Effect of Sb-Doped SnO$_2$ Nanostructures on Electrocatalytic Performance of a Pt Catalyst for Methanol Oxidation Reaction

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Abstract: In this study, antimony-doped tin oxide (ATO) support materials for a Pt anode catalyst in direct methanol fuel cells were prepared and electrochemically evaluated. When the heating temperature was increased from 300 to 400 $^\circ$C, the ATO samples exhibited a slightly decreased specific surface area and increased electrical conductivity. In particular, the ATO sample heated at 350 $^\circ$C in an air atmosphere showed improved electrical conductivity (1.3 S cm$^{-1}$) with an optimum specific surface area of ~34 m$^2$ g$^{-1}$. The supported Pt catalysts were synthesized using a polyol process with as-prepared and heated ATO samples and Vulcan XC-72R as supports (denoted as Pt/ATO, Pt/ATO-350, and Pt/C, respectively). In the methanol oxidation reaction (MOR), compared to Pt/C and Pt/ATO, Pt/ATO-350 exhibited the best electrocatalytic activity and stability for MOR, which could be attributed to Pt nanoparticles on the relatively stable oxide support with high electrical conductivity and interaction between the Pt catalyst and the heated ATO support.

Keywords: Sb-doped SnO$_2$; metal oxide support; supported catalyst; methanol oxidation reaction

1. Introduction

Direct methanol fuel cells (DMFCs) have attracted attention due to the ease of storage and transport of methanol as a liquid fuel and its high energy density, as well as the simplicity of the system for various applications from portable devices to vehicle power sources [1–4]. However, poor methanol oxidation reaction (MOR) activity at the anode and the high cost of noble metal catalysts are major issues for the practical development of DMFCs [5–11]. The main challenge for DMFCs is to find a catalyst with excellent catalytic activity and stability. In particular, the cost and limited availability of Pt as a catalyst hamper the commercialization of DMFCs as power sources for fuel cell vehicles and portable devices [11,12]. Thus, to reduce the utilization of Pt catalysts, various research attempts have been made, including the fabrication of Pt-based alloys, nanostructure design of pure Pt or Pt-based alloys, and synthesis of supported catalysts [13].

Supported catalysts, in particular, have been utilized as an effective catalyst structure by depositing Pt nanoparticles on supporting materials [14,15]. The essential characteristics of these supporting materials are high specific surface area to support the nano-sized Pt nanoparticles, high electrical conductivity for efficient electron transport in electrochemical reactions, electrochemical stability, and porous structure to effectively transport product and by-products [12,16–18]. Carbon nanostructured materials, such as carbon black, carbon nanotubes, carbon nanofibers, graphene, and graphite nanosheets, have been extensively utilized as supports [9,16,19]. However, the oxidation of carbon-based materials as a degradation mechanism of the electrocatalyst (Equation (1)) needs to be prevented in order to improve
electrode stability [17,20]. Although the electrochemical reaction at 25 °C is likely to be sluggish in that potential range, the oxidation rate of carbon at potentials above 0.9 V vs. SHE, i.e., Standard Hydrogen Electrode, can be rapidly accelerated even at 25 °C [21]. Thus, the electrocatalytic activity and stability of carbon-supported catalysts can deteriorate due to a collapse in their structure [22].

\[
\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \quad \text{E}^\circ = 0.207 \text{ V vs. SHE}
\]

To overcome the electrochemical oxidation of carbon materials in supported catalysts, transition metal oxides, such as WO₃, TiO₂, and SnO₂, have been proposed as supports in proton-exchange membrane fuel cells (PEMFCs) [19,23]. Among these oxides, SnO₂ is attractive because of its electrochemical stability, non-toxicity, and abundance [23,24]. However, a wide energy band gap of >3.6 eV for SnO₂ as a semiconductor can deteriorate its electrochemical performance in PEMFCs because of relatively poor electrical conduction during the electrochemical reactions [25–27]. In general, the introduction of dopants in a semiconductor is the best way to increase its electrical conductivity of a semiconductor [23,26,28]. Thus, antimony (Sb⁵⁺) utilized as a dopant in SnO₂ (antimony-doped tin oxide, ATO) can produce extra electrons, thereby improving electrical conductivity in the SnO₂ structure [23,26,29,30]. In this study, mesoporous ATO nanostructures as supports for a Pt anode catalyst were synthesized using the Adams fusion method and a heating process at different temperatures. The Pt anode catalysts for the MOR were deposited on the ATO supports using the polyol process. Furthermore, the electrocatalytic activity and stability of the anode catalysts for MOR were evaluated using typical electrochemical cells. Specifically, compared to literature, in this study, we found that the electrocatalytic performance of the catalysts for the MOR could be attributed to Pt nanoparticles on the relatively stable oxide support with electrical conductivity and interaction between the Pt catalyst and the ATO support heated at a varying temperature [31–33].

2. Results and Discussion

Figure 1 shows XRD patterns for the bare ATO and the samples heated at different temperatures in air. All the samples exhibited the main characteristic peaks corresponding to the (110), (101), (200), and (211) planes at 26°, 34°, 38°, and 52°, respectively, in a tetragonal SnO₂ structure with a = b = 4.74 Å and c = 3.19 Å (P42/mn(136) group, Powder Diffraction File (PDF) 88-0287) [24,29]. This demonstrated that the heated samples maintained a crystal structure identical to that of the ATO before heating, without other phases. Compared to pure SnO₂ and bare ATO, the diffraction peak shift towards higher angles demonstrated the substitution of Sn with Sb in the SnO₂ structure without other Sb-related structures [34,35]. The average crystallite sizes of ATO, ATO-300, ATO-350, and ATO-400 were determined to be 8.6, 8.9, 8.9, and 8.7 nm, respectively, by the Scherer equation. Figure 2 shows the TEM images of the as-prepared and heated ATO samples. Overall, the samples appeared spherical in shape. The average crystallite sizes of ATO, ATO-300, ATO-350, and ATO-400 were 8.6, 8.8, 8.9, and 8.7 nm, respectively, which was in accordance with those obtained by the XRD results. Furthermore, as the heating temperature was increased from 300 to 400 °C, the size of the ATO samples slightly decreased due to a slight aggregation of the ATO particles. From the high-resolution TEM images, the ATO samples were indexed as tetragonal SnO₂ with an interplanar spacing of 1.4 Å corresponding to the dominant (110) plane, which was in agreement with the XRD analysis.
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Figure 1. XRD patterns of the antimony-doped tin oxide (ATO) samples heated at different temperatures from 300 to 400 °C in an air atmosphere. (A tetragonal SnO$_2$ structure with $a = b = 4.74$ Å, $c = 3.19$ Å (P42/mn(136) group, PDF 88-0287)).

Figure 2. TEM images, size distributions, and high-resolution TEM images of ATO (a,e,i), ATO-300 (b,f,j), ATO-350 (c,g,k), and ATO-400 (d,h,l).

To confirm the specific surface area and pore structure of the samples, N$_2$ adsorption/desorption characteristic curves were obtained, as shown in Figure 3 and Table 1. All the samples exhibited type IV curves, indicating a mesoporous structure for the ATO samples synthesized by the Adams fusion method. The specific surface areas of ATO, ATO-300, ATO-350, and ATO-400 were 37, 36, 34, and 31 m$^2$ g$^{-1}$, respectively. Furthermore, the dominant pore sizes of ATO, ATO-300, ATO-350, and ATO-400 were 19.4, 20.0, 21.2, and 22.5 nm, respectively. As the heating temperature increased, the specific surface area decreased, and the pore size increased due to a slight aggregation of the ATO particles. To investigate the chemical state of Sb in the ATO-samples, XPS analysis was performed.
(Figure 4). The amount of Sb measured by XPS in the ATO samples was determined to be ~5%, which is close to an optimum value for Sb [36]. The Sb 3d spectrum consists of two characteristic peaks for 3d_{3/2} and 3d_{5/2}, located at ~540 and ~531 eV, respectively, because of spin-orbit interactions [37–39]. Practically, it is hard to analyze the accurate valence state of antimony by fitting the Sb 3d_{3/2} peak because of overlap with the O 1s peak. Thus, the Sb 3d_{3/2} peaks in the samples were fitted into the two chemical states of Sb^{3+} and Sb^{5+} at ~539.74 and ~540.71 eV, respectively. As shown in Table 2, with increasing heating temperature, the ratio of Sb^{5+} in the entire Sb state increased from 85% to 95%.

The content of Sb^{5+} as a dopant in the SnO\(_2\) structure could be significantly related to its electrical behavior, i.e., conductivity. In other words, Sb^{5+} might play the role of the donor to enhance electrical conductivity, producing extra electrons in the conduction band of the Sb-doped SnO\(_2\) structure as an n-type semiconductor [38,39]. The electrical conductivities in the Sb-doped SnO\(_2\) samples heated at different temperatures were compared (Figure 5). The average conductivity values of ATO, ATO-300, ATO-350, and ATO-400 were 0.32, 0.68, 1.30, and 0.86 S cm\(^{-1}\), respectively. Compared to the ATO, the heated samples exhibited improved electrical conduction due to more activation of Sb^{5+} as a dopant in the SnO\(_2\) structure. Furthermore, the conductivity of the ATO samples increased with increasing heating temperature. The improved electrical conductivity of the doped ATO samples could be attributed to an increased Sb^{5+} ratio, i.e., an increased concentration of the activated Sb donors (Table 2). However, since annealing in air at 400 °C might lead to a decreased Sb^{5+} ratio due to an air-rich atmosphere, resulting in decreased electrical conductivity of the ATO-400, thus, the ATO-350 heated at 350 °C in the air could have an optimum conductivity.

![Figure 3](image-url) **Figure 3.** \(\text{N}_2\) adsorption-desorption isotherms and pore size distributions for ATO (a,e), ATO-300 (b,f), ATO-350 (c,g), and ATO-400 (d,h).

### Table 1. Comparison of the specific surface area, pore size, and particle size of the antimony-doped tin oxide (ATO) samples.

| Sample    | Specific Surface Area (m\(^2\) g\(^{-1}\)) | Pore Size (nm) | Crystalline Size (nm) |
|-----------|------------------------------------------|----------------|-----------------------|
| ATO       | 37                                       | 19.4           | 8.6                   |
| ATO-300   | 36                                       | 20.0           | 8.8                   |
| ATO-350   | 34                                       | 21.2           | 8.9                   |
| ATO-400   | 31                                       | 22.5           | 8.7                   |
Figure 4. XPS Sb3d3/2 spectra of (a) ATO, (b) ATO-300, (c) ATO-350, and (d) ATO-400.

Table 2. Comparison of the Sb\(^{5+}\) ratio and electrical conductivity of the ATO samples.

| Sample  | \(\frac{\text{Sb}^{5+}}{\text{Sb}^{3+} + \text{Sb}^{5+}} \times 100\) | Conductivity (S cm\(^{-1}\)) |
|---------|-------------------------------------------------|-----------------------------|
| ATO     | 48%                                            | 0.32                        |
| ATO-300 | 49%                                            | 0.68                        |
| ATO-350 | 66%                                            | 1.30                        |
| ATO-400 | 64%                                            | 0.86                        |
In general, the essential requirements for the supporting materials are high electrical conductivity, specific surface area, and stability. Specifically, as shown in Figure 5, among these ATO samples, ATO-350 exhibited a high electrical conductivity with the optimum specific surface area. Thus, to investigate the effect of the heated ATO support on the electrocatalytic performance of Pt catalyst, we prepared Pt nanoparticles as catalysts deposited on ATO and ATO-350 supports (Pt/ATO and Pt/ATO-350). Figure 6 shows XRD patterns for the Pt nanoparticles as catalysts deposited on ATO and ATO-350 as supports, denoted as Pt/ATO and Pt/ATO-350, respectively. All the samples exhibited the main characteristic XRD peaks corresponding to the (111), (200), and (220) planes at 39.7°, 46.2°, and 67.4°, respectively, in a face-centered-cubic (fcc) structure in Pt. Furthermore, the ATO structure in the Pt/ATO was the same as that of the ATO, without any change during the synthesis of the Pt nanoparticles. As shown in Figure 7 (TEM images), the Pt nanoparticles formed by the polyl process were deposited on the supports. Compared to Pt/C, Pt/ATO and Pt/ATO-350 exhibited an aggregation of Pt nanoparticles on the ATO supports because of the relatively low specific surface area of the ATO samples. The average crystallite sizes of the Pt catalysts in the Pt/ATO, Pt/ATO-350, and Pt/C were 2.2, 2.5, and 2.7 nm, respectively. From the high-resolution TEM images, the Pt nanoparticles were found to have an interplanar spacing of 2.2 Å corresponding to the (111) plane of an fcc structure.

![Figure 5](image5.png)  
**Figure 5.** Comparison of the specific surface area and electrical conductivity of the samples.

![Figure 6](image6.png)  
**Figure 6.** XRD patterns of Pt/C, Pt/ATO, and Pt/ATO-350.
Cyclic voltammograms (CVs) of the catalysts were measured in Ar-saturated 0.5 M H$_2$SO$_4$ at a scan rate of 50 mV s$^{-1}$ (Figure 8a). All the catalysts showed typical CVs of a polycrystalline Pt electrode containing electrochemical characteristic peaks corresponding to hydrogen oxidation/reduction and oxygen oxidation/reduction. In particular, the electrochemically active surface area (EASA) of the Pt catalysts could be calculated by the following equation [9]:

$$\text{EASA} \left[ \text{m}^2 \text{g}^{-1} \right] = \frac{Q_H}{0.21 \times M_{Pt} \times}$$  

where $Q_H$ is the charge amount of hydrogen adsorbed on the Pt catalyst, 0.21 mC cm$^{-2}$ is the Coulombic charge ($Q_H$) associated with hydrogen adsorption of the polycrystalline Pt electrode, and $M_{Pt}$ is an amount of the Pt loading on the working electrode. The EASAs of the Pt/C, Pt/ATO, and Pt/ATO-350 were determined to be ~9.5, ~4.3, and ~18.6 m$^2$ g$_{Pt}^{-1}$, respectively. To compare the electrocatalytic activity of the catalysts for the MOR, CVs were measured in Ar-saturated 0.5 M H$_2$SO$_4$ + 2 M CH$_3$OH at a scan rate of 50 mV s$^{-1}$ in the potential range 0.1–1.3 V (vs. SHE) (Figure 8b). The specific activities of Pt/C, Pt/ATO, and Pt/ATO-350 measured at 0.65 V, close to the onset potential for the MOR, were 0.26, 0.22, and 0.47 A cm$^{-2}$, respectively (Table 3). Furthermore, the mass activities of Pt/C, Pt/ATO, and Pt/ATO-350 were 0.39, 0.27, and 0.58 A g$_{Pt}^{-1}$, respectively. Overall, the electrocatalytic activity of Pt/ATO-350 was superior to that of Pt/ATO because of the improved electrical conductivity of ATO heated at 350 °C with an unchanged specific surface area of ATO. Compared to Pt/C, the electrochemical performance of Pt/ATO-350 could be attributed to the supported catalyst structure of the Pt nanoparticles.
deposited on the doped oxide support with high electrical conductivity and an optimum specific surface area [19]. Compared to oxide-supported Pt catalysts reported in the literature, Pt/ATO-350 exhibited improved electrocatalytic activity toward the MOR (Table 4) [7,24,40]. Furthermore, the electrocatalytic stability of the supported catalysts was evaluated by measuring the variation of current density at a constant potential of 0.7 V for 3600 s in Ar-saturated 0.5 M H₂SO₄ + 2 M CH₃OH (Figure 9). The initial current values of Pt/C and Pt/ATO-350 were 0.91 and 4.37 A g⁻¹Pt, respectively. After 3600 s, the MOR current densities of Pt/C and Pt/ATO-350 dropped to 0.12 and 0.73 A g⁻¹Pt, respectively. Compared to Pt/C, Pt/ATO-350 exhibited superior electrocatalytic stability for the MOR, which could be attributed to Pt nanoparticles on the relatively stable oxide support with high conductivity and interaction between the Pt catalyst and the heated ATO support [24]. As shown in Figure 10, the average crystallite sizes of Pt/C and Pt/ATO-350 after the stability tests were ~4.4 and ~3.5 nm, respectively, increasing by 160% and 140%, respectively, from the values before the stability tests. However, compared to Pt/C, the relatively less increased catalyst size of Pt/ATO-350 indicated the superior stability of Pt/ATO-350 during the MOR. Figure 11 shows the Pt4f XPS spectra of Pt/C and Pt/ATO-350. Compared to Pt/C, the relatively lower binding energy shift of Pt4f in Pt/ATO-350 demonstrated a strong coupling effect between Pt and ATO with electron transfer between the ATO and the Pt [41–43]. Such an electronic effect between Pt and ATO could lead to the favorable adsorption of OH on Pt sites by facilitating the cleavage of intermediates during the MOR, resulting in an improved MOR activity. In addition, the strong metal-oxide support interaction could prevent aggregation of Pt nanoparticles during the MOR, resulting in an enhanced MOR stability.

### Table 3. Comparison of the methanol oxidation reaction (MOR) activities and electrochemically active surface areas (EASAs) of the supported Pt catalysts.

| Sample       | Current Density (A cm⁻²) | Current Density (A cm⁻²) | Current Density (A g⁻¹Pt) | EASA (m² g⁻¹Pt⁻¹) |
|--------------|--------------------------|--------------------------|----------------------------|-------------------|
| Pt/C         | 0.26                     | 0.09                     | 0.39                       | 9.5               |
| Pt/ATO       | 0.22                     | 0.90                     | 0.27                       | 4.3               |
| Pt/ATO-350   | 0.47                     | 0.52                     | 0.58                       | 18.6              |

### Table 4. Comparison of the Pt catalysts supported by oxide supports.

| Sample        | Condition                | Mass Activity (A g⁻¹Pt⁻¹@0.65 V) | Ref.     |
|---------------|--------------------------|----------------------------------|----------|
| Pt/ATO-350    | 0.5 M H₂SO₄ + 2 M CH₃OH  | 0.58                             | In this study |
| Pt/SnO₂       | 0.5 M KOH + 2 M CH₃OH    | 0.30                             | 7        |
| Pt/InSnO₂     | 0.5 M KOH + 2 M CH₃OH    | 0.41                             | 7        |
| Pt/SbSnO₂     | 0.5 M H₂SO₄ + 2 M CH₃OH  | 0.64                             | 24       |
| Pt/RuO₂/CNT   | 1 M HClO₄ + 1 M CH₃OH    | 0.49                             | 35       |
Figure 8. Cyclic voltammograms (CVs) for Pt/C, Pt/ATO, and Pt/ATO-350 measured with a scan rate of 50 mV s\(^{-1}\) (a) in Ar-saturated 0.5 M H\(_2\)SO\(_4\) and (b) Ar-saturated 0.5 M H\(_2\)SO\(_4\) + 2 M CH\(_3\)OH at 25 °C. (c) Comparison of specific and mass activities of the supported catalysts measured at 0.65 V.

Figure 9. Plots of current density vs. time for Pt/C and Pt/ATO.
Figure 9. Plots of current density vs. time for Pt/C and Pt/ATO.

Figure 10. TEM images and size distributions of Pt/C (a,c) and Pt/ATO-350 (b,d) after the methanol oxidation reaction (MOR) stability test.

Figure 11. XPS Pt4f spectra of (a) Pt/ATO-350 and (b) Pt/C.

Table 4. Comparison of the Pt catalysts supported by oxide supports.

| Sample Condition               | Mass Activity (A gPt$^{-1}$@0.65 V) | Ref. |
|-------------------------------|------------------------------------|------|
| 0.5 M H$_2$SO$_4$ + 2 M CH$_3$OH | 50 mV s$^{-1}$ 0.58               | In this study |
| 0.5 M KOH + 2 M CH$_3$OH       | 20 mV s$^{-1}$ 0.30               | 7    |
| 0.5 M KOH + 2 M CH$_3$OH       | 20 mV s$^{-1}$ 0.41               | 7    |
| 0.5 M H$_2$SO$_4$ + 2 M CH$_3$OH | 50 mV s$^{-1}$ 0.64               | 24   |
| 1 M HClO$_4$ + 1 M CH$_3$OH    | 100 mVs$^{-1}$ 0.49               | 35   |

To confirm the stability of the supports without Pt catalysts, CVs were compared before and after potential cycling between 0.1 and 1.3 V for 100 cycles in Ar-saturated 0.5 M H$_2$SO$_4$ (Figure 12). The variation of the area in the CVs before and after potential cycling demonstrates the degradation of the stability of the supporting material [18]. The carbon support in Pt/C showed an increased area in the CV due to surface oxidation of the carbon, whereas the CV area for ATO-350 was maintained before and after cycling, thereby indicating high stability of the Sb in ATO [36,44,45]. Thus, compared...
To confirm the stability of the supports without Pt catalysts, CVs were compared before and after potential cycling between 0.1 and 1.3 V for 100 cycles in Ar-saturated 0.5 M H₂SO₄ (Figure 12). The variation of the area in the CVs before and after potential cycling demonstrates the degradation of the stability of the supporting material [18]. The carbon support in Pt/C showed an increased area in the CV due to surface oxidation of the carbon, whereas the CV area for ATO-350 was maintained before and after cycling, thereby indicating high stability of the Sb in ATO [36,44,45]. Thus, compared to carbon support, Pt/ATO-350 showed superior electrochemical stability, which could be attributed to the excellent electrochemical stability of ATO-350 between 0.1 and 1.3 V in an acid solution. The superior electrocatalytic activity and stability of Pt/ATO-350 could be attributed to the relatively stable conductive oxide support and interaction between the Pt catalyst and the ATO support.

![Figure 12](image-url)  
**Figure 12.** CVs for (a) carbon and (b) ATO-350 after 100 cycles between 0.1 and 1.3 V with a scan rate of 50 mV s⁻¹ in Ar-saturated 0.5 M H₂SO₄ at 25 °C.

3. Materials and Methods

3.1. Synthesis of ATO Supported Pt Catalysts

The ATO sample was synthesized by the Adams fusion method [27,46]. To prepare ATO, the desired amount of SnCl₂·5H₂O (Sigma-Aldrich, 98%) was dissolved in 100 mL of de-ionized (DI) water with stirring for 30 min, and 5% SbCl₃ was then added, calculated based on tin chloride, and continually stirred for 24 h. Subsequently, excessive NaNO₃ (Sigma-Aldrich, 99%) was added to the solution under sonication with stirring for 30 min. The solvent in the solution was evaporated at 80 °C for 4 h. The remaining powder was calcined under an air atmosphere at different temperatures from 300 to 400 °C for 5 h. The calcined powders were washed and filtered with a 0.5 M HCl solution and then dried at 50 °C for 12 h. To prepare ATO supported Pt (20 wt%) catalysts, Pt nanoparticles were formed using the polyol process and deposited on the ATO samples. Ethylene glycol (Sigma-Aldrich, 99.8%) was used as both the solvent and reductant in the polyol process [14]. An amount of 0.225 g of H₂PtCl₆ (Sigma-Aldrich, 99.9%) was dissolved in 95 mL of ethylene glycol (Samchun, 99.5%) with continuous stirring. NaOH (Sigma-Aldrich, 97%) was added until a pH of 11.5 was reached in the precursor solution, and stirring was continued for 30 min. Then, the mixed solution was heated to 180 °C, and the temperature was maintained at 180 °C for 1 h with stirring for complete reduction of the Pt precursor. The support materials (0.427 g) were added to the colloidal solution of Pt nanoparticles at 25 °C with sonication for 30 min and overnight stirring, and the ξ-potential of the ATO samples was adjusted to pH 2.0 using 1 M H₂SO₄. The supported catalysts (Pt/ATO) were washed with ethanol and DI water and dried in a 50 °C oven for 12 h. For comparison, Pt (20 wt%) catalyst deposited on Vulcan XC-72R as support (Pt/C) was prepared using the same procedure as the Pt/ATO.

3.2. Structural Analysis of ATO Supported Pt Catalysts

The crystal structure of the samples was analyzed by an X-ray diffractometer (XRD, Bruker D2 Phaser system, Geumcheon, Korea) with Cu Kα radiation (λ = 0.15418 nm) and a Ni filter operating at an accelerating voltage of 30 kV and a current of 10 mA. The specific surface area and pore structure
of the samples preheated under a pressure of 100 mmHg at 473 K for 360 min were characterized by nitrogen adsorption/desorption analyzer (Micromeritics ASAP 2020 instrument, Norcross, GA, USA). The morphology of the samples was observed using a Cs-corrected spherical aberration-corrected scanning transmission electron microscope (JEM-ARM 200F microscope, Akishima, Tokyo, Japan) working at an accelerating voltage of 200 kV. To characterize the surface composition and chemical species of the samples, X-ray photoelectron spectroscopy (XPS, K-Alpha, Waltham, MA, USA) was carried out with an Al Kα X-ray of 1468.8 eV and beam power of 200 W under a chamber pressure of 7.8 × 10⁻⁹ Torr. The sample was loaded in a Teflon-coated stainless steel container, and its electrical conductivity was measured under a pressure of ~5 bar as the following equation:

\[ \sigma = \frac{L}{A} \times \frac{I - I_0}{V - V_0} \text{ (S·cm}^{-1}) \]  

(3)

where \( \sigma \) is electrical conductivity, \( L \) is the length of the pressed powder sample, \( A \) is the area of the pressed powder sample, \( V_0 \) is the initial voltage, \( V \) is the final voltage, \( I_0 \) is the initial current, and \( I \) is the final current.

3.3. Electrochemical Analysis of ATO Supported Pt Catalysts

The electrochemical properties of the samples were characterized in a three-electrode cell at 25 °C. Pt wire and Ag/AgCl (in 3 M KCl) were used as counter and reference electrodes, respectively. The working electrode was prepared by loading the prepared sample on the glassy carbon (GC) electrode of a rotating disk electrode system. The ink was prepared by mixing the sample powder with DI water, isopropyl alcohol (Sigma-Aldrich, 99.7%), and Nafion (Sigma-Aldrich, 5 wt% Nafion® ionomer) and then dropped on the GC electrode. After drying in an oven at 50 °C for 10 min, the loading amount of the catalyst deposited on the GC electrode was 80 µgPt cm⁻². The electrochemical properties of the catalysts were characterized in Ar-saturated 0.1 M H₂SO₄ using cyclic voltammetry (CV, Metrohm Autolab PGSTAT302N instrument, Netherlands) in the potential range 0–1.2 V (vs. Ag/AgCl) with a scan rate of 50 mV s⁻¹. To evaluate the electrocatalytic stability of the MOR, the electrocatalysts were kept at 0.7 V (vs. Ag/AgCl) for 3600 s in Ar-saturated 0.1 M H₂SO₄ + 2.0 M CH₃OH. All electrode potentials were converted to the SHE potentials using the Nerst equation.

4. Conclusions

In summary, we synthesized Sb-doped SnO₂ nanostructure supports for Pt catalyst for the MOR in an acid solution. The ATO-350 heated at 350 °C in air exhibited the best electrical conductivity (1.30 S cm⁻¹) caused by a high Sb⁵⁺ ratio (95%) and the optimum specific surface area (34 m² g⁻¹) with a mesoporous structure. Compared to Pt/C and Pt/ATO, Pt/ATO-350 showed the best electrochemical performance, i.e., electrocatalytic activity (0.58 A g⁻¹ Pt at 0.65 V) and stability, for the MOR, resulting from the relatively stable conductive oxide support and interaction between the Pt catalyst and ATO support.

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