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SnO_2-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 SnO_2-modified Pt (C–Pt/SnO_2, SnO_2–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 NH_3. The ammonia oxidation current achieved during the LSVs was in the order C–Pt/SnO_2 > SnO_2–Pt/C > Pt/C. In addition, the apparent activation energies for ammonia oxidation calculated from the CAs for C–Pt/SnO_2, SnO_2–Pt/C, and Pt/C at various temperatures were 52, 58, and 67 kJ mol^{-1}, respectively. These results indicated that SnO_2 activated the dehydrogenation of ammonia over Pt. Moreover, the *I–V* characteristics of an ammonia-fueled anion exchange membrane fuel cell with the SnO_2–Pt/C anode clearly achieved a higher performance than with the Pt/C anode.

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 CO_2 [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 HCO_3^- and CO_3^{2-} derived from CO_2 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 Vooys 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

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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 $Pt(NO_2)_2(NH_3)_2$ 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 $m^2 g^{-1}$) was mixed with the desired amount of an aqueous solution of $Pt(NO_2)_2(NH_3)_2$. 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 cm^2) 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 μg 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 NH_3–1 M KOH solution prepared using a 28 wt% NH_3 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 ($\Delta Q_H{}^0$) in each CV, referenced to $\Delta Q_H{}^0 = 0.21$ 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 SnO_2–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 cm^2 (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 H_2 or 50% NH_3–N_2 was fed to the anode, and O_2 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

Fig. 1 shows TEM images of (a) C–Pt/SnO_2 and (b) SnO_2–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/SnO_2 and 2.4 ± 0.4 nm for SnO_2–Pt/C. The Pt particles in C–Pt/SnO_2 were finely dispersed over the entire surface of the SnO_2 support and had an average particle size slightly larger than that of the SnO_2–Pt/C and commercial Pt/C (~2–3 nm) particles [36–38], even though the BET surface area of the SnO_2 support was exceedingly low compared to that of the carbon support (5 and 1270 $m^2 g^{-1}$, respectively [39]). In the SnO_2–Pt/C, large dark-colored SnO_2 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. Fig. 2 shows the CVs of the C–Pt/SnO_2, SnO_2–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 SnO_2–Pt/C was nearly the same as that for Pt/C. For C–Pt/SnO_2, the adsorptions/desorptions for hydrogen and OH were also observed, indicating that electrochemically active Pt was deposited on the SnO_2 support. In addition, considering the BET surface areas of SnO_2 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