH over 3h

Results of Pt/HPA-C Preparation

- Dispersion of HPA-C material in water via ultrasonication (20 minutes)
- Addition of Pt colloid followed by ultrasonication for an additional 20 min
- Catalyst separation via Büchner filtration
- Drying at 200°C for 2 h

δ_{Pt} \cong 3.5 \text{ nm (XRD)}

STEM EDX analysis, FEI F20 UT, 200 kV, spot size 7, from red square area
Progress of Pt ALD on WO$_x$ materials

Initial ALD resulted in high Pt loading with large particle sizes.

With a higher flux (higher precursor temp) the nucleation was more uniform, leading to smaller particles throughout the sample.

Saturated exposure leads to more uniform coverage

60 Cycles
Pt precursor temperature = 70$^{\circ}$C
(14.1 wt% Pt)
NREL Atomic Layer Deposition of Pt

Current deposition capabilities

Smaller Pt particle size

Demonstrated Pt loading 1 – 23 wt% (not controlled)

Continue to increase the uniformity of Pt coverage.
Pt ALD on WO$_3$ – Scaling with Dual Rotary Reactor

Dual rotary reactor for uniform Pt particle growth on WO$_3$ nanorods at large scale.

- Computer controlled spinning enables uniform deposition.
- This system can hold a volume of 60 cm$^3$.
- Based on the powder density of WO$_3$, this corresponds to ~420 g / deposition.

New NREL Rotary ALD system for uniform scalable Pt deposition on WO$_x$ Powders

Able to coat powders or flat surfaces
Equipped for two heated and two room temperature precursors
Reactor volume ~100 cm$^3$

Funded by NREL LDRD
Electrochemical Characterization
Results: ECA Determination of Pt/WO$_x$

Formation of Hydrogen Tungsten Bronzes ($H_{0.18}WO_3$ and $H_{0.35}WO_3$)
$WO_3 + xH^+ + xe^- = H_xWO_3$ ($0 < x < 1$)

Formation of Substoichiometric Oxides
$WO_3 + 2yH^+ + 2ye^- = WO_{3-y} + yH_2O$ ($0 < y < 1$)

Results of Cu UPD on Pt/Vu Electrocatalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu UPD</th>
<th>CO</th>
<th>HUPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>47 wt% Pt/Vu</td>
<td>65</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>Pt Black</td>
<td>19</td>
<td>17</td>
<td>17</td>
</tr>
</tbody>
</table>
Cu UPD on Pt/WO$_x$ Electrocatalysts

![Graph showing Cu UPD on Pt/WO$_x$](image)

- **Cu Stripping**
- **Final CV**
- **Initial CV**

E vs RHE [V]

**Table: Cu UPD on Pt/WO$_x$ Electrocatalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu UPD</th>
<th>CO</th>
<th>HUPD*</th>
<th>$\delta_{\text{particle}}$</th>
<th>ECA</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 wt% Pt/WO$_x^a$</td>
<td>53</td>
<td>30</td>
<td>65</td>
<td>$5^c$</td>
<td>56</td>
</tr>
<tr>
<td>22 wt% Pt/WO$_x^b$</td>
<td>16</td>
<td>12</td>
<td>16</td>
<td>$9^d$</td>
<td>31</td>
</tr>
</tbody>
</table>

- **a)** ALD Deposited Pt on HWD WO$_x$ Nanorods
- **b)** Wet Chemistry Pt/WO$_x$

- **Catalyst**
- **Cu UPD** [m$^2$/g$_{Pt}$]
- **CO** [nm]
- **HUPD** [nm]
- **$\delta_{\text{particle}}$**
- **ECA** predicted

*From TEM, $^d$from XRD
Results: Conductivity of $\text{WO}_x$

**HWCVD 4 point probe for pellets**

$\text{WO}_x$ powders from wet chemistry @ RT, 500 N/cm$^2$, Au coated Cu plates
Results for Mass Activity: Pt/WO$_x$

**NREL Pt ALD on WO$_x$**

- Baseline Pt/C
- ALD Pt/WO$_x$
- ALD Pt/WO$_x$ + C

**NREL Pt Colloids on WO$_x$**

- Baseline Pt/C
- 20:80
- 16:64:20
- 10:40:50

Pt:WO$_x$:GCNF
Results: Impact on Mass Activity for HPA Loading on Carbon

Peak in mass activity observed at an HPA loading of ~3.5% - 18% improvement

<table>
<thead>
<tr>
<th>Loading SiW(_{11}) (wt% of support)</th>
<th>6,000 cycles</th>
<th>30,000 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0-1.6 V</td>
<td>Pt/C</td>
<td>57%</td>
</tr>
<tr>
<td>0.6-1.0 V</td>
<td>Pt/HPA-C</td>
<td>92%</td>
</tr>
</tbody>
</table>

7% HPA on carbon, mass activity retention (NREL Protocol)
Pt/SnO₂ Electrocatalysts

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Electrode Loading (mg/cm²)</th>
<th>Wt % Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SnO₂</td>
<td>18</td>
<td>29</td>
</tr>
<tr>
<td>Pt/SnO₂ + C</td>
<td>18.8</td>
<td>29</td>
</tr>
<tr>
<td>Pt/SnO₂ + C</td>
<td>9.2</td>
<td>12</td>
</tr>
<tr>
<td>Pt/SnO₂ + C</td>
<td>9.4</td>
<td>23</td>
</tr>
</tbody>
</table>

Electrocatalysts were evaluated in RDEs ‘as is’ as well as with 2 different amounts of added carbon black (GCNF) to increase the electronic conductivity of the catalyst layer. GCNF was used as it is a more durable carbon black than Ketjen black®.
Pt/SnO₂ Electrocatalysts: ORR Activity

Lower electronic conductivity—one of the causes for lower activity of Pt/SnO₂ electrocatalysts; the other being electrode dispersion.
Pt/SnO₂ Electrocatalysts: Cyclic Durability

0.6–1.0V, RT, 500 mV/s

1.0V–1.6V, RT, 100 mV/s

- Protocol (0.6–1.0V, RT, 500 mV/s) applied to baseline Pt/C and Pt/SnO₂ show similar losses in ECA. Losses are likely to be due to Pt dissolution which is independent of the support.
- Protocol (1.0V–1.6V, RT, 100 mV/s) applied to baseline Pt/C and Pt/SnO₂ show higher losses for Pt/C catalysts since the SnO₂ support is more corrosion resistant.
Collaborations

• **CU Boulder: subcontractor – University**
  – ALD growth of Pt on $WO_x$

• **CSM: subcontractor – University**
  – Synthesis of $WO_3$ and preparation and attachment of HPA to Pt/$WO_3$

• **3M: subcontractor – Company**
  – Advice on thin films electrocatalysts

• **NTCNA: consultant – Automotive Company**
  – Support on fuel cell testing & AST protocols

• **Tanaka Kikinzoku Kyogo (TKK) — Commercial Electrocatalyst Manufacturer**
Future Work (2012)

1. Complete a systematic conductivity of WO$_x$ films with and without conductive matrices to guide catalyst ink formulations.

2. Improve wet-chemistry Pt deposition and ALD Pt deposited on WO$_x$ and characterize electrochemically with and without a conductive matrix to obtain mass activities comparable to Pt/C
   - Decision on ALD Pt/WO$_x$ vs. wet-chemistry Pt/WO$_x$ for meeting program goals (December 2012)

3. Evaluate alternative catalysts such as Pt-alloys (on WO$_x$ + conductive matrix) in RDE for higher activities. (2013)

4. Scale-up selected electrocatalyst system synthesis process to prepare Pt/WO$_x$ + conductive matrix in gram quantities for MEA preparation (2013, 2014)

5. Evaluation of HPA incorporation into catalyst layers of MEA to ascertain proton conduction and durability impacts (2013, 2014)

Summary

1. WOₓ was prepared using HWCVD having BET surface area of ~ 50 m²/g; WOₓ also prepared using wet-chemistry techniques

2. CU-Boulder deposited Pt using ALD:
   - These materials did not initially produce small and uniform particles of Pt/WOₓ
   - On refinement of the ALD conditions, smaller particles of Pt were obtained
   - The wt% of Pt/WOₓ is still very low and not suitable for electrochemical characterization
   - A rotary system is being used currently to increase the yield of ALD Pt/WOₓ and improve the Pt particle distribution

3. NREL also attempted ALD of Pt/WOₓ; these materials had a reasonable Pt wt % and electrochemical characterization resulted in a mass activity of ~100 mA/mg (ALD Pt/WOₓ with inclusion of carbon black)

4. Conductivity of WOₓ pellets was measured using Vander Paw technique as well powders in an in-house conductivity cell.

5. AST protocols for evaluating durability of alternative supports were developed with the DWG

6. ECA issues were addressed using three different protocols.

7. Pt colloids were prepared (CSM) that were subsequently deposited on HPA functionalized C; these materials were electrochemically characterized and exhibited ~15–20% higher mass activity that Pt/C and improved durability under cycling.

8. Pt/SnO₂ obtained from a commercial catalyst supplier (TKK) was evaluated in RDE. These catalysts also achieved activities comparable to baseline Pt/C after the inclusion of graphitized carbon black to the ink formulation. These materials demonstrated higher cyclic durability compared to baseline Pt/C
Pt/C Activity Benchmarks: RDE, 0.1M HClO₄, Nafion®-based Inks

1. Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs, H Gasteiger, S Kocha, B Sompalli, F Wagner, Applied Catalysis B Environmental (2005), Volume: 56, Issue: 1-2, Publisher: ELSEVIER SCIENCE BV, Pages: 9-35.


### Literature on Oxide Supports 2012

<table>
<thead>
<tr>
<th>Reference</th>
<th>System Evaluated</th>
<th>Key Results: $d_p$, ORR Activity, e-conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z. Sun, H. C. Chiu, A.C.C. Tsueng—Univ. Greenwich, UK</td>
<td>10wt% Pt/WO$_3$/C&lt;br&gt;0.5M H$_2$SO$_4$;</td>
<td>$d_p = 1–3$ nm&lt;br&gt;ORR Activity Pt/WO$_3$/C &gt; Pt/C</td>
</tr>
<tr>
<td>Saha, Banis, Zhang, Li, Sun, Cai, Wagner—General Motors</td>
<td>15 mm long, 20–60 nm dia&lt;br&gt;Nanowires W$<em>{18}$O$</em>{49}$&lt;br&gt;Grown on carbon microfiber paper</td>
<td>$d_p = 2–4$ nm&lt;br&gt;ORR activity Pt/W$<em>{18}$O$</em>{49}$ on C = x4 Pt/C</td>
</tr>
<tr>
<td>Suzuki, Nakagawa, Ishihara, Mistushima, Ota—Yokohama Nat’l Univ.</td>
<td>Pt/WO$_3$; Pt/V$_2$O$_5$, Pt/SnO$_2$; Pt/Cr$_2$O$_3$; Pt/GC&lt;br&gt;RF Sputtering onto C</td>
<td>ORR activity Pt/V$_2$O$_5$ &gt; Pt/WO$_3$ = Pt/C</td>
</tr>
<tr>
<td>Savadogo and Beck—Ecole Polytech, Quebec</td>
<td>5%Pt- 40%WO$_3$&lt;br&gt;PAFC, 180$^\circ$C</td>
<td>ORR activity $\sim$ x2 Pt/C</td>
</tr>
<tr>
<td>Huang, Ganeshan, Popov;—Univ. S. Carolina</td>
<td>Rutile Phase–Nb$<em>{0.25}$Ti$</em>{0.75}$O$_2$&lt;br&gt;0.5M H$_2$SO$_4$; RDE</td>
<td>$d_p = 3–4$ nm&lt;br&gt;ORR Activity Pt/Nb$<em>{0.25}$Ti$</em>{0.75}$O$_2$ = x1 Pt/C</td>
</tr>
</tbody>
</table>

Equal or enhanced ORR electrocatalytic activities have been reported in the literature—generally requiring a conductive matrix like carbon black or doping of the oxide support and often have been compared to Pt/C that have lower values than obtainable today for commercial electrocatalysts.
Optimal Synthesis Conditions Result in a Single Crystalline Phase

**X-ray Diffraction (XRD)**
- Single Crystalline $\gamma$-monoclinic $\text{WO}_3$ Phase
- Multiple Phases
- Crystalline / Amorphous
- Amorphous

**Raman Spectroscopy**
- Single Crystalline $\gamma$-monoclinic $\text{WO}_3$ Phase
- Multiple Phases
- Crystalline / Amorphous
- Amorphous

300°C, 4% $\text{O}_2$ in Ar, filament ~ 2000°C
Pt ALD Reaction Sequence

D.N. Goldstein, S.M. George Thin Solid. Film. 5339 (2011) 519
HPA Background

• **Benefits**
  – Acts like 1 nm spheres of WO$_x$
  – Enhances the ORR
  – Stabilizes Pt nano-particles
  – Decomposes peroxide
  – Improves CO tolerance
  – Excellent proton conductors

• **Challenges**
  – Soluble in water
  – Possible mass transport issues

Challenges may be overcome by immobilizing HPA via covalent linkages to the carbon