

## IV.C.2 Low-Platinum Catalysts for Oxygen Reduction at PEMFC Cathodes

*Karen Swider-Lyons (Primary Contact), Peter J. Bouwman, Margaret E. Teliska and Wendy S. Baker*

*Naval Research Laboratory*

*Surface Chemistry Branch, Code 6171*

*Washington, DC 20375-5342*

*Phone: (202) 404-3314; Fax: (202) 767-3321; E-mail: karen.lyons@nrl.navy.mil*

*DOE Technology Development Manager: Nancy Garland*

*Phone: (202) 586-5673; Fax: (202) 586-9811; E-mail: Nancy.Garland@ee.doe.gov*

*Subcontractor:*

*Wojtek Dmowski, University of Tennessee*

### Objectives

- Create low-cost, acid-stable electrocatalysts for oxygen reduction.
- Evaluate the activity and durability of the catalysts.
- Characterize active materials to resolve key catalytic mechanisms.

### Technical Barriers

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

- O. Stack Materials Cost
- Q. Electrode Performance
- P. Durability

### Approach

- Synthesize oxides and phosphates that are catalytically active for oxygen, good proton conductors, and stable in acid, and impregnate them with Pt and other noble metals.
- Evaluate the electrocatalytic properties of the new compounds with a rotating disk electrode method.
- Characterize the physical, chemical, and structural attributes of the catalysts with techniques including X-ray absorption spectroscopy, pair-density function analysis of X-ray diffraction, X-ray photoelectron spectroscopy, and thermogravimetric analysis.

### Accomplishments

- Demonstrated a 10% platinum-tantalum phosphate/Vulcan carbon catalyst with 2 to 3 times the mass activity of a 20% Pt/Vulcan carbon standard.
- Showed that the activity of gold and palladium is enhanced when the catalyst is supported on hydrous tin oxide.
- Completed an in-situ spectroscopic study of a platinum iron phosphate catalyst to establish the oxidation state of the platinum during use in a fuel cell.
- Established a preliminary mechanism to explain the electrocatalyst functions.

## Future Directions

- Determine the stability of the catalysts in operational proton exchange membrane fuel cells (PEMFCs).
- Improve ink formulations of the catalysts to simplify testing by third parties.
- Develop reliable methods for making nanoscale particles of the catalysts.
- Continue to develop understanding of how the properties of the catalysts affect the electrocatalysis of oxygen reduction.

## Introduction

The cost of the fuel cells and imports of noble metals can be drastically reduced by using little or no Pt in fuel cell electrodes, thereby improving the commercialization potential of fuel cells. The most Pt is used at the fuel cell cathode, where the oxygen reduction reaction (ORR) is kinetically limited. We are investigating several materials that may be able to serve as low-cost, stable electrocatalysts in fuel cell cathodes, including Pt-FePO, Pt-TaPO, and Pt-SnO. Selected hydrous phosphates and hydrous oxides can serve as catalytic supports for Pt because of their ability to activate molecular oxygen (O<sub>2</sub>) to prerequisite species in the ORR mechanism (O<sup>2-</sup> and <sup>-</sup>OOH)<sup>1</sup> and their microporous or open-framework structures that promote oxygen storage and high proton conductivity.<sup>2</sup> By satisfying the need for oxygen activation and proton (H<sup>+</sup>) conductivity, the ORR (in Equation 1) can be improved. In addition to studying their electrocatalytic properties, the physical, chemical, and structural attributes of the catalysts must be investigated to deconvolve the catalytic mechanisms. The Pt can be substituted by Au and other metals to study the interactions between the noble metals and the support.

Oxygen reduction reaction:



## Approach

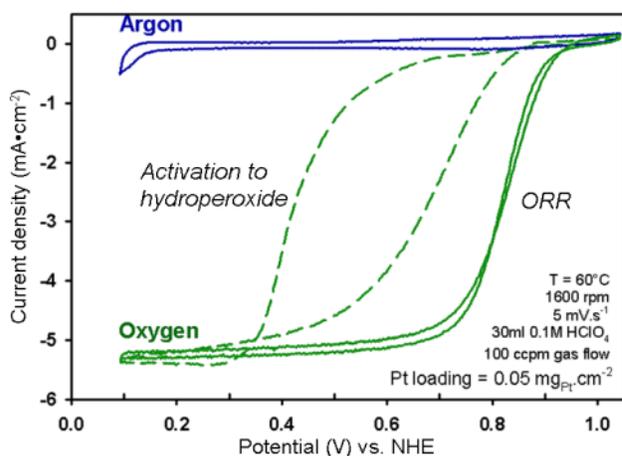
Hydrous phosphates and oxide catalysts are made in aqueous solutions from commercially available chemicals, then filtered and dried in air. The materials are then heated to 150°C, but retain >0.2 mole percent water in their structure. The powdered materials are mixed with 20 to 80 wt% Vulcan carbon to improve their electronic conductivity.

The performance of noble-metal-doped phosphate and oxide materials is evaluated using standard procedures for a rotating disk electrode (RDE) for platinum electrocatalysts.<sup>3</sup> The materials may also be used in membrane electrode assemblies for testing in PEMFCs using the procedures developed and optimized by Los Alamos National Laboratory.<sup>4</sup> The catalysts are evaluated for stability by determining their chemical composition and electrochemical activity before and after stirring in 1.0 M sulfuric acid at 90°C for 12 to 24 hours. A key criterion is that the catalysts show no evidence of dissolution in the acid.

The physical properties of the catalysts are characterized using a variety of tools. The BET method is used to evaluate surface area and microporosity, and thermal analysis is used to determine water content and thermal stability. The structure of the materials is characterized by the pair-density-function analysis of high-energy X-ray diffraction patterns, which is able to resolve the local and medium-range structure of the materials from 0.2 to 1.5 nm, the size region that has the greatest impact on the ensuing catalytic results. The oxidation states of the catalysts are studied ex-situ with X-ray photoelectron spectroscopy (XPS) and in-situ with X-ray absorption near-edge spectroscopy (XANES).

## Results

The Pt-SnO, Pt-TaPO, and Pt-FePO can withstand acid environments and show high electrocatalytic activity for the ORR. The voltammetry of a hydrous Pt-TaPO RDE is shown in Figure 1. The RDE data for the phosphates can be compared to that of Pt standards by their relative activity at 0.9 V vs. a normal hydrogen electrode, as shown in Figure 2. This plot shows that the Pt-FePO

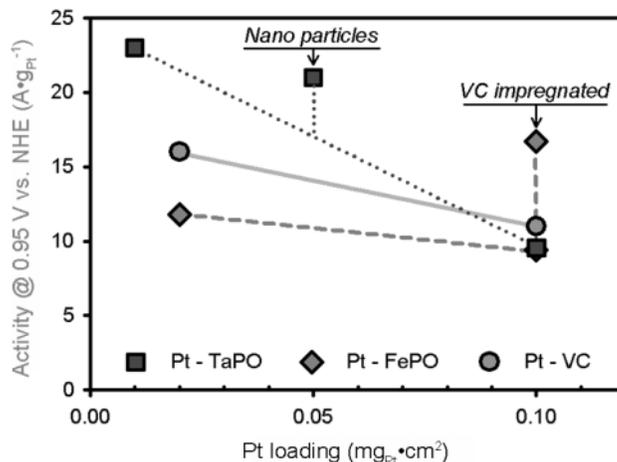


**Figure 1.** RDE of 5% Pt-TaPO/VC. After electrochemical activation (dashed line), the material shows excellent activity for the ORR under oxygen (bottom solid line). The Pt-TaPO shows no characteristic features for Pt metal when cycled under Ar (top solid line).

and Pt-TaPO have higher activity per unit Pt than Pt/VC standards, particularly when the materials are prepared as nanoparticles. Clearly, optimizing synthetic methods for the phosphate nanoparticles will lead to improved activity.

The Pt-TaPO, and the other active oxides and phosphates, must be electrochemically activated between 0.6 and 0.4 V (vs. a normal hydrogen electrode, NHE) before they exhibit high activity for the ORR, as shown in the voltammetry in Figure 1. The electrochemical activation occurs whether or not the material contains Pt, indicating that the process is innate to the phosphate and oxide. The materials are electrochemically deactivated only when cycled to  $>1.6$  V. It should be noted that oxygen evolution is only observed at  $>1.8$  V, which is about 0.5 V higher than the onset potential for oxygen evolution on Pt metal.

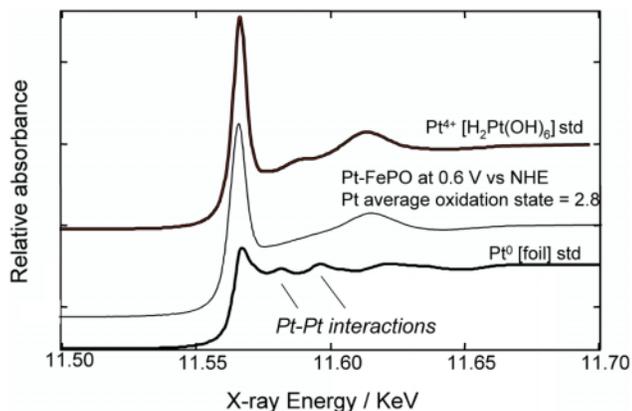
There are numerous indications that the active forms of the catalysts, particularly Pt-FePO, have no surface-confined Pt metal. The most electrochemically active materials have none of the characteristic adsorption features of Pt metal, such as hydrogen adsorption at  $<0.2$  V and oxygen adsorption at  $>0.8$  V, as is shown for the Pt-TaPO under Ar in Figure 1. XPS measurements and XANES measurements on Pt-FePO indicate that its



**Figure 2.** Relative activity of Pt-FePO and Pt-TaPO catalysts vs. a Pt/VC standard as measured by RDE voltammetry in oxygen-saturated 0.1 M HClO<sub>4</sub> at 60°C, 1600 rpm, and a sweep rate of 5 mV·s<sup>-1</sup>

Pt is in an oxidized state (Pt<sup>2+</sup> and Pt<sup>4+</sup>), even after the material has been electrochemically activated (Figure 3). The spectra lack features of Pt–Pt metal interactions, and the intensity of the main absorption curve indicates an average oxidation Pt state of +2.8 after the material has been electrochemically activated and held at 0.6 V in the electrochemical cell. High-energy X-ray diffraction measurements also show that there are minimal Pt–Pt metal interactions in the materials, as would be expected for Pt metal. It should be noted, however, that the Pt-TaPO and Pt-SnO show a mixture of Pt oxides and metal, by both XPS and XANES, and it is possible that both Pt metal and Pt oxides can be active in the ORR mechanism.

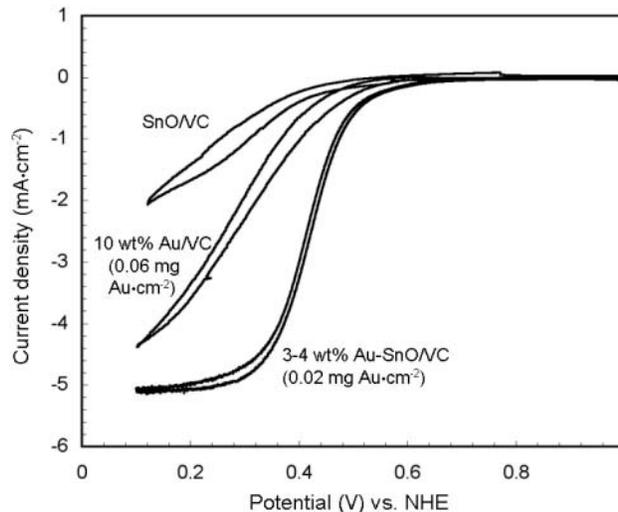
The XPS and XANES analyses of the Pt-FePO also indicate that there is no significant reduction of the Pt or Fe during the activation of the catalysts. We attribute the reduction reaction associated with electrochemical activation to the formation of a hydroperoxide species on the surface of the FePO. The formation of the Fe–OOH group requires the consumption of electrons, presumably with the occupation of an oxygen vacancy in the FePO lattice, thus explaining the reduction peak, constant oxidation states of the metal ions, and high voltage needed for electrochemical deactivation of the materials. Surface hydroperoxide groups are common to iron phosphates.<sup>1</sup>



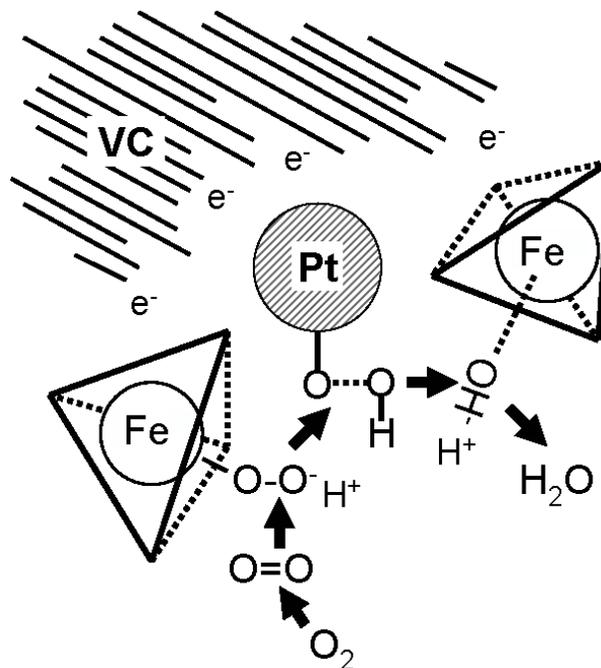
**Figure 3.** XANES of  $\text{Pt}^0$  and  $\text{Pt}^{4+}$  Standards vs. a Pt-FePO Sample at 0.6 V. The linear combination of the Pt standards indicates that the Pt-FePO has an average oxidation state of +2.8. There are no apparent peaks from Pt-Pt interactions in the Pt-FePO, suggesting that there is no Pt metal.

To probe the mechanism for the activity of the catalysts, we studied the activity of catalysts when doped with Au and Pd, as they are less active for the ORR than Pt, thus allowing the role of the support to be discerned. The RDE data for Au/VC, SnO/VC and Au-SnO/VC are shown in Figure 4. As expected, the Au and SnO have poor activity for the ORR. The Au is inactive for the ORR without the presence of hydroxyl ( $\text{OH}^-$ ) groups, which are scarce in acid.<sup>5</sup> The RDE data for our Au-SnO in acidic media shows higher activity than is expected from the pure Au (or SnO), suggesting that it is not starved of OH when in the presence of SnO.

A bifunctional mechanism for the Au on SnO (and Pt-FePO, etc.) can be proposed in terms of the accepted pathway for the ORR (see reference 5). The ORR occurs via the following steps: the oxygen physisorbs on the catalyst surface, dissociates, and finally recombines with protons to form water. The “slow” or rate-determining step in the reaction is understood to be the oxygen dissociation step. Whereas Au is a poor catalyst for oxygen dissociation in acid, SnO is able to adsorb molecular oxygen and dissociate it to form hydroperoxides, or  $\text{SnO-OH}$ , thus providing the needed hydroxyl groups. Once hydroperoxides are present on the SnO, the Au carries out the next step of recombining the hydroperoxides to water. A similar mechanism is



**Figure 4.** RDEs of Au/VC, SnO/VC and Au-SnO/VC. The Au impregnated on SnO shows higher activity than that expected from the individual materials, suggesting a synergistic effect.



**Figure 5.** Mechanism for Oxygen Reduction on Pt-FePO. The FePO dissociates molecular oxygen to hydroperoxides, and the  $\text{Pt}^{2+/4+}$  recombines hydroperoxides into water.

expected in the Pt-FePO and is shown schematically in Figure 5.

Further work may clarify the mechanisms and lead to the improved design of the catalysts and ultimately catalysts containing no precious metals.

### **Conclusions**

- Metals and metal oxides that are understood to be poorly active for the ORR (e.g., Pt<sup>2+</sup>, Pt<sup>4+</sup>, and Au) are activated when supported on hydrous oxide or phosphate catalysts that interact strongly with oxygen to form hydroperoxides.
- Pt-TaPO and Pt-FePO show higher activity per unit Pt than Pt-metal standards, particularly when prepared as nanoparticles.

### **References**

1. K. Otsuka, Y. Wang, *Appl. Catal. A*, 222, 145 (2001).
2. P. Colomban, Ed., "Proton conductors: solid, membranes and gels – materials and devices," Cambridge University Press, Cambridge (1992).
3. T.J. Schmidt, U.A. Paulus, H.A. Gasteiger, R.J. Behm, *J. Electroanal. Chem.*, 508, 41 (2001).
4. M. S. Wilson, J. A. Valerio, S. Gottesfeld, *Electrochim. Acta*, 40, 355 (1995).
5. B. B. Blizanac, C. A. Lucas, M. E. Gallagher, M. Arenz, P. N. Ross, N. M. Markovic, *J. Phys. Chem. B*, 108, 625 (2004).

### **FY 2004 Publications/Presentations**

1. W. Dmowski, T. Egami, K. E. Swider-Lyons, D. R. Rolison, P. J. Bouwman, "Atomic structure of disordered hydrous RuO<sub>2</sub>, Pt-Ru and Pt-FePO<sub>4</sub>," Symposium on Advanced Materials for Fuel Cells and Batteries, 204th Meeting of The Electrochemical Society, 12-17 October 2003, Orlando, FL.
2. P. J. Bouwman, W. Dmowski, K. E. Swider-Lyons, "Hydrous Pt-FePO<sub>x</sub> catalysts for oxygen reduction in proton exchange membrane fuel cells," Symposium on Advanced Materials for Fuel Cells and Batteries, 204th Meeting of The Electrochemical Society, 12-17 October 2003, Orlando, FL.
3. K. Swider-Lyons, P. J. Bouwman, W. Dmowski, "The use of nanocomposite materials to lower the platinum content of fuel cells and potential environmental payoffs," Symposium on Nanotechnology and the Environment: Nanotech-enabled Green Energy, 227th ACS National Meeting, 28 March - 1 April 2004, Anaheim, CA.
4. P. J. Bouwman, W. Dmowski, J. Stanley, G. B. Cotten, K. E. Swider-Lyons, "Platinum iron phosphates for oxygen reduction in PEMFCs," *J. Electrochem. Soc.*, Volume 151, No. 12, in press.