

# V.A.7 Tungsten Oxide and Heteropoly Acid-Based Systems for Ultra-High Activity and Stability of Pt Catalysts in PEM Fuel Cell Cathodes

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## Subcontractors:

- University of Colorado Boulder (UC-Boulder), Boulder, CO
- Colorado School of Mines (CSM), Golden, CO

Project Start Date: May 2010

Project End Date: April 2014

## Overall Objectives

Improve electrocatalyst and membrane electrode assembly (MEA) durability and activity through the use of Pt/WO<sub>x</sub> (tungsten oxide) and Pt/HPA-C (heteropoly acid) modifications to approach automotive proton exchange membrane (PEM) fuel cell activity targets (0.44 mA/mg Pt) and durability targets (5,000 h/10 y).

- Optimize Pt anchoring to support:
  - To suppress loss in Pt electrochemical area (ECA) under start-stop and load cycling operations
  - Enhance electrocatalytic activity
- To demonstrate lower support corrosion:
  - Suppress Pt agglomeration/electrode degradation
  - Increase durability under automotive start-up/shut-down operation

## Fiscal Year (FY) 2013 Objectives

- Determine viability of scaling up hot-wire chemical vapor deposition (HWCVD) WO<sub>x</sub> synthesis and atomic layer deposition (ALD) of Pt to gram quantities
- Optimize the Pt in WO<sub>x</sub> system and make a Go/No-Go decision based on its performance vs. PtC

## Technical Barriers

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

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

## Technical Targets

This project addresses the activity and durability of Pt-supported catalysts in automotive applications during start-up and shut-down. This regime is where corrosion and electrode degradation take place in PEM fuel cells and can ultimately limit the lifetime. Our target is to synthesize alternative supports such as WO<sub>x</sub> and HPA-functionalized carbon blacks and to evaluate them for improved corrosion resistance while maintaining or improving activity in comparison to conventional Pt/C supports. 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 mA/mg<sub>Pt</sub>
- Durability under start-up/shut-down cycling: ECA loss <40%

## FY 2013 Accomplishments

- Synthesized well-distributed and high-wt% Pt/WO<sub>x</sub> using ALD for Pt and HWCVD for tungsten oxide.
- Scaled up WO<sub>x</sub> preparation to gram levels for ALD platinum deposition.
- Deposited ALD Pt/WO<sub>x</sub> (UC-Boulder) that was scaled up to g quantity. However, mass activity of scaled-up ALD Pt/WO<sub>x</sub> was low.
- Prepared Pt colloids (CSM) that were subsequently deposited on HPA-functionalized carbons. These were scaled up to generate 1 g quantity.
- Obtained gram quantities of Pt/SnO<sub>2</sub> from a commercial catalyst supplier (TKK), and evaluated Pt/SnO<sub>2</sub> in RDE with and without Nafion®.
- Prepared Pt/SnO<sub>2</sub> catalyst-coated membranes and began subscale testing.

- Studied alternative support materials for conductivity and corrosion resistance.
- Performed a subscale test run comparing Pt/C MEA to a Pt/HPA-C MEA.



## INTRODUCTION

Start-up and shut-down operations in automotive fuel cells can cause significant degradation in conventional Pt/C nanoparticle electrocatalysts. Potentials at the cathode approaching ~1.6 V for short times lead to carbon corrosion and subsequent loss of Pt activity. For this project we are evaluating alternative supports for Pt for greater stability and corrosion resistance than conventional carbon blacks. These alternative supports could allow the fuel cell system balance of plant to be simplified, lowering the costs while simultaneously increasing the durability and leading to a more commercially viable product.

## APPROACH

Oxide supports such as  $\text{WO}_x$  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 blacks but have drawbacks in terms of lower surface area and lower electronic conductivity as compared to 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  $\text{WO}_x$  or HPA-C. Durability cycling protocols that simulate start-up/shut-down were developed to

quantify the suppression of degradation with the alternative corrosion resistant supports.

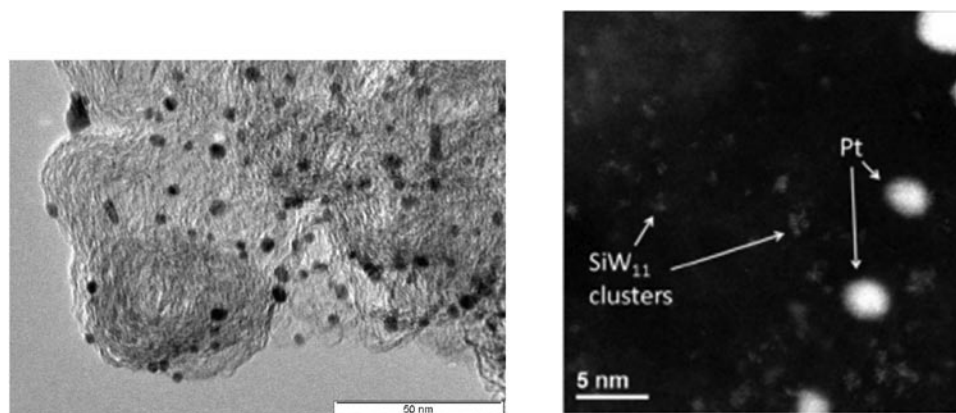
## RESULTS

### Synthesis

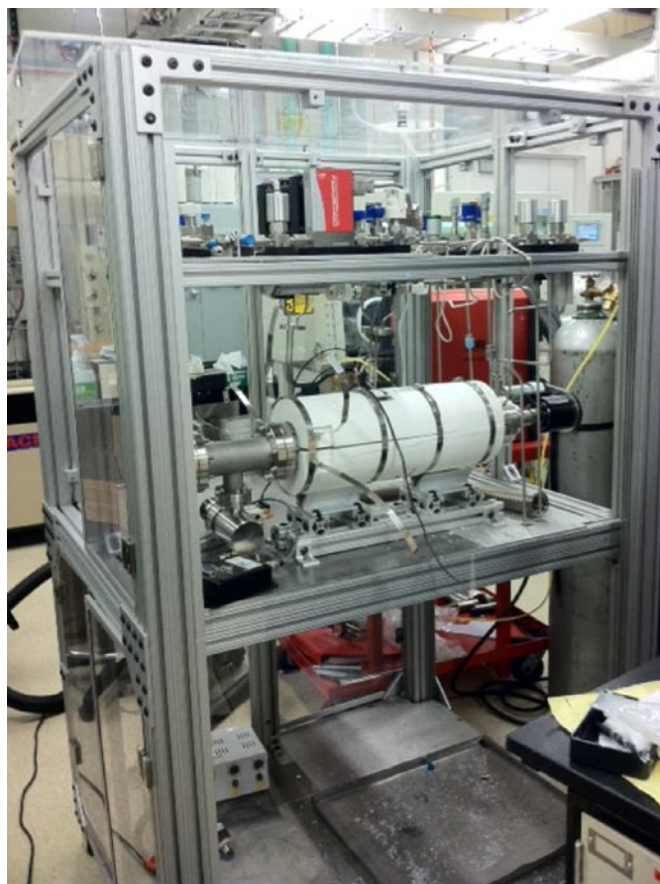
HPA functionalization of carbon was carried out to: i) shield carbon against corrosion; ii) stabilize nano-metallic particles; iii) decompose peroxide; iv) alter electrochemistry on the Pt surface; and v) conduct protons. These functionalized carbons were used as supports for depositing Pt nanoparticles that were synthesized using a colloidal preparation. A literature recipe [1] was modified significantly to synthesize small controlled Pt nanoparticles with controlled sizes by: decreasing the temperature to 80°C; bubbling dilute CO into solution; and gradually adding 0.25 M NaOH over 3 h. This method was used to scale up the catalyst synthesis to g quantities in order to prepare MEAs for testing in subscale fuel cells. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images of the synthesized catalysts are shown in Figure 1.  $\text{Pt}/\text{WO}_x$  was scaled up to g quantities using ALD deposition on HWCVD  $\text{WO}_x$ . Figure 2 illustrates the NREL Rotary ALD system for uniform scalable Pt deposition on  $\text{WO}_x$  powders.

### Conductivity and Corrosion Measurements

Conductivity and corrosion measurements were carried out on non-carbon support materials that showed promise as a substitute for the conventional carbon blacks. Conductivity measurements were carried out in an in-house experimental setup that consisted of Au-coated Cu plates. The density and conductivity of various support materials as well as supports mixed with various amounts of a graphitized carbon were determined at various loads and were reported previously.



**FIGURE 1.** TEM and Z-contrast STEM image of  $\text{Pt}/\text{SiW}_{11}\text{-C}$  showing spatial distribution of Pt (~3–5 nm bright white spots) and  $\text{SiW}_{11}$  (~1 nm dull gray spots). Catalysts synthesized by wet-chemistry from Pt precursors and HPA-functionalized carbon black.



**FIGURE 2.** NREL Rotary ALD system for uniform scalable Pt deposition on  $\text{WO}_x$  powders.

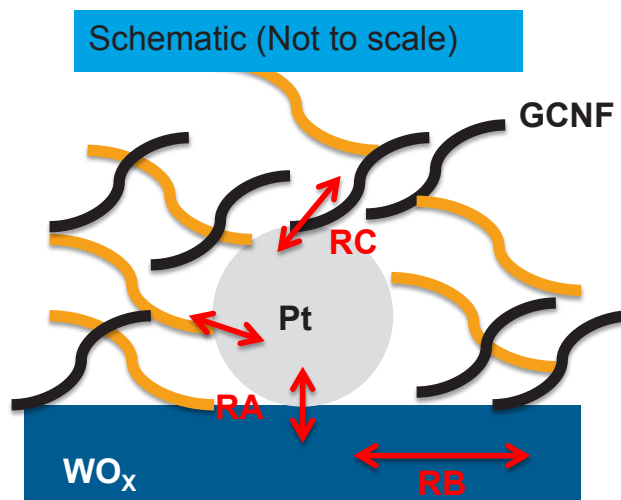
The challenges that result from the lower conductivity of alternative supports are illustrated in Figure 3.

### Corrosion of Supports

Corrosion studies were carried out in RDE cells, and the working electrodes were subjected to high anodic potentials to estimate the onset of corrosion currents. Figure 4 (a and b) depicts the conductivity and corrosion currents for the support materials that were evaluated.  $\text{TiO}_2$ , TaC, and  $\text{WO}_3$  showed the highest corrosion resistances, while TiC had the lowest corrosion resistance.

### Durability Protocols

Durability protocols were established for evaluating the corrosion resistance of alternate supports in collaboration with the DOE Durability Working Group [2]. Figure 5 depicts the durability protocol that simulated start-stop degradation in the voltage range 1–1.6 V. The measurements are designed to be conducted at room temperature and atmospheric pressure in RDE setups.



**FIGURE 3.** Illustration of the challenges that result from the lower conductivity of alternative supports. Shown are the electron pathways that impact conductivity. 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  $\text{WO}_x$  and C not shown: (RNafion). Addition of carbon matrix such as graphitized carbon black nano-fibers (GCNFs) enhances the overall conductivity, but does not address RA and RB.

### Electrochemical Characterization

**Pt Black- $\text{WO}_x$  Mixtures:** We completed a study that evaluated Pt black mixed with various amounts of a graphitized carbon black nano-fiber (GCNF). 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  $\text{WO}_x$  or other low conductivity, corrosion-resistant oxide supports are used. Utilizing the established DOE protocols, durability tests of these materials with and without the addition of GCNF were also conducted and the results are summarized in Figure 6. The mixed Pt black-GCNF materials show activity and durability that are better than that of the conventional Pt/C baseline materials from TKK.

**Pt/ $\text{WO}_x$ :** The mass activity of ALD-deposited Pt/ $\text{WO}_x$  improved to ~175 mA/mg when measured in RDE half-cells (Figure 7). This activity is a significant improvement but falls short of the activity of baseline Pt/C. Pt/ $\text{WO}_x$  was scaled up to g quantities using ALD deposition on HWD  $\text{WO}_x$ ; however, the scaled-up Pt/ $\text{WO}_x$ -C did not show these improvements. The lower activity of Pt/ $\text{WO}_x$  is primarily due to the low electronic conductivity of the  $\text{WO}_x$  as seen by the doubling in activity with the addition of 50 wt% carbon black. Based on these results, further work on Pt/ $\text{WO}_x$  has been given a No-Go and alternative paths are being pursued.

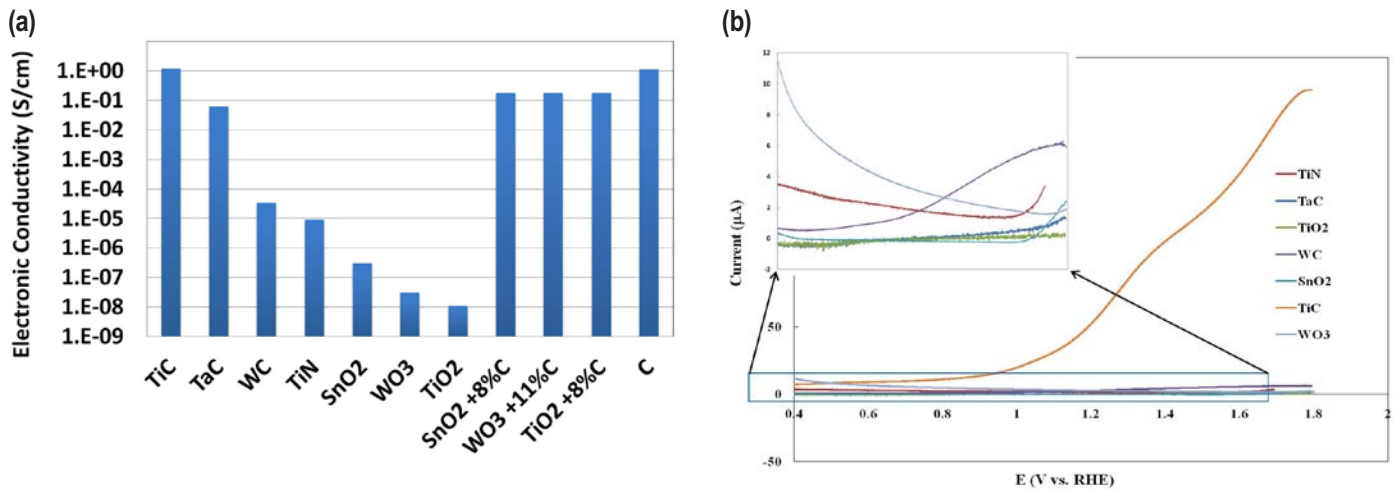


FIGURE 4. a) Conductivity of alternative supports. b) Corrosion currents (corrected) of alternative support materials. Gold disk used.

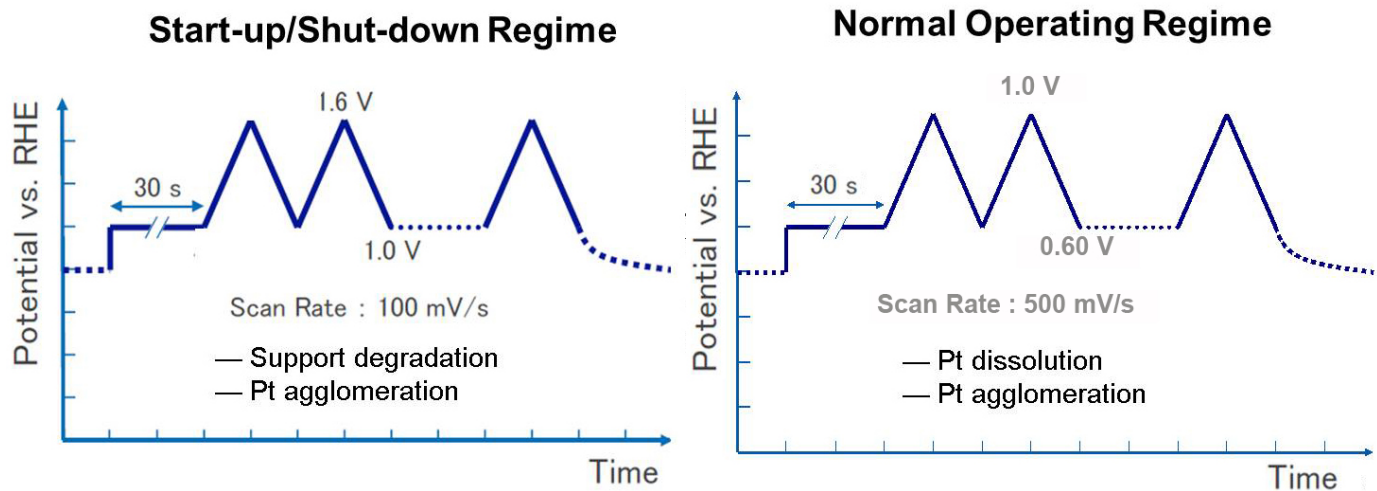


FIGURE 5. Durability protocols simulating start-stop degradation in the voltage range 1–1.6 V as well as the normal operating regime.

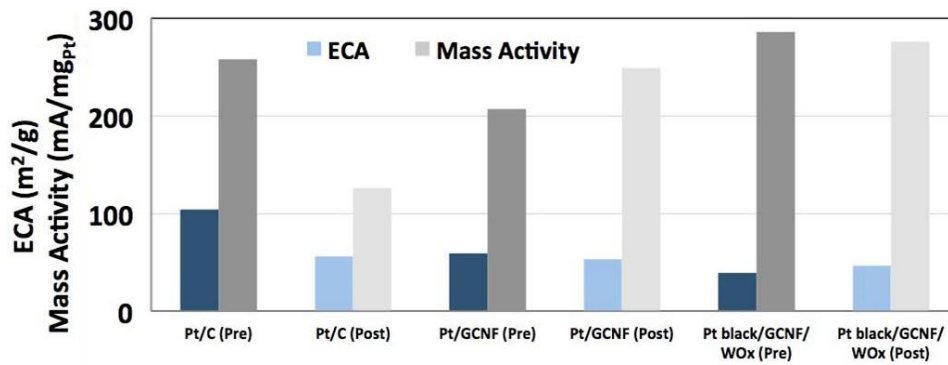


FIGURE 6. Durability comparisons for Pt black + GCNF + WO<sub>x</sub> systems. Pt and GCNF from TKK, WO<sub>x</sub> from NREL (1.0–1.6 V protocol).

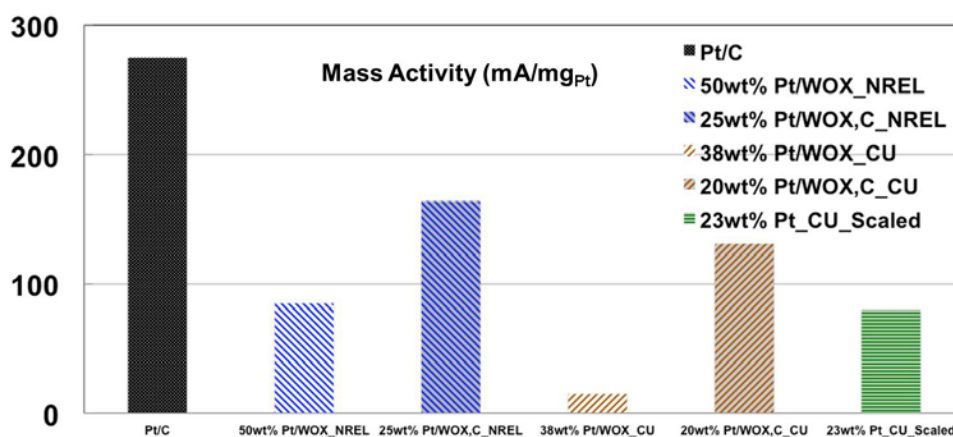


FIGURE 7. Mass activity of Pt/WO<sub>x</sub> synthesized using various techniques measured in RDE half-cells.

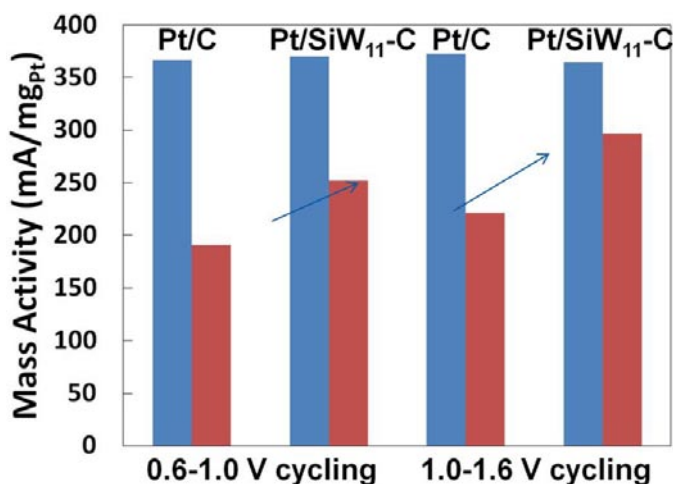


FIGURE 8. Durability results for Pt/HPA-C conducted using previously developed protocols. HPA loading was chosen such that initial activity was near equal to that of Pt/C. (0.6–1.0 V cycling, 30,000 cycles, 500 mV/s; 1.0–1.6 V cycling, 6,000 cycles, 100 mV/s)

**Pt/HPA-C:** Durability results on Pt/HPA-C were conducted using the previously developed DOE protocols. Results of durability tests are shown in Figure 8. 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) was used to evaluate support corrosion. HPA loading was chosen such that initial activity was nearly equal to that of Pt/C. In both cases, HPA helped maintain catalyst activity by slowing particle growth. MEAs were also prepared with scaled-up catalyst and tested in subscale fuel cells for initial activity.

**Pt/SnO<sub>2</sub>:** The performance of a Pt/SnO<sub>2</sub> electrocatalyst produced by a commercial catalyst manufacturer (TKK) was evaluated in RDE studies. For this catalyst, with the addition of a graphitized carbon black to enhance conductivity, values

close to the benchmark Pt/C activity of 275 mA/mg<sub>Pt</sub> were achieved. These activities were found to be even higher for ink formulations that were Nafion®-free. The catalyst was spray-coated onto Nafion® membranes and evaluated in subscale fuel cells. Initial results were lower than what we found in RDE studies, and ink optimization and modification will be necessary to achieve higher activity values in fuel cells.

## CONCLUSIONS AND FUTURE DIRECTIONS

The following conclusions summarize the work conducted in FY 2013:

- Pt/WO<sub>x</sub> was scaled up to gram quantities using the ALD technique and evaluated for activity in RDE setups.
- Pt/HPA-C was synthesized in larger quantities and spray-coated onto a membrane to form MEAs that were tested in subscale fuel cells.
- Pt/HPA-various carbon blacks were synthesized in larger quantities and evaluated for activity in RDE setups.
- Pt/SnO<sub>2</sub> was obtained in larger quantities and spray-coated onto a membrane to form MEAs that were tested in subscale fuel cells.
- Various alternative supports were evaluated for conductivity and corrosion resistance.
- Pt was deposited onto TiN support and electrochemically characterized in RDE half-cells

Due to the low electronic conductivity of WO<sub>x</sub> and consequent low activity of Pt/WO<sub>x</sub> catalysts, no further work will be conducted in this area. Future work will use alternative nitride and carbide supports as well as the HPA-modified graphitized carbons in an attempt to meet the DOE targets.

**FY 2013 PUBLICATIONS/PRESENTATIONS**

1. Kocha, S.S., et al. "Influence of Ink Composition on the Electrochemical Properties of Pt/C Electrocatalysts." Presentation at the Fall ECS Meeting, Honolulu, HI, 2012.
2. Kocha, S.S., et al. "Influence of Ink Composition on the Electrochemical Properties of Pt/C Electrocatalysts." *ECS Transactions* 50.2 (2013): 1475-1485.
3. Kocha, S.; Garsany, Y.; Myers, D. "Testing Oxygen Reduction Reaction Activity with the Rotating Disc Electrode Technique." Webinar, March 12, 2013. [http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/webinarslides\\_rde\\_technique\\_031213.pdf](http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/webinarslides_rde_technique_031213.pdf).
4. Mason, K.S.; Neyerlin, K.; Kuo, M.; Horning, K.; Kocha, S.S.; Turner, J.A.; Herring, A. "Durability Enhancement of Pt/C Catalysts via Support Functionalization with Silicotungstic Acid." Poster presentation at the 222<sup>nd</sup> ECS Meeting, Honolulu, HI, October 2012.
5. Hurst, K.; Parilla, P.; Kocha, S.; Zack, J.; Neyerlin, K.C.; Turner, J. "Tungsten oxide nanowire supports for PEM cathode catalysts." Presentation at the Spring MRS Meeting, San Francisco, CA, April 3, 2013.

**REFERENCES**

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.