

V.D.9 Tungsten Oxide and Heteropoly Acid Based System for Ultra-High Activity and Stability of Pt Catalysts in PEM Fuel Cell Cathodes

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Project Start Date: May 2010

Project End Date: April 2014

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project addresses the precipitous corrosion and electrode degradation that takes place when using carbon-supported Pt catalysts (Pt/C) in automotive applications during start-up and shut-down operations. Alternative supports such as WO_x as well as HPA-functionalized carbon blacks are being synthesized and evaluated for improved corrosion resistance while maintaining or improving on the activity in comparison to conventional Pt/C. Studies are first being conducted in rotating disk electrode (RDE) setups due to the small quantity of materials synthesized and will be followed by testing in fuel cells. The following targets are being addressed:

- Mass activity: $>275 \text{ mA/mg}_{Pt}$
- Durability under start-up/shut-down cycling: ECA loss $<40\%$

Fiscal Year (FY) 2012 Objectives

Improve Pt electrocatalyst and membrane electrode assembly (MEA) durability and activity through the use of tungsten oxide (Pt/WO_x) and heteropoly acid (HPA) catalyst support modifications to approach DOE targets for activity (0.44 mA/mg Pt) and durability (5,000 hours/10 years) for automotive polymer electrolyte membrane fuel cells.

- Enhance Pt anchoring to support:
 - Suppress loss in Pt electrochemical area (ECA) under load cycling operations.
 - Enhance electrocatalytic activity.
- Lower support corrosion:
 - Increase durability under automotive startup/shutdown operation. Suppress Pt agglomeration and electrode degradation.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

FY 2012 Accomplishments

- Synthesized well-distributed and high wt% Pt/WO_x using atomic layer deposition (ALD) for Pt and hot-wire chemical vapor deposition (HWCVD) for tungsten oxide.
- Synthesized Pt nanoparticles using a colloidal technique and deposited onto carbon functionalized with HPA.
- Established protocols to evaluate and benchmark the durability of alternative supports.
- Measured the electronic conductivity of WO_x and WO_x mixed with carbon powders.
- Measured the electrochemical activity of Pt black- WO_x mixtures and determined the amount of carbon black required to meet the activity of baseline Pt/C.
- Determined the most accurate and relevant method of determining the surface area of Pt/WO_x catalysts.
- Obtained electrochemical areas for Pt/WO_x that exceeded $25 \text{ m}^2/\text{g}$.
- Synthesized and evaluated Pt/WO_x in RDE with a mass activity of 175 mA/mg_{Pt} .
- Synthesized and evaluated Pt/C-HPA with a mass activity of 300 mA/mg_{Pt} .
- Demonstrated improved durability of Pt/C-HPA over Pt/C.
- Demonstrated activity of Pt/SnO_2 to meet that of Pt/C and durability exceeding that of Pt/C.



Introduction

Conventional nanoparticle Pt/C electrocatalysts used in automotive fuel cells suffer significant degradation during start-up and shut-down operations. Under these conditions the potential at the cathode approaches ~1.6 V for short bursts of time, leading to carbon corrosion. In this project we evaluate alternative supports for Pt that might be more stable and corrosion resistant than conventional carbon blacks. Developing such a support will allow the fuel cell system to be simplified, lowering the costs and simultaneously increasing the durability.

Approach

Oxide supports such as WO_x are grown using a HWCVD method and then ALD or wet-chemistry is used to deposit Pt nanoparticles on the support. These oxide supports are inherently more stable than carbon black but have drawbacks in terms of lower surface area and lower electronic conductivity as compared to the carbon blacks. Therefore the electronic conductivity and the electrochemical activity as a function of adding small quantities of highly graphitized carbon blacks/fibers are being studied. The added graphitized carbon is not susceptible to corrosion because the Pt nanoparticles have a closer interaction with the WO_x or C-HPA. Durability cycling protocols that simulate start-up/shut-down were developed to quantify the suppression of degradation with the alternative corrosion resistant supports.

Results

Synthesis: Tungsten oxide nanostructures were prepared using HWCVD. Material synthesis employing sequential depositions at room temperature led to rod-like nanostructured growth as shown in Figure 1 (a,b). The stoichiometry and crystalline structure of WO_x nanoparticles can be controlled by subsequent annealing in air, as demonstrated by the X-ray diffraction spectra (not shown). Near edge X-Ray absorption fine structure spectroscopy data were obtained from the Stanford Linear Accelerator Center to provide insight into oxygen bonding on tungsten oxide. Our initial ALD work resulted in a high Pt loading with large particle sizes and agglomeration. By increasing the precursor temperature, a higher flux of Pt enabled more uniform nucleation, leading to smaller particles throughout the sample. Figure 1 (c) depicts the Pt nanoparticles on tungsten oxide rods with a fairly uniform distribution for a 25 wt% Pt material. Recent work has resulted in materials with up to 50–60 wt% Pt loadings. At this high loading, the particles almost reach full coverage of the WO_x surface, as shown in Figure 1 (d). This has been achieved by performing ALD in a stop flow configuration with increased dosing time of the

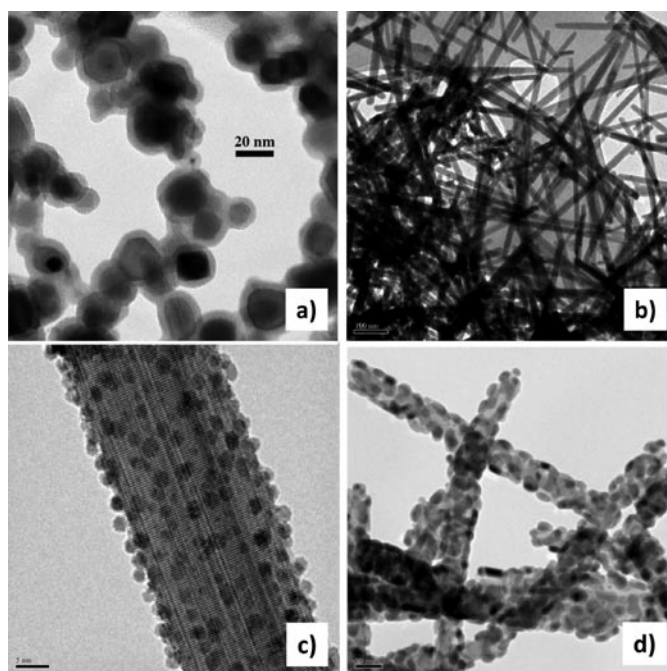


FIGURE 1. TEM micrographs (a, b) for WO_x after a few and after 60 cycles showing nanorods; (c) Pt/ WO_x at 25 wt% Pt; and (d) Pt/ WO_x at 50 wt% Pt

platinum precursor as well as increased soak times during deposition.

HPA functionalization of carbon was carried out to: i) shield carbon against corrosion; ii) stabilize nano-metallic particles; iii) decompose peroxide; iv) alter electrochemistry on Pt surface; and v) conduct protons. These functionalized carbons were used as supports for depositing Pt nanoparticles that were synthesized using a colloidal preparation. A literature recipe [1] was modified significantly to synthesize small controlled Pt nanoparticles by decreasing the temperature to 80°C; bubbling dilute CO into solution; and gradually adding 0.25 M NaOH over 3 h. Figure 2 (a) illustrates the transmission electron microscope (TEM) image and particle size distribution of the synthesized colloids. The Pt colloids were deposited onto the HPA-functionalized carbon, Figure 2 (b), by the following process: i) dispersion of HPA-C material in water via 20 min ultrasonication; ii) addition of Pt colloid followed by ultrasonication for an additional 20 min; iii) catalyst separation via Buchner filtration; and iv) drying at 200°C for 2 h.

Conductivity: Conductivity measurements were carried out in an in-house experimental setup that consisted of Au-coated Cu plates. The density and conductivity of WO_3 and WO_2 as well as WO_x mixed with various amounts of a graphitized carbon were determined at various loads and are reported in Figure 3 at 500 N/cm². The bulk conductivity of the WO_x materials was also investigated by four-point probe measurement in the Van der Pauw geometry. The as-produced materials were pressed into a pellet and the

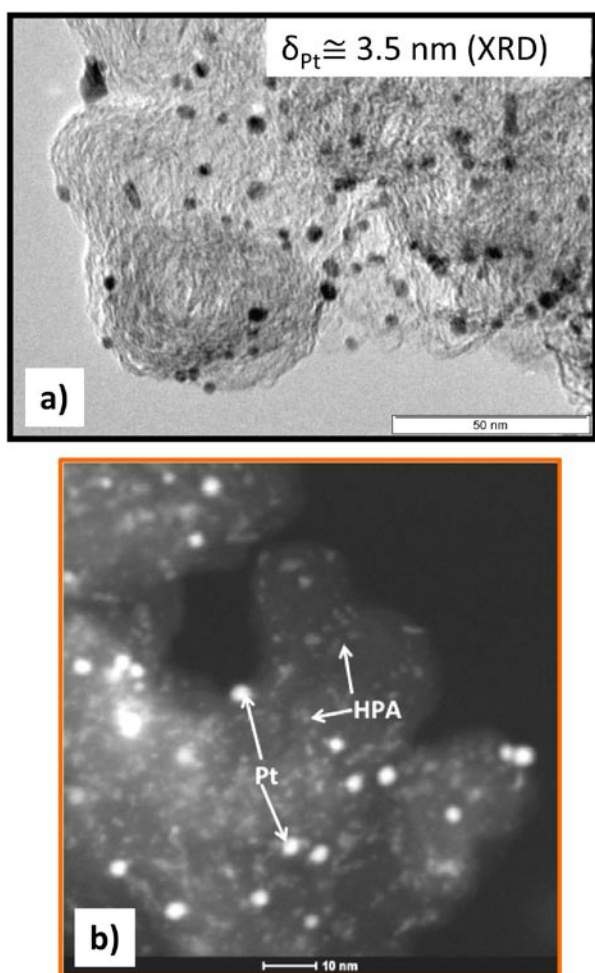


FIGURE 2. TEM micrograph showing Pt colloids (a); dark field image showing Pt and HPA on carbon support (b)

conductivity was measured over a range of pellet pressing pressures. The average conductivity was ~ 0.25 (ohm cm^{-1}).

Electrochemical Area Measurements: Because of the formation of tungsten bronzes that produces a peak in the same voltage domain as the hydrogen underpotential deposition, the accurate determination of the ECA of Pt/ WO_x becomes difficult. We have used CO stripping as well as Cu underpotential deposition to determine the Pt area for these electrocatalysts. Cu underpotential deposition is preferred because CO appears to get oxidized and shows an anodic peak that complicates the determination of a good baseline for the CO stripping area.

Durability Protocols: Durability protocols were established for evaluating the corrosion resistance of alternate supports in collaboration with the DOE Durability Working Group [2]. The measurements are designed to be conducted at room temperature in RDE setups.

Mass Activity Measurements, Pt black- WO_x Mixtures: To support the conductivity studies and verify the necessity

of carbon black addition to achieve high mass activities, we conducted a study that evaluated Pt black mixed with various amounts of carbon black. For very thin films (low loadings) with the addition of carbon black, it was possible to meet the baseline Pt/C oxygen reduction reaction activity values. The results verify that electronic conductivity issues will be encountered when WO_x or other corrosion-resistant oxide supports are used as a support due to their low conductivity.

Pt/ WO_x and Pt/HPA-C: The mass activity of Pt/ WO_x was found to be ~ 100 mA/mg by both wet-chemistry and ALD deposition methods, Figure 4 (a,b). More recently, the 50 wt% Pt/ WO_x has shown a higher activity of about 175 mA/mg_{Pt} (not shown). This is a significant improvement but falls short of the activity of baseline Pt/C. Pt/HPA-C was found to have comparable mass activity to Pt/C of more than 300 mA/mg_{Pt}.

Pt/ SnO_2 : Since the mass activity of Pt/ WO_x has not yet met the benchmark values for commercial Pt/C in RDE studies, we investigated the performance of a Pt/ SnO_2 electrocatalyst produced by a commercial catalyst manufacturer (TKK). For these catalysts, with the addition of a graphitized carbon black to enhance conductivity, values close to the benchmark Pt/C of 275 mA/mg_{Pt} were achieved. Figure 4 (c) shows the activity of these catalysts in comparison to baseline Pt/C.

Conclusions and Future Directions

Tungsten oxides provide durable supports for Pt catalysts, and while their lower conductivity limits the activity, the activity can be restored by adding a conductive matrix.

Future work will include the following:

- Complete a systematic conductivity analysis of WO_x films with and without conductive matrices to guide catalyst ink formulations.
- Improve wet-chemistry Pt deposition and ALD Pt deposition on WO_x and characterize electrochemically, with and without a conductive matrix, to obtain mass activities comparable to Pt/C.
- Make decision on using ALD Pt/ WO_x versus wet-chemistry Pt/ WO_x for meeting project goals. (December 2012)
- Evaluate alternative catalysts such as Pt-alloys (on WO_x + conductive matrix) in RDE for higher activities. (2013)
- Scale up the selected electrocatalyst system synthesis process to prepare Pt/ WO_x + conductive matrix in gram quantities for MEA preparation. (2013, 2014)
- Evaluate HPA incorporation into catalyst layers of MEA to ascertain proton conduction and durability impacts. (2013, 2014)
- Optimize catalyst inks for MEA preparation and evaluation in subscale cells. (2013, 2014)

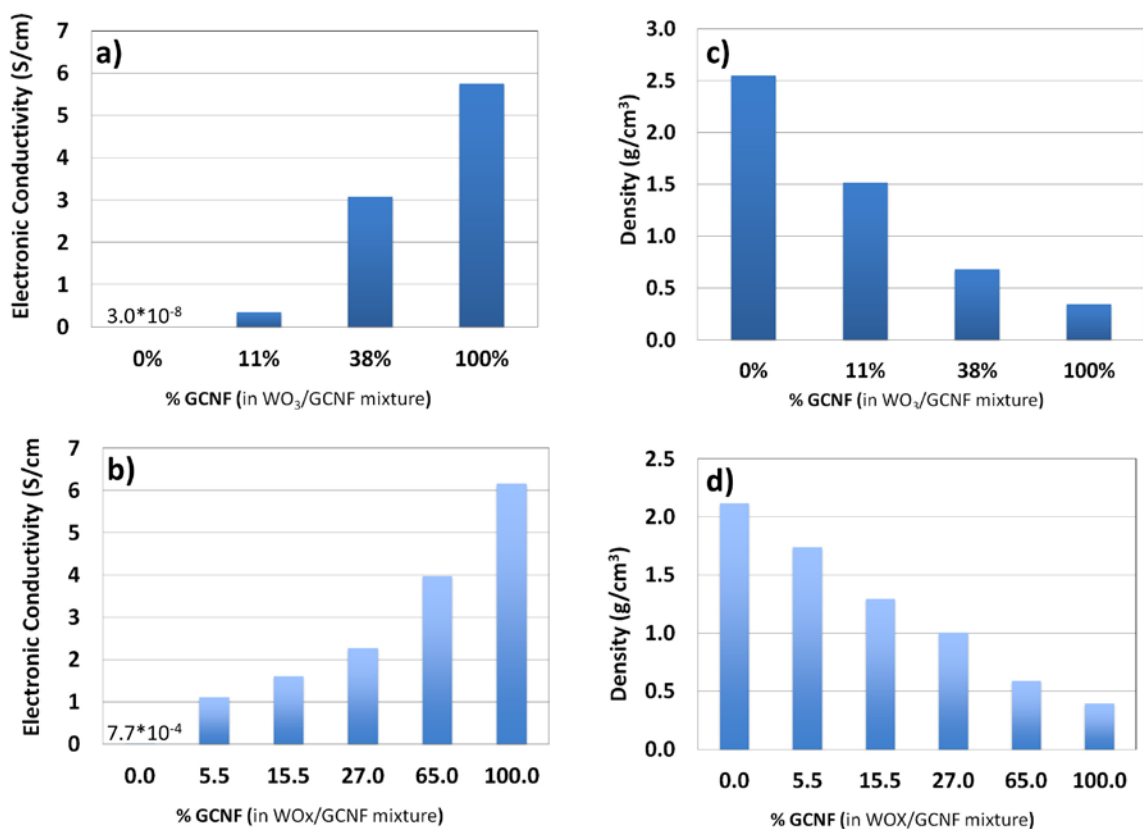


FIGURE 3. Electronic conductivity of WO_3 (a) and WO_x (b) with various additions of graphitized carbon nano-fibers (GCNF). Corresponding density of each mixture is shown in (c) and (d) respectively.

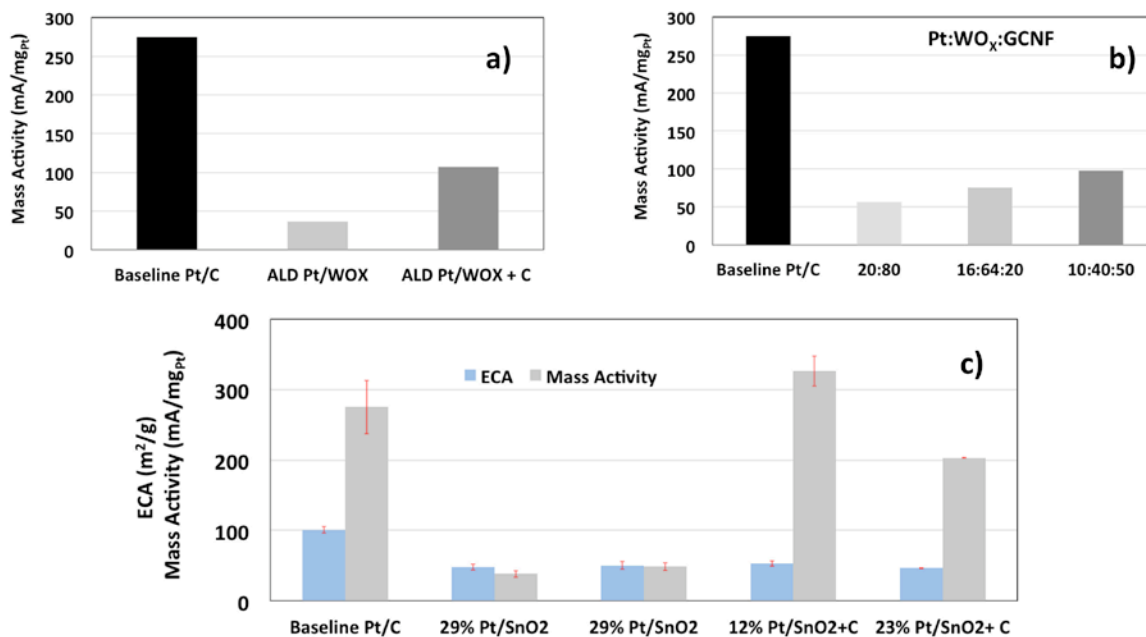


FIGURE 4. Mass activity (a) of various ALD Pt/WO_x with and without carbon addition; (b) based on samples from wet-chemistry Pt colloid deposition; and (c) for Pt/SnO₂ with and without carbon addition.

FY 2012 Publications/Presentations

1. “Nano-Pt and Tungsten Oxides as a Novel PEM Cathode Catalyst,” Katherine E. Hurst, Virginia R. Anderson, Steve Christensen, Shyam Kocha, K.C. Neyerlin, Jason Zack, Kim Jones, Steven George, John Turner, and Anne Dillon. Talk given at the American Chemical Society Fall Meeting, Denver, Colorado, August 31, 2011.
2. “Atomic Layer Deposition of Platinum on Tungsten Oxide as a Novel PEM Cathode Catalyst,” Katherine E. Hurst, Virginia R. Anderson, Steven T. Christensen, Arrelaine A. Dameron, Shyam S. Kocha, K.C. Neyerlin, Jason Zack, Steven M. George, John Turner, and Anne C. Dillon. Talk given at ALD2012, Dresden, Germany, June 18, 2012.
3. “Effect of Silicotungstate Functionalization on Carbon Black Supported Platinum Electrocatalysts”, K. Mason, M. Kuo, S. Kocha, K. Neyerlin, J. Turner, and A. Herring, Abstract 66, 221st Meeting of the Electrochemical Society, May 6–10, 2012, Washington State Convention Center, Seattle, Washington.

4. “Investigation of a Silicotungstic Acid Functionalized Carbon on Pt Activity and Durability for the Oxygen Reduction Reaction”, K. Mason, M. Kuo, K. Horning, K. Neyerlin, and A. Herring, *Journal of the Electrochemical Society* (Submitted June 2012).
5. “Durability Enhancement of Pt/C Catalysts via Support Functionalization with Silicotungstic Acid”, K. Mason, K. Neyerlin, M. Kuo, K. Horning, S. Kocha, J. Turner, and A. Herring, Abstract 1418, 222nd Meeting of the Electrochemical Society, October 7–12, 2012, Hawaii Convention Center, Honolulu, Hawaii.

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1. Wang, Y.; Ren, J.; Deng, K.; Gui, L.; Tang, Y. *Chem. Mater.* **2000**, *12*, 1622.
2. Kocha, S.; Myers, D.; Borup, R. *Accelerated stress tests for oxide supports*, DOE-EERE Durability Working Group Meeting, Boston, MA, 2011.