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Mesoporous Tin Oxide as an Oxidation-Resistant Catalyst Support for Proton Exchange Membrane Fuel Cells

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Mesoporous catalyst support based on tin oxide (SnO2) is synthesized with high surface area of 205 m² g⁻¹ and with narrow pore size distribution. Modified polylol method is used to deposit platinum on SnO2. The physical properties of the support and the SnO2-supported Pt catalyst (Pt/SnO2) are characterized by using the Brunauer, Emmett, and Teller method, X-ray diffraction, and transmission electron microscopy. The electrochemical stability and durability of the Pt/SnO2 catalyst are investigated by the accelerated stress tests proposed by the U.S. Department of Energy. Pt/SnO2 catalyst exhibits electrochemical activity in fuel cells comparable to that of Pt/C. More importantly, the electrochemical stability of the Pt/SnO2 catalyst significantly improves when compared with the commercial Pt/C catalyst at high potentials (~1.2 V vs reversible hydrogen electrode).

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The performance and stability of proton exchange membrane fuel cells (PEMFCs) is mainly controlled by platinum-particle dissolution and sintering,1,4 carbon support corrosion, and membrane thinning. Carbon due to its large surface area, high electrical conductivity, and well-developed pore structure is commonly used as a catalyst support material for PEMFCs.5,6 However, porous carbon support is susceptible to corrosion at the cathode interface under PEMFC operating conditions such as high water content, low pH, and high temperature from 50 to 90°C. Furthermore, Reiser et al. 9 reported that when the anode is partially exposed to hydrogen and partially exposed to oxygen during start–stop procedures, this causes flow of current opposite to the normal fuel cell mode at the oxygen-exposed region and raises the cathode interfacial potential difference to 1.44 V, which, in the presence of Pt nanoparticles, results in a cathode severe corrosion following the reaction10

\[
C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad (0.207 \text{ V vs RHE, 25°C})
\]

where RHE is reference hydrogen electrode.

Carbon oxidation results in the hydrophobic effects that prevent water removal and thus leads to increased mass-transport losses and decreased thickness of the catalyst layer, which increases the cell resistance. Carbon corrosion also leads to electrically isolated Pt particles that are detached from the support. These factors finally cause a rapid degradation in the Pt catalysts in PEMFCs. Jarvi et al.11 investigated the platinum catalyzed effect on corrosion of carbon supports with various Pt mass fractions under PEMFC conditions. Carbon-only (or Pt-free) electrodes in membrane electrode assembly (MEA) had low CO2 emission at high potentials, whereas the CO2 emission rates were much higher in the presence of Pt. In addition, the CO2 generation rates increased with higher Pt mass fraction in the electrodes.12-15

It is desirable to use more robust noncarbon materials such as metal oxides as catalyst supports in PEMFCs. A variety of conducting oxides with high oxidation-resistant properties such as titanium oxides,16 niobium oxides,17 niobium-doped titanium oxides,18 indium tin oxides (ITO),19 iridium oxides,20 antimony-doped tin oxides,21 and tungsten oxides22 have been studied as potential catalyst-support candidates. Even though improved stability in PEMFC performance was achieved using these metal oxides, the low electrical conductivity and the surface area resulted in the poor dispersion of Pt on the supports, leading to low electrochemical activity. In this paper, tin oxide (SnO2) was prepared as a catalyst support due to its unique electrical, chemical, and physical properties.

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Material characterizations.— The physical properties of the SnO2 support and Pt/SnO2 catalysts were characterized by the Brunauer, Emmett, and Teller method (BET) (Quantachrome Instrument), X-ray diffraction (XRD), and transmission electron microscopy (TEM). XRD analysis was performed using a Rigaku X-ray diffractometer in a 2θ range 20-90° with Cu Kα radiation. A tube voltage of 30 kV and a current of 15 mA were used during the scanning. TEM was carried out using a JEOL-2100F microscope equipped with a field-emission electron gun source operated at 200 kV.

RRDE and CV measurements.— Electrochemical characterizations were performed in 0.5 M H2SO4 using a Pine bipotentiostat (model AFCBP1), Pt wire counter electrode, and Hg/HgO reference electrode of 0.68 V vs RHE. The rotating ring-disk electrode (RRDE) with a Pt ring and a glassy carbon disk (0.247 cm²) was...
used as the working electrode. The catalyst ink was prepared by blending the catalyst powder with ethanol in an ultrasonic bath. The required amount of the catalyst ink was deposited onto the glassy carbon disk using a micropipette. 5 μL of Nafion solution (0.25 wt % Nafion) was added on top of the catalyst layer to minimize anion adsorption effects on the catalysts.23

The electrolyte was purged with nitrogen (99.999%), and cyclic voltammograms (CVs) were recorded before the O2 reduction measurements. The CV was recorded in aqueous electrolyte purged with nitrogen to obtain the background capacitive currents and electrochemical surface area (ECSA) of the Pt. The ECSA of the Pt was determined by charge integration under the hydrogen desorption peaks, assuming a charge of 210 μC cm−2 for the electroactive Pt surface. The electrolyte was purged with oxygen (99.999%) for 30 min before measurement. The linear sweep voltammograms were recorded at different rotation speeds of the RRDE. The oxygen reduction current was calculated from the difference between currents measured in the nitrogen- and oxygen-saturated electrolytes.

**PEMFC performance.**—The cathode catalyst ink was prepared by ultrasonically blending the catalyst powder with Nafion solution (5 wt %) and ethanol for 4 h. The catalyst ink was then spray-coated onto a gas diffusion layer (GDL, ELAT LT1400W, BASF). The weight ratio of Pt catalyst to Nafion was kept at 4:1. Commercially available catalyzed GDL (LT140EW low temperature ELAT GDE microporous layer, BASF) was used as the anode for all fuel cell experiments. The anode catalyst loading was 0.5 mg Pt cm−2. The fuel cell tests were carried out in a single cell with an electrode area of 5 cm2. H2 gas (99.999%) humidified at 77°C [relative humidity (RH) 100%] and O2 gas (99.999%) humidified at 75°C (RH 100%) were supplied to the anode and cathode compartments, respectively, each at a flow rate of 150 mL min−1. Polarization experiments were conducted using a fully automated test station (Fuel Cell Technologies Inc.) at 75°C.

**Accelerated stress tests.**—The electrochemical durability and stability of the Pt/C and Pt/SnO2 cathode catalysts were examined using accelerated stress test protocols (ASTP) suggested by U.S. DOE.25 The tests were carried out in a single cell with an electrode area of 25 cm2. In ASTP I, the catalyst support durability of both types of catalysts was compared by holding the cell potential at 1.2 V with the anode and cathode exposed to hydrogen and nitrogen, respectively. To further characterize the catalyst support properties, polarization curves and full-scale CVs (50 mV s−1) recorded over the voltage range from 0 to 1.2 V were measured every 24 h. As suggested in ASTP II, continuous potential cycling between 0.7 and 1.2 V at 50 mV s−1 at various temperatures with periodic measurements of polarization curve and ECSA was performed to determine the electrochemical stability of the Pt/C and Pt/SnO2 catalysts. TEM and electrochemical impedance spectra were used to measure the Pt particle size and resistance in the MEAs before and after the ASTP II tests.

**Results and Discussion**

**Structural characterization.**—The synthesized SnO2 nanoparticles and the Pt/SnO2 catalyst were analyzed by XRD. The bottom diffractogram in Fig. 1 shows the typical polycrystalline diffraction of cassiterite SnO2, as indicated by three predominant peaks from the (110), (101), and (211) planes. The size of the SnO2 nanoparticles was calculated from the (110) peak using Scherrer’s equation at 6.1 nm. The Pt/SnO2 catalyst exhibited a characteristic pattern of polycrystalline Pt diffraction. The diffraction peaks at approximately 39, 46, 68, and 80° are due to diffractions at the Pt(111), (200), (220), and (311) planes, respectively. The Pt particle size calculated from the (111) peak using Scherrer’s equation was 5.2 nm. For the Pt/C, the patterns of the Pt characteristic peaks were too broad to be resolved, indicating very small Pt particles (~2.5 nm confirmed by the TEM image, as shown in Fig. 1a).

The details of the BET analysis for surface area, pore size, and pore volume are summarized in Table 1. The SnO2 nanoparticles showed a high BET surface area of 205 m² g⁻¹ and an average pore diameter of 13.4 nm, indicating the presence of a mesoporous framework. When Pt was deposited on the SnO2 support, the values of the BET specific surface area, pore size, and pore volume of the Pt/SnO2 catalyst decreased compared to those of pure SnO2. This is because the Pt nanoparticles were dispersed within the pores of the porous SnO2 support, leading to blocking of the pore channels and a consequent decrease in the measured surface area, pore size, and pore volume.27

**Electrochemical characterizations.**—The electrochemical properties of SnO2 and the commercial carbon supports (Ketjen Black EC-300J and Vulcan XC-72) were examined using CV. Figure 4 shows CV curves for SnO2, Ketjen Black EC-300J, and Vulcan XC-72 obtained at a scan rate of 50 mV s⁻¹ in 0.5 M H2SO4. The potential was scanned from 0 to 1.3 V vs RHE. In the positive direction sweep, below 0.9 V, only the double-layer charging current was observed for all three supports. At potentials above 0.9 V, the anodic current for Ketjen Black EC-300J and Vulcan XC-72 carbon increased with the increase in the potentials, whereas only a small anodic current was observed for the SnO2 support up to 1.3 V, suggesting its high resistance toward oxidation when subjected to high positive potentials, indicating its high resistance toward oxidation when subjected to high positive potentials.

To evaluate the electrochemical activity of the Pt/SnO2 catalyst, the oxygen reduction reaction (ORR) was studied using RRDE with

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**Figure 1.** XRD patterns of (a) SnO2 support, (b) Pt/C, and (c) Pt/SnO2 catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m² g⁻¹)</th>
<th>BJH pore size (nm)</th>
<th>BJH pore volume (ml g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vulcan XC-72</td>
<td>230</td>
<td>5.9</td>
<td>0.339</td>
</tr>
<tr>
<td>SnO2</td>
<td>205</td>
<td>13.4</td>
<td>0.346</td>
</tr>
<tr>
<td>Pt/SnO2</td>
<td>102</td>
<td>6.6</td>
<td>0.197</td>
</tr>
</tbody>
</table>
different Pt loadings (60, 80, 100, and 120 µg cm⁻²) on the glassy carbon electrode. Figure 5 shows the polarization curves for ORR with the Pt/SnO₂ catalyst. The polarization curve of pure SnO₂ indicated that SnO₂ was electrochemically inert to the oxygen reduction and showed negligible current. At high potentials, the ORR is under the kinetic-diffusion control region, followed by a purely diffusion-limited region between 0.55 and 0.1 V vs RHE. The limiting currents increased with the increase in Pt loading levels on the glassy carbon electrode.

Figure 2a shows the compared polarization curves for ORR on Pt/SnO₂, Pt black, and Pt/C, each with the same amount of Pt loading. The limiting current of Pt/SnO₂, which was similar to that of Pt/C, was much higher than that of Pt black. Figure 6b depicts the mass activities for all three Pt catalysts, obtained from the kinetic currents divided by the Pt mass at 0.85 V. The mass activity of Pt/SnO₂ was slightly higher than that of the Pt black catalyst. The improved activity of Pt/SnO₂ may be attributed to the good dispersion of Pt nanoparticles on the nanosized SnO₂ support. In addition to the dispersion effect on the catalyst, an interaction between the Pt/SnO₂ catalyst and SnO₂ showed very well-defined mass-transfer regions similar to those obtained for oxygen reduction on conventional Pt/C catalysts. The ORR was under mixed kinetic-diffusion control in the high potential region, followed by the region where the diffusion-limiting currents were observed. Single-step reduction waves with well-developed limiting-current plateaus were observed at all rotation speeds. Furthermore, the low peroxide for-
information (<2%, not shown here) implied that the Pt/SnO2 catalyst was highly selective for the ORR via the four-electron process.29

The stability from CV measurement.—The durability of the Pt/SnO2 catalyst was characterized for up to 1600 cycles in a N2-saturated 0.5 M H2SO4 solution at room temperature by voltage cycling at higher potentials and compared with the Pt/C catalyst. A considerable corrosion of carbon supports, associated with a decrease in the catalyst layer thickness due to carbon electro-oxidation and with aggregation and growth of Pt nanoparticles at high potentials approaching 1.3 V, has been reported.30,31

Figure 6. (Color online) (a) Linear sweep voltammograms and (b) mass activity at 0.85 V of the Pt/SnO2, Pt black, and Pt/C catalysts for the ORR.

Figure 7. (Color online) Tafel slopes derived from the kinetic currents for the Pt/SnO2, Pt black, and Pt/C catalysts.

Figure 8. (Color online) Linear sweep voltammograms of the Pt/SnO2 catalyst for the ORR at various rotation speeds (inset: Amount of H2O2 produced on Pt/SnO2 for ORR).

Figure 9. (Color online) CVs of (a) Pt/SnO2 and (b) Pt/C at a scan rate of 50 mV s⁻¹ in 0.5 M H2SO4.
hydrogen adsorption/desorption peaks in the CVs of Pt/C shown in Fig. 9b changed significantly, whereas those of the Pt/SnO2 CVs (shown in Fig. 9a) were unchanged. Pt/C peak positions shifted dramatically as the surface area was reduced by 40% over 600 cycles, while the Pt/SnO2 CV shapes again remained nearly unchanged. The electrochemically active surface area, however, was reduced by only 20% after 1600 cycles. Similar results were observed by other researchers when ITO was used as a catalyst support. A 40 wt % Pt supported on Vulcan carbon suffered a loss of almost all of its active area after 50 cycles during potential cycling from 0.6 to 1.8 V, whereas the Pt reduction peak for Pt/ITO did not shift even after 100 cycles at the same potential cycling range. Evidence has also been presented that tin oxide supports could bear more severe oxidation conditions up to 1.5 V.

Figure 10 shows the normalized ECSA as a function of the cumulative number of potential cycles for the Pt/SnO2 and Pt/C catalysts. Both samples exhibited a gradual decline in surface area with successive potential cycling, probably due to Pt dissolution or migration and growth of Pt particles on/off the supports. The total surface area loss in the Pt/C sample was about 60%. The surface area losses were 40% for the Pt/SnO2 catalyst, which indicated that the Pt/SnO2 catalyst was much more electrochemically stable than the Pt/C catalyst. The smaller surface area loss for the Pt/SnO2 catalyst during potential cycling test could be attributed to the relatively high corrosion resistance of the SnO2 support. The greater corrosion resistance of SnO2 over commercial carbon supports in an acid environment was demonstrated by CV, as previously shown in Fig. 4.

Fuel cell initial performance.— Each single cell of 5 cm2 MEA was operated on ambient pressure of saturated hydrogen/oxygen until performance had stabilized. Figure 11 shows the polarization curves of PEMFCs using Pt/SnO2, Pt black, and Pt/C as cathode catalysts. In this figure, the current densities at 0.7 V reached to 0.61, 0.48, and 0.72 A cm⁻² with maximum power densities of 0.74, 0.58, and 0.81 W cm⁻² for the Pt/SnO2, Pt black, and Pt/C catalysts, respectively. The fuel cell performance of the Pt/SnO2 was comparable to that of the Pt/C catalyst. This may be due to the difference in thickness of the cathode catalyst layers. At the targeted Pt loading, the thickness of the catalyst layer with Pt/C was ~10 μm, whereas an ultrathin catalyst layer (~1 μm) was observed.

Table II. ASTP I.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Hold at 1.2 V for 24 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total time</td>
<td>Continuous operation for 200 h</td>
</tr>
<tr>
<td>Temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>RH</td>
<td>Anode/cathode 100/100%</td>
</tr>
<tr>
<td>Fuel/oxidant</td>
<td>Hydrogen/nitrogen</td>
</tr>
<tr>
<td>Pressure</td>
<td>150 kPa absolute</td>
</tr>
</tbody>
</table>

Figure 12. (Color online) Polarization curves for PEMFCs with (a) Pt/C and (b) Pt/SnO2 catalysts after potential holding tests (ASTP I).
potential holding tests. Figure 12 shows polarization curves of the Pt/C and PtSnO2 catalysts before and after potential holding tests. To carefully compare the properties of both types of catalysts, the ECSA must be normalized because the CV intensity for the Pt/C catalysts remains nearly unchanged even after a corrosion time of 190 h, while the ECSA of the Pt/C was reduced by 80% after 48 h as Pt/C peak positions shifted dramatically (indicated by the arrow in Fig. 13).

Furthermore, the potential losses at 0.4 A cm\(^{-2}\) as a function of corrosion time for both types of catalysts are compared in Fig. 14b. The Pt/C catalyst suffered a large potential loss with an increase in corrosion time. This is attributed to the thermodynamic instability of carbon supports at high potentials. Additionally, a new peak in the double-layer region of Pt/C catalysts was observed. As shown in Fig. 13b, the Pt/SnO2 catalyst remained ~60% of its initial ECSA even after 190 h, while the ECSA of the Pt/C was reduced by 80% after 48 h as Pt/C peak positions shifted dramatically (indicated by the arrow in Fig. 13).

Table III. ASTP II.

<table>
<thead>
<tr>
<th>Electro catalyst cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle</td>
</tr>
<tr>
<td>Number</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>RH</td>
</tr>
<tr>
<td>Fuel/oxidant</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
</tbody>
</table>
is the most stable compound in the Sn–H2O system under conditions similar to a typical PEMFC operation. In other words, SnO2 as a catalyst support is much robust against electro-oxidation at high potentials. SnO2 as an oxidation-resistant catalyst support is targeted to be used in the unitized regenerative fuel cell (URFC) applications, which operates at very positive potentials (>1.5 V) when URFC is used in the water electrolyzer mode. Medium temperature fuel cells such as phosphoric acid fuel cell can also benefit with SnO2 support.

**ASTP II for Pt particle sintering.**—To investigate the issue of Pt particle sintering in proton exchange membrane MEAs, the potential cycling tests between 0.7 and 1.2 V were applied to the MEAs with Pt/C and Pt/SnO2 cathode catalysts as described in Table III. The initial polarization curves and ECSA for both cases were measured before the potential sweeping started. The cycling tests were periodically stopped, and then the current–voltage curves and ECSA were measured. Figure 15 shows the polarization curves of the Pt/C and Pt/SnO2 before and after potential holding tests (ASTP II) at 80°C. From Fig. 15, the performance loss of the Pt/C catalyst was clearly much more significant than that of the Pt/SnO2 catalyst after only 1000 cycles. Changes in ECSA, catalyst activity, overall MEA impedance, and mass transport could mainly contribute to this performance loss.

The potential cycling tests were repeated with a new set of MEAs but at different cell temperatures (70, 75, 80, 85, and 90°C). The normalized ECSA vs potential cycling numbers for the Pt/C and Pt/SnO2 catalysts at all the temperatures are shown in Fig. 16. In the Pt/SnO2 catalyst, the normalized ECSA stabilized at around 60% for all temperatures after 5000 cycles, while the ECSA of the Pt/C catalyst decreased by more than 90% in the first 1000 cycles. To provide further evidence from potential cycling, the CVs of the Pt/C and Pt/SnO2 catalysts after potential holding tests (ASTP II) at 80°C are shown in Fig. 17.
Pt/SnO₂ catalysts cycled at 80°C, for example, are shown in Fig. 17. The results indicated that the potential cycling led to proportional drops in such surface-area-dependent processes as electrochemical adsorption and desorption of hydrogen (0–0.4 V), double-layer charging (0.4–0.6 V), and Pt–OH formation and reduction (0.6–1.2 V). The hydrogen adsorption–desorption peaks were poorly defined on Pt/C catalyst after 1000 cycles, finally leading to a continuous decrease in ECSA with an increase in cycling numbers. The Pt–OH reduction peaks shifted to high potentials and decreased in intensity (shown in Fig. 17a). This shift reflects a decrease in the adsorption of the oxygen-containing species on the carbon surfaces, which are believed to lower the ORR activity.34 Such shift is mainly due to the growth of Pt particle size because electrochemical oxidation of carbon supports causes the agglomeration of Pt catalyst particles, which were initially separated from each other by the supports. This modification of the catalyst properties was more remarkable in the potential cycling tests than in the potential holding experiments.

TEM images of the Pt/C and Pt/SnO₂ catalysts are shown in Fig. 18 to provide further evidence of Pt particle growth and agglomeration. Pt particles on the order of 2–3 nm with a narrow distribution in the pristine MEA cathode with Pt/C catalyst have grown up to 5.1 nm in the cycled MEA cathode at 80°C. In contrast, Pt particle size (initially ~5.1 nm) has increased only to ~7.5 nm in the MEA cathode during the potential cycling tests at the same temperature. The degree of Pt nanoparticles agglomeration on carbon support is higher than that on SnO₂ support. The anchoring effect on the Pt/SnO₂ catalyst is due to the strong interaction between SnO₂ and Pt metal because SnO₂ support has rough surfaces. Carbon support, on the contrary, has smooth surfaces on which the interaction between carbon and Pt metal is weak. Kamiuchi et al.35 carefully studied the interaction between Pt and tin oxide in a reoxidation atmosphere. They concluded that the inhibition of Pt migration and agglomeration was attributed to the formation of a Pt–Sn bond. As to the Pt/C catalyst, the Pt particle growth behavior during potential cycling is under control by a combination of Pt dissolution/reprecipitation and Pt particle coalescence because Pt particle size distributions become broader but do not shift completely to larger particle size ranges.30 For instance, as shown in Fig. 18c, an increased number of larger Pt particles are observed, but in the mean time, a fraction of smaller Pt particles (<5 nm) remains after potential cycling tests though the total particle number decreases. Pt

| Table IV. A summary of average Pt particle size before and after ASTP II. |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                            | 70°C | 75°C | 80°C | 85°C | 90°C |
| Pt/C                       | 2.5  | 5.8  | 7.1  | 8.8  | 10.4 | 12.2 |
| Pt/SnO₂                    | 5.1  | 6.2  | 6.9  | 7.5  | 8.8  | 9.5  |

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Figure 18. (Color online) TEM images of the Pt/C [(a) initial and (c) after ASTP II at 80°C] and Pt/SnO₂ [(b) initial and (d) after ASTP II at 80°C] catalysts.
coalescence occurs when Pt particles are close to each other and stick together to form larger particles or clusters. 26 Bi and Fuller developed a simple model to predict the Pt dissolution rates during potential cycling. Taking into account Pt particle size effect, they concluded that the Pt dissolution rates decreased with potential cycling due to the increase in the Pt particle size. Pt particle size distribution shifts to a higher and wider range as a consequence of Pt growth and aggregation after potential cycling tests. Table IV summarizes the average Pt particle size for the Pt/C and Pt/SnO2 catalysts before and after ASTP II at various temperatures. The average Pt particle size in the Pt/C catalyst increased dramatically with an increase in testing temperatures. Although the average Pt particle size on the Pt/SnO2 catalyst has also been dependent on operation temperatures, it has still exhibited a narrow distribution (shown in Fig. 18d) and has a much smaller particle size than the Pt/C catalyst. To investigate the contribution of MEA impedance to the degradation behavior of single cells, electrochemical impedance spectra for the Pt/C and Pt/SnO2 catalysts were obtained by the ac impedance technique to determine the ohmic ($R_{\text{ohm}}$) and charge-transfer resistances ($R_{\text{ct}}$) of the MEAs before and after potential cycling tests. It has been reported that the cell impedance measured at low overvoltage with pure hydrogen for the anode and high airflow for the cathode is to minimize the anode effect and to lessen the mass-transport effect of the cathode, respectively. Thus, the impedance of the full fuel cell almost equals the cathode impedance due to the fast hydrogen oxidation reaction. In principle, the intersection with the $x$ axis at the high frequency represents the total ohmic resistance, which is the sum of the contributions from contact resistances between components and ohmic resistances of the cell components such as the membrane, catalyst layer, GDL, and bipolar plates. 37 The diameter of the semicircle measures the charge-transfer resistance of the ORR, which is a good indicator of the properties of the cathode such as the catalyst surface area, catalyst loading, and catalyst utilization. 38 As shown in Fig. 19, the standard semicircle appears in all experimental cases. The ohmic resistance (~0.03 $\Omega$ cm$^2$ for Pt/C and ~0.01 $\Omega$ cm$^2$ for Pt/SnO2) of the MEAs did not significantly change in any case, implying that the membrane resistance was not affected by the potential cycling tests. However, the charge-transfer resistance increased with an increase in cycling numbers, suggesting that the ORR was greatly influenced by the potential cycling tests. The charge-transfer resistance of the Pt/C catalyst increased dramatically from 0.7 to 3.0 $\Omega$ cm$^2$ after 5000 cycles, whereas that of the Pt/SnO2 catalyst increased slowly (from 0.75 to 2.5 $\Omega$ cm$^2$) over 5000 cycles. In a more specific case, the charge-transfer resistance of the Pt/C catalyst over 1000 cycles was slightly higher than that of the Pt/SnO2 catalyst after 5000 cycles, indicating that the fuel cell performance of the former was much lower than that of the latter. This was also confirmed by the polarization curves shown in Fig. 15.

Conclusions

In this study, mesostructured SnO2 nanoparticles with high surface areas were successfully synthesized as a promising cathode catalyst support for PEMFCs. The Pt/SnO2 catalyst showed good electrochemical activity for ORR and, more importantly, much better stability in CV cycling tests (up to 1.3 V) than the commercial Pt/C catalyst. In addition, to mimic the conditions during the start/shutdown cycle in automotive application, the accelerated stress tests were applied to MEAs with the Pt/C and Pt/SnO2 catalysts. In ASTP I, SnO2 sustains a high potential (1.2 V) for almost 200 h with a slight decay, while carbon supports showed a large decrease in surface area due to the electro-oxidation of carbon itself. The durability of the Pt/C and Pt/SnO2 catalysts was investigated by the potential cycling tests. According to the results from ASTP II, the Pt/SnO2 catalyst is more stable than Pt/C. The Pt/SnO2 catalyst approached a maximum of 50% ECSA loss in 5000 cycles, whereas Pt/C lost nearly 90% of the initial ECSA over only 1000 cycles. After potential cycling tests, the Pt/C catalyst showed a dramatic increase in the Pt particle size and a remarkable shift in Pt particle size distribution to a broader range. In contrast, the Pt particle size of the Pt/SnO2 increased slowly due to the strong interaction between platinum metal and tin oxide.

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