ABSTRACT

Proton-exchange membrane fuel cells (PEMFCs) can be made more affordable by reducing their noble metal (platinum) content. Traditional fuel cells often use 10 wt% Pt on Vulcan carbon (10% Pt/VC), but we show that this platinum content can be lowered by the utilization of metal oxide supports for the Pt at the cathode. New low-Pt catalysts of hydrous tin oxide (Pt-SnO\textsubscript{x}) are compared to 10% Pt/VC in both half-cell and PEMFC measurements. Half-cell voltammetric evaluation with a rotating disk electrode shows that Pt-SnO\textsubscript{x}/VC has higher activity for oxygen reduction than the standard 10% Pt/VC even though it contains 5\times less Pt. Preliminary PEMFC measurements are made using a Pt-SnO\textsubscript{x}/VC cathode and a Pt/VC anode at room temperature using humidified hydrogen and oxygen. The Pt-SnO\textsubscript{x}/VC catalyst performs well in PEMFCs compared to 10% Pt/VC catalysts, despite having a 23\times lower platinum loading.

INTRODUCTION

Proton-exchange membrane fuel cells (PEMFCs) are under development as high-efficiency fuel conversion devices, however several technological problems must be solved before they are available for wide-scale consumer use. For instance, the PEMFC electrodes contain platinum, which makes the fuel cells costly and subject to fluctuations in the market availability of the noble metal. The Pt content of the electrodes is lowered by dispersing nanoscale particles on Vulcan carbon (VC), but the amount of Pt is still too high (ca. 0.1 mg Pt cm\textsuperscript{-2}) for fuel cells to be affordable to consumers (1).

Our goal is to further lower the platinum content of PEMFCs by dispersing the Pt on an oxide support, and then supporting that oxide on VC. We are targeting the fuel-cell cathode, where oxygen is reduced by protons and electrons to yield water via the oxygen reduction reaction (ORR) in Eq. [1]. The kinetics limitations of this four-electron reaction are alleviated by the catalytic properties of the platinum. The slow transport of molecular oxygen and/or protons can also hinder the ORR at high current densities, (2, 3, 4).

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}
\]  

[1]
Hydrous transition-metal oxides are ideal supports for platinum in PEMFCs, because they are good proton and water conductors (5). Oxides are also less prone to poisoning than metals, and some oxide catalysts are resistant to dissolution under the highly corrosive conditions at the PEMFC cathode. More importantly, the catalytic activity of platinum can be improved by using the appropriate oxide support.

Our previous electrochemical and structural studies on hydrous Pt-FeOx indicate that the catalysts having the highest ORR activities have open-framework structures (6,7). The ~0.5-nm micropores in the FeOx structure are ideal for rapid proton conduction. Unfortunately the Fe-based catalysts are prone to corrosion and therefore are not viable PEMFC catalysts.

In this paper, we discuss new catalysts for PEMFC cathodes comprising hydrous tin oxides that are loaded with low amounts of Pt. These hydrous metal oxides are targeted due to their stability in acidic environments plus their likelihood for catalytic activity. Pt-SnOx catalysts have already been recognized for their high ORR activity in alkaline solutions (8). The chemical, physical, and structural properties of our catalysts are determined via characterization with inductively coupled plasma (ICP) analysis, Brunauer-Emmett-Teller (BET) analysis, and powder X-ray diffraction (XRD). The oxygen reduction activity of the Pt-SnOx catalysts is evaluated using a rotating disk electrode (RDE) in argon- and oxygen-saturated H2SO4 at 60 °C and compared to a 10% Pt/VC standard catalyst. The ORR activity of the catalysts is noted from the difference in their voltammetric sweeps under Ar and O2 and in Tafel plots of the ORR. The performance of these catalysts is also compared in a PEMFC operated on humidified H2 and O2 at room temperature.

**EXPERIMENTAL**

The standard electrocatalyst is 10 wt% Pt on Vulcan carbon (Alfa Aesar) having approximately 2.5 nm Pt particles. This Pt/VC is used as received.

Hydrous SnOx is prepared by dissolving SnSO4 (Alfa) in 18 MΩ cm H2O and then neutralizing the solution with NH4OH. The resulting precipitate is vacuum filtered and air dried. The hydrous SnOx powder is stirred in a solution of Pt in H2SO4, filtered, and dried at 150 °C. The material has 7.12 wt% Pt and 59.95 wt% Sn, according to ICP (Galbraith Lab, Knoxville TN). The surface area and pore size distribution of the Pt-SnOx is determined via BET analysis under N2 to 77K (Micromeretics ASAP 2010). The crystal phase composition of the powders is surveyed with XRD (Bruker D-8 Advance with Göbel mirrors and Cu Kα radiation).

For the RDE measurements, the catalysts are ground with 73 wt% Vulcan carbon XC-72R (Cabot) so that the total Pt content of the Pt-SnOx/VC catalysts is 1.9 wt%. Inks are made by stirring together a 1:6 mixture of a catalyst (1.9% Pt-SnOx/VC or 10 wt% Pt/VC) and a Nafion® ionomer solution (5 wt% solids: Ion Power). A 6 μL drop of the ink is pipetted onto a polished 5-mm-diameter glassy-carbon RDE (Pine Instrument Company) and dried at 150 °C (9). The RDE is submerged in 0.1 M H2SO4 prepared from high purity H2SO4 (Optima, Fisher) and 18 MΩ cm H2O. The electrolyte is heated...
at 60 °C, and sparged with Ar and O₂ for deaeration and saturation, respectively. A Pt mesh is used as the auxiliary electrode and a charged Pd wire is used for reference to a normal hydrogen electrode (NHE). The speed of the RDE is controlled at 1000 rpm using a single element rotator (Pine Instrument Company). Voltammetric analysis is carried out at 10 mV/s using a potentiostat (PAR/EG&G Instruments model 263a).

Tafel plots are generated from the difference in the currents (I) of the RDEs under O₂ and Ar when swept from 1.3 and 0.2 V using Eq. [2], where 0.196 cm² is the electrode area (9). The limiting current (Iₘₐₓ) is obtained from the average current density at 0.1 ± 0.01 V. Eq. [3] is used to calculate the Tafel current (9).

\[
I (mA/cm^2) = 1000 \times \left( I_{O_2} - I_{Ar} \right) / 0.196 \ cm^2 \tag{2}
\]

\[
I_{tafel} = (I_{lim} \times I) / (I_{lim} - I) \tag{3}
\]

The Los Alamos National Laboratory protocol is used to make catalyst inks for evaluation in PEMFCs (1). The Pt-SnOₓ catalyst is ground with 80 wt% VC. An ink made of 0.063 g of catalyst (Pt-SnOₓ/VC or Pt/VC) and 0.5 g of Nafion® ionomer solution is stirred for 1 h and then 0.25 g of glycerol is added. After stirring for 30 min, two drops of as-received tetra-n-butylammonium hydroxide (TBAOH, 31% in methanol, Alfa) are added and the solution is stirred again for 1 h. Another 0.2 g of glycerol is added before stirring the solution overnight. The inks are applied to a 2.5 cm² carbon cloth (E-TEK) using a paintbrush. The painted cloths are oven dried at 150 °C. Catalyst loadings are calculated from the difference in the weight of the as-received carbon cloth and that of the dried, painted cloth.

To make the membrane electrode assembly (MEA) for the PEMFC, a Nafion 117 solid electrolyte is cleaned and protonated by boiling sequentially in 3% H₂O₂ (Fisher), 18 MΩ·cm H₂O, and 0.5 M H₂SO₄ solutions for 1 h each. The H⁺-Nafion® 117 is sandwiched between the painted cathode and anode carbon cloths and pressed at 200 °C. The resulting MEA is boiled in 0.1 M H₂SO₄ for several hours. The MEA is tested in PEMFC hardware (ElectroChem Inc) with two graphite blocks having a serpentine flow pattern. H₂ and O₂ are humidified at room temperature by bubbling through water and then fed to the anode and cathode, respectively. Current is collected using a potentiostat, and the cell voltage is reported after 60 s under the target current.

RESULTS AND DISCUSSION

BET results on Pt-SnOₓ show a surface area of 36 m²/g, an average pore size of 3.8 nm and a pore volume of 0.016 cm³/g. The data indicate that there are predominantly micropores rather than mesopores in the catalyst. Microporous walls are excellent proton conductors (5). We previously correlated the presence of micropores to increased ORR activity in the Pt-FeOₓ compounds (7).
XRD analysis reveals that the Pt-SnOₓ has a phase composition of SnO₂ and Pt; SnO₂ is present as the major phase. The material is partially crystalline with crystallites less than 100 nm and an amorphous portion.

Voltammetric results are shown in Fig. 1(a) and 1(b) for the 10% Pt/VC and 1.94 wt% Pt-SnOₓ/VC RDEs, respectively. The RDEs are swept to negative potentials under Ar and O₂. A greater cathodic current is measured under the O₂ flow than under Ar because of the electrocatalytic reduction of oxygen on the electrodes, and the difference between O₂ and Ar curves (O₂ - Ar) reflects the total current of the ORR. The Pt-SnOₓ/VC has a high ORR activity despite a low Pt content of 1.94% and behaves similarly to the 10 wt% Pt/VC catalyst when cycled under Ar and O₂. In comparison, the voltammetry of Pt-free SnOₓ/VC has no electrocatalytic response to the O₂ (not shown). We surmise that the SnOₓ phase improves the electrocatalytic properties of the Pt, though, because the Pt-SnOₓ/VC electrocatalyst has higher activity than the Pt/VC standard despite having 5x less Pt (Fig. 1 (b)). The Tafel plots of the ORR for the catalysts reflect the same trends, as shown in Fig. 2.

Figure 1. Voltammetric response of RDEs of (a) 10 wt% Pt/VC and (b) 1.94% Pt-SnOₓ/VC. The ORR activity is derived from the difference of the O₂ and Ar sweeps (O₂ - Ar) measured in 0.1 M H₂SO₄ at 1000 rpm, 60 °C, and 10 mV/s.
Figure 2. Tafel plots of the ORR on 1.94 wt% Pt-SnOx/VC and 10 wt% Pt/VC as calculated from the voltammetry data in Fig. 1.

Figure 3. Polarization curves for PEMFCs having Pt-SnOx/VC and Pt/VC cathode catalysts under H2/O2 and H2/air at 25 °C and ambient pressure. The Pt loadings of the cathodes are 0.0109 mg Pt cm² for the Pt-SnOx/VC and 0.26 mg Pt cm² for the Pt/VC PEMFCs. Both anodes are prepared from 10% Pt/VC and contain 0.29 mg Pt cm².
Figure 3 compares the performance of the Pt-SnOx/VC and Pt/VC catalysts in H2/O2 PEMFCs. The Pt loadings of the Pt-SnOx/VC PEMFC are 0.0109 mg Pt cm⁻² at the cathode and 0.29 mg Pt cm⁻² at the anode. The Pt/VC standard PEMFC has 0.29 mg Pt cm⁻² at both the cathode and anode. Note that the standard 10 wt% Pt/VC catalyst is used at the anode in both of the PEMFCs. Under our test conditions of H2/O2 at 25 °C and ambient pressure, the Pt-SnOx/VC and Pt/VC PEMFCs have open circuit voltages of 0.927 and 0.951 V, respectively. At low current densities (<2 mA cm⁻²), the performance of the fuel cells is nearly identical, even though the Pt loading at the Pt-SnOx/VC PEMFC is 23× lower than that of the standard Pt/VC PEMFC. Under a current density of 20 mA cm⁻², the Pt-SnOx catalyst has a higher overpotential than the standard Pt/VC PEMFC, as the former drops to 0.4 V while the latter to 0.6 V. The source of this overpotential is under investigation and is likely due to the room-temperature operation of these fuel cells and/or inadequate humidification. Improvements to the MEA fabrication and fuel cell operation conditions will likely be able to decrease this difference between the indications from the Tafel data and the PEMFC results.

Observations to date indicate that the Pt-SnOx/VC materials are stable to corrosion. Voltammetry inks are reused months after being prepared with no change to their ORR activity, and the Pt-SnOx/VC MEAs show no degradation of performance after removal from and then reassembly in a PEMFC.

CONCLUSIONS

The use of hydrous tin oxide as a support for Pt provides a means for lowering the Pt content of PEMFC cathodes. The ORR activity per weight % Pt is higher when the Pt is dispersed in hydrous tin oxide vs. in a standard 10 wt% Pt/VC catalyst. Future work will focus on improving the Pt-SnOx catalysts by tuning the preparation of the metal oxides and the MEA fabrication procedures (e.g. heating conditions). Further testing of the electrocatalysts in a fuel cell test station operating at higher temperature and pressures will also give insight into the properties of these catalysts. Ultimately, using a metal-oxide-supported electrocatalyst with low Pt loadings will significantly reduce the cost of PEMFCs.

ACKNOWLEDGMENTS

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. We also thank Jason Stanley for preparing the SnOx, and Dr. Francisco Uribe (LANL) for guidance on the preparation of the fuel cell inks. NPU is a visiting graduate student from the University of Texas-El Paso.
REFERENCES

1. M. S. Wilson, J. A. Valerio, and S. Gottesfeld, *Electrochim. Acta*, 40, 355 (1998).
2. F. Jouen, G. Lindbergh, and G. Sundholm, *J. Electrochem. Soc.*, 149, A437 (2002).
3. J. Ihonen, F. Jouen, G. Lindbergh, A. Lundblad, and G. Sundholm, *J. Electrochem. Soc.*, 149, A448 (2002).
4. M. Eikerling and A. A. Komshev, *J. Electroanal. Chem.*, 453, 89 (1998).
5. P. Colomban, Ed., *Proton Conductors: Solids, Membranes and Gels – Materials and Devices*, Cambridge University Press, Cambridge (1992).
6. K. Swider Lyons, G. B. Cotton, J. A. Stanley, W. Dmowski, and T. Egami, “Low-platinum and platinum-free catalysts for oxygen reduction at proton-exchange membrane fuel cell cathodes,” *2001 Progress Report for Fuel Cells for Transportation*, U.S. Department of Energy Office of Transportation Technologies, December 2001, 159-162.
7. K. Swider Lyons, G. B. Cotton, J. A. Stanley, W. Dmowski, and T. Egami, “Low-platinum catalysts for oxygen reduction at proton exchange membrane fuel cell cathodes,” *2002 Progress Report for Fuel Cells for Transportation*, U.S. Department of Energy Office of Transportation Technologies, in press.
8. M. Watanabe, S. Venkatesa, and H. A. Laitinen, *J. Electrochem. Soc.*, 130, 59 (1983).
9. S. Lj. Gojkovic, S. K. Zecevic, and R. F. Savinell, *J. Electrochem. Soc.*, 145, 3713 (1998).