

## V.A.6 Tungsten Oxide and Heteropoly Acid-Based System for Ultra-High Activity and Stability of Pt Catalysts in Proton Exchange Membrane Fuel Cell Cathodes

John A. Turner

National Renewable Energy Laboratory (NREL)  
15013 Denver West Pkwy  
Golden, CO 80401  
Email: John.Turner@nrel.gov

DOE Manager

David Peterson  
Phone: (720) 356-1747  
Email: David.Peterson@ee.doe.gov

Subcontractors

University of Colorado, Boulder, CO  
Colorado School of Mines, Golden, CO

Project Start Date: May 1, 2010

Project End Date: April 30, 2014

during unmitigated start-up and shut-down operations. The following are the targets that are being addressed.

- Mass Activity:  $>275 \text{ mA/mg}_{\text{Pt}}$
- Durability under start-up/shut-down cycling: electrochemical surface area (ECA) loss  $<40\%$

The cost of the fuel cell system will be lowered with system simplification if the fuel cell vehicle can be subject to start-stop cycles without any complex system mitigation involved.



### 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  $\sim 1.5\text{--}1.6 \text{ V}$  for short bursts of time leading to carbon support 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. Alternative supports such as  $\text{WO}_x$  as well as HPA-functionalized carbon blacks were synthesized and evaluated for improved corrosion resistance while maintaining or improving on the activity in comparison to conventional Pt/C. Studies were primarily conducted in half-cell rotating disk electrode (RDE) experimental set-ups due to the small quantity (tens of mg) of catalyst materials that were typically synthesized. Only catalysts that met the activity and durability target in RDE studies would be considered for further evaluation as MEAs in subscale proton exchange membrane fuel cells.

### APPROACH

Oxide supports such as  $\text{WO}_x$  are grown using a hot-wire chemical vapor deposition (HWCVD) method and atomic layer deposition (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 known drawbacks in terms of lower surface area and lower electronic conductivity as compared to conventional carbon black supports. Therefore, the electronic conductivity and the electrochemical activity of the supports and Pt-catalyzed supports as a function of small added quantities of highly

### Overall Objectives

- Replace carbon in the fuel cell cathode with tungsten oxide ( $\text{WO}_x$ ) to reduce support corrosion.
- Utilize heteropolyacid (HPA)-functionalized supports (carbon and  $\text{WO}_x$ ), to increase platinum stability.

### Fiscal Year (FY) 2014 Objectives

Quantify the mass activity, electrochemical active surface area and durability of HPA-functionalized carbon blacks

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (A) Durability (of catalysts and membrane electrode assemblies [MEAs])
- (B) Cost (of catalysts and MEAs)
- (C) Performance (of catalysts and MEAs)

### Technical Targets

This project addresses the severe corrosion and fuel cell cathode electrode degradation that takes place when using carbon-black-supported Pt catalysts in automotive applications

graphitized carbon blacks/fibers was studied in parallel with measurement of the oxygen reduction reaction (ORR) activity of the materials. The overall approach in terms of collaboration with the various subcontractors and institutions is schematically depicted in Figure 1. Durability cycling protocols that simulate start-up/shut-down were not available at the beginning of the project and were developed along with the DOE Durability Working Group to quantify the suppression of degradation achieved with the novel supports. We delineate the choice of protocols that were selected by the Durability Working Group for evaluating cyclic durability of the novel supports in comparison to carbon blacks in RDE studies.

## Materials and Catalyst Synthesis and Scale-Up and Conductivity Measurements

### Tungsten Oxide Hot Wire Deposition

Tungsten oxide nanostructures were synthesized by HWCVD in an atmosphere of argon and oxygen. Material synthesis employing sequential depositions at room temperature leads to rod-like nanostructure growth 10–50 nm in diameter, and up to microns in length. The yield of one batch was approximately 25 mg. We increased the  $WO_x$  HWCVD yield to 50 mg/synthesis by increasing the length of the reaction zone. Our initial synthetic runs resulted in the fabrication of mixed phases; fully ( $x=3$ ) and sub-stoichiometric ( $x<3$ )  $WO_x$  material. The fabrication of the sub-stoichiometric material is more desirable owing to

its higher electrical conductivity. We were able to decrease the amount of  $WO_3$  by conditioning, or flowing current through the filament, in an Ar-only atmosphere prior to the addition of oxygen to the reaction zone. This generated sub-stoichiometric material, where the bulk  $WO_x$  synthesized was  $x=1.39$  as determined by thermo-gravimetric analysis. The  $WO_x$  nanoparticle stoichiometry and crystalline structure can also be controlled by subsequent annealing in air, as demonstrated by the X-ray diffraction spectra in Figure 2a. Near edge X-ray absorption fine structure data were obtained from the Stanford Linear Accelerator Center to provide insight into oxygen bonding on tungsten oxide, illustrated in Figure 2b. However, in situ and post-synthetic attempts to increase the conductivity of the  $WO_x$  substrates were not observable in the electrochemical characterization.

Another method to produce tungsten oxide nanorods was the pyrolysis of the precursor compound  $((C_4H_9)_4N)_4W_{10}O_{32}$ . The precursor compound, was synthesized by using  $Na_2WO_4 \cdot 2H_2O$  and tetrabutylammonium bromide as the starting materials. The precursor was recrystallized in hot dimethyl formamide to give yellow crystals. The pyrolysis of  $((C_4H_9)_4N)_4W_{10}O_{32}$  to synthesize  $WO_3$  nanorods is carried as follows: 1 g of the precursor compound was taken in an alumina crucible and introduced inside a tubular furnace and heated at 450°C under an Ar atmosphere for 3 hours followed by heating under air atmosphere at the same temperature for 3 hours. Then it was gradually cooled to room temperature to obtain  $WO_3$  nanorods. Scanning electron microscopy

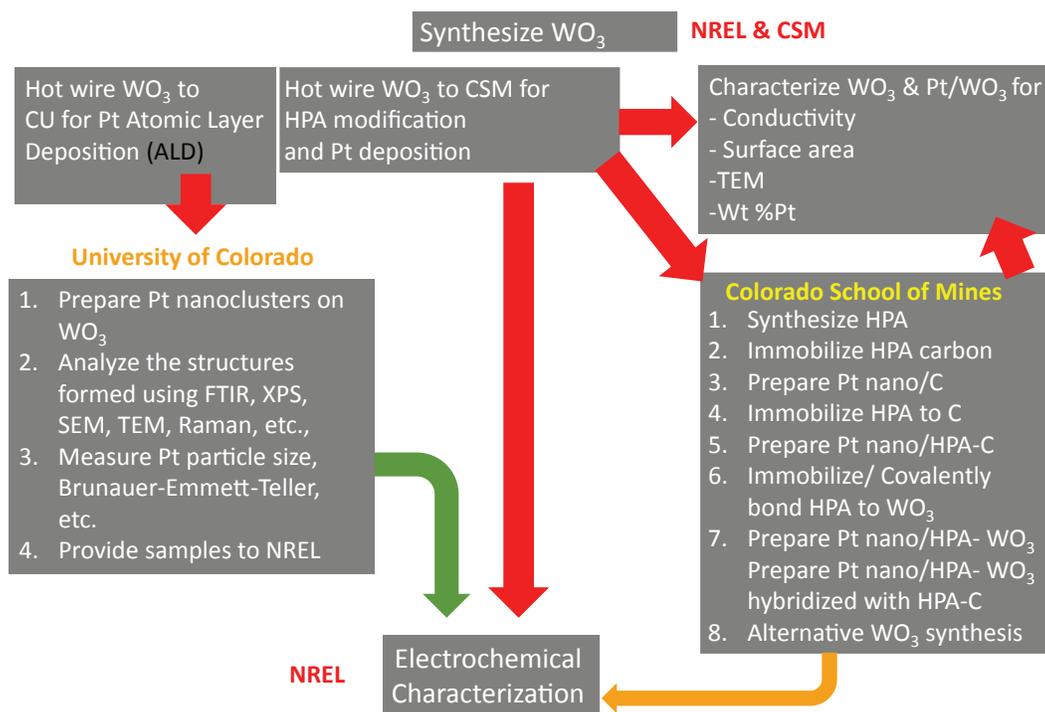


FIGURE 1. Operational Flow Diagram

was employed to observe the morphology of  $\text{WO}_3$ . The as-synthesized  $\text{WO}_3$  showed the formation of one-dimensional nanorods (Figure 3) in high yields. The rods were poly-dispersed with an average width of 15 nm.

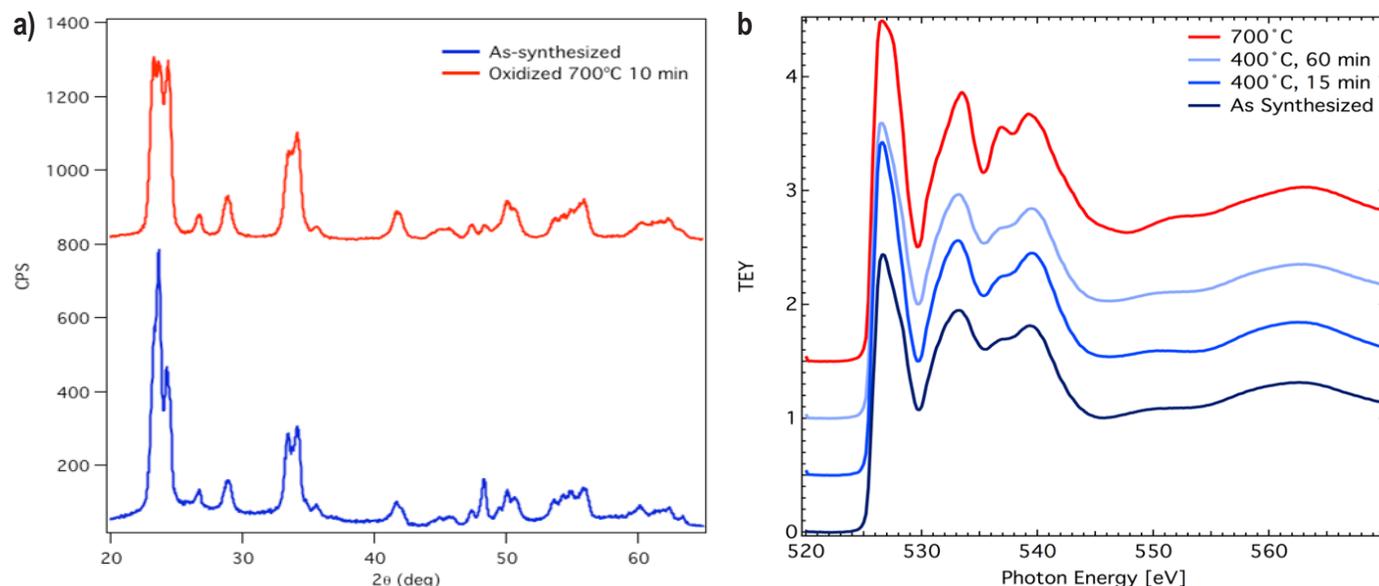
### Vand der Pauw Technique

The bulk conductivity of the  $\text{WO}_x$  materials was investigated by four-point probe measurement in the Van der Pauw geometry. The as-produced materials were pressed into a pellet and the conductivity was measured over a range

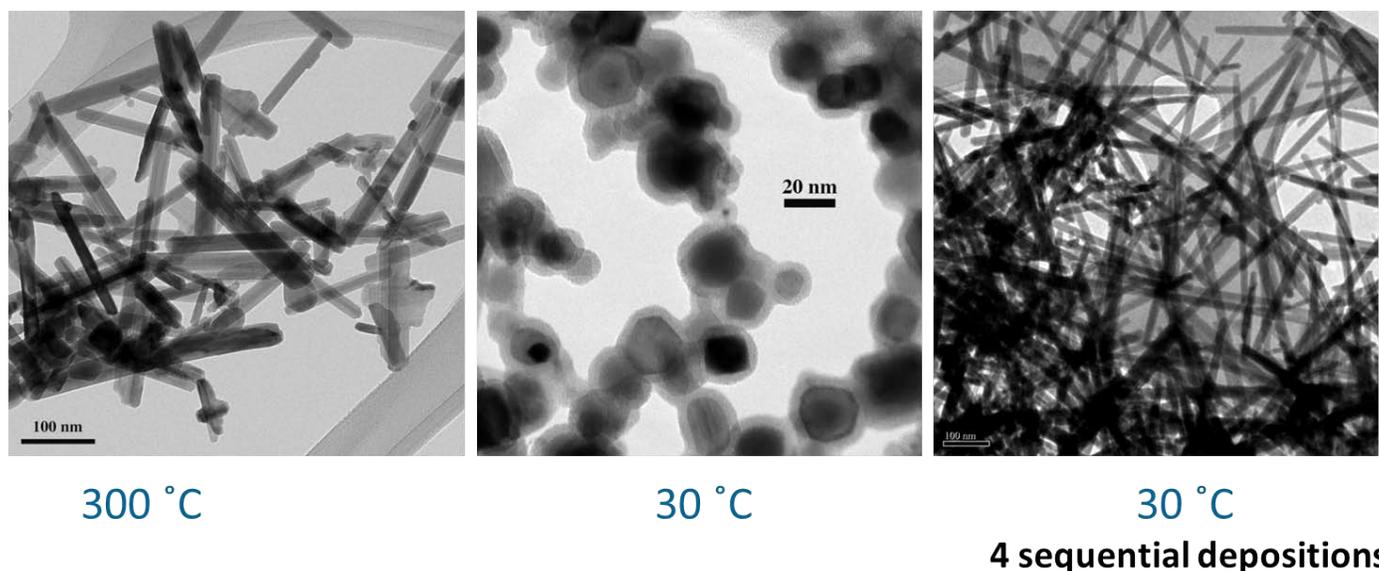
of pellet pressing pressures. The average conductivity was  $\sim 0.25 \text{ (ohm cm)}^{-1}$ .

### In-House Electronic-Conductivity Cell Measurements

Conductivity measurements were carried out in an in-house experimental set-up 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. The challenges that result from



**FIGURE 2.** a) X-Ray Diffraction and b) Near Edge X-ray Absorption Fine Structure of HWCVD  $\text{WO}_x$  Materials

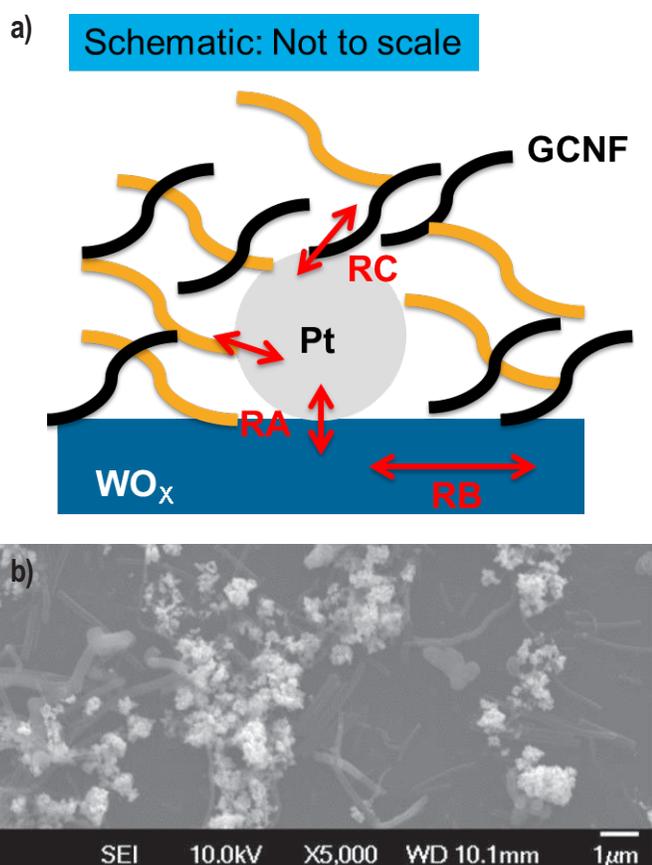


**FIGURE 3.** HWCVD production of tungsten oxide nanostructures. Synthesis at 150 Torr 4%  $\text{O}_2$  in Ar, filament temperature  $\sim 2,000^\circ\text{C}$ . Showing dramatic change in particle morphology with lower furnace temperature and that sequential depositions lead to rod growth.

the lower conductivity of alternative supports are illustrated in Figure 4a. Three electronic pathways are illustrated in the figure: i) electronic contact between Pt and the support or Pt and ionomer covered support; ii) conductivity through the bulk support, and iii) electronic pathway between Pt/support agglomerates through added carbon support. We note that, although currently used carbon black supports have extremely high electronic conductivity (~10-100 S/cm), novel corrosion resistance supports with lower conductivity in the range (~1-10 S/cm) might be acceptable, since the limiting resistance in the cathode catalyst layer of proton exchange membrane fuel cells are the result of protonic resistances of the ionomer (~0.1 S/cm). A micrograph of the mixture is given in Figure 4b.

#### ALD Deposition of Pt on $WO_x$

Platinum was deposited on the  $WO_x$  nanoparticles by ALD using sequential dosing of (methylcyclopentadienyl) trimethylplatinum IV ( $Me_3PtMeCp$ ) precursor and oxygen. We investigated different methods to alter the morphology



**FIGURE 4.** a) Electronic pathways in a Pt/support mixed with carbon black structure; RA: electronic contact between Pt and the support or Pt and ionomer covered support; RB: conductivity through the bulk support; and RC: electronic pathway between Pt/support agglomerates through added carbon support GCNF. b) Micrograph of  $WO_x$ /Pt/GCNF.

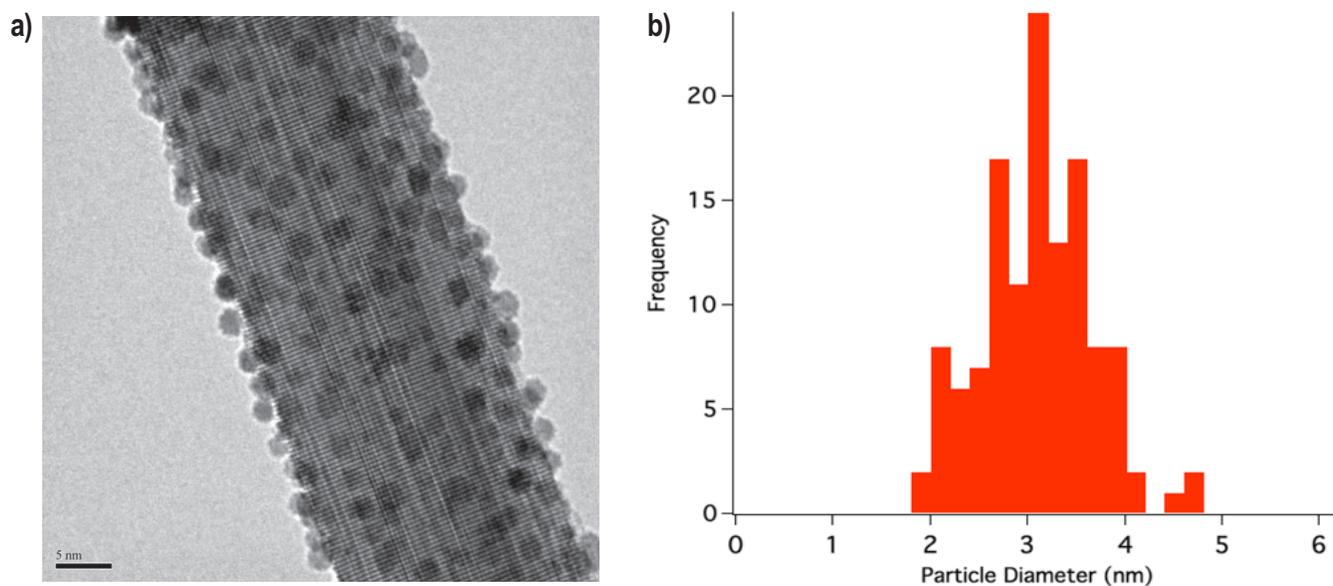
of the Pt deposition. Our initial ALD work resulted in a high Pt loading with large particle sizes and agglomeration. By increasing the precursor temperature, a higher flux of Pt enabled more uniform nucleation, leading to smaller particles throughout the sample. Uniform deposition of Pt nanoparticles on tungsten oxide, with a diameter distribution of 2-4 nm is shown in Figure 5. We developed control of uniform deposition in the range of 0-60 wt% Pt loadings. For high loadings of Pt, the particles almost reach full coverage the  $WO_x$  surface as shown in Figure 6a. This has been achieved by performing ALD in a stop-flow configuration with increased dosing time of the platinum precursor as well as increased soak times during deposition. The ALD deposition process was scaled up to accommodate gram size quantities of  $WO_x$  with new capabilities at NREL using a rotary ALD system.

The effect of temperature is demonstrated by performing the same deposition conditions, (number of cycles, precursor temperature, flow rates, and dose and soak times) with changing the reactor temperature. Figures 6a and 6b show 20 cycles of Pt deposition on  $WO_x$  substrates for the reactor temperature of 270°C and 300°C, respectively. The Pt deposited at higher temperature results in rounder particles owing to the greater mobility and higher surface energy of Pt. ALD of thin Pt films was also attempted on the  $WO_x$  substrates. Wetting of a Pt film on a substrate, however, requires a material with higher surface energy such as W metal. Therefore, a thin W layer was deposited using  $WF_6 + Si_2H_6$  on the  $WO_x$  substrate prior to Pt ALD.

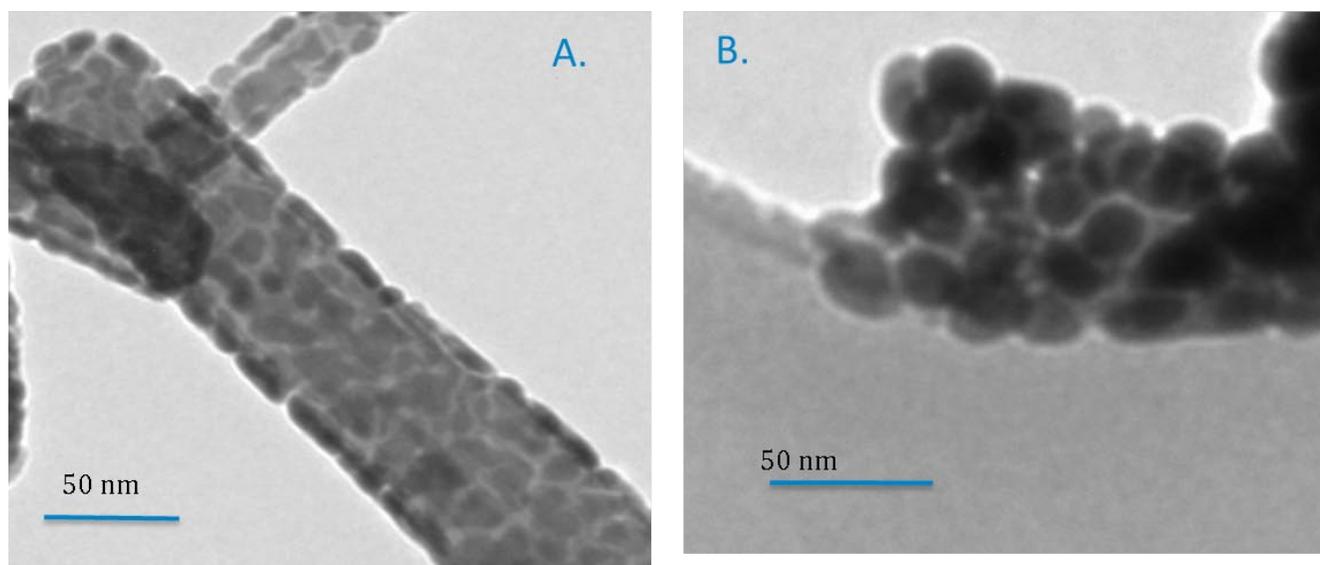
The use of Pt II hexafluoroacetylacetonate,  $Pt(hfac)_2$ , precursor was also considered. This work was done by the University of Colorado. Our intent was to use the hfac ligand chemistry as site-blocking species to enable greater control over the spacing and Pt particle size. This concept was previously demonstrated for the deposition of Pd particles using  $Pd(hfac)_2$ . This method was scaled up from the initial synthesis of mg samples to gram size samples by the use of a rotary ALD system. However, high metal loadings were difficult to achieve using this precursor. Although novel chemistry of Pt ALD was demonstrated, it was shown that this was not an efficient route for fuel cell catalyst development. The addition of a plasma source to the ALD rotary system may provide a route to increase Pt loadings.

#### Deposition of Pt Nanoparticles on HPA-Functionalized Carbon Black

HPA functionalization of carbon was carried out to i) shield carbon against corrosion, ii) stabilize nano-metallic particles, iii) decompose peroxide, iv) alter electrochemistry at 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 was modified significantly to synthesize small controlled Pt nanoparticles by decreasing the temperature to 80°C, bubbling dilute CO into solution,



**FIGURE 5.** (A) TEM Image of Pt ALD on  $\text{WO}_x$  and (B) Associated Particle Size Distribution



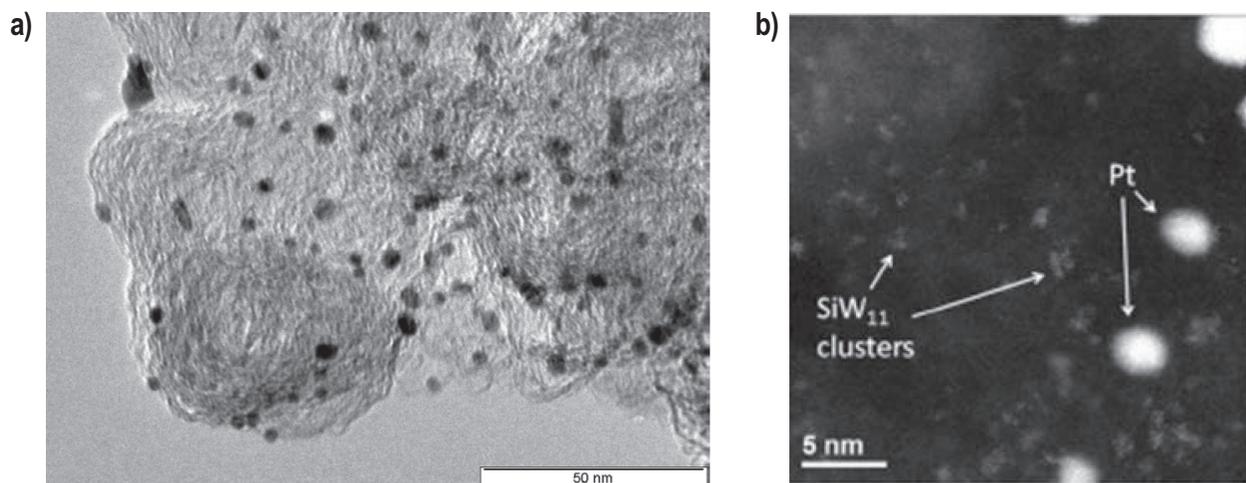
**FIGURE 6.** For high loadings of Pt, the particles almost reach full coverage of the  $\text{WO}_x$  surface. 20 cycles of Pt ALD deposited on  $\text{WO}_x$  with a reactor temperature at A) 300°C and B) 270°C.

and gradually adding 0.25M NaOH over 3 hours. Figure 7a illustrates the transmission electron micrograph (TEM) and particle size distribution of the synthesized colloids that were deposited onto the HPA-functionalized carbon 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 Buechner filtration; and (iv) drying at 200°C for 2 hours. Figure 7b illustrates the Z-contrast scanning TEM (STEM) image of Pt/SiW11-C showing spatial

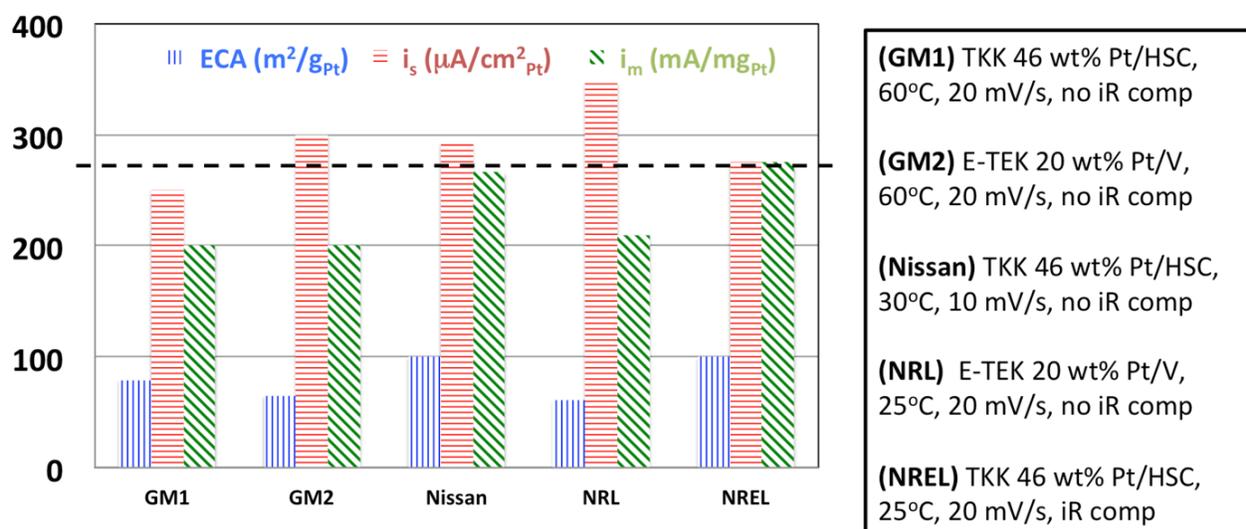
distribution of Pt (bright white spots ~3-5 nm) and SiW11 (~1 nm dull gray spots).

### Electrochemical Characterization and Analysis

Prior to evaluating novel materials for electrochemical ORR activity, we established benchmarks for the activity of baseline commercial Pt/C materials. The ORR activity and ECA of the novel synthesized materials were then compared to the benchmarks to determine if they performed well enough to be taken to the next stage of scale up of synthesis



**FIGURE 7.** (a) Illustrates the TEM and particle size distribution of the synthesized colloids that were deposited onto the HPA-functionalized carbon. Scaled up to produce 1 g of electrocatalyst for MEA preparation. (b) Z-contrast STEM image of Pt/SiW<sub>11</sub>-C showing spatial distribution of Pt (bright white spots ~3-5 nm) and SiW<sub>11</sub> (~1 nm dull gray spots).

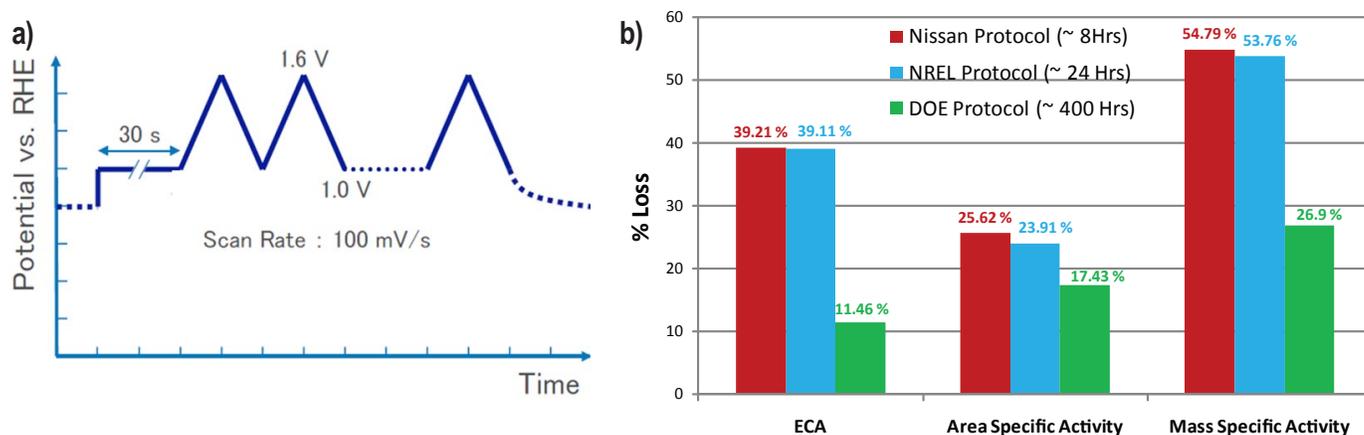


**FIGURE 8.** Baseline Pt/C Activity Benchmarks in RDE at NREL and Other Labs

and evaluation of material durability. Figure 8 illustrates the performance of the baseline Pt/C materials and comparison to other values in the literature for measurements conducted under approximately similar conditions.

Because of the formation of tungsten bronzes that produces a peak in the same voltage domain as hydrogen underpotential deposition, the accurate determination of the ECA of Pt/WO<sub>x</sub> 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 since CO appears to get oxidized and shows an anodic peak that complicates the determination of a good baseline for CO stripping area.

Durability protocols were established for evaluating the corrosion resistance of alternate supports in collaboration with the DOE Durability Working Group. Figure 9a depicts the durability protocol that simulated start-stop degradation in the voltage range 1–1.6 V. Nissan and NREL protocols result in comparable losses for ECA,  $i_s$  and  $i_m$  (Figure 9b). Nissan protocol (60°C) takes only 8 hours due to higher temperature accelerant. NREL protocol is conducted at room temperature and takes 24 hours using low-scan-rate accelerant and was selected due to environmental, health and safety issues of making measurements at temperature at NREL.



**FIGURE 9.** a) Illustrates the durability protocol that simulated start-stop degradation in the voltage range 1–1.6 V (start-up/shut-down regime) used to evaluate the corrosion resistance of alternative supports. b) Two equivalent protocols for measurements at room temperature and 60°C. DOE protocol is 1.2 V constant hold for 400 hr.

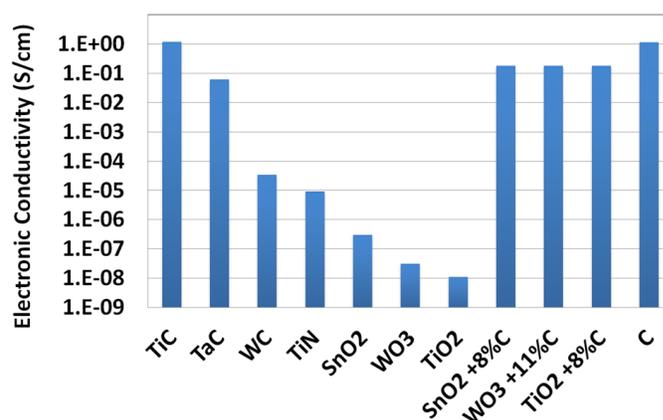
## Corrosion of Supports

Corrosion studies were carried out in RDE cells and the working electrodes were subjected to high potentials reaching 1.8 V in perchloric acid. The onset and magnitude of corrosion currents was determined and compared. Figures 10 and 11 depict the conductivity and corrosion currents for the set of support materials that were evaluated.  $\text{TiO}_2$ , TaC and  $\text{WO}_3$  exhibited the highest corrosion resistances while TiC had the lowest corrosion resistance. WC also exhibited less than ideal behavior. The preferred materials are those that possess both a high electronic conductivity and corrosion resistance.

## Pt/ $\text{WO}_x$

Based on the conductivity measurements of  $\text{WO}_x$ , it was clear that the conductivity of  $\text{WO}_x$  was significantly lower than that of carbon black. As a result, electrochemical measurements were performed using catalyst inks with and without incorporation of carbon black. The results with the incorporation of carbon black would allow us to estimate the losses incurred due to electronic conductivity issues.

Pt/ $\text{WO}_x$  was scaled up to g quantities using ALD deposition on HWCVD  $\text{WO}_x$ . The mass activity of Pt/ $\text{WO}_x$  was found to be ~175 mA/mg when measured in RDE half-cells ( $\text{WO}_x$ ). This is a significant improvement but falls short of the activity of baseline Pt/C. 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 to it. Based on these results further work on Pt/ $\text{WO}_x$  was discontinued and alternative paths were deemed appropriate at the end of FY 2013.



**FIGURE 10.** Electronic Conductivity for Various Support Material Candidates

## Pt Black/ $\text{WO}_x$

Although conductivity studies provide some insight into the potential of using a support material, actual mixtures of Pt black, (an unsupported catalyst) with various amounts of tungsten oxide and carbon black allows us to evaluate the materials electrochemically for ORR activity. 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. The detailed studies revealed that only for very thin films (low catalyst loadings), was it possible to meet the baseline Pt/C ORR activity values. The results indicated that electronic resistance of the support would be an impediment when  $\text{WO}_x$  or other corrosion-resistant oxide supports are used as a support due to their low electronic conductivity. Extremely low loadings/thin films/high added carbon black content would be necessary for the catalyst to perform at acceptable levels of activity. Figure 13 indicates that the

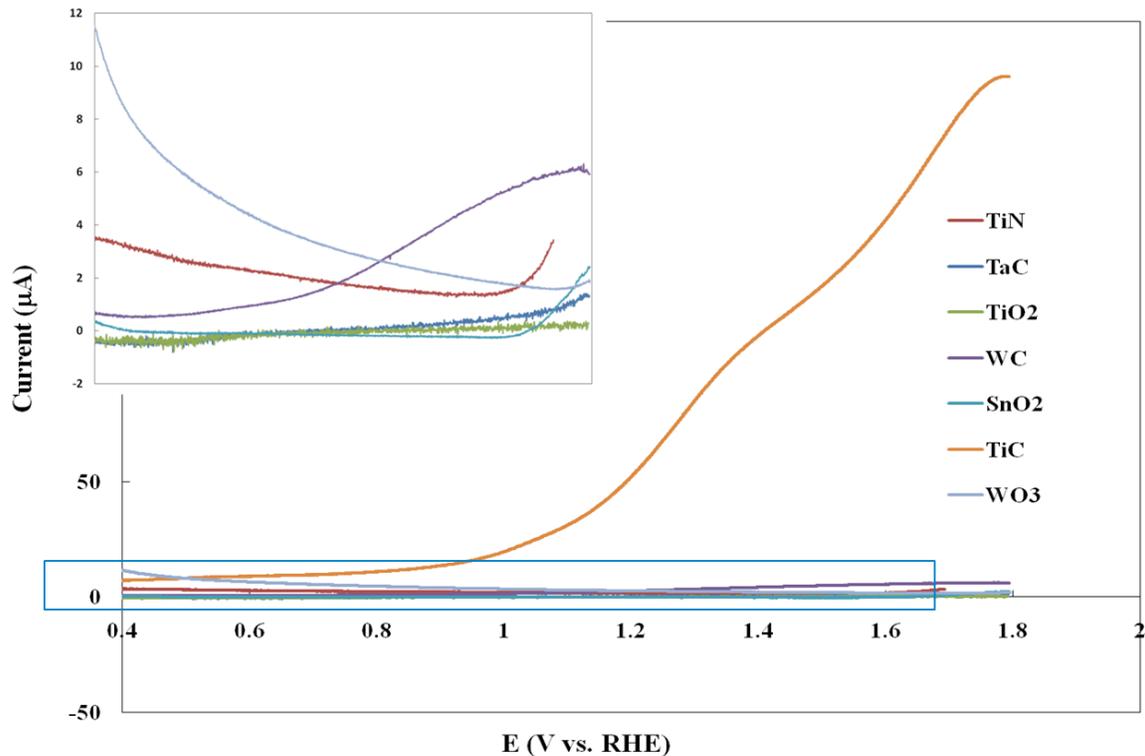


FIGURE 11. Corrosion Currents for Various Support Material Candidates

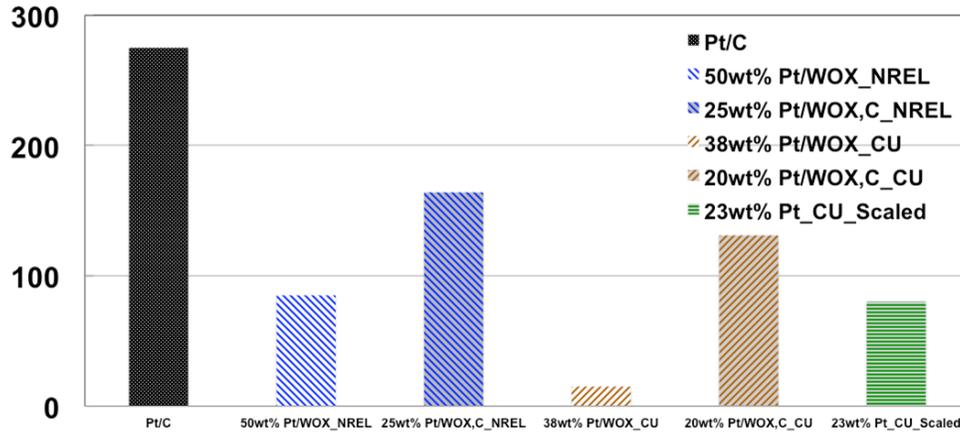


FIGURE 12. Mass Activity of Various Pt/WO<sub>x</sub> in Comparison to Baseline Pt/C

durability of Pt/GCNF as well as the best case of Pt black/graphitized carbon nano-fibers (GCNFs)/WO<sub>x</sub> has higher durability than baseline Pt/C.

**Pt/SnO<sub>2</sub>**

Since the mass activity of Pt/WO<sub>x</sub> had not yet met the benchmark values for commercial Pt/C in RDE studies, we investigated the performance of a Pt/SnO<sub>2</sub> 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 benchmark Pt/C of 275 mA/mgPt were achieved. The ORR activities were found to be even higher for ink formulations that were Nafion<sup>®</sup>-free. The catalyst was spray-coated onto Nafion<sup>®</sup> membranes and evaluated in subscale fuel cells. Initial results were lower than that found in RDE, and ink optimization and modification were attempted without success to attain the same activity as in RDE studies

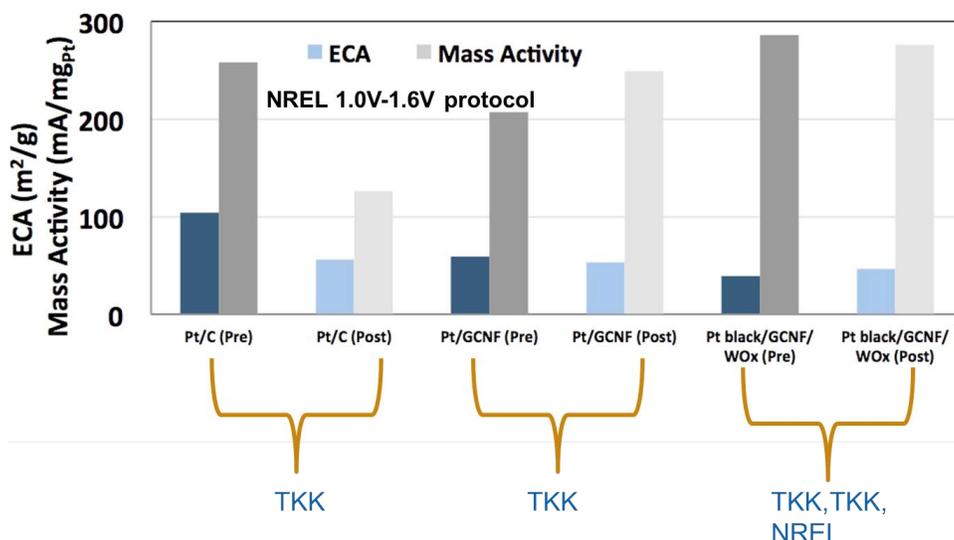


FIGURE 13. Mass Activity and Durability of Pt Black/GCNF/WO<sub>x</sub> Mixtures

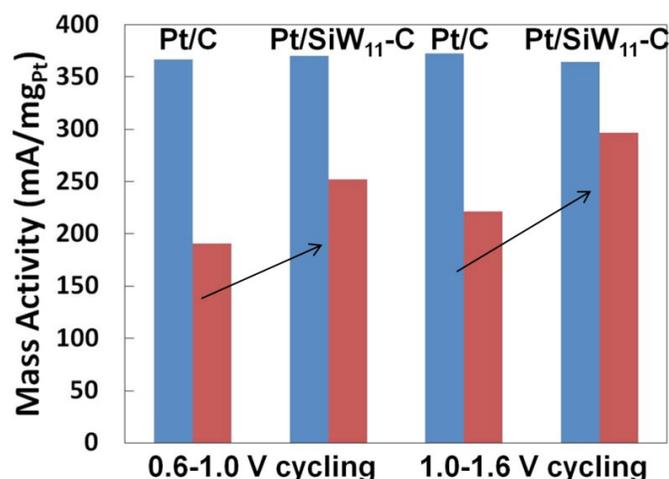


FIGURE 14. The 0.6-1.0 V cycling (30,000 cycles, 500 mV/s) was used to evaluate Pt dissolution, while 1.0-1.6 V cycling (6,000 cycles, 100 mV/s) evaluated support corrosion. HPA loading was chosen such that initial activity was near equal to Pt/C. In both cases, HPA helped maintain catalyst activity by slowing particle growth.

### Pt/C-HPA

Durability results on Pt/HPA-C were conducted using previously developed protocols. Results of durability are shown in Figure 14. 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 nearly equal to Pt/C. In both cases, HPA helped maintain catalyst activity by slowing particle growth.

Graphitized carbons treated with HPA were the new focus of research during the first and second quarters of

ECA (m <sup>2</sup> /g <sub>Pt</sub> ); ECA Loss (%); EOL @ 5000 cycles
<b>Pt/Ketjen Black Baseline:</b> BOL= 100 m <sup>2</sup> /g <sub>Pt</sub> ; EOL= 46 m <sup>2</sup> /g <sub>Pt</sub> ; 39.5% Loss
<b>Pt/GCNF:</b> BOL= 82 m <sup>2</sup> /g <sub>Pt</sub> ; EOL=71 m <sup>2</sup> /g <sub>Pt</sub> ; 13.4% Loss
<b>Pt/GCNF-HPA:</b> BOL= 68 m <sup>2</sup> /g <sub>Pt</sub> ; EOL=52 m <sup>2</sup> /g <sub>Pt</sub> ; 23.5% Loss

FIGURE 15. Cyclic Durability of Pt/C and Pt/C-HPA. Pt/GCNF exhibits improved durability compared to baseline, but post-HPA treatment, the losses are higher. HPA treatment does not result in an improvement on the durability of the catalyst system.

FY 2014. The expectation was that we might be able to maintain the activity similar to Pt/C-HPA while improving the durability even further with the use of more durable graphitized carbon blacks. Various graphitized carbon blacks were modified with HPA and Pt deposited on them using ALD or wet chemistry. Samples with Pt-ALD did not meet the activity requirements. Our results indicated that Pt deposited by wet-chemistry onto GCNFs, showed excellent activity and cyclic durability. Modifying the GCNF with HPA did not affect the activity significantly and actually lowered the cyclic durability. As a result, even though Pt/HPA-GCNF met the durability requirement, it was not a result of the HPA treatment and hence a No-Go decision was made as is not a viable option. Figure 15 summarizes the ECA loss for baseline Pt/C, Pt/GCNF and Pt/GCNF-HPA.

## CONCLUSIONS

Pt deposited by ALD or wet chemistry technique on  $WO_x$  supports did not meet the ORR activity requirements of commercial Pt/C primarily due to the low electronic conductivity of  $WO_x$ . ECAs were also lower than conventional Pt/C. A higher Pt wt% on the support as well as incorporating carbon black to the catalyst resulted in improved ORR activities that were still lower than the baseline Pt/C materials. Pt deposited by wet chemistry on HPA modified conventional high surface area carbon (Ketjen Black) met the requirements for ORR activity in RDE studies. The most durable catalyst was wet chemistry Pt deposited on GCNFs from TKK. Pt/GCNF exhibited activity and durability in RDE studies that were significantly higher than Pt/Ketjen Black baseline materials. However, Pt deposited on HPA-modified graphitized carbons including GCNF did not show any additional improvements due to the HPA functionalization; the durability of these materials was slightly lower than untreated Pt/GCNF. As a result, even though Pt/HPA-GCNF met the durability requirement, it was not a result of the HPA treatment and hence a No-Go decision was made. HPA functionalized Pt/GCNF were not evaluated in subscale fuel cells, but Pt/GCNF based subscale cells were evaluated and compared to Pt/Ketjen Black to demonstrate improved durability under cyclic durability protocols.

## 2014 PUBLICATIONS AND PRESENTATIONS

1. “Atomic Layer Deposition of Platinum Particles on Titanium Oxide and Tungsten Oxide” Virginia R. Anderson, Noemi Leick, Joel W. Clancey, Katherine E. Hurst, Kim M. Jones, Anne C. Dillon, Steven M. George. Submitted to J. Phys Chem C. 2014.
2. Mason, K. Sykes, Kenneth C. Neyerlin, Mei-Chen Kuo, Kiersten C. Horning, Karren L. More, and Andrew M. Herring. “Investigation of a Silicotungstic Acid Functionalized Carbon on Pt Activity and Durability for the Oxygen Reduction Reaction.” Journal of The Electrochemical Society 159, no. 12 (2012): F871-F879.