

Low-Platinum Catalysts for Oxygen Reduction at Proton Exchange Membrane Fuel Cell Cathodes

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Objectives

- Decrease the platinum content of the oxygen reduction catalysts in fuel cell cathodes to meet the DOE 2010 precious-metal-loading goals of 0.2 g/rated kW and electrode costs of \$5/kW.
- Achieve catalyst loadings of 0.02 mg Pt/cm² and stability greater than 5000 hours.
- Optimize catalyst performance for low overpotentials.

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 R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance

Approach

- Disperse platinum on selected hydrous-oxide and hydrous-phosphate supports to enhance the proton transport to and catalytic activity of the platinum sites.
- Evaluate the electrochemical performance of the low-platinum catalysts in standardized half-cell and fuel-cell measurements.
- Perform stability studies of the catalysts in aggressive chemical solutions, in the presence of gaseous poisons, and in operating fuel cells.
- Identify the structure-property relationships of the active materials by studying nanoscale features with various characterization tools, including pair density function analysis of X-ray diffraction.
- Collaborate with industry and university contacts for independent evaluation of the catalysts.

Accomplishments

- Identified stable platinum/hydrous iron phosphate catalysts that have approximately 10× less platinum than the platinum/Vulcan carbon catalysts.
- Observed lack of adsorption of carbon monoxide on Pt-FePO_x catalysts in half-cell measurements.

- Developed new, stable platinum/hydrous tin-oxide catalysts that exhibit excellent electrochemical performance at 10× lower platinum loadings compared to a standard platinum/Vulcan carbon catalyst.
- Improved electrochemical testing methods (half cell and fuel cell) by internal developments and collaborations with industry.
- Operated fuel cells having cathode catalysts of either platinum iron phosphate or platinum tin oxide.
- Characterized nanoscale structure and platinum oxidation state of active phosphate and oxide catalysts.

Future Directions

- Continue to identify optimum platinum loadings of catalysts for maximum performance.
- Develop methods to make high surface-area, nanoscale particles of the phosphate and oxide catalysts.
- Test tolerance of the catalysts to poisons such as carbon monoxide and sulfur dioxide in the air streams of proton exchange membrane fuel cells (PEMFCs).
- Improve methods for the preparation of fuel cell cathodes having the new oxide and phosphate catalysts via research at the Naval Research Laboratory (NRL) and collaboration with industry.
- Test new catalysts in PEMFCs at NRL and with collaborators, and evaluate long-term stability.

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. Researchers recognized years ago that the Pt content of PEMFC electrodes could be reduced by dispersing nanoscale Pt particles on a porous, electronically conductive media (Vulcan carbon) and adding a proton conducting media (a perfluorosulfonic membrane, Nafion[®])(1). When surrounded by Vulcan carbon and Nafion, the Pt serves more effectively as an electrocatalyst for hydrogen oxidation and oxygen reduction because there are ample transport paths for protons and electrons. Whereas the catalytic activity of the Pt is critical, the electrode reactions are mediated by the rate of the transport of the gases, protons, electrons and water to and from the Pt surfaces.

We are investigating three types of catalyst that may be able to serve as low-cost, stable electrodes in fuel cells: Pt-FePO_x, Pt-NbPO_x, and Pt-SnO_x. Selected hydrous phosphate and oxides can serve as catalytic supports for Pt because of their innate activity and their microporous or open-framework structures that enhance proton conduction (2). Hydrous iron phosphates are known as corrosion barriers, paint additives and friction coatings; anhydrous phosphate-based catalysts can be used for

direct conversion of methane into oxygenates and oxidative dehydrogenation (3); and lithiated FePO₄ is also being tested as a positive electrode in Li-ion batteries (4). Anhydrous Pt-SnO_x materials have been previously investigated for use in PEMFC anodes by other researchers (5), but proved to be unstable under reducing conditions.

Approach

Hydrous phosphates and oxide catalysts are made in aqueous solutions from commercially available chemicals, filtered, air dried, and then heated from 150 to 200°C. By heating below 200°C, the materials retain >0.2 mole % water in their structure. The powdered materials are mixed with 50 to 80 weight % Vulcan carbon to improve their electronic conductivity and for fabrication into electrodes.

The Pt-doped phosphate and oxide materials are evaluated for their performance in PEMFCs using a modified recipe for a rotating disk electrode (RDE) for platinum electrocatalysts (6). They are also formed into membrane electrode assemblies for testing in PEMFCs using the procedures developed and optimized by Los Alamos National Laboratory (7). The stability of the catalysts is evaluated by heating the powdered catalysts (without carbon) in 1.0 M sulfuric acid at 90°C for 1 to 12 h and then testing the electrochemical performance of the

recovered powders. A key criterion is that the acid has no evidence of metal dissolution.

The physical properties of the catalysts are characterized using a variety of approaches, including surface area measurements, thermal analysis, transmission electron microscopy, X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy. The materials are generally amorphous to conventional X-ray diffraction, so their structure is characterized by the pair-density-function analysis of high-energy X-ray diffraction patterns. The pair-density-function analysis has been particularly useful for this group of catalysts because it is able to resolve the local and medium-range structure of the materials from 0.2 to 1.5 nm, or the size region that has the greatest impact on the ensuing catalytic results.

Results

Nanoscale Pt-FePO_x particles dispersed on Vulcan carbon have excellent electrocatalytic activity for oxygen reduction, as shown in the cyclic voltammetry plot in Figure 1. The activity is exemplified by the precipitous drop in the activity

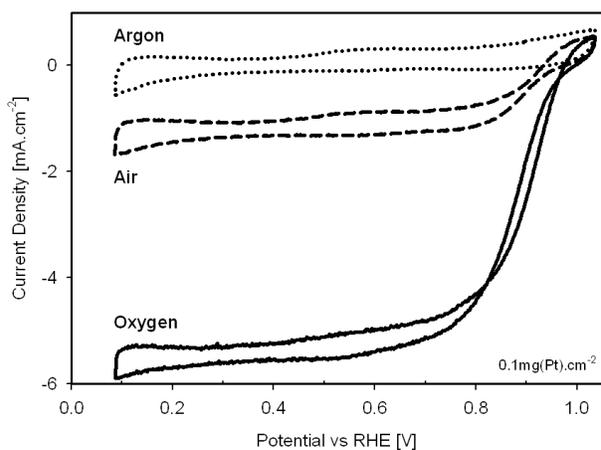


Figure 1. Cyclic voltammetry of a rotating disk electrode of 10% Pt-FePO_x mixed with Vulcan carbon under Ar, air and oxygen. The RDE is prepared using the method in reference 7. The data shown is in 0.1 M HClO₄ at 60°C at a rotation rate of 1600 rpm and at a scan rate of 5 mV/s using a Pd/H reference electrode that is corrected to RHE. The Pt loading of the RDE is approximately 0.1 mg Pt/cm².

between 1.0 and 0.7 V vs. a real hydrogen electrode (RHE), giving a half-wave potential of 0.91 V, as shown in the Tafel plot in Figure 2. By comparison, a standard 20% Pt/Vulcan carbon catalyst has a half-wave potential of 0.89 V. The active Pt-FePO_x catalysts have ~0.3 nm micropores, and the Pt is dispersed throughout the phosphate tetrahedra and is lodged in interstitial sites throughout the structure, creating disorder and opening micropores. X-ray photoelectron and absorption spectroscopies indicate that the Pt is oxidized, most likely in a 2+ or 4+ state. An advantage of Pt^{x+} catalyst sites is that they are poisoned less easily than Pt-metal sites. In fact, Pt²⁺/Pt⁴⁺ is not poisoned by sulfur, but rather catalytically oxidizes it to benign sulfate species (8). Because the Pt is an oxidized form in these phosphate catalysts, they appear to be unpoisoned by carbon monoxide. Typically, carbon monoxide adsorbs on the surface of platinum and blocks it from further catalysis, but these phosphate catalysts show no evidence of carbon monoxide adsorption and/or poisoning when tested in a half cell. These Pt-FePO_x materials have been successfully fabricated into membrane electrode assemblies and tested in a PEMFC at NRL. The ultimate test of these materials' viability will be their long-term performance in a PEMFC, as trace iron will degrade Nafion (9).

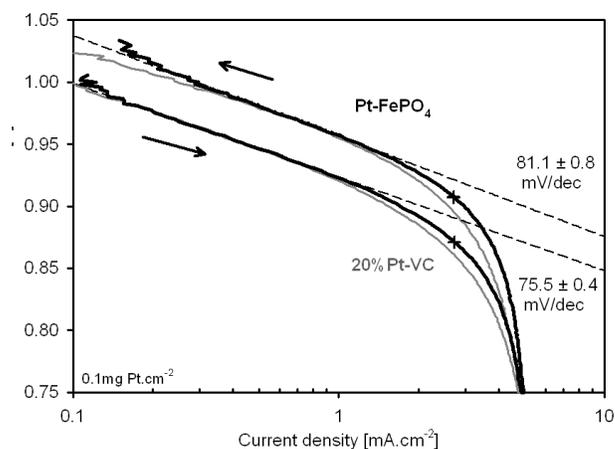


Figure 2. Tafel plots of Pt-FePO_x on Vulcan carbon vs. a 20% Pt/Vulcan carbon standard as calculated from cyclic voltammetry experiments carried out using the conditions described in the caption for Figure 1. The Pt loading is 0.1 mg Pt/cm² in both RDEs. Crosses indicate the half-wave potentials of the catalysts.

The Pt-NbPO_x materials are attractive because of their high stability in acid, and they perform well for oxygen reduction when doped with Pt. However, the materials have relatively low open circuit potentials (OCPs) that are 0.8 V vs. RHE, compared to the expected 1.0 V for Pt/Vulcan carbon. These low OCPs are a detriment to PEMFCs, as they cut down on the cell voltage and therefore the power. Because of this drawback, these catalysts have not yet been tested in PEMFCs, but efforts are underway to increase the OCP via doping with other transition metals.

The Pt-SnO_x materials also have excellent electrochemical performance. The performance of the catalysts in a PEMFC is shown in Figure 3. In this experiment, the Pt loading of the cathode is 0.02 mg Pt/cm² of Pt-SnO_x/Vulcan carbon, and the anode is 0.2 mg Pt/cm² of 20% Pt/Vulcan carbon. When normalized to current, these Pt-SnO_x catalysts outperform the Pt/Vulcan carbon standard by a factor of 3.5, per weight Pt. Further improvements are anticipated as the Pt loading of the SnO_x is optimized and the particle size is reduced. The Pt-SnO_x

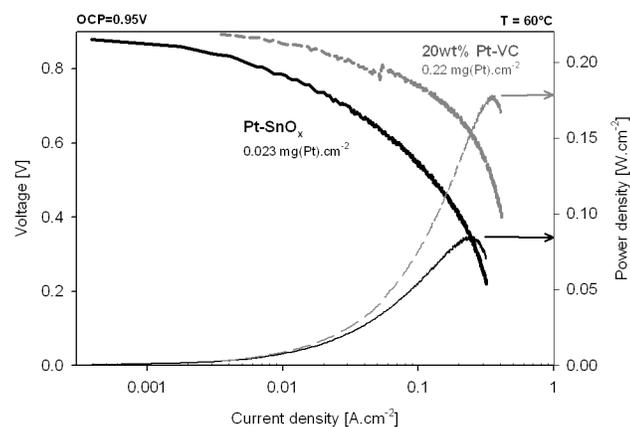


Figure 3. Comparison of PEMFCs having cathodes of 0.023 mg Pt/cm² of Pt-SnO_x/Vulcan carbon and 0.22 mg Pt/cm² of 20 wt% Pt/Vulcan carbon at 60°C, under humidified H₂/O₂ at atmospheric pressure, and using Nafion 112 membranes. Both anodes have loadings of 0.2 mg Pt/cm² of 20-wt% Pt/Vulcan carbon. The standard PEMFC has a power of 0.18 W/cm² at a current density of 0.34 A/cm², while the Pt-SnO_x PEMFC has a maximum power 0.09 W/cm² at a current density of 0.26 A/cm², despite having 10× lower Pt at the cathode.

catalysts are stable to heating in sulfuric acid; however, we also observe that the catalysts are not stable at fuel cell anodes. Like the phosphate materials above, these SnO_x-based materials are microporous, as shown in Figure 4.

Conclusions

- Hydrous metal oxides and phosphates doped with platinum may be viable candidates as high-activity, inexpensive oxygen reduction catalysts for PEMFC cathodes.
- The microporous structures of the catalysts appear to influence the performance of the catalysts.
- The catalysts are stable under aggressive acid treatment, and therefore are likely to have long-term stability under the operating conditions of a PEMFC cathode.
- The catalysts can be successfully fabricated as stable cathodes for PEMFCs.
- These phosphate and oxide catalysts may prove to be more stable than Pt metal over long-term tests because their platinum is in an oxidized state (Pt²⁺/Pt⁴⁺) and therefore is less prone to poisoning.

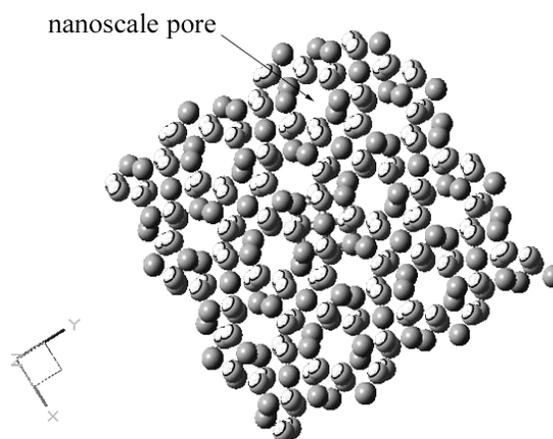


Figure 4. Schematic of the microporous structure of Pt-doped hydrous SnO_x. The nanoscale pores are conducive to proton conduction.

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FY 2003 Publications/Presentations

1. N. P. Ugarde, K. E. Swider-Lyons, "Low-Platinum Tin-Oxide Electrocatalysts for PEM Fuel Cell Cathodes," in the Proceedings of the Symposium on Polymer Fuel Cells, Electrochemical Society Proceedings Series, October 2002, in press.
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3. P. J. Bouwman, J. A. Stanley, G. B. Cotten, K. E. Swider-Lyons, W. Dmowski, T. Egami, "Low-Platinum, Oxide-Based Electrocatalysts for Oxygen Reduction in PEM Fuel Cells," Gordon Research Conference on Fuel Cells, RI, 27-31 July 2003.
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Special Recognitions & Awards/Patents
Issued

1. Patent disclosure: K. S. Lyons, P. J. Bouwman,
"Hydrous phosphate catalysts with low platinum,"
Navy Case No. 84,631, 26 March 2003.
2. Patent disclosure: K. S. Lyons, N. P. Ugarte,
"Platinum-impregnated hydrous tin oxide
catalysts," Navy Case No. 84,632, 26 March 2003.