SnO₂-modified Pt electrocatalysts for ammonia-fueled anion exchange membrane fuel cells

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Abstract

The electrochemical oxidation of ammonia over two types of SnO₂-modified Pt (C–Pt/SnO₂, SnO₂–Pt/C) and Pt/C electrocatalysts was evaluated in alkaline aqueous solutions. Linear sweep voltammograms (LSVs) and chronoamperograms (CAs) were obtained in a 1 M KOH solution with 0.1 M NH₃. The ammonia oxidation current achieved during the LSVs was in the order C–Pt/SnO₂ > SnO₂–Pt/C > Pt/C. In addition, the apparent activation energies for ammonia oxidation calculated from the CAs for C–Pt/SnO₂, SnO₂–Pt/C, and Pt/C at various temperatures were 52, 58, and 67 kJ mol^{−1}, respectively. These results indicated that SnO₂ activated the dehydrogenation of ammonia over Pt. Moreover, the *I*–*V* characteristics of an ammonia-fueled anion exchange membrane fuel cell with the SnO₂–Pt/C anode clearly achieved a higher performance than with the Pt/C anode.

Keywords: Ammonia oxidation, Tin oxide, Platinum, Direct ammonia fuel cell, Anion exchange membrane

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1. Introduction

Hydrogen is a promising fuel source for stationary, mobile, and transportation applications, particularly for fuel cells, but its storage and delivery are still major issues. To overcome these problems, hydrogen has been stored and transported via other chemical compounds, such as ammonia, alcohols, hydrocarbons, etc.

Ammonia is a promising potential hydrogen carrier due to its high hydrogen density,

ease of liquefaction at ambient temperature, and low production cost [1,2]. In addition, ammonia is a carbon-free fuel, which makes it ideal for low emission power supply systems such as fuel cells. However, conventional proton exchange membrane fuel cells (PEMFCs) employing acidic membranes, such as Nafion[®], are not compatible with ammonia because the presence of trace ammonia in the anode fuel degrades cell performance [3,4]. However, ammonia can be used as a fuel for alkaline fuel cells (AFCs) using KOH [5–7], molten NaOH–KOH [8,9], and anion exchange membranes (AEMs) [10,11] as the electrolytes. Unlike KOH-based electrolytes, which suffer from the problem of carbonate salt formation via the chemical reaction between KOH and CO₂ [12,13], in AEMs such carbonate salts are not formed [14]. Moreover, in AEMFCs, OH[−] generated in the cathode during the operation purges a portion of the HCO₃[−] and CO₃^{2−} derived from CO₂ in the air, leading to enhancement of cell performance [15–17]. Therefore, AEMs are promising electrolytes for direct ammonia fuel cells.

Ammonia-fueled AFCs do, however, suffer from some serious limitations: (1) the overpotential for ammonia oxidation on anode catalysts is high [11,19] and (2) atomic nitrogen (N_{ad}) produced during the dehydrogenation of ammonia acts as a poisoning species on anodes [11,18,19]. To investigate these problems in detail, several studies have focused on electrochemical ammonia oxidation over Pt group metals in alkaline media [11,19,20]. De Vooy et al. [19] confirmed that the peak current value for ammonia oxidation varied in the order Ru < Rh < Pd < Ir < Pt, while the onset potential of ammonia oxidation for the 4d metals (Ru, Rh, and Pd) was considerably lower than that for Pt and Ir. This difference is due to the stronger N_{ad} adsorption energies on 4d metals.

To enhance the electrocatalytic activity of Pt for ammonia oxidation, various bimetallic catalysts have been investigated, e.g., PtIr, PtRu, PtPd, PtCu, and PtNi [11,21–26]. In particular, PtIr alloys are considered to be promising electrodes due to their good catalytic activity and enhanced stability for ammonia oxidation as determined by several studies [21–26]. Endo et al. reported that the onset potential for ammonia oxidation on PtIr alloys is reduced by approximately 0.1 V compared to that on monometallic Pt, because Ir participates in ammonia dehydrogenation [22]. Allagui et al. also concluded that PtIr alloys exhibit superior results with a better stability and durability compared to monometallic Pt due to the change in the electronic state of the Pt surface when alloyed with Ir [26]. However, the maximum current for ammonia oxidation achieved with PtIr alloys is still lower than that for monometallic Pt. In addition, the high cost and limited availability of Ir pose serious concerns.

Another effective approach for enhancing the catalytic activity of Pt electrocatalysts is

to modify the Pt with metal oxides, which have rarely been evaluated for the electrochemical oxidation of ammonia. Moreover, metal oxides can provide OH_{ad} , which is an active species in the dehydrogenation of ammonia [18]. In particular, oxygen vacancies and other defect sites at the surface of SnO_2 may play an important role in water dissociation, indicating that SnO_2 can effectively provide OH groups [27,28]. In fact, SnO_2 -modified Pt catalysts have been widely applied as CO-tolerant anode catalysts in PEMFCs [29,30] and highly active catalysts for ethanol oxidation [31–33] due to their capacity of SnO_2 to supply OH species. In the present study, therefore, the effect of SnO_2 modification of Pt catalysts on their ammonia oxidation behavior was investigated. The performance of an ammonia-fueled AEMFC with an SnO_2 -modified Pt anode was also evaluated.

2. Experimental

2.1. Catalyst preparation and characterization

Two types of SnO_2 -modified Pt catalysts were prepared. Pt supported on SnO_2 (Pt/SnO_2) was produced using the impregnation method. An aqueous solution of $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ and commercial SnO_2 (Wako Pure Chemical) were used as the Pt source and support, respectively. After calcination of the SnO_2 at 800°C for 5 h in air, the SnO_2 powder (BET surface area: $5.0 \text{ m}^2 \text{ g}^{-1}$) was mixed with the desired amount of an aqueous solution of $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$. The Pt loading on SnO_2 was 10 wt%. The mixture was heated on a steam bath at 80°C until the solution evaporated, yielding a powder. The dried powder was heated at 400°C for 0.5 h in air. Carbon black (Lion, Ketjen Black 600JD) was then added to the suspension in order to enhance the electronic conductivity of the catalyst. The weight ratio of Pt to carbon black was 1:1 in the catalyst, which was denoted as C– Pt/SnO_2 . Another SnO_2 -modified catalyst (SnO_2 – Pt/C) was prepared by simply mixing the calcined SnO_2 powder with a commercial Pt/C catalyst (Tanaka Kikinzoku Kogyo, TEC10E50E, 46.1 wt% Pt on Ketjen Black) in an agate mortar. The weight ratio of Pt to SnO_2 was 1 to 9 for the SnO_2 – Pt/C catalyst.

The morphology and particle size distribution of the C– Pt/SnO_2 and SnO_2 – Pt/C catalysts were observed using a transmission electron microscope (TEM, JEOL, JEM-2100F).

2.2. Electrochemical measurements

All electrochemical measurements were conducted in a conventional three-electrode cell. The electrodes were a glassy carbon (GC) disk electrode (geometric area: 0.196

cm²) with a Pt counter electrode and a reversible hydrogen electrode (RHE) as the reference. A suspension containing the catalyst in water was ultrasonically dispersed for 2 h then dropped onto the GC disk electrode. For each catalyst, the amount of Pt loaded on the electrode was 28 $\mu\text{g cm}^{-2}$. The water was allowed to evaporate, and then the electrode surface was covered with 10 μl of an anion exchange ionomer solution (Tokuyama, AS-4, diluted to 1 wt% solution with ethanol). Cyclic voltammograms (CVs), linear sweep voltammograms (LSVs), and chronoamperograms (CAs) were obtained in a 1 M KOH or 0.1 M NH₃–1 M KOH solution prepared using a 28 wt% NH₃ solution (Wako Pure Chemical), KOH (Sigma-Aldrich, >85 wt%), and ultrapure water (Millipore, Milli-Q). After the electrochemical cell was purged for 30 min with Ar, each electrochemical measurement was conducted using a potentiostat (Hokuto Denko, HSV110). The CVs were recorded between 0.05 and 0.90 V vs. RHE at 25°C. The CAs were obtained at 0.6 V for 3 min at several temperatures (5, 25, 45, and 60°C). The electrochemically active surface area (ECSA) was determined from the hydrogen adsorption charge (ΔQ_{H}^0) in each CV, referenced to $\Delta Q_{\text{H}}^0 = 0.21 \text{ mC cm}^{-2}$ for clean polycrystalline Pt [34,35].

2.3. Fuel cell operation

The basic properties of the AEM (A201, Tokuyama) used in this study have been described previously [11]. A commercial Pt/C catalyst (Tanaka Kikinzoku Kogyo, TEC10E50E, 46.1 wt% Pt on Ketjen Black) was applied to the cathode in all cases, while the anode was composed of either a Pt/C or SnO₂–Pt/C catalyst. A catalyst slurry was prepared by mixing each catalyst with the anion exchange ionomer solution such that the weight ratio of the polymer content was 0.8 with respect to carbon for both the anode and the cathode. The slurry was directly screen-printed on the membrane. The geometric electrode area was 1.0 cm² (1.0 cm × 1.0 cm), and the Pt loadings were set at 0.4 mg cm⁻² for both electrodes. A membrane electrode assembly (MEA) was constructed by sandwiching the catalyst-coated membrane between two microporous gas diffusion layers (24BC, SGL). The MEA was mounted in a single-cell holder composed of two carbon separator plates with ribbed single serpentine flow channels.

The cells were operated at 50°C and ambient pressure under high humidity conditions (95% relative humidity (RH) for both electrodes). Humidified H₂ or 50% NH₃–N₂ was fed to the anode, and O₂ to the cathode. The flow rate for all of the feed gases was 100 ml min⁻¹. The *I*–*V* characteristics were determined at a scanning rate of 10 mV s⁻¹ using a Solartron 1470E potentiostat.

3. Results and discussion

3.1. Characterization of the electrocatalysts

Figure 1 shows TEM images of (a) C–Pt/SnO₂ and (b) SnO₂–Pt/C, together with the corresponding Pt particle size distribution histograms. Approximately 400 particles were subjected to a particle size analysis for each catalyst. The average particle size and standard deviation were 3.2 ± 1.2 nm for C–Pt/SnO₂ and 2.4 ± 0.4 nm for SnO₂–Pt/C. The Pt particles in C–Pt/SnO₂ were finely dispersed over the entire surface of the SnO₂ support and had an average particle size slightly larger than that of the SnO₂–Pt/C and commercial Pt/C (~2–3 nm) particles [36–38], even though the BET surface area of the SnO₂ support was exceedingly low compared to that of the carbon support (5 and 1270 m² g^{−1}, respectively [39]). In the SnO₂–Pt/C, large dark-colored SnO₂ particles (~50–100 nm) were mixed with the Pt/C particles.

The electrochemical properties of the electrocatalysts were studied in alkaline aqueous solutions using cyclic voltammetry. Figure 2 shows the CVs of the C–Pt/SnO₂, SnO₂–Pt/C, and Pt/C electrocatalysts in 1 M KOH at a scanning rate of 20 mV s^{−1}. For Pt/C, typical hydrogen and OH adsorption/desorption was observed at approximately 0.05–0.40 V and 0.60–0.90 V, respectively, which was in agreement with the results previously obtained for the electrochemical behavior of a Pt/C electrocatalyst in an alkaline aqueous solution by Tripkovic et al. [40]. The shape of the voltammogram for SnO₂–Pt/C was nearly the same as that for Pt/C. For C–Pt/SnO₂, the adsorptions/desorptions for hydrogen and OH were also observed, indicating that electrochemically active Pt was deposited on the SnO₂ support. In addition, considering the BET surface areas of SnO₂ and carbon black, most of the double-layer capacity was expected to be derived from the carbon black. In fact, it can be seen in Fig. 2 that the double layer capacities for all of the catalysts were nearly identical. Therefore, it was concluded that the added carbon black successfully contributed to the enhancement of the electronic conductivity of the Pt/SnO₂ electrocatalyst. Moreover, no redox peaks derived from SnO₂ were detected for either SnO₂–Pt/C or C–Pt/SnO₂.

The ECSA of each catalyst was determined using the CVs shown in Fig. 1. C–Pt/SnO₂ exhibited a slightly lower ECSA value (38 m² g^{−1}_{Pt}) compared to that for Pt/C (43 m² g^{−1}_{Pt}). This result is reasonable considering the average Pt particle size in the electrocatalysts determined from the TEM images. Furthermore, the ECSA value for SnO₂–Pt/C (30 m² g^{−1}_{Pt}) was slightly less than that for the other electrocatalysts, which may be attributed to coverage of some of the electrochemically active Pt sites by the added SnO₂.

3.2. Durability of the electrocatalysts in an alkaline aqueous solution

The durability of the electrocatalysts was evaluated using cyclic voltammetry (1000 cycles) in an alkaline aqueous solution. Figure 3 shows the CVs per 200 cycles for (a) C–Pt/SnO₂ and (b) Pt/C in 1 M KOH at a scanning rate of 200 mV s⁻¹. Figure 4 displays the changes in the (a) ECSA and (b) normalized ECSA over the course of 1000 cycles for the C–Pt/SnO₂ and Pt/C catalysts (*Note*: Normalized ECSA = ECSA at cycle x /ECSA at the initial state $\times 100$). It has been generally recognized that Pt dissolves during potential cycling to a higher potential region [41]. In addition, corrosion of the catalyst support is an issue to be avoided because it most likely causes agglomeration of the detached Pt [42]. As can be seen in Fig. 3, the current density corresponding to the adsorption/desorption of hydrogen and OH, decreased with potential cycling for both electrocatalysts. In contrast, the current density corresponding to the electric double layer at ~0.4–0.6 V remained nearly unchanged for each electrocatalyst, even after 1000 cycles. These results indicated that a portion of the Pt dissolved due to potential cycling, while corrosion of the carbon black did not occur. In fact, as shown in Fig. 4(a), the ECSA gradually decreased with potential cycling for both electrodes. Furthermore, the normalized ECSA was reduced by around 20% after 1000 cycles for C–Pt/SnO₂ and Pt/C (Fig. 4(b)). Bagotzky et al. reported that Pt dissolution occurred over the potential range 0.85–1.37 V vs. RHE, and the complex ion [Pt(OH)₆]²⁻ was formed in alkaline solutions [43]. In the present study, it is reasonable to assume that Pt dissolution occurred during the potential cycles between 0.05 and 0.90 V vs. RHE. If the SnO₂ support dissolved during potential cycling, the agglomeration of Pt would be accelerated, leading to a significant decrease in the ECSA. In addition, SnO₂ is thermodynamically unstable at high pH [44]. In this study, however, such degradation was not observed. Therefore, it can be concluded that the SnO₂ support was stable at least under the present experimental conditions.

3.3. Ammonia oxidation in an alkaline aqueous solution

The electrochemical oxidation of ammonia over the electrocatalysts was studied using linear sweep voltammetry and chronoamperometry in an alkaline aqueous solution containing ammonia. Figure 5 shows the LSVs for the C–Pt/SnO₂, SnO₂–Pt/C, and Pt/C electrocatalysts, each in a 1 M KOH solution with 0.1 M NH₃, at a scanning rate of 20 mV s⁻¹. Ammonia oxidation over polycrystalline Pt in alkaline aqueous solutions is known to begin at ~0.45 V vs. RHE [11,21,45]. In this study, the onset potentials for ammonia oxidation were ~0.45 V regardless of the electrocatalyst, indicating that SnO₂ modification did not affect the onset potential for ammonia oxidation over Pt. In the

higher potential region above 0.45 V, however, a difference in the ammonia oxidation current was observed for the electrocatalysts. The maximum current density was in the order C–Pt/SnO₂ > SnO₂–Pt/C > Pt/C, and the maximum value for C–Pt/SnO₂ was 26% higher than that for Pt/C. This result also clarified that the presence of SnO₂ near Pt positively affected electrochemical ammonia oxidation, even when the Pt was not supported on the SnO₂. The slightly higher performance of C–Pt/SnO₂ compared to SnO₂–Pt/C is due to the difference in the numbers of Pt particles in contact with the SnO₂ in each catalyst.

Chronoamperometric measurements were also performed in order to evaluate in detail the effect of SnO₂ modification on the ammonia oxidation activity of Pt. The CAs obtained at 25°C for C–Pt/SnO₂, SnO₂–Pt/C, and Pt/C are compared in Fig. 6. It can be clearly seen that the two SnO₂–modified Pt catalysts maintained a high current density during the analysis. In particular, the current density for C–Pt/SnO₂ after 3 min was approximately three times higher than that for Pt/C. A series of measurements was also performed at 5, 45, and 60°C, and the Arrhenius plots were constructed using the current density after 3 min for each catalyst (see Fig. 7). The estimated apparent activation energies for C–Pt/SnO₂, SnO₂–Pt/C, and Pt/C were 52, 58, and 67 kJ mol^{−1}, respectively. The activation energy for C–Pt/SnO₂ was slightly lower than that for SnO₂–Pt/C due to the difference in the numbers of Pt particles in contact with the SnO₂ in each catalyst. Therefore, these results demonstrated that SnO₂ activated the ammonia oxidation reaction over Pt. With regard to the role of SnO₂ in ammonia oxidation, it is thought that the SnO₂ provides OH species to the Pt surface, which accelerates the dehydrogenation of NH₃ and/or intermediates, i.e., NH₂ and NH, as is the case for ethanol oxidation according to Kowal et al. [31].

3.4. *I-V characteristics of fuel cells*

The ammonia oxidation activity of the SnO₂–Pt/C electrocatalyst was also investigated using a practical AEMFC. Figure 8(a) and (b) shows the *I-V* characteristics of single cells employing two different anodes with a supply of either hydrogen or ammonia fuel, respectively. As shown in Fig. 8(a), both cells exhibited nearly the same open circuit voltage (OCV) of 0.96 V, regardless of the anode materials. Notably, this value was lower than the theoretical value of 1.23 V and is partially due to permeation of the reactant hydrogen and oxygen gases across the very thin AEM (≈ 28 μm). In addition, the performance of the cell with the SnO₂–Pt/C catalyst was lower than that with the Pt/C catalyst, likely due to the decrease in the ECSA of the anode resulting from SnO₂ addition.

As shown in Fig. 8(b), the OCV for each cell with NH_3 as the fuel was significantly lower (≈ 0.40 V) than the theoretical value of 1.17 V, which was in agreement with previously reported data [10,11]. The high overpotential for ammonia oxidation on each anode is considered to be the reason for the low OCV. This conclusion is also supported by the results in Fig. 5, which show that the onset potential for ammonia oxidation over the $\text{SnO}_2\text{-Pt/C}$ catalyst was nearly the same as that for Pt/C. The permeation of the ammonia fuel throughout the AEM as another possible reason for the lower OCV value [11].

Note that the cell with the $\text{SnO}_2\text{-Pt/C}$ anode clearly provided a higher current density compared to that for the Pt/C anode under ammonia-fueled conditions. This result corresponds to the fact that the SnO_2 modification activated the ammonia oxidation reaction over Pt in alkaline aqueous solutions, as discussed above. Therefore, it was successfully demonstrated with the practical AEMFCs that SnO_2 improved the ammonia oxidation activity of the Pt catalyst.

In addition, to confirm the morphology of the $\text{SnO}_2\text{-Pt/C}$ catalyst layers, a TEM image of the $\text{SnO}_2\text{-Pt/C}$ catalyst and the anion exchange ionomer as-prepared from the catalyst slurry was obtained. As can be seen in Fig. 9, the SnO_2 particles ($\sim 50\text{--}100$ nm) formed aggregates ($\sim 100\text{--}300$ nm) and were mixed with the Pt/C. This result was similar to that for the $\text{SnO}_2\text{-Pt/C}$ without the anion exchange ionomer (Fig. 1(b)). If the dispersibility of the SnO_2 in the catalyst layer can be improved, the ammonia oxidation activity of the anode catalyst may be enhanced due to an increase in the number of SnO_2 particles in contact with Pt. Moreover, sufficient dispersibility of SnO_2 , which is an insulator, may enhance the resistivity of the catalyst layer, resulting in improved cell performance.

4. Conclusions

The effect of SnO_2 modification of Pt catalysts on their ammonia oxidation activity was investigated under alkaline conditions. For both SnO_2 -modified electrocatalysts (C-Pt/SnO_2 , $\text{SnO}_2\text{-Pt/C}$), the apparent activation energy for ammonia oxidation was lower than that for a Pt/C catalyst, which indicated that SnO_2 activated the dehydrogenation of ammonia over Pt. Moreover, it was confirmed that SnO_2 enhanced the ammonia oxidation activity of the Pt catalysts in a practical AEMFC and in alkaline aqueous solutions.

Furthermore, the stability of the SnO_2 in the modified catalysts was also examined in 1 M KOH solutions. The decreasing rate of the normalized ECSA for C-Pt/SnO_2 was nearly equal to that for Pt/C after 1000 potential cycles between 0.05 and 0.90 V vs. RHE, indicating that SnO_2 was stable under such conditions.

Therefore, SnO₂ was found to be a promising anode material for ammonia-fueled AEMFCs.

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Figure captions

Fig. 1. TEM images and particle size distribution histograms of (a) C–Pt/SnO₂ and (b) SnO₂–Pt/C. The histograms were obtained for 400 particles in each corresponding TEM image.

Fig. 2. Cyclic voltammograms of the C–Pt/SnO₂ (solid line), SnO₂–Pt/C (dashed line), and Pt/C (dotted line) electrocatalysts in 1 M KOH at 25°C. Sweep range: 0.05–0.90 V vs. RHE; scanning rate: 20 mV s^{−1}.

Fig. 3. Cyclic voltammograms of the (a) C–Pt/SnO₂ and (b) Pt/C electrocatalysts in 1 M KOH at 25°C. Sweep range: 0.05–0.90 V vs. RHE; scanning rate: 200 mV s^{−1}.

Fig. 4. (a) ECSA and (b) normalized ECSA over the course of 1000 potential cycles from 0.05 to 0.90 V vs. RHE for the C–Pt/SnO₂ (●) and Pt/C (▲) electrocatalysts.

Fig. 5. Linear sweep voltammograms of the C–Pt/SnO₂ (solid line), SnO₂–Pt/C (dashed line), and Pt/C (dotted line) electrocatalysts in 1 M KOH plus 0.1 M NH₃ solutions at 25°C. Sweep range: 0.05–0.90 V vs. RHE; scanning rate: 20 mV s^{−1}.

Fig. 6. Chronoamperograms of the C–Pt/SnO₂ (solid thick line), SnO₂–Pt/C (solid thin line), and Pt/C (dashed line) electrocatalysts obtained at 0.6 V vs. RHE in 1 M KOH plus 0.1 M NH₃ solutions at 25°C.

Fig. 7. Current density at 0.6 V as a function of the reciprocal temperature for the C–Pt/SnO₂ (●), SnO₂–Pt/C (▲), and Pt/C (■) electrocatalysts in 1 M KOH plus 0.1 M NH₃ solutions at 0.6 V. The plotted current density was measured after 3 min.

Fig. 8. *I*–*V* characteristics of AEMFCs with SnO₂–Pt/C (solid line) and Pt/C (dotted line) anodes. Operating temperature: 50°C; anode gas: (a) H₂ (95% RH) and (b) 50% NH₃–N₂ (95% RH); cathode gas: O₂ (95% RH); scanning rate: 10 mV s^{−1}.

Fig. 9. TEM image of the SnO₂–Pt/C electrocatalyst including the anion exchange ionomer.

Fig. 1 (T. Okanishi et al.)

Fig. 2 (T. Okanishi et al.)

Fig. 3 (T. Okanishi et al.)

Fig. 4 (T. Okanishi et al.)

Fig. 5 (T. Okanishi et al.)

Fig. 6 (T. Okanishi et al.)

Fig. 7 (T. Okanishi et al.)

Fig. 8 (T. Okanishi et al.)

Fig. 9 (T. Okanishi et al.)