

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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catalysts based on tungsten oxide and/or heteropolyacid/C supported Pt.

Technical Barriers

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

- (A) Durability (of catalysts and membrane electrode assemblies)
- (B) Cost (of catalysts and membrane electrode assemblies)
- (C) Performance (of catalysts and membrane electrode assemblies)
- (D) Start-up and Shut-down Time and Energy/Transient Operation (Support Corrosion)

Technical Targets

This project synthesizes novel Pt-based electrocatalysts on alternative oxide supports. The project has targets outlined in the Multi-Year Research, Development and Demonstration Plan for both electrocatalysts for transportation applications (Table 3.4.12) and MEAs (Table 3.4.13). An enhancement in electrocatalytic activity by a factor of 4x (from the benchmark Pt/C metrics) and the ability to withstand 30,000 start-up/shut-down cycles and open circuit voltage holds with an electrochemically available surface area (ECA) loss of <30% are included.

Background

One of the critical goals to achieve the automotive commercialization targets is improved durability. Although durability of the fuel cell system has been improved, some of the improvements come with increased system complexity and cost. This project addresses the issue of catalyst support degradation during normal operation and especially under start-stop conditions when the fuel cell cathode experiences high transient potentials approaching 1.6 V. Typical carbon blacks used today corrode easily under these conditions and complex systems operations are being employed to mitigate it at this time. We propose to use corrosion-resistant oxide supports as a solution. In addition to corrosion resistance, this project will attempt to strengthen the support-Pt anchoring and also lower the total Pt loading in the cathode of the catalyst layer.

Fiscal Year (FY) 2011 Objectives

To help DOE address critical shortcomings in catalyst performance and durability by synthesizing novel

FY 2011 Accomplishments

- Prepared different stoichiometries of nano-WO₃ for Pt deposition by atomic layer deposition (ALD) and characterized the material using X-ray diffraction and Brunauer-Emmett-Teller. Demonstrated and characterized improved structure Pt/WO₃.
- Evaluated Pt catalyzed support corrosion as a baseline for stability of Pt/WO₃. Evaluated Pt/WO₃ in electrochemical half-cells for ECA and oxygen reduction reaction (ORR) activity. Investigated several alternative methods for the measurement of ECA accurately.
- Completed following milestones:
 - 5.7.0 Demonstrate nano-structured Pt on WO₃, heteropoly acid (HPA), or a combination of the two. (100% completed) 09/2010.
 - 5.7.1 Demonstrate controlled nano-structured Pt placement and loading on WO₃, HPA, or a combination of the two. (100% completed) 12/2010.

- 5.7.2 Obtain cyclic voltammograms (CVs) and mass activity for Pt on WO₃, HPA, or a combination of the two. (100% completed) 2/28/11
- 5.7.3 Prepare high surface area catalyst electrodes based on tungsten oxide and tungsten-based heteropoly acids (HPAs), test electrochemically in half-cells, and compare to the corrosion of typical carbon blacks for proton exchange membrane fuel cells (PEMFCs) up to 1.5 V. (100% completed) 4/2011
- 5.7.4 Obtain CVs and mass activity for Pt on WO₃, HPA or a combination of the two with ECAs greater than 10 m²/g Pt. (100% completed) 9/2011.



Introduction

Before polymer electrode membrane fuel cells (PEMFCs) can be fully commercialized, improvements in cost and durability must be achieved [1]. Key to the PEMFC operation is the catalysis of the ORR on the cathode. An ideal ORR catalyst efficiently converts O₂, protons, and electrons to water, produces no peroxide byproducts, and is inexpensive and durable. The sluggish kinetics of the ORR on Pt-based electrocatalysts used today requires a high loading of Pt-based catalyst on the cathode with consequent concurrent increased costs. PEMFC cathode catalysts are supported on high surface area carbon blacks that are known to be thermodynamically unstable in the entire fuel cell operating regime. The kinetics of carbon corrosion are slow below 1 V, but catastrophic losses are observed when the cathode sees transient fluctuations in the 1-1.6 V regime (during start-up shut-down phenomena). Under these conditions, Pt nanoparticles are susceptible to agglomeration. Clearly there is a need for an improved corrosion-resistant support that strongly anchors the Pt strongly to the support and synergistically enhances the catalyst system ORR activity [2,3].

Approach

Our approach is multi-pronged and addresses the catalyst, support, catalyst/support interaction and functionalization of the support. Examination of Pourbaix diagrams reveals that the metals that are fairly stable in acid conditions at the potentials of interest are Ir, Pt and Au, and candidate metal oxides that are thermodynamically stable include Ti, Zr, Nb, Ta and W [2,3]. Various stoichiometries and crystallinities of WO_x nanorods are being grown using hot wire deposition (HWD); wet chemistry is also being pursued to produce different nanostructures of WO_x. These supports are projected to provide the desired higher corrosion resistance at these high transient potentials. Pt nanoparticles are being deposited on WO_x using ALD and wet-chemical methods. Heteropoly acid (HPA) materials being synthesized and characterized at CSM are candidates

for co-catalysts because they can be readily synthesized and assembled into nano-ordered ensembles on many electrode materials. The most promising HPA structures are being attached to the WO_x nanoparticles and carbon blacks. Part of the approach is to combine a high surface area carbon electrode with a tungsten oxide and/or HPA that can enable enhanced activity of Pt for the ORR and enhanced stability of the Pt catalyst particles [4,5]. The challenge is to develop i) electrode support materials that are resistant to corrosion in the entire PEMFC operating environment, ii) electrode support materials that strongly anchor the Pt nanoparticles to prevent agglomeration, iii) electrode support and functionalized materials that have sufficient conductivity to provide both electronic and protonic conduction paths, iv) catalyst-support systems that lower peroxide generation, and v) electrode structures that have the optimal electrode structure/porosity/hydrophobicity/hydrophilicity to minimize mass-transport losses. Overall, our approach is to develop a catalyst system that approaches the DOE activity, performance and cost benchmarks.

Results

Commercial Pt/C electrocatalysts were evaluated by rotating disk electrodes (RDEs) and characterized for ECA, specific and mass activity [6-8]. These catalysts were found to meet and even exceed literature benchmarks (Figure 1) validating our measurement and preparation methods. Baseline and newly synthesized materials were also screened for corrosion resistance in electrochemical half-cells. Because standardized protocols for evaluating Pt/alternative supports do not exist, a durability working group sub-team lead by NREL that includes members from Los Alamos National Laboratory, NTCNA and Illinois Institute of Technology are working jointly to develop these protocols. The protocols under development involve potential cycling in the typical automotive regime of 0.6–1.0 V as well as in the start-up/shut-down regime of 1.0–1.6 V. Furthermore, in preparation for testing of selected Pt/alternative support candidates as fuel cell electrodes, baseline Pt/C catalysts were evaluated in subscale fuel cells at NREL and demonstrated to meet and even exceed the DOE benchmarks of ORR electrocatalytic activity (Table 1).

WO_x support materials were prepared by HWD as well as wet chemistry, as shown in Figures 2 and 3 respectively. Pt was deposited onto WO_x supports using ALD but was initially found to have a non-uniform distribution. Using TiO₂ as a proxy support allowed us to monitor in situ the loading of Pt as a function of number of ALD cycles. We were then able to optimize the process and significantly improve Pt nanoparticles dispersed on WO_x (Figure 4). The materials were screened for morphology, surface area, and electrochemical stability by excursions to high potentials. We found them to possess superior stability as compared to carbon blacks. These studies confirmed that WO_x supports are more stable than carbon blacks and Pt/WO_x is more stable than Pt/C (Figure 5).

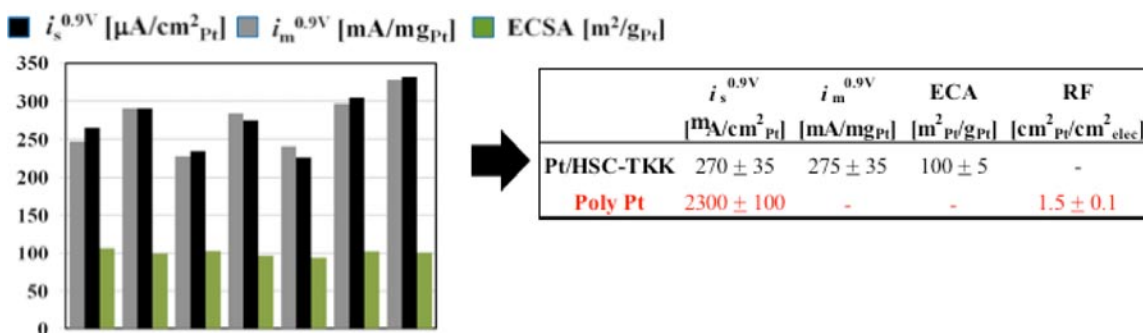


FIGURE 1. Accuracy and Reproducibility of RDE Measurements of ECA and ORR Activity for Baseline Pt/C and Poly-Pt (The x-axis corresponds to the different samples characterized for electrochemical benchmarking.)

TABLE 1. Baseline Pt/C ECA and activity results in RDE and subscale fuel cells tested at NREL and compared to DOE benchmarks.

	Specific Activity ($\mu\text{A}/\text{cm}^2_{\text{Pt}}$)	Mass Activity ($\text{mA}/\text{mg}_{\text{Pt}}$)
DOE 2015 Target in MEA ¹	720	> 440
DOE 2011 Status	720 ³	240 ⁴
NREL Pt/C status in MEA ¹	290 ± 10	225 ± 10
NREL Pt/C status in RDE ²	270 ± 30	270 ± 30

¹MEAs 900 mV, 50 cm² subscale fuel cells, 15 min/point, 150 kPa

(PO₂ = 100 kPa), 80°C, 100% RH, Nafion[®] membrane.

²RDE half-cell - 900 mV, 20 mV/s, 25°C, 0.1 M HClO₄

³Pt nanostructured catalysts, at 900 mVIR-free

⁴Achieved by 3M

Preliminary Pt/WO_x materials produced by ALD as well as wet chemistry were evaluated in half-cell RDE set-ups

for ECA and activity. Two issues arise with electrochemical measurements: In measuring CVs, we find that the WO_x contributes charge to the hydrogen underpotential deposition (UPD) region due to formation of tungstates (Figure 6). This issue can be bypassed by using Cu UPD or CO chemisorption to measure the ECA and has been performed (Figure 7). ECA values are in the range of 10–14 m²/g. In measuring ORR current-voltage curves, high stoic WO₃ with lower electronic conductivity resulted in lower activity; the impact could be partially mitigated by mixing small amounts of carbon black to the ink formulation (Figure 8). At this time, the highest specific activity measured is comparable to that of conventional Pt/C while the mass activity is lower due to the lower surface area.

Commercial Pt/C (2.5 nm Pt nanoparticles on high surface area carbon) was functionalized with HPA by CSM

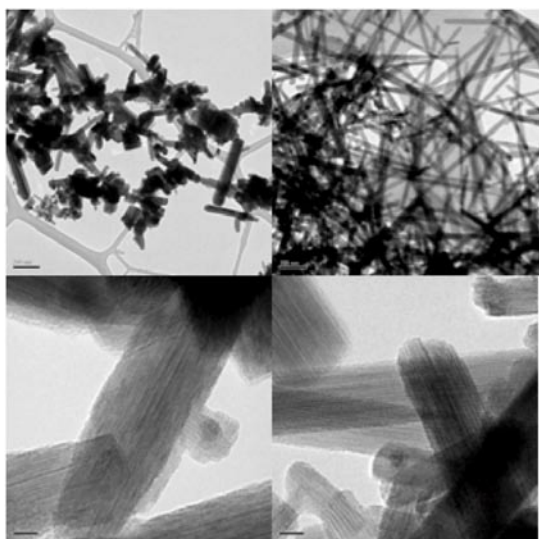
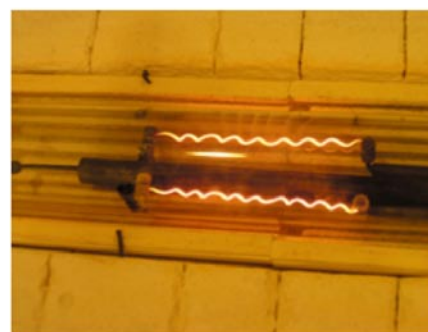
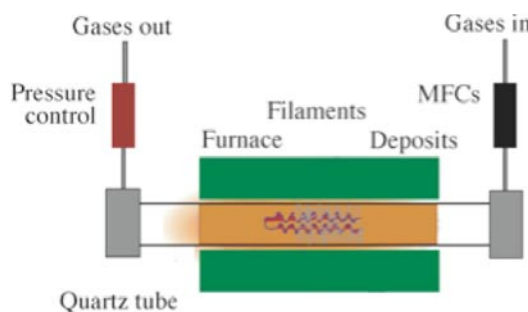


FIGURE 2. Preparation Method of WO_x using HWD and Transmission Electron Microscopy (TEM) Micrographs



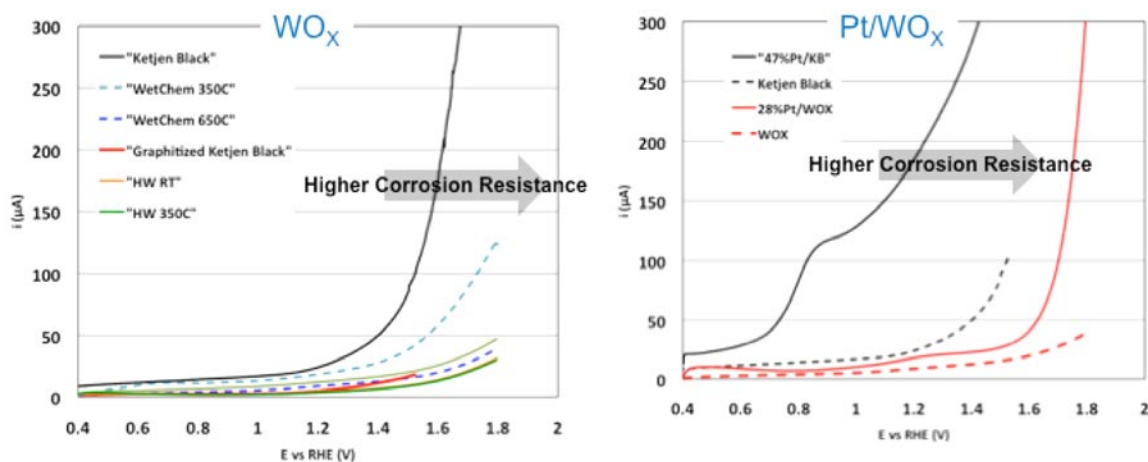


FIGURE 5. Half-Cell Electrochemical Screening Test Showing Onset and Magnitude of Corrosion Currents for Carbon, Pt/C and WO_x and Pt/ WO_x

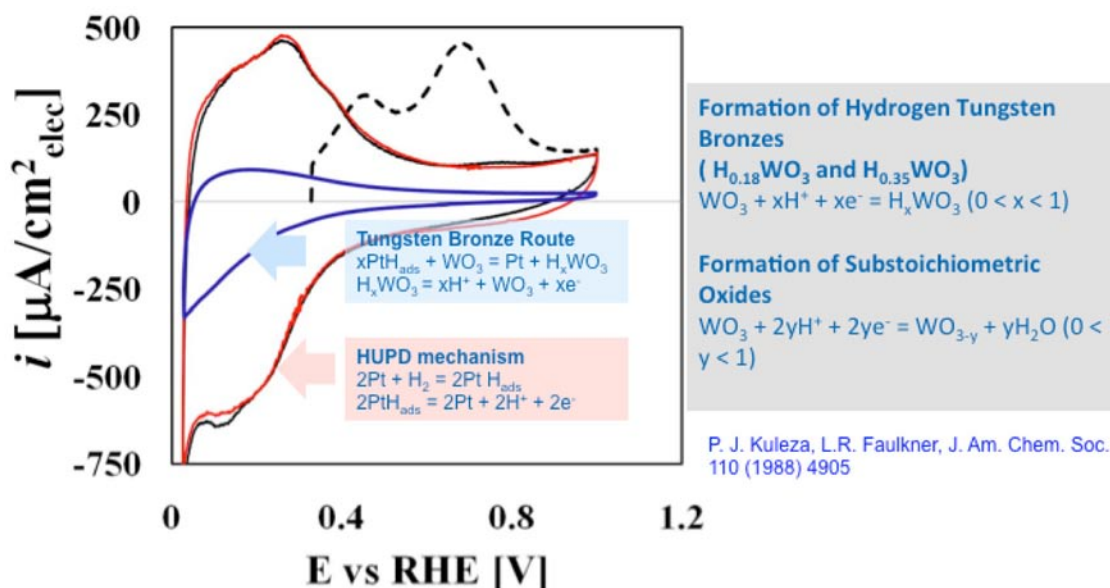


FIGURE 6. CVs showing the impact of contribution from WO_x in the HUPD region. Cu UPD might give a better estimate of ECA since hydrogen UPD region includes charge due to formation of H_xWO_3 as well as spill over effects.

the evaluation of alternative catalyst support durability. Demonstrate electrochemical (RDE) durability of Pt/ WO_x as a function of the initial ECA using the developed protocols. Achieve specific and mass activity for Pt/ WO_x /HPA that is comparable to and eventually higher than conventional Pt/C.

FY 2011 Publications/Presentations

1. John Turner, “ WO_3 and HPA based system for ultra-high activity and stability of Pt catalysts in PEMFC cathodes”, 2011 DOE AMR, May 10th, 2011, project FC084, http://www.hydrogen.energy.gov/pdfs/review11/fc084_turner_2011_o.pdf

2. Shyam Kocha, “Protocols for Alternative Supports for PEMFCs”, Durability Working Group Meeting, 2011 DOE AMR Meeting, VA (2011).

3. Shyam S. Kocha, K.C. Neyerlin and Bryan Pivovar, “Electrocatalyst Durability in Automotive PEMFCs”, PBFC-5, August 1–4, 2011, ANL, Argonne, IL.

4. K.C. Neyerlin, S. Kocha, B. Pivovar and H. Dinh, Cu UPD as a diagnostic technique for the determination of electrochemical surface area of unsupported Pt, Pt/C, Pt/ WO_x , and PtRu alloys, 242nd ACS National Meeting Denver, CO August 28 – September 1, 2011.

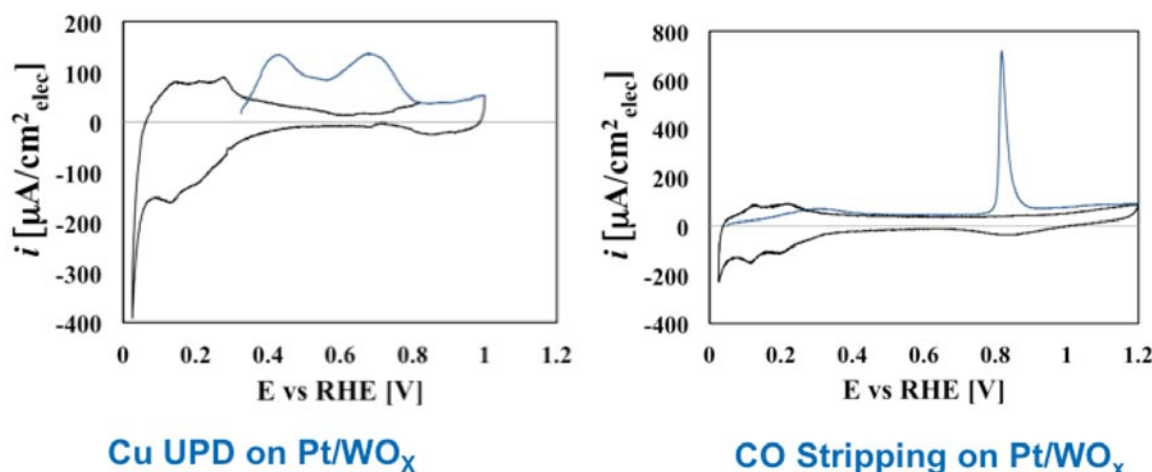


FIGURE 7. Application of Cu UPD and CO stripping to measure ECA. Cu UPD ($\sim 14 \text{ m}^2/\text{g}$) and CO ($\sim 10 \text{ m}^2/\text{g}$) stripping on identical Pt/WO_x samples.

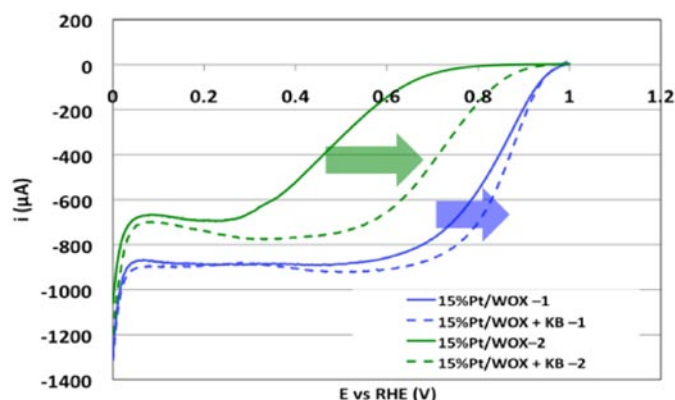


FIGURE 8. Impact of addition of electronically conductive carbon black to Pt/WO_x ORR current-voltage curves. RDE electrode ink modification improves activity and addition of carbon black improves dispersion and electronic conductivity.

5. Supporting platinum on nano-structured metaloxides for proton exchange membrane cathodes. A.M. Herring, M.-C. Kuo, R.J. Stanis, and N. Danforth, Prepr. Pap.-Am. Chem. Soc., Div. Fuel. Chem., 2011, 56, 100.
6. Kelly S. Mason, "Use of Heteropoly Acids and Tungsten Oxides Toward Improved Performance of the PEMFC Cathode Electrocatalyst" 242nd ACS National Meeting, Denver, CO, Aug. 2011.
7. Kelly S. Mason, "Preparation and Characterization of Heteropoly Acid and Tungsten Oxide Modified Pt Electrocatalysts" 220th ECS Meeting, Boston, MA, Oct. 2011. http://ecsmect2.peerexpress.org/ms_files/ecsmect2/2011/04/29/00003426/00/3426_0_art_0_lkg4d5.pdf
8. "Supporting platinum on nano-structured metal oxides for proton exchange membrane cathodes." A.M. Herring, M.-C.Kuo, R.J. Stanis, and N. Danforth, oral presentation, presented at the 241st ACS Meeting, Anaheim, CA, March 2011.

9. A.C. Dillon "WO₃ Nanorods for Electrochromic and Fuel Cell Catalyst Applications" SSPC, "Key-Note" SSPC15, Santa Barbara, July, 2010.
10. Katherine Hurst, Virginia Anderson, Robert Tenent, Shyam Kocha, Kenneth Neyerlin, Jason Zack, Steven George, John Turner, and Anne Dillon "Deposition of Pt on tungsten oxide nanoparticles for PEM cathodes" presented at the 241st ACS Meeting, Anaheim, CA, March 2011.
11. Katherine E. Hurst, Virginia R. Anderson, Shyam S. Kocha, Steven M. George, John A. Turner and Anne C. Dillon "Nano-Pt and tungsten oxides as a novel PEM cathode" 242nd ACS National Meeting, Denver, CO, Aug. 2011.

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