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Preparation of Nanoparticles of Pt and SnO₂ Highly Dispersed on Carbon Black Support and Their Activity for Ethanol Oxidation Reaction

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Received January 21, 2010 ; Accepted March 11, 2010

Double nanoparticles of Pt and SnO₂ with different Pt/Sn ratios highly dispersed on Ketjen Black (denoted as Pt/SnO₂/CB) were prepared by the modified Bönemann method. The average size and standard deviation of the Pt and SnO₂ nanoparticles were 3.1 ± 0.5 nm and 2.5 ± 0.3 nm for the Pt/SnO₂(3 : 1)/CB, 3.0 ± 0.5 nm and 2.6 ± 0.3 nm for Pt/SnO₂(1 : 1)/CB, 2.8 ± 0.5 nm and 2.5 ± 0.3 nm for Pt/SnO₂(1 : 3)/CB. The Pt/SnO₂(3 : 1)/CB showed the highest specific activity and lowest overpotential for ethanol oxidation reaction (EOR) in the present study, and was superior to a Pt/CB electrode. These were ascribable to the synergistic effect of Pt and SnO₂ nanoparticles.

Key Words : Pt/SnO₂/CB, Ethanol Oxidation Reaction, Nanoparticle, DEFC

1 Introduction

Direct alcohol fuel cells (DAFCs) have attracted much interest as a primary power source for portable electronic devices. The popular DAFCs are the direct methanol type,¹⁾ which is the simplest, and the direct ethanol type.²⁾ Especially, ethanol is an attractive fuel for fuel cell vehicles because it is nontoxic and can be easily produced in large quantity by carbon neutral processes such as the fermentation of sugar-containing raw materials. For improving the slow EOR, Pt-M (M = Ru, Rh, etc.) alloys^{3,4)} have been developed. Several authors have reported that some Pt-Sn alloy catalysts were superior to the other Pt-based alloy catalysts on the ethanol oxidation reaction (EOR) activity.^{2, 5-7)}

In general, carbon-supported Pt-based alloy nanoparticles are prepared by the impregnation method⁸⁾ and microemulsion method⁹⁾ together with the following heat-treatment. Bönemann *et al.* first prepared tetraalkylammonium ions (NR₄⁺ (R = C₄-C₂₀))-stabilized bimetallic particles with average particle sizes less than 2 nm and narrow size distribution in an Ar atmosphere at room temperature.^{10, 11)} In this way, the Bönemann's method can control not only particle size but its distribution, which would contribute to the reduction of Pt consumption. Our original plan was to prepare the monodispersed Pt-Sn alloy nanoparticles as an electrocatalyst for EOR by the Bönemann's method. However, Pt and SnO₂ double nanoparticles actually were produced instead because our method was a little different from the original one. It is known that the Pt-loaded SnO₂ bulk catalysts show high catalytic activity for EOR,⁶⁾ but the EOR activity of the double nanoparticles has not been evaluated yet, to our knowledge. Recently, some research groups have reported that Au-CeO₂ and Au-TiO₂ double nanoparticles had high activity for the water-gas shift reaction in spite that neither bulk Au nor bulk CeO₂ and TiO₂ were inactive.^{12, 13)} In this case, the Au nanoparticles partially cov-

ered by CeO₂ or TiO₂ nanoparticles had high activity because of a synergistic effect of the nanoparticles based on direct participation of the oxide-Au interface. In the present study we characterize the Pt and SnO₂ double nanoparticles we firstly prepared and evaluate their EOR activity.

2 Experimental

Tetraoctylammonium triethylhydroborate (N(Oct)₄(BEt₃H)) as a reducing agent and stabilizer was prepared in a THF solution according to the Ref. 10. To prepare the Pt/SnO₂(3 : 1) catalyst, 12 mL of 0.3 M N(Oct)₄(BEt₃H) in THF solution was added dropwise to 100 mL of a vigorously stirred solution containing 0.177 (0.67 mol) g of PtCl₂ and 0.043 g (0.23 mol) of SnCl₂ at 30 °C, followed by stirring for 3 h, resulting in a black suspension with colloidal Pt₃Sn[N(Oct)₄Cl]₈. 15 mL of acetone was added to the suspension to oxidize surplus N(Oct)₄(BEt₃H) and then stirred for 30 min. Each procedure was carried out in an Ar atmosphere. The Pt₃Sn[N(Oct)₄Cl]₈ in the suspension was separated by suction filtration, followed by drying in vacuo for 16 h at room temperature, yielding black solid. The procedure in the air, which was not in the original method, is likely to cause the oxidation of Sn.

The resultant black solid was redispersed in ethanol and then 67 mg of Ketjen Black was added into it, followed by sonicating for 10 min. After suction filtration, residual black powder was collected. The resultant black powder was heat-treated at 200 °C in the air for 30 min to remove N(Oct)₄Cl. Total content of Pt and SnO₂ in the black powder is *ca.* 67 wt. %. The product is denoted as Pt/SnO₂(3 : 1)/CB. We also prepared the Pt/SnO₂/CB with different mole fractions of Pt and SnO₂, Pt/CB and SnO₂/CB in the same manner. The products are denoted as Pt/SnO₂(1 : 1)/CB, Pt/SnO₂(1 : 3)/CB, Pt/CB and SnO₂/CB, respectively.

The microstructure of the Pt/SnO₂(3 : 1)/CB catalyst was observed by field-emission transmission electron microscopy (FE-TEM). Specimens were prepared by pipetting a drop of the catalyst dispersed in ethanol to a copper grid coated with a collodion membrane and evaporating the solvent. Size distribution and lattice fringes of Pt and SnO₂ nanoparticles were obtained by directly measuring size for 500 of Pt nanoparticles and 100 of SnO₂ nanoparticles randomly chosen in several high revolution TEM images. Structural analysis of the obtained catalysts was carried out using an X-ray diffractometry (XRD). Chemical states of each catalyst were measured by X-ray photoelectron spectroscopy (XPS). The X-ray source was MgK α with 1253.6 eV operating at 8 kV and 30 mA. The base pressure of the system was 1.3×10^{-7} Pa. Bulk composition of the each catalyst was evaluated by energy dispersive X-ray analysis (EDX).

0.063 g of each catalyst powder was dispersed in 50 mL of 99.5 % ethanol solution (Wako), followed by sonicating for 10 min. After that, 20 μ L of the resultant dispersed solution was cast on a glassy carbon substrate (5 mm ϕ), followed by drying overnight. 10 μ L of 0.05 wt. % Nafion (Aldrich) (diluted with ethanol) solution was cast on the top of the dried catalyst layer to yield the film thickness of 0.1 μ m,¹⁴ followed by heat-treating in the air at 120 $^{\circ}$ C for 1 h, resulting in each catalyst electrode coated with the thin Nafion film. A Pt plate and a reversible hydrogen electrode (RHE) were used as the counter and reference electrodes, respectively. EOR activity for the electrodes was evaluated at 30 $^{\circ}$ C by cyclic voltammetry (CV).

3 Results and Discussion

Figure 1 shows TEM images with different magnifications for the Pt/SnO₂(3 : 1)/CB catalyst. Figure 1 (a) clearly shows the existence of nanoparticles on CB. In Fig. 1 (b), two kinds of lattice fringes with inter-fringe distances of 0.225 nm and 0.333 nm were observed. These were approximately in accord with the lattice spacing of the (111) plane (0.227 nm) in the face-centered cubic (fcc) Pt crystal and the (110) plane (0.335 nm) in the tetragonal SnO₂ crystal, respectively, suggesting that not Pt₃Sn alloy nanoparticles but Pt and SnO₂ double nanoparticles were loaded on CB probably because Sn atoms in the Pt₃Sn alloy were preferentially oxidized and segregated to form nanoparticles. The average size and standard deviation of the Pt and SnO₂ nanoparticles were 3.1 ± 0.5 nm and 2.5 ± 0.3 nm for the Pt/SnO₂(3 : 1)/CB, 3.0 ± 0.5 nm and 2.6 ± 0.3 nm for Pt/SnO₂(1 : 1)/CB, 2.8 ± 0.5 nm and 2.5 ± 0.3 nm for Pt/SnO₂(1 : 3)/CB. The average particle size of the Pt nanoparticles obtained by TEM analysis was quite in good agreement with that evaluated by XRD analysis.

In the XPS analysis for each catalyst, there were no peaks in the N1s and Cl2p core level spectra, suggesting that N(Oct)₄Cl as a stabilizer has been completely removed away during heat-treatment. In the Pt4f spectra for the Pt/SnO₂(3 : 1)/CB, the intense doublets assigned to metallic Pt (Pt⁰) were observed at 71.1 and 74.4 eV, while there were not any peaks assigned to Pt

Fig. 1 TEM images of Pt/SnO₂(3 : 1)/CB catalyst with (a) $\times 100000$ and (b) $\times 500000$.

oxides, suggesting that surface Pt was not oxidized. On the other hand, in the Sn3d spectra, the intense doublets assigned to Sn⁴⁺ were clearly observed at 495.1 and 486.7 eV,¹⁵ while the doublets assigned to metallic Sn were not observed, suggesting that Sn was oxidized to SnO₂. This result showed quite in good agreement with that evaluated by XRD. The Pt4f and Sn3d spectra for the Pt/SnO₂(1 : 1)/CB and Pt/SnO₂(1 : 3)/CB were in agreement with those for the Pt/SnO₂(3 : 1)/CB.

The mol ratio of Pt and SnO₂ (Pt/Sn ratio) for the Pt/SnO₂(3 : 1)/CB, Pt/SnO₂(1 : 1)/CB and Pt/SnO₂(1 : 3)/CB determined by EDX was quite close to that of Pt and Sn precursors, respectively, suggesting that the Pt/Sn ratio of the Pt/SnO₂/CB catalysts can be controlled by the content of Pt and Sn precursors.

Figure 2 shows linear sweep voltammograms for various Nafion-coated electrodes in an Ar-saturated 0.5 M H₂SO₄ solution containing 1 M ethanol. In this figure, current density per real Pt surface area, specific activity (SA), is used for current. Figure 2 shows that the onset potential of oxidation current density shifts in the less positive direction as the Pt/Sn ratio of Pt/SnO₂/CB increases. The onset potential for the Pt/SnO₂(3 : 1)/CB electrode (*ca.* 0.15 V) is *ca.* 0.25 V less positive than that for the Pt/CB electrode (*ca.* 0.40 V), suggesting that the former has smaller overpotential for EOR than the latter. These results clearly indicate that SnO₂ synergistically enhances the EOR activity of Pt. In addition, the Pt/SnO₂

Fig. 2 Linear sweep voltammograms of various Nafion-coated electrodes in an Ar-saturated (1 M C₂H₅OH + 0.5 M H₂SO₄) solution at 30 $^{\circ}$ C. Sweep rate = 20 mV s⁻¹. $w_{\text{Pt/SnO}_2}$ = 12.8 μ g cm⁻², w_{CB} = 5.5 μ g cm⁻².

(3 : 1)/CB electrode was superior to bimetallic Pt-Sn/CB,²⁾ Pt/SnO_x/CB⁶⁾ and Pt microparticles-dispersed SnO₂ thin film¹⁶⁾ on overpotential for EOR, suggesting strongly that the combination of Pt nanoparticles with SnO₂ nanoparticles is the best on EOR activity in catalysts composed of Pt and Sn species.

For each curve in Fig. 2, the SAs for EOR at 0.4 and 0.6 V were evaluated and plotted against mole fraction of Pt in Fig. 3. In both cases the Pt/SnO₂(3 : 1)/CB electrode with the mole fraction of Pt of 0.79 shows the maximum SAs (0.51 mA Pt·cm⁻² at 0.4 V and 0.86 mA Pt·cm⁻² at 0.6 V), which were *ca.* 25 times at 0.4 V and 4 times at 0.6 V higher than that for the Pt/CB electrode. In addition, the SA at 0.40 V for the Pt/SnO₂(3 : 1)/CB electrode is superior to catalysts with high EOR activity like PtSn,⁷⁾ PtSnIr¹⁷⁾ and PtMo.¹⁸⁾ The Pt/SnO₂(1 : 1)/CB electrode, which had the similar real surface area to the Pt/CB electrode, also had higher SA than the Pt/CB electrode. On the other hand, EOR activity for the Pt/SnO₂(1 : 3)/CB electrode was lower than that of Pt/CB electrode. It is known that higher surface contents of bulk SnO₂ with poor electronic conductivity lead to lower anode electronic conductivity,⁶⁾ significantly decreasing the EOR activity. The SnO₂/CB electrode was inactive toward EOR.

The synergistic effect arising from the combination of Pt nanoparticles with SnO₂ nanoparticles is ascribable to the bi-functional mechanism^{7, 19)} in which SnO₂ adjacent to Pt supply oxygen-containing species for the oxidative removal of intermediate CO-like species strongly adsorbed on Pt. The Pt/SnO₂(3 : 1)/CB electrode with the highest SA probably has the most Pt-Sn interface, and significantly accelerates the oxidative removal of intermediate CO-like species formed on the Pt surface in EOR.

Fig. 3 Specific activity of EOR at 0.4 and 0.6 V for various Nafion-coated Pt/SnO₂/CB electrodes.

4 Conclusion

The Pt/SnO₂/CB catalysts with different contents of Pt and SnO₂ were prepared by the modified Bönemann method. TEM images of the Pt/SnO₂(3 : 1)/CB catalyst showed not only Pt nanoparticles but also SnO₂ nanopar-

ticles, and their average size and standard deviation were 3.1 ± 0.5 nm and 2.5 ± 0.3 nm, respectively. The average size and standard deviation of the Pt and SnO₂ nanoparticles for the Pt/SnO₂(1 : 1)/CB and Pt/SnO₂(1 : 3)/CB were 3.0 ± 0.5 nm and 2.6 ± 0.3 nm, 2.8 ± 0.5 nm and 2.5 ± 0.3 nm, respectively. Pt4f and Sn3d core level spectra of all Pt/SnO₂/CB catalysts showed that they were composed of Pt⁰ and SnO₂. The Pt/Sn ratio for each catalyst was quite close to that for Pt and Sn precursors. The onset potential of EOR for the Pt/SnO₂(3 : 1)/CB electrode in an Ar-saturated 0.5 M H₂SO₄ containing 1 M C₂H₅OH solution is about 0.25 V less positive than that for the Pt/CB electrode and the SAs at 0.4 and 0.6 V for the former were *ca.* 25 and 4 times higher than those for the latter, respectively, indicating the significant improvement of the activity of EOR due to the synergistic effect of Pt and SnO₂.

Acknowledgement

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan through a Grant-in-Aid for Young Scientists (B) (No. 19750170).

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