LOW-PLATINUM OXIDE-BASED ELECTROCATALYSTS FOR OXYGEN REDUCTION IN PROTON EXCHANGE MEMBRANE FUEL CELLS

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Introduction

Proton-exchange membrane fuel cells (PEMFCs) produce energy at high fuel efficiencies and low pollution levels, however several technological problems must be solved before they are available for wide-scale consumer use. For instance, the high platinum content of the cathode and anode makes the fuel cells costly and subject to fluctuations in the market availability of the noble metal. The oxygen reduction reaction (ORR) at the cathode also suffers from high overpotentials, reducing the efficiency of the fuel cell.

The catalytic activity of the ORR is slow, presumably because it is a 4-electron mechanism:

$$O_2 + 4H^+ + 4e^- = 2\ H_2O$$

For this reaction to proceed unencumbered, the catalyst site must also have a supply of oxygen, protons, and electrons, and must be able to transport away water. The reaction above becomes limited when the transport of any of these four species is slow.

We are designing new low-Pt electrocatalysts for oxygen reduction at PEMFC cathodes. Catalysts are targeted based on their ability to transport the following species: (1) molecular oxygen, (2) protons, (3) electrons, and (4) water. We have targeted "amorphous" nanocomposites of oxides with low amounts of platinum to fulfill these transport criteria. All catalysts are transition-metal oxide based, because hydrous transition-metal oxides are good proton and water conductors. Oxides are also less prone to poisoning than metals, and some mixed-oxide catalysts also have the ability to mimic Pt. Some oxide catalysts may also be resistant to dissolution under the highly corrosive conditions at the PEMFC cathode.

The electrocatalytic activities of hydrous oxide catalysts for ORR are compared to their physical and structural properties to select and design high-performance PEMFC cathode catalysts. Several transition metal oxide systems have been studied, but this presentation will focus on our research on the Pt-FeO_x system.

Experimental

Materials preparation. Catalyst powders are prepared from aqueous solutions in ambient conditions and then heated in various atmospheres at temperatures between 100 and 200 °C to adjust their water content. For electrochemical evaluation, the catalysts are mixed with carbon and a 5 wt% Nafion solution to make a conductive ink that is applied to a glassy-carbon rotating disk electrode (RDE) and dried at 75 °C.[1] Some inks are also prepared from mixtures of the catalysts carbon, Nafion and glycerin, and dried on the RDE at 150 °C.[2]

Electrochemical analysis. A RDE loaded with catalyst ink is submerged in 0.1 M H_2SO_4 and cycled under both Ar and O_2 at 5 mV/s between -0.01 and 1.3 V vs RHE at 60 °C using rotation rates from 1000 to 1750 rpm. The activity of the new transition metal catalysts is estimated by comparison to a standard RDE with 10 wt% Pt/Vulcan carbon catalyst (Alfa). Tafel plots are calculated from the RDE data from the difference in the voltammetric sweeps in Ar and O_2 as described in the literature.

Physical and structural characterization. The physical and structural properties of the catalysts are determined via characterization with X-ray photoelectron spectroscopy (XPS), thermal analysis (TA), surface-area measurements (BET), energy dispersive X-ray spectroscopy (EDS) in conjunction with transmission electron microscopy (TEM), powder X-ray diffraction (XRD). Additionally, high-energy XRD is carried out at beamline X7-A of the National Synchrotron Light Source on samples in air in the symmetric reflection geometry with the incident x-ray wavelength (λ) of 0.0574 nm. The high-energy XRD data are analyzed by pair-density function (PDF) analysis.[3]

Results and Discussion

The cyclic voltammetry of the FeO_x phase changes dramatically when over 0.5 wt% of Pt is added, and it begins to resemble pure Pt. The FeO_x phase has excellent oxygen reduction activity when it contains 3 to 6 weight % Pt. The Tafel plot of a ~3% wt% Pt-FeO_x phase mixed with 80 wt% Vulcan carbon [0.6 wt% Pt/19.4% FeO_x/80% VC)] is shown compared to that of 10% Pt:VC in **Figure 1**. When normalized for Pt content, the 3% Pt-Fe_x:VC has 20X the activity of the standard fuel-cell-grade 10% Pt/VC.

The ORR performance of the Pt-FeO_x catalysts varies as a function of the following factors: the type of carbon black (Vulcan carbon vs. acetylene black), the heating temperature, the heating atmosphere, the weight % of Pt, and the method for adding the Pt during synthesis. Catalysts are active only when prepared with the appropriate synthetic and heating procedures.

The analyses from XRD (with a Cu anode), BET, and EDS-TEM indicate little discernable difference between Pt-FeO_x samples with excellent and poor performance. However the PDF analysis of the high-exergy XRD data suggest that there is a significant difference in the medium-range structure between active and unactive samples, as observed with deviations in their PDF from 0.22 to 0.3 nm.

Over time, the performance of all of the Pt-FeO_x samples degrades after they have been suspended in the Nafion inks for several days, presumably due to dissolution of the FeO_x phase.

Conclusions

We have demonstrated that the ORR activity of Pt can be enhanced 20X by dissolving it in a matrix that is a good proton and

water conductor, such as a hydrous FeO_x phase. The ability of the FeO_x to transport molecular oxygen is also likely to improve its activity for ORR. Extensive physical characterization of the active and inactive Pt-FeO_x materials indicates that the medium range structure of the sample (~0.3 nm) is most likely to affect its catalytic activity.

The Pt-FeO_x phases undergo dissolution over time in acidic media. Other transition-metal oxide systems with high corrosion resistance are being developed using the same approach pursued for the Pt-FeO_x phases to generate a new class of low-cost, high activity electrocatalysts for PEMFC cathodes.

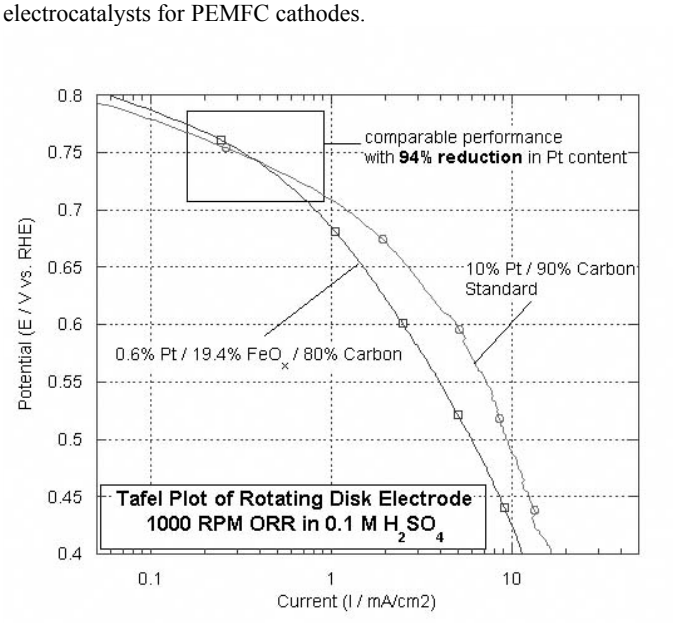

Figure 1. Tafel plots comparing the oxygen reduction activity of 3 wt%Pt-FeO_x mixed with 80% Vulcan carbon (0.6 wt% Pt/19.4% FeO_x/80% VC) compared to a 10% Pt / VC standard. Cyclic volatammetry conditions: sweep rate = 5 mV/s; electrolyte: 0.1 M H_2SO_4; rotation rate = 1250 rpm; temperature = 60 °C.

Acknowledgements

The authors are grateful for financial support provided by the Department of Energy Office of Transportation Technologies (contract DE-A101-00EE50639) and the Office of Naval Research. The National Synchrotron Light Source is supported by the Department of Energy Division of Materials Sciences and Chemical Sciences. Dr. Francisco Uribe (Los Alamos National Laboratory) facilitated the preparation of our catalyst inks.

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