

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

Karen Swider Lyons (Primary Contact), Margaret Teliska, Wendy Baker, Jeremy Pietron

Naval Research Laboratory

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

Start Date: June 1, 2001

Projected End Date: December 30, 2006

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 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

A DOE goal for hydrogen fuel cell power systems for transportation is to cut the total platinum loading of the anode and cathode from 1.1 g/kW (rated) in 2004 to 0.2 g/kW in 2015, or to decrease the Pt amount by a factor of 5.5. Naval Research Laboratory (NRL) cathode catalysts show 6× the mass activity of standard platinum catalysts, indicating that 6× less platinum will be needed in a fuel cell. Verification of the activity of the catalysts in full fuel cells is in progress.

Table 1. Comparison of the Activity of Oxygen Reduction Catalysts at 0.9 V (NRL catalysts have 2x the activity of state-of-art catalysts and exceed 2010 stack targets by 27%. NRL catalyst measurements are made with half cells, and correlated to stack performance according to reference 1.)

| State-of-art Current (A) per mg Pt | DOE 2010 stack target Current (A) per mg Pt | NRL Platinum-Tantalum Phosphate Current (A) per mg Pt |
|---------------------------------------|--|--|
| 0.28 | 0.44 | 0.56 |

Approach

- Select and synthesize combinations of noble metals and phosphates or oxides that are acid stable and can promote metal-support interactions.
- 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, X-ray photoelectron spectroscopy, and thermogravimetric analysis.

Accomplishments

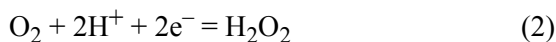
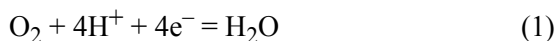
- Improved the activity of a 10% platinum-tantalum phosphate/Vulcan carbon catalyst from 3× to 6× the activity per unit mass of platinum of a 20% Pt/Vulcan carbon standard.
- Demonstrated for the first time the 4-electron oxygen reduction reaction on gold in acid by supporting the gold on tin oxide (non-Pt catalyst).
- Established mechanisms to explain the electrocatalyst activity based on metal-support interactions.

Future Directions

- Improve the stability of the catalysts.
- Evaluate the activity of the catalysts in fuel cells.
- Continue to explore opportunities for non-Pt catalysts, such as Au-SnO.

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 (O_2) to water (H_2O) via a reaction with protons (H^+). Catalysts with poor ORR activity often convert the O_2 to hydrogen peroxide (H_2O_2) 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 not only shifts the electronic state of the platinum, but

also serves as a proton-conducting medium for the transport of water. Additionally, we show for the first time that gold (Au) can be used as an oxygen-reduction catalyst because it becomes active when supported on hydrous tin oxide (SnO). We propose that the electronic states of the Au are shifted higher by the SnO to improve the metal interaction with O_2 .

Approach

Materials combinations are selected by their acid stability and their electronic states. Candidate materials are illustrated in the periodic table in Figure 1. The circled elements are non-toxic and predicted by Pourbaix diagrams to withstand the highly corrosive conditions at the PEMFC cathodes (pH ~1 and potential ~1 V). These elements include Ti, Zr, Nb, Ta, W, Al, Si, Ge, Sn, Ir, Pt and Au. To design new catalysts, Pt is combined with the electron-

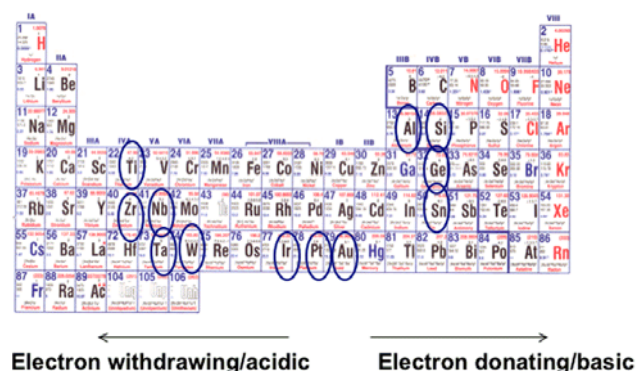


Figure 1. Periodic Table Showing Which Elements Are Stable under the Conditions at PEMFC Cathodes, and Denoting Which Trend Results in Electron-Withdrawing Compounds (acidic), and Which Are Electron-Donating (basic)

withdrawing compounds to the left (e.g., Ta) and Au is supported on basic supports to the right (e.g., Sn). The supports are either metal hydrous phosphates or hydrous oxides, due to the high stability of these materials to corrosion and their ability to transport water and protons, key components of the ORR.

The catalyst activity is evaluated using standard rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) methods. Both methods use a rotating disk 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 . For these electroanalytical tests, the catalysts are mixed with Vulcan carbon and a Nafion ionomer and dispersed as a thin film on the tip of the glassy-carbon disk, which is then submerged in an electrolyte of perchloric acid and referenced to a hydrogen electrode. 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 oxidation states of the catalysts are studied ex-situ with X-ray photoelectron spectroscopy (XPS) and in-situ with X-ray absorption spectroscopy (XAS).

Results

This year, we showed that the mass activity of our Pt-TaPO catalysts is twice that of the state-of-the-art. A representative cyclic voltammogram from a Pt-TaPO RDE is shown in Figure 2. The high activity of the Pt-TaPO is represented by the steep reduction current between 1.0 and 0.8 V; below 0.6 V, the catalyst activity plateaus due to the diffusion limitations of the RDE method. Evaluation of the catalysts with the RRDE method confirms that ORR is complete (eq. 1) and negligible H_2O_2 is produced (eq. 2). Physical characterization shows that the hydrous TaPO support is microporous and covered with 1.7 nm Pt metal particles.

The activity of the Pt-TaPO catalyst is compared to that of a Pt/VC standard in a Tafel plot of potential vs. mass activity (A per mg of Pt , $\text{A mg}_{\text{Pt}}^{-1}$) in Figure 3. At 0.9 V, or at low currents where the ORR is not diffusion limited, the Pt-TaPO has 2 \times the mass activity vs. standard catalysts, as reported in Table I.

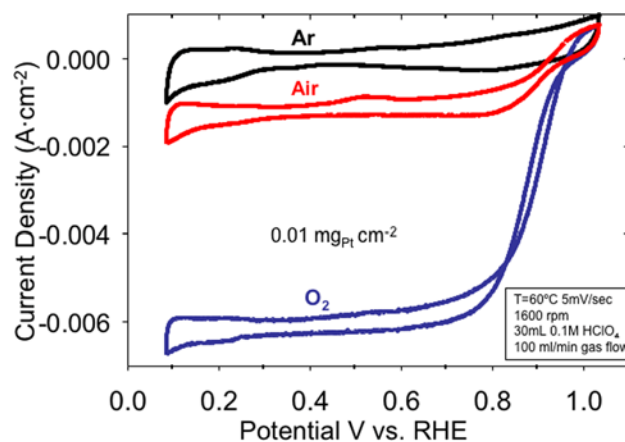


Figure 2. Cyclic Voltammograms of Pt-TaPO RDEs in Ar, Air and O_2

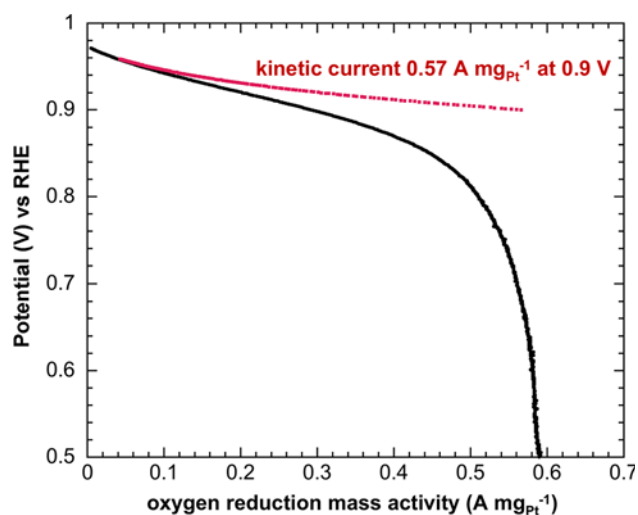


Figure 3. Tafel Plots Showing the Mass Activity of Pt-TaPO in O_2

That is, the mass activity of the Pt-TaPO is $0.56 \text{ A mg}_{\text{Pt}}^{-1}$ at 0.9 V, while state-of-the-art catalysts have $0.24 \text{ A mg}_{\text{Pt}}^{-1}$. The mass activity of these catalysts exceeds that of the DOE 2010 goals of $0.44 \text{ A mg}_{\text{Pt}}^{-1}$ by 27%. The actual activity of the Pt-TaPO catalysts will be confirmed in a fuel cell.

The improved mass activity of these Pt-TaPO catalysts is attributed to the MSI between the Pt and TaPO. The TaPO is electron-deficient compared to the Pt (or to the left of Pt on the periodic table), and therefore is electron-withdrawing or acidic. The contact of the two materials results in a lowering of the density of states in the Pt or decrease in the Fermi level, and an increase in the activity of the Pt [2].

The effect of the substrate interaction is likely improved by the phosphorous in the structure, as we observe poor ORR activity for Pt on hydrous tantalum oxide. Unfortunately, the electron-withdrawing effect on the Pt not only improves its catalytic nature, but it also makes the Pt more prone to oxidation. We observe a loss of activity of the Pt-TaPO when it is stored in air due to the conversion of the Pt metal to PtO₂, an inactive catalyst. The PtO₂ can be reduced to Pt metal by applying a negative bias to the catalyst in the electrochemical cell. We are investigating strategies to stabilize the active Pt metal when it is stored in air.

The opportunities for MSI in ORR catalysis are clear from our studies of gold supported on hydrous tin oxide (Au-SnO). Au is a well-known catalyst for the ORR under basic conditions, but it is active in acid only for the reduction of oxygen to hydrogen peroxide (equation 2), making this relatively inexpensive noble metal non-viable for PEMFCs. The Au has poor activity for the ORR in acid because its reaction mechanism relies on hydroxyl (OH⁻) groups, which are scarce in proton-dominated acidic media [3].

The success of the ORR in acid on Au-SnO is shown in Figure 4. While the Au and SnO individually are inactive for the ORR, the combination of the two materials results in an excellent catalyst. The bottom part of the voltammetric plot shows that the reduction current in the active Au-SnO increases between 0.6 and 0.4 V from the baseline to its diffusion-limited value of -6 mA cm⁻², indicative of the 4-electron ORR reaction. The reduction currents from the Au and SnO catalysts are much less and do not reach the limiting current. The top section of the plot shows the response of the Pt ring due to current generated by H₂O₂ oxidation. Negligible current is measured at the Pt ring when Au-SnO is used as the catalyst at the disk electrode, indicating that no H₂O₂ byproducts from the catalysis reaction are generated at the Au-SnO film. In comparison, the Au and SnO catalysts show significant current due to H₂O₂ oxidation at the ring electrode, confirming that they are poor ORR catalysts in acid.

The activity of the Au catalyst is clearly improved by the MSI with the SnO, presumably

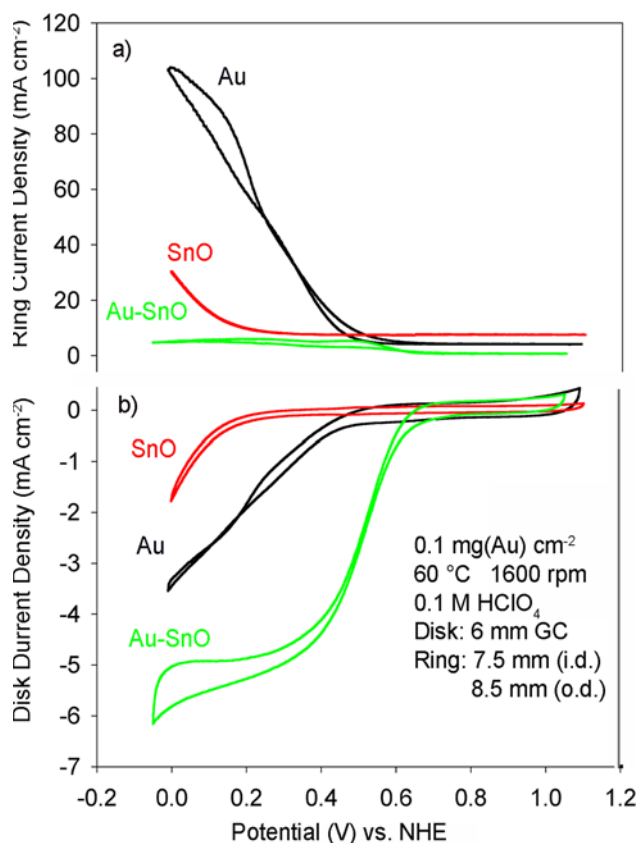


Figure 4. Oxygen Reduction at Au, SnO, and Au-SnO Electrodes (bottom curves, b) Compared to the Oxidation of Residual Peroxide at the Pt Ring (top curves, a)

because the SnO contributes electrons to the Fermi level of the Au. Unlike the Pt, the Au activity is improved by making it more basic. The surface species on the hydrous SnO (e.g., OH⁻ groups) may also influence the activity of the Au. The Au-SnO is not appropriate for a PEMFC cathode catalyst because the high overvoltage of the catalysis on the Au-SnO (resulting in the ORR reaction starting at 0.6 V vs. 0.95 V on the Pt) indicates that the catalyst is too inefficient to be practical, despite its low cost.

Conclusions

We conclude that there are significant opportunities from the effects of MSIs. Catalysis on Pt and Au have both been improved and even modified. Although there are limitations to the materials that can be used under the highly corrosive conditions at the PEMFC cathodes, the improvements achieved by combining the

appropriate elements, plus selecting modifying ligands (e.g. phosphorous), suggest that there are paths forward to even more low-Pt and Pt-free catalysts.

FY 2005 Publications/Presentations

1. 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.*, 151 (2004) A1989-A1998.
2. W. S. Baker, P. J. Bouwman, W. Dmowski, K. E. Swider-Lyons, "Platinum and Non-Platinum-Metal Tin Oxide Supported Catalysts for PEMFC Cathodes," 206th Meeting of the Electrochemical Society, 3-8 October 2004, Honolulu, HI.
3. P. J. Bouwman, M. Teliska, W. Dmowski, K. E. Swider Lyons, "Increased Poisoning Tolerance of Pt-MO_x Oxygen-Reduction Catalysts," 206th Meeting of the Electrochemical Society, 3-8 October 2004, Honolulu, HI.
4. K. E. Swider Lyons, P. J. Bouwman, W. S. Baker, M. E. Teliska, W. Dmowski, "Oxide- and Phosphate-Based Catalysts for Oxygen Reduction at PEMFC Cathodes," Symposium on Materials Aspects of Fuel Cells, Materials Research Society Meeting, 29 November – 3 December 2004, Boston, MA.
5. W. Dmowski, P. J. Bouwman, K. E. Swider Lyons, "Atomic Structure of Platinum-Iron Phosphate Electrocatalysts," Symposium on Materials Aspects of Fuel Cells, Materials Research Society Meeting, 29 November – 3 December 2004, Boston, MA.
6. M. Teliska, W. Baker, J. Pietron, T. Schull, K. Swider Lyons, "Tantalum-Phosphate-Supported Platinum Catalysts for PEMFC Cathodes," Symposium on Nanostructured Materials for Energy Storage and Conversion, 207th Meeting of the Electrochemical Society, 15-20 May 2005, Quebec City, Canada.
7. W. S. Baker, P. J. Bouwman, M. E. Teliska, W. Dmowski, K. E. Swider-Lyons, "Platinum and Non-Platinum-Metal Tin Oxide Supported Catalysts for PEMFC Cathodes," in *Proton Conducting Membrane Fuel Cells IV*, 2004, ed M. Murthy, et al., Electrochemical Society Proceedings 2004, in press.
8. P. J. Bouwman, M. E. Teliska, K. Swider Lyons, "Increased Poisoning Tolerance of Pt-FePO Oxygen Reduction Catalysts," in *Proton Conducting Membrane Fuel Cells IV*, 2004, ed M. Murthy, et al., Electrochemical Society Proceedings 2004, in press.
9. M. Teliska, W. Baker, T. Schull, K. Swider Lyons, "Tantalum-Phosphate-Supported Platinum Catalysts for PEMFC Cathodes," in *Nanostructured Materials for Energy Storage and Conversion*, ed. K. Zaghbi, et al., Electrochemical Society Proceedings 2005, in press.

References

1. Gasteiger, H. A.; Kocha, S. S.; Sampalli, B.; Wagner, F. T.; *Appl. Catal. B-Envir.*, 2005, 56, 9.
2. Oudenhuijzen, M. K.; van Bokhoven, J. A.; Ramaker, D. E.; Koningsberger, D. C.; *J. Phys. Chem. B*, 2004, 108, 20247.
3. Blizanac, B. B.; Lucas, C. A.; Gallagher, M. E.; Arenz, M.; Ross, P. N.; Markovic, N. M.; *J. Phys. Chem. B*, 2004, 108, 625.