

V.C.3 Low-Platinum Catalysts for Oxygen Reduction at PEMFC Cathodes

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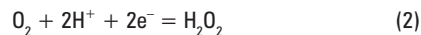
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- Preliminary durability studies of peroxide generation.
- Established high activity of gold supported on titanium oxide in base.

Introduction

The cost of proton exchange membrane fuel cells (PEMFCs) can be drastically reduced by using little or no platinum (Pt) in the electrodes. However, Pt is the only catalyst proven to date to withstand thousands of hours of operation in the highly corrosive, acidic conditions at PEMFC electrodes. The oxygen reduction reaction (ORR) in equation (1) occurs at the PEMFC cathode and requires relatively large loadings of Pt because it is a complex, 4-electron process requiring the activation and conversion of molecular oxygen (O₂) to water (H₂O) via a reaction with protons (H⁺). Catalysts with poor ORR activity often convert the O₂ to hydrogen peroxide (H₂O₂) via the two-electron reaction in equation (2). Hydrogen peroxide should be avoided in PEMFCs because it degrades the electrolyte membrane.



The activity of noble metal catalysts can be improved and/or modified by metal-support interactions (MSIs), whereby the support affects the electronic state of the metal. This is the standard approach used with heterogeneous catalysts for reforming, as the activity of the catalysts can be tuned and their stability improved. In this research effort, we show that the activity of Pt for the ORR is improved when it is supported on acidic phosphates, such as hydrous tantalum phosphate (TaPO). The electron-withdrawing, hydrous metal phosphate shifts the electronic state of the platinum to improve catalysis. We also studied gold (Au) as a model compound because it is known only to be active for oxygen reduction in base, but we have been able to change its ORR activity in acid properties by supporting it on tin oxide and titanium oxide. Gold is also significantly less expensive than platinum and is also highly acid stable.

Objectives

- Create low-cost, low-Pt, acid-stable electrocatalysts for oxygen reduction.
- Evaluate the activity and durability of the catalysts.
- Resolve key catalytic mechanisms.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

TABLE 1. Mass Activity of NRL Catalysts vs. DOE Targets - Metric: (A mg_{Pt}⁻¹) at 0.9 V

NRL Status (Cell)	DOE 2004 Status (Cell)	DOE 2004 Status (Stack)	DOE 2010 Target (Stack)
0.25 to 0.56	0.28	0.11	0.44

Accomplishments

- Developed method to improve air stability of supported Pt catalysts.
- Improved synthesis to achieve up to 5x surface activity of Pt.

supported on both basic and acidic supports, such as tin oxide and titanium oxide, respectively.

The catalyst activity for the oxygen reduction reaction in equation (1) is evaluated using standard rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) methods. This approach has been identified as an accurate means to correlate the activity of the oxygen reduction reaction kinetics to actual performance in PEM fuel cell membrane electrode assemblies [1]. A rotating disk is used to measure the current-voltage relationship of the reduction of oxygen, and the RRDE apparatus has an additional Pt ring that reports current from the oxidation of any residual H_2O_2 that might be formed by incomplete oxygen reduction equation (2). The specific activity of the Pt per unit surface area is measured by hydrogen adsorption (HAD) from the cyclic voltammetry of the catalysts under an inert atmosphere. For these electroanalytical tests, the catalysts are mixed with Vulcan carbon (VC) and a Nafion[®] ionomer and dispersed as a thin film on the tip of the glassy-carbon disk, which is then submerged in an acidic or basic liquid electrolyte. The physical properties of the catalysts are characterized using a variety of tools. The Bruner, Emmett and Teller method is used to evaluate surface area and microporosity, and thermal analysis is used to determine water content and thermal stability, and transmission electron microscopy is used to visualize catalyst dispersion. The oxidation states of the catalysts are studied *ex-situ* with x-ray photoelectron spectroscopy (XPS). Proton conductivity is measured with impedance spectroscopy.

Results

Last year, we used the RDE method to measure a mass activity of $0.56 \text{ A mg}_{Pt}^{-1}$ at 0.9 V for our Pt-TaPO/VC catalysts, which is a 2x improvement over the state-of-the-art catalysts with the RDE method. The catalysts lost activity upon storage in air due to the irreversible oxidation of the platinum to a platinum oxide. We also measured significant variation in our catalyst activity but were unsure whether it was due to catalyst preparation or due to activity fade over time.

Our first achievement for this year was to resolve the air stability problems with the catalysts, which

we did by additional heating steps. This success was critical for the overall viability of this catalyst system and also allowed us to send catalysts to industry for their evaluation without a time constraint on the testing and to determine the variability between samples. We showed with RRDE measurements that the Pt-TaPO/VC catalysts are highly efficient and produce little peroxide, which is critical for the long-term stability and durability of the PEMFC.

We confirmed this year that the activity of the catalysts is highly variable with synthesis, and focused on measuring which variables are vital to catalyst activity. We learned that catalysts that are made with chloride-free precursors are most active, and those with a ratio of Ta:P 1:1 in the synthesis are also the best. The catalysts cannot be heated at high temperatures, but heating under hydrogen at around 200°C improves the activity of some of the catalysts.

We also measured the proton conductivity of the tantalum phosphates because we have observed that they are better supports when hydrated and have speculated that the proton conductivity of the support may be critical to the ORR mechanism. The conductivity of the tantalum phosphates is approximately $1 \times 10^{-6} \text{ S cm}^{-1}$ at room temperature, or about 5 orders of magnitude lower than that of Nafion[®]. Therefore, the phosphates are not serving as a proton-conducting electrolyte. The conductivity measurements, however, prove that the protons in the materials are labile and can be donated to the platinum to change its electronic state presumably through the phosphate group [2].

The activity comparison of a Pt/VC standard to our Pt-TaPO/VC catalysts is shown in Table 2 for RDE measurements at room temperature (25°C). The Pt/VC results are comparable to those reported in the literature [1]. We report lower mass activity (A mg_{Pt}^{-1}) than last year. The problem is due to low Pt dispersion, as evidenced by the high platinum specific activity ($\mu\text{A cm}_{Pt}^{-2}$) or the activity per unit of platinum metal surface area as measured by hydrogen adsorption. Accordingly, the Pt-TaPO catalysts have 5x the specific activity of the highly dispersed Pt on VC. The low dispersion of the Pt on our TaPO catalysts is confirmed by transmission electron microscopy; as shown in Figure 1, the Pt is clumped non-uniformly on the phosphate.

TABLE 2. Activity of standard Pt/VC catalyst vs. Pt-TaPO/VC catalyst via rotating disk electrode measurements. RDE conditions: sweep rate is 20 mV/s; temperature is 25°C; electrolyte is 0.1 M HClO₄; rotation rate is 1600 rpm.

catalyst	HAD [m^2/g_{Pt}]	Pt loading, $\mu\text{g}_{Pt}/\text{cm}^2$	A mg_{Pt}^{-1} at 0.9V	A mg_{Pt}^{-1} at 0.85V	$\mu\text{A cm}_{Pt}^{-2}$ at 0.9V	$\mu\text{A cm}_{Pt}^{-2}$ at 0.85V
20% Pt/VC Standard	50	20	0.24	0.66	480	1330
Pt-TaPO/VC	8.8	11	0.25	0.72	2800	8140

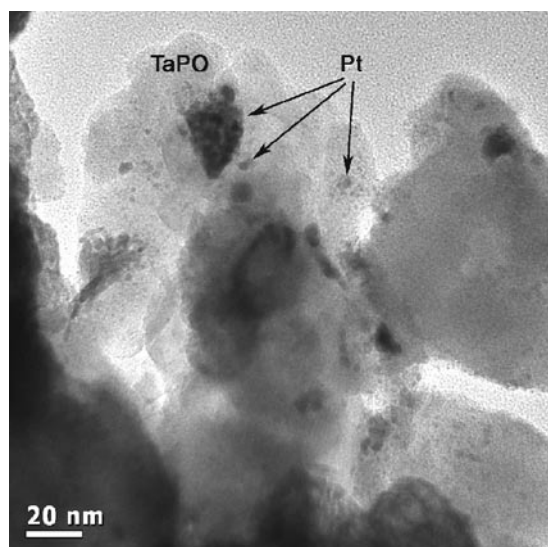


FIGURE 1. Transmission electron micrograph of platinum on tantalum phosphate (Pt-TaPO) showing poor dispersion of Pt nanoparticles (acknowledgement: K. Pettigrew, NRL).

Our task now is to improve the Pt dispersion on the TaPO. Much work was invested in the past to optimized Pt/VC materials. We can leverage methods developed for Pt/VC and also for commercial catalysts such as Pt on aluminum oxide.

Some of our Pt-TaPO/VC catalysts were also independently evaluated by General Motors. They reported a mass activity of $0.19 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ at elevated temperatures (60°C) using a sweep rate of 5 mV/s and rotation rate of 1600 rpm . Their mass activity for Pt-TaPO is only slightly higher than that for Pt/VC under these conditions. But, they also confirmed an approximate 5x-increase in the Pt specific activity of the Pt-TaPO/VC vs. Pt/VC.

The TaPO clearly affects the activity of the platinum, possibly because the acidic support affects the electronic state of the metal. A notional mechanism is shown in Figure 2, whereby the proton on the phosphate group is donated to the platinum, resulting in the withdrawal of electrons and a lowering of the platinum Fermi level. Such an effect has been modeled in alloys, and showed increased activity via increased oxygen adsorption, with complications from the increase in an oxide scale that inhibits the Pt activity [3]. Electronic effects can be studied with *in situ* methods such as x-ray absorption spectroscopy.

We continued with some limited studies of supported gold catalysts. Last year we proved that we could change the catalysis mechanism of oxygen on gold in acid significantly by supporting it on tin oxide.

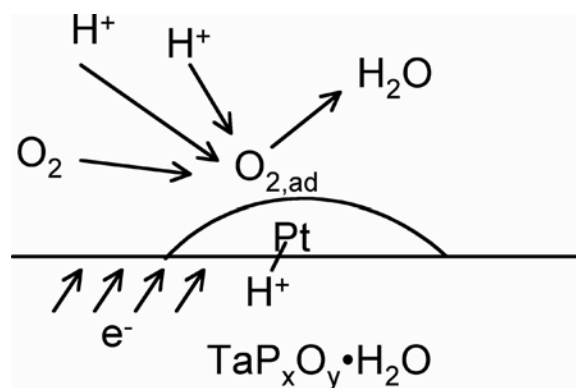


FIGURE 2. Notional mechanism for the improved activation of oxygen on Pt by an electronic effect of the proton-donating hydrous tantalum phosphate support, which acts as an electron sink.

Gold on carbon (Au/VC) only has almost no activity for oxygen reduction in acid, as shown by the low currents of the Au/VC RDE curves in Figure 3a compared to Pt/VC. Gold is inactive in acid because it only weakly adsorbs oxygen molecules, and therefore cannot initiate the reduction mechanism [4]. By supporting the gold on tin oxide (AuSnO_x/VC), the reaction changes to a 4-electron reaction, as evidenced by the higher current density. We have proposed that this catalyst is active either because the tin oxide adsorbs the oxygen molecules, or the electronic state of the gold is modified by the tin, improving its adsorption properties [5].

This year, we studied gold on titanium oxide (AuTiO_x/VC) because this is a well-known catalyst for carbon monoxide oxidation. Titanium dioxide is also very acidic vs. the basic nature of the tin oxide surface, giving an opportunity to further probe the effect of the oxide support. We observe that the gold on titanium oxide is an excellent oxygen reduction catalyst in base, and far outperforms gold on carbon and the gold on tin oxide, and approaches the activity of platinum on carbon. In the acidic electrolyte representative of the PEMFC, the gold on titanium oxide loses activity, while the gold on tin oxide is a good performer. The lack of activity of the gold on titanium oxide in acid electrolyte implies the necessity of a basic support for gold, as is supplied by the tin oxide. The gold on titanium oxide might outperform the gold on carbon standard in the basic solution (Figure 3b) by enhancing the adsorption of the hydroxyl groups (OH) which are critical to its oxygen reduction mechanism [3]. Significant improvements in the activity of these gold catalysts are still be needed to make them viable fuel cell catalysts, however, we show again the strong influence of oxide-based supports on gold catalysis.

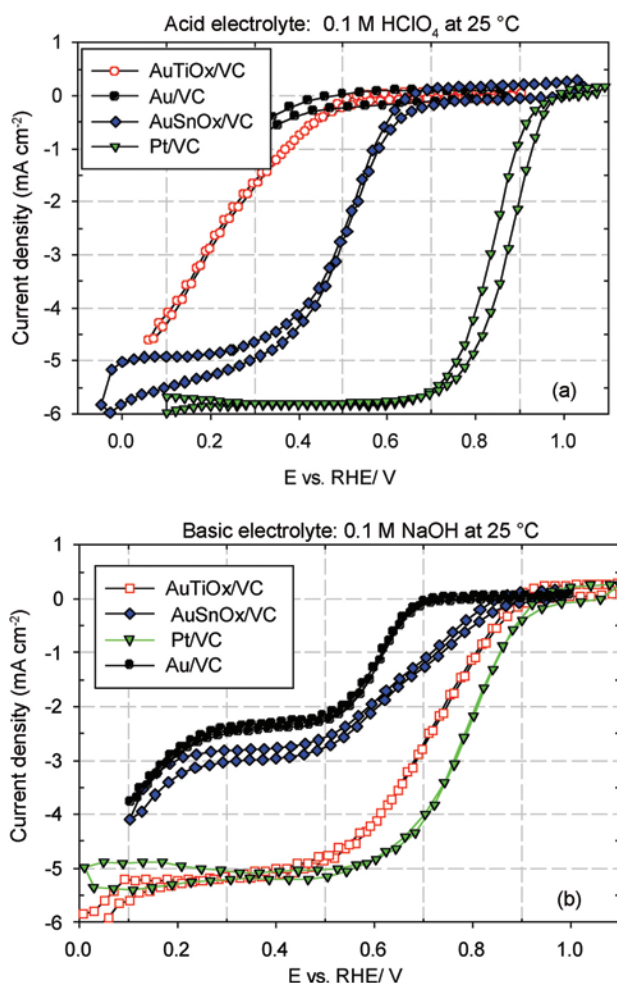


FIGURE 3. Rotating disk electrode voltammetry of four different catalysts mixed with Vulcan carbon in (a) acid and (b) base. We compare a standard of platinum (Pt/VC) to gold (Au/VC), gold on tin oxide (AuSnO_x/VC), and gold on titanium oxide (AuTiO_x/VC). Electrode conditions: 1,600 rpm, 20 mV s⁻¹, 20 mg_{Pt} cm⁻² for Pt/VC electrode, 80 mg_{Au} cm⁻² for Au-based electrodes.

Conclusions and Future Directions

We conclude that there are significant opportunities for improving Pt catalysis by metal support interactions. This approach is an important alternative to that taken with alloying, because oxide-based supports are highly stable in acid. When normalized to surface area, these catalysts have approximately 5x the specific activity of standard platinum on carbon catalysts, but the actual mass activity realized must be improved to

make these catalysts a viable alternative. Our next goal is to optimize Pt dispersion on the TaPO to increase utilization. It is also important to further study the mechanism to determine how the TaPO is affecting the platinum electronic state, and whether oxides can be used in the same way as alloys to change the catalysis.

The catalysis of oxygen reduction on gold is significantly affected by its oxide support, suggesting that there may be opportunities with this metal. Gold catalysis might be further improved by selecting alternative supports.

FY 2006 Publications/Presentations

1. "Enhanced Oxygen Reduction Activity in Acid by Tin-Oxide Supported Au Nanoparticle Catalysts," W. S. Baker, J. J. Pietron, M. E. Teliska, P. J. Bouwman, D. E. Ramaker, and K. E. Swider-Lyons, *J. Electrochem. Soc.*, **153**, A1702 (2006).
2. "Leveraging Metal-support Interactions to Improve the Activity of PEMFC Cathode Catalysts," K. E. Swider-Lyons, M. E. Teliska, W. S. Baker, P. J. Bouwman, J. J. Pietron, *ECS Transactions*, Vol 1, Issue 6, 97 (2005).
3. "Leveraging Metal-Support Interactions to Improve The Activity of PEMFC Cathode Catalysts," K. E. Swider-Lyons, M. E. Teliska, W. S. Baker, J. J. Pietron, *Fifth International Symposium On Proton Exchange Membrane Fuel Cells*, 208th Meeting of the Electrochemical Society, Los Angeles, CA, 16-21 October 2005.
4. "Using Metal Oxide and Phosphate Supports to Improve Oxygen Electrocatalysts in PEM Fuel Cells," Electrochemistry Gordon conference, Buellton, CA, 12-17 February 2005.

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