PLATINUM AND NON-PLATINUM-METAL TIN OXIDE SUPPORTED CATALYSTS FOR PEMFC CATHODES

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ABSTRACT

This paper details the physical and electrochemical characterization of hydrous tin-oxide supported noble-metal PEMFC cathode catalysts. The hydrous tin oxide (SnO\textsubscript{x-y}H\textsubscript{2}O) is precipitated from aqueous tin salt solutions by addition of NH\textsubscript{4}OH, and then impregnated with Au, Pd, or Pt metal ions. The physical and structural properties of the noble metal-SnO\textsubscript{x-y}H\textsubscript{2}O catalysts are investigated using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), nitrogen physisorption surface-area analysis, and powder X-ray diffraction (XRD). The SnO\textsubscript{x-y}H\textsubscript{2}O and noble metal-SnO\textsubscript{x-y}H\textsubscript{2}O catalysts are electrochemically evaluated by rotating disk electrode (RDE) voltammetry. Tafel plots indicate that all catalysts are active for oxygen reduction. In the case of the Au-SnO\textsubscript{x-y}H\textsubscript{2}O catalyst enhanced catalytic activity is observed relative to Au or SnO\textsubscript{x-y}H\textsubscript{2}O alone, suggesting a synergy between the noble metal and oxide support. These results demonstrate the potential use of metal oxide supports for the successful preparation of ORR-active Pt-free catalysts.

INTRODUCTION

The widespread commercial application of proton-exchange membrane (PEM) fuel cells is contingent upon overcoming a variety of well-recognized technological hurdles including improved membrane performance, effective water-management, preparation of mass-transport optimized electrode structures, and development of low-cost poison-resistant catalysts.\textsuperscript{1-3} The high cost of current state-of-the-art Pt catalysts represents a major obstacle in the path of PEMFC commercialization, which is currently being addressed by investigations focused on the use of Pt alloys. Studies of alloys have provided useful structural and mechanistic insights for the development of new PEMFC catalysts, and resulted in the preparation of promising new alloy materials including Pt-Cr, Pt-Ni, Pt-Fe, and Pt-Co.\textsuperscript{4-7} However, problems associated with the long-term stability of metal alloys have yet to be resolved, and the goal of stable, poison-resistant, viable non-Pt catalysts remains to be achieved.\textsuperscript{8,9}

An objective of our research is to develop alternative catalysts from inexpensive
hydrous metal oxides and noble metal/hydrous metal-oxide composites. We have
developed a series of metal-oxide-supported noble-metal catalysts which are active for
the oxygen reduction reaction (ORR). Our previous studies of carbon-supported
Pt/hydrous iron phosphate (FePO) catalysts showed enhanced activity for the ORR
relative to standard 20 wt% Pt/Vulcan carbon, despite lower Pt loadings. While the
practical application of the Pt-FePO catalyst is ultimately limited by slow corrosion-
related degradation of the cathode under PEMFC operating conditions, the results point
to opportunities for metal-oxide supports to reduce noble-metal loading in fuel cells.

The enhanced catalysis of the Pt-FePO catalyst is associated with three key
characteristics of the metal-oxide structure including (1) its activity for oxygen
dissociation, (2) its open pore structure, and (3) the presence of hydrous surface
functionalities. The proton-conducting nature of the hydrous surface is particularly
advantageous for promoting the ORR (Eq 1) because it provides a ready supply of
protons as well as a pathway for shuttling water away from the catalyst.

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O_2 + 4H^+ + 4e^- = 2 H_2O \]  \[1\]

An additional advantage of using metal oxide composites in fuel cell electrodes is lower
susceptibility to poisoning than pure and alloyed metals. As with all new catalysts for
fuel cells, the materials must also be resistant to dissolution under the highly corrosive
conditions at the PEMFC cathode.

In this paper, we discuss new low-Pt tin-based hydrous oxide catalysts that were
chosen based their catalytic activity and predicted resistance of tin to corrosive
dissolution. Structural and chemical properties of the materials are described and
correlated with ORR behavior as measured by rotating disk electrode (RDE) voltammetry
for the purpose of optimizing future catalyst preparations for both lowered Pt loading and
improved ORR electroactivity.

EXPERIMENTAL

The hydrous tin oxide catalyst powders are prepared by dissolving SnCl\(_2\) (Aldrich) in
high-purity H\(_2\)O (18 M\(\Omega\)-cm, NANOpure, Barnstead International) followed by drop-
wise addition of 1 M NH\(_4\)OH (Aldrich, ACS grade) until a white precipitate forms under
mildly acidic conditions. Following a series of repeated washings with high-purity water
and centrifugation steps, the resulting powder is isolated and air-dried.

The tin oxide support is impregnated with noble metal ions by stirring with known
concentration of aqueous PdCl\(_2\) (Johnson Matthey, 99.9%), HAuCl\(_4\) \(\times\) H\(_2\)O (Alfa Aesar),
or H\(_2\)PtCl\(_6\) \(\times\) H\(_2\)O (Aldrich) for 1-2 h. Next, the material is repeatedly washed, isolated,
and dried before being heated to 150 °C in air for 12 h. The heat-treated material is then
stirred in boiling, high-purity H\(_2\)O for up to two hours. The final product is isolated by
vacuum filtration. The corrosion resistance of the SnO\(_x\) \(\times\) yH\(_2\)O and M-SnO\(_x\) \(\times\) yH\(_2\)O
materials was investigated using gravimetric and XPS analysis. For the gravimetric
analyses, the materials were weighed before and after boiling for 3 h in dilute acid (0.1 M
HClO₄). XPS elemental analysis was performed on the as-prepared material and after electrochemical cycling in oxygen-saturated 0.1 M HClO₄ for at least 1 h.

For electrochemical evaluation, the noble-metal hydrous tin-oxide (M-SnOₓ·yH₂O) catalysts are mixed with Vulcan carbon (VC) (Cabot, XC-72) in a 2:1 mass ratio to improve the electronic conductivity of the metal oxide composite. Inks for the RDE experiments are prepared by mixing 5-20 mg of the M-SnOₓ·yH₂O/VC composite with 2-3 g of a prepared solution composed of 20 ml isopropanol (Mallinckrodt, ACS grade), 79.6 ml 18 MΩ-cm H₂O, and 0.4 ml 5 wt% Nafion (Ion Power, Liquion 1100). The catalyst suspension is sonicated for 30-45 min before a 12 μl drop is placed on a 5-mm-diameter glassy carbon electrode and dried in a partially-closed humid container for several hours. An additional 4 μl drop of 0.025 wt% Nafion solution is placed on the electrode prior to experimentation and dried in air. This RDE electrode preparation is based on a strategy previously described by Paulus et al. and modified in-house and through consultation with General Motors Fuel Cell Activities.

The glassy carbon electrode loaded with catalyst ink is submerged in 0.1 M HClO₄ (J. T. Baker, ACS reagent grade) and cycled under both Ar and O₂ at 60 °C using rotation rates from 1000 to 1600 rpm. Tafel plots are calculated from the RDE data using the difference in the voltammetric sweeps obtained in O₂ and Ar. All electrochemical experiments are performed using an EG&G-PAR model 263A potentiostat, a Pine AFCPRB rotator. The cell contains a Pt gauze counter electrode and a Pd/H bead reference electrode which has been soaked in concentrated HNO₃, rinsed in H₂O, and charged cathodically prior to each experiment. The actual Pd/H bead reference potential is measured versus a Pt electrode under H₂.

The physical and structural properties of the catalysts are determined with X-ray photoelectron spectroscopy (XPS) (Fisons 220iXL, monochromatic Al Kα X-ray, spot size 250 x 1000 μm), thermal analysis (TA) (Rheomatic Scientific STA), nitrogen physisorption surface-area measurements (ASAP 2010 Micromeritics surface area and porosimetry system), scanning electron microscopy (SEM) (Leo Supra 55) and powder X-ray diffraction (XRD) (Bruker AXS D8). For the XPS studies, SnOₓ·yH₂O powders are first mixed with acetylene black (Alfa Aesar, 99.99%) in a 1:1 ratio to prevent charging and then deposited on carbon paper.

RESULTS AND DISCUSSION

SEM micrographs of the SnOₓ·yH₂O and impregnated Au-SnOₓ·yH₂O powders are shown in Figure 1. The images show that the as-prepared SnOₓ·yH₂O is well-dispersed and crystalline prior to impregnation with the noble metal catalyst. Heating the SnOₓ·yH₂O to 150 °C causes the metal oxide to become amorphous, while inclusion of Au, Pt, or Pd ions prior to heating lends local order to the long-range amorphous structure. The qualitative observations with SEM are supported by XRD. The as-prepared SnOₓ·yH₂O is crystalline and matches the JCPDS reference card for tin oxide hydroxide (SnO₆(OH)₄, JCPDS card #84-2157). The surface area of the SnOₓ·yH₂O is 7.0 m²/g, as indicated by Brunauer-Emmett-Teller (BET) isotherm modeling of nitrogen physisorption data.

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Acid-stability studies of the SnO$_x$·yH$_2$O and M-SnO$_x$·yH$_2$O materials showed that as much as 70 wt% of the material was retained for short boiling periods in 0.1 M HClO$_4$ (45 min) while prolonged or repeated boiling resulted in near-complete dissolution of the non-noble-metal fraction of the catalyst. XPS analysis confirms the stability of the M-SnO$_x$·yH$_2$O for short-term electrochemical experimentation. No statistically significant change is observed in the atomic ratio of M/Sn before and after ORR electrocatalysis, indicating that the SnO$_x$·yH$_2$O shows short-term stability to corrosion in 0.1 M HClO$_4$ while sequestered within the M-SnO$_x$·yH$_2$O/VC/Nafion electrode ink environment. Although our synthetic protocol has resulted in the production of acid-soluble hydrous tin oxide ($\alpha$-oxide) we are in the process of preparing a modified, acid-stable form ($\beta$-oxide) which will provide more practical corrosion-resistance for PEMFC application.

Cyclic voltammograms depicting the ORR activity of selected Pt-SnO$_x$·yH$_2$O, Pd-SnO$_x$·yH$_2$O, and Au-SnO$_x$·yH$_2$O catalysts are shown in Figure 2. The voltammograms indicate that the overpotentials for the ORR increase in the following order: Pt-SnO$_x$·yH$_2$O/VC, Pd-SnO$_x$·yH$_2$O/VC and Au-SnO$_x$·yH$_2$O/VC, as predicted by ORR overpotentials of the native noble metals. Potentials for Pt-SnO$_x$·yH$_2$O/VC are within 100 mV of those of 20 wt% Pt/VC and at high Pt loadings exhibit similar mass activities. The mass activity data of the catalysts may be improved through the use of thinner
Figure 3 contrasts the ORR behavior of the Au-SnO$_x$-yH$_2$O/VC composite with that of 10 wt% Au/VC and SnO$_x$-yH$_2$O/VC. The ORR activity of Au is typically low in acidic conditions, as indicated by the voltammogram for 10 wt% Au/VC. The voltammetry for the Au-SnO$_x$-yH$_2$O/VC composite shows that the presence of SnO$_x$-yH$_2$O lowers the overpotential of Au for the ORR, providing greatly enhanced activity and improved electrochemical reversibility. The voltammogram shown for SnO$_x$-yH$_2$O/VC alone is distinctly different, exhibiting even lower activity for the ORR than Au/VC. These results show that the improved ORR behavior of the Au-SnO$_x$-yH$_2$O/VC composite is not attributable to tin oxide or Au behaving independently of one another. The finding in Figures 2 and 3 are summarized in the Tafel plots shown in Figure 4 which indicate that all catalyst powders are active for the ORR, with hysteresis apparent in the cyclic voltammetry of the three composite materials. A similar hysteresis is commonly observed in Pt voltammetry where a less oxidized surface promotes lower ORR overpotentials on the return (anodic) voltammetric scan.14

Although our previous studies of Pt-FePO catalysts indicated that Pt remains in ionic form after cycling cathodically to ORR promoting potentials, the Pt-SnO$_x$-yH$_2$O catalyst forms metallic Pt during electrochemical cycling. This finding is supported indirectly by the hysteresis previously described in the cyclic voltammetry of the composite materials, and directly by XPS. The spectra shown in Figure 5a shows that much of the Pt is in an ionic or oxidized state prior to being used for ORR electrocatalysis, with two distinct Pt4f$\gamma$/2 peaks centered at binding energies of 72.6 eV.
and 74.7 eV(—). The 72.6 eV peak occurs in the Pt(OH)$_2$ region and the 74.7 eV peak, which is lost upon boiling in dilute acid solution, is likely due to adsorbed Pt(IV) halide. After the powders are employed for ORR electrocatalysis, the Pt4f$_{7/2}$ signal profile changes, with the largest peak now being present at 71.4 eV(—). This shows that much of the Pt has been transformed into metallic form during the potential cycling involved in the ORR experiment. It is possible that the remaining ionic signal observed in Figure 5b is attributable to incomplete electronic contact with Pt ions in the electrode ink.

Experiments are underway to investigate this issue, as well as the oxidation state of the Pd and Au-SnO$_x$·yH$_2$O/VC composites before and after electrochemical experimentation.

**CONCLUSIONS**

M-SnO$_x$·yH$_2$O/VC composite electrode inks exhibit desirable overpotentials for the ORR and point to the opportunity for developing effective, inexpensive catalysts based on metal-oxide composite materials. The experiments showed that Pt, Pd, and Au-SnO$_x$·yH$_2$O/VC composites promote the ORR, and that the Au-SnO$_x$·yH$_2$O/VC composite shows enhanced catalytic activity relative to Au/VC and SnO$_x$·yH$_2$O/VC alone. XPS studies point to the conversion of noble metal ions to metallic form upon electrochemical cycling for the ORR studies.

Efforts are underway to characterize the electrochemical performance of the acid-stable β-oxide form of the M-SnO$_x$·yH$_2$O support, as well as optimize the RDE ink methodology to maximize electronic conductivity and minimize film-generated mass transport effects so that true kinetic mass activities can be readily assessed. Cathodic performances in an MEA are being investigated, and the role of protonic conductivity is being probed by impedance analysis. Additionally, the effects of CO and sulfur poisoning on the ORR activity of M-SnO$_x$·yH$_2$O/VC electrodes are being studied.

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