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

2014 DOE Hydrogen and Fuel Cells Program Review

John Turner

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Overview

Timeline
• Start date: 05/01/2010
• End date: 04/30/2014
• Percent complete: 100%

Budget
• Total funding spent: $2.9M
• Total Project value: $2.9M
• Cost Share percentage: 9%

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/WO\textsubscript{3} and Heteropoly Acid (HPA) modification of carbon support to approach automotive PEMFC activity (\(0.44 \text{ mA/mg}_{\text{Pt}}\)) 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

Simplify and lower system cost
Develop Accelerated Tests for Durability Support: Protocols

**RDE Accelerated Test for Support Corrosion**

<table>
<thead>
<tr>
<th></th>
<th><strong>Nissan</strong></th>
<th><strong>NREL</strong></th>
<th><strong>DOE</strong></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>Time to complete the test</strong></td>
<td>~ 8 Hrs</td>
<td>~ 24 Hrs</td>
<td>~ 402 Hrs</td>
</tr>
</tbody>
</table>
**Protocol Comparisons – Pt/C Results**

- 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.
Approach

**NREL**

Supply WO₃ to CU for Pt ALD deposition
Supply WO₃ to CSM for HPA modification and Pt deposition
Charac. WO₃ & Pt/WO₃ for - Conductivity - BET surface area - TEM

**CU – Steve George**

1. Prepare Pt nanoclusters on WO₃
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 WO₃
7. Prepare Pt nano/HPA- WO₃ Prepare Pt nano/HPA- WO₃ hybridized with HPA-C
8. Alternative WO₃ synthesis

**Electrochemical Characterization**

NATIONAL RENEWABLE ENERGY LABORATORY
Pt/WOx Electrocatalysts

Accomplishments

Other oxides, carbide and nitrides were also screened.
HWCVD Production of Tungsten Oxide Nanostructures
Synthesis at 150 Torr 4% O₂ in Ar, filament temperature ~ 2000°C.

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

Controlling the stoichiometry of $\text{WO}_x$ by subsequent oxidation in air.

- Different oxide phases are made upon oxidation
- Sub-stoichiometric material should have higher conductivity
- The stoichiometry of $\text{WO}_x$ may impact subsequent Pt deposition

Samples are heterogeneous
Tungsten Oxide Wet Chemistry Synthesis

Pyrolysis of \(((C_4H_9)_4N)_4W_{10}O_{32}\).

XRD pattern—as synthesized \(WO_3\) nanorods.

Raman

Nanorods

Spindles

Needles

Plates

Porous
Pt Colloid Synthesis (outcome)

- A literature recipe* was modified significantly to synthesize Pt nanoparticles of controlled size by:
  - Decreasing the temperature to 80°C
  - Bubbling dilute CO into solution
  - Gradually adding 0.25M NaOH over 3h

Tungsten Bronze Formation Interferes with Standard Electrochemical Surface Area Measurements Techniques

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)

Cu UPD on Pt/WO$_x$ Electrocatalysts

![Graphs showing CVs with Cu Stripping, Final CV, and Initial CV](image)

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

### Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu UPD</th>
<th>CO</th>
<th>HUPD*</th>
<th>ECA [m$^2$/g$_{Pt}$]</th>
<th>$\delta_{\text{particle}}$ [nm]</th>
<th>ECA predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 wt% Pt/WO$_x^a$</td>
<td>53</td>
<td>30</td>
<td>65</td>
<td>56</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>31</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$_x$
- $^c$ From TEM
- $^d$ from XRD
Mass activity of ALD Pt/WO$_x$ is low due to low conductivity of WO$_x$.

Adding carbon (graphite nanofibers – GNF) improves conductivity, but still far short of baseline.

From NREL ALD
Challenges: Electronic Conductivity

- Oxides supports have low electronic conductivity
- Addition of carbon matrix enhances the overall conductivity
- 3 electron pathways
  - Contact point between Pt and support: RA
  - Electronic conductivity through the support: RB
  - Electronic conductivity through the added carbon matrix: RC
  - Coating of Nafion® ionomer on Pt and WO_x and C not shown: R_Nafion
Mass Activity of Pt/C vs. ALD Pt/WO$_x$

WO$_x$ based electrocatalysts did not meet Pt/C baseline activity.
WO$_3$ Semiconductor Energetics

- WO$_3$ will block carrier transport for reactions in the gap.
- Sub-stoichiometric WO$_3$ doesn’t provide conductive path.
- To obtain good conductivity, states must be created in the gap via alloying.
- Impact of alloying on the stability is unknown.

Intergap states could provide conducting pathway.
Strategy for Continuous Pt ALD Films Using W Adhesion Layer

Continuous film of Pt would help conductivity, but needs a continuous W adhesion layer. Attempted to make a W film via a hydrogen plasma, but didn’t work for mesostructured WO₃.
Results for Pt ALD on WO$_x$ Particles in Plasma Reactor used for Flat Substrates

200 cycles - MeCpPt(IV)Me$_3$ with H$_2$ plasma at 120ºC

Attempt to produce a W film via a hydrogen plasma to make a continuous film of Pt, but didn’t work for mesostructured WO$_3$. Pt particles are still the result.
Atomic Layer Deposition of Platinum Nanoparticles on Titanium Oxide and Tungsten Oxide Using Pt(hfac)$_2$ and Formalin as the Reactants

Virginia R. Anderson, Noemi Leick, Joel W. Clancey, Katherine E. Hurst, Kim M. Jones, Anne C. Dillon and Steven M. George

$^1$Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, 80309; $^2$Technische Universiteit Eindhoven, P.O. Box 513, 5600 MB Eindhoven; $^3$National Renewable Energy Laboratory, 1617 Cole Blvd, Golden, Colorado, 80401; $^4$Dept. of Mechanical Engineering, University of Colorado, Boulder, Colorado, 80309

ACKNOWLEDGEMENTS

This work is dedicated to Dr. Anne C. Dillon who was a former student and collaborator. Her early passing took away a colleague with deep insight and infectious enthusiasm. This work was funded by the DOE under the EERE Fuel Cell Technology Program. We thank Dr. Andrew Cavanagh for X-ray photoelectron spectroscopy (XPS) sample analysis. We also appreciate useful conversations on Pt ALD with Dr. Layton Baker who is now at the Jet Propulsion Laboratory.
Corrosion Currents on Au disk (Corrected)

Results:
• TiC is the worst. From the inset WC is also less than ideal, and TiN is questionable.
• TiO₂, TaC, and WO₃ appear to be the best for corrosion resistance.
Pt/SnO$_2$ Electrocatalysts: SEM

Better dispersion

29 wt% Pt/SnO$_2$

12 wt% Pt/SnO$_2$ + C

Pt/SnO$_2$ Carbon nanofibers providing interconnects
Lower electronic conductivity—one of the causes for lower activity of Pt/SnO₂ electrocatalysts; the other being electrode dispersion.
Nafion-free results are better due to Nafion blocking or slowing down oxygen diffusion. Note: this only works for an RDE.
Pt/SnO₂ Electrocatalysts: Cyclic Durability

- 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.

**Graphs:**
- **0.6- 1.0V, RT, 500 mV/s**
  - Baseline Pt/C
  - Pt/SnO₂
- **1.0V- 1.6V, RT, 100 mV/s**
  - Pt-HSC
  - Pt-Vu
  - Baseline Pt/C
Pt/HPA-Graphitized C Electro catalysts

Accomplishments

Based on FY13 work on Pt/Ketjen Black-HPA, Fuel Cell Tech Team and DOE recommendation was to evaluated Pt/graphitized carbon-HPA.
**HPA Functionalization to C, Pt/C, WO₃ and Pt/WO₃**

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

**Immobilized HPAs as Catalyst Supports**

HPA functionalization of Carbon black confirmed by EDX spectra.

Wells-Dawson Sandwich

Fe₄⁺ (H₂O)₂(P₂W₁₅O₅₆)₁₆⁻
The strong effect on the Pt edge with increasing HPA loading implies to us that Pt is preferentially binding at the HPA locations. In contrast, there is very little change in the W edge implying that the Pt-W interaction remains approximately unchanged as HPA loading is increased.

The maximum observed in Pt mass activity is likely a result of competing effects of the Pt-W interactions shown here and occupation of preferential binding sites by the HPA.
Pt/HPA-C Durability

The 0.6-1.0 V cycling (30,000 cycles, 500 mV/s) was used to evaluate Pt dissolution, while 1.0-1.6 V cycling (6,000 cycles, 100 mV/s) evaluated support corrosion. HPA loading was chosen such that initial activity was near equal to Pt/C (blue bars). In both cases, HPA helped maintain catalyst activity by slowing particle growth (red bars).

*All scale bars are 20 nm.
**Insets show Pt particle size distribution in 0.5 nm increments starting from 1.5 nm.

In this next set of experiments (to slide 34) however, this data shows a decrease in the activity after HPA modification. The reason for the difference is not clear.
Electrochemical Activity for Wet Chemistry Catalysts (Pt/V, Pt/HT-V)

Mass Activity Target = 275 mA/mg_{Pt}; 380 mA/mg_{Pt}

![Bar chart showing specific activity, mass activity, and ECA for different Pt/V and Pt/HT-V benchmarks. The chart compares various compositions such as 46wt%Pt/HSC, 46%Pt/V, 31%Pt/V, 31%Pt/HT-V, and 32%Pt/HT-V (3.2%HPA). The targets are indicated with dashed lines.]
Electrochemical Activity for Wet Chemistry Catalysts (Pt/G-KB)

Mass Activity Target = 275 mA/mg_{Pt}

![Bar graph showing specific activity, mass activity, and mass activity per gram of Pt for different samples. The target is indicated by a horizontal line.](image-url)
Electrochemical Activity for Wet Chemistry Catalysts (Pt/GCNF)

Mass Activity Target = 275 mA/mg$_{Pt}$

Wet chemistry based

Pt/GCNF

- Specific Activity $\mu$A/cm$^2_{Pt}$
- Mass Activity mA/mg$_{Pt}$
- ECA m$^2$/g$_{Pt}$

Target
Pt/Ketjen Black **Baseline:**
BOL= 100 m²/gₚt; EOL= 46 m²/gₚt; 39.5% Loss

Pt/GCNF:
BOL= 82 m²/gₚt; EOL=71 m²/gₚt; 13.4% Loss

Pt/GCNF-HPA:
BOL= 68 m²/gₚt; EOL=52 m²/gₚt; 23.5% Loss

Pt/GCNF exhibits improved durability compared to baseline, but for post-HPA treatment, the losses are slightly higher.
For these samples, the HPA treatment does not result in an improvement of the durability of the catalyst system.
FY 2014 1st Quarter Milestone

• Meet the Pt/C baseline activity of \(275 \text{ mA/mg}_{\text{Pt}}\) mass activity at 0.90 V, 100 kPa with either the HPA modified carbons or the non-carbon supports, but show a 2x greater cyclic durability in RDE tests.  

12/31/2013

Milestone has been met; but HPA treatment itself does not cause any improvement in durability of a graphitized carbon support.

2nd and Final Quarter Milestone

• Evaluate remainder of the Pt/HPA treated carbons with RDE

MEA testing was a no-go and the program was ended early with some cost saving to DOE

3/31/2014