Radiochemical synthesis of a carbon-supported Pt-SnO₂ bicomponent nanostructure exhibiting enhanced catalysis of ethanol oxidation

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Abstract

Carbon-supported Pt-SnO₂ electrocatalysts with various Sn/Pt molar ratios were prepared by an electron beam irradiation method. These catalysts were composed of metallic Pt particles approximately 5 nm in diameter together with low crystalline SnO₂. The contact between the Pt and SnO₂ in these materials varied with the amount of dissolved oxygen in the precursor solutions and it was determined that intimate contact between the Pt and SnO₂ significantly enhanced the catalytic activity of these materials during the ethanol oxidation reaction. The mechanism by which the contact varies is discussed based on the radiochemical reduction process.

Keywords

Electron beam irradiation; Pt; SnO₂; Nanoparticle; Direct ethanol fuel cell

1. Introduction

Bicomponent nanoparticle materials containing two phases, such as a metal and a ceramic, have attracted significant attention from materials scientists due to their interesting and potentially important properties. Through the appropriate choice of the constituent phases and the morphology of the primary catalyst and its promoter, the catalytic activities of these materials may be significantly enhanced. Jiang *et al.* have reported that a structure composed of Pt and Sn showed enhanced catalysis of the ethanol oxidation reaction (EOR) occurring at the electrode of a direct ethanol fuel cell (DEFC) (Jiang *et al.*, 2004, Jiang *et al.*, 2005, Zhou *et al.*, 2003). They attributed this increased catalytic activity to the contact between a SnO₂ phase and the Pt metal, which was partially alloyed with Sn. Li *et al.* (2010) reported a catalyst composed of PtRh-SnO₂ that also showed enhanced EOR activity. These improvements are believed to be associated with multi-valence states of the non-noble metal generated through the bicomponent contact. In these prior reports, the optimum composition of such materials is discussed, but the degree of contact obtained between the Pt and the SnO₂ is not made clear. It is important to both understand and control the extent of contact between the two components, although it is not an easy task to prepare samples with controlled bicomponent contact. Therefore, it is necessary to employ various methods of synthesis under a number of different conditions to assess the best means of producing appropriate samples.

In this work, we report the radiochemical synthesis of carbon-supported Pt-SnO₂ and its enhanced electrocatalytic activity in the EOR. The radiochemical

synthesis of bimetallic alloy and core-shell nanoparticles has been reported by Belloni (2006). However, there have been only a few reports on radiochemical synthesis of nanoparticles containing different phases. We have previously succeeded in synthesizing bicomponent nanoparticles immobilized on supports, such as Pt-Cu alloy and CuO in close contact with one another supported on γ -Fe₂O₃ (Kugai et al., 2011, Yamamoto et al., 2010). We have also reported the application of this radiochemical method to the synthesis of Pt-SnO₂ nanoparticles (Okazaki et al., 2014). In the present study, we attempted to control the extent of contact between the Pt and SnO₂ phases by changing the dissolved gas in the precursor solution. The resulting degrees of contact were analyzed by scanning transmission electron microscopy (STEM) images and the synthetic process is discussed from a radiochemical point of view.

2. Experimental

2.1. Material Synthesis

The procedure and mechanism associated with the electron beam irradiation method are described only briefly here, since the details have been previously reported (Seino et al., 2008). A 66.6 mg quantity of carbon powder (Vulcan XC-72R, Cabot) was dispersed in an aqueous solution containing the metal precursors H₂PtCl₆·6H₂O (Wako) and SnCl₄·5H₂O (Wako). Five different precursor mixtures, each 50 mL in volume, were prepared by varying the Sn concentration so as to produce Sn/Pt molar ratios from 0 to 4, keeping the Pt concentration constant at 0.5 mM. The resulting products are designated herein as “Pt1Sn_x,” where *x* is the molar ratio. The total metal concentration in each reaction mixture, Pt+Sn, ranged from 6.82 to 20.1 wt.%. In addition, 1 vol.% 2-propanol (Wako) was added to scavenge oxidative hydroxyl radicals formed during the irradiation. Dissolved air was removed from some reactant mixtures by purging with Ar gas for 10 minutes. Samples produced in a reaction mixture in which air remained dissolved are herein designated by appending “_air” to the sample name, while samples produced with Ar purging are designed with “_Ar.” In each case, the reaction solution was well mixed and sealed in a 100 mL glass vial. As noted, each sample was denoted in accordance with its preparation conditions, and the samples are summarized in Table 1. Each vial was irradiated with a 4.8 MeV electron beam for several seconds at room temperature to a surface dose of 20 kGy. The Gy is a unit identifying the energy absorbed by a given mass of substance and is equivalent to 1 J/g. The irradiated samples were subsequently washed with pure water and dried at 60 °C overnight to obtain samples in powder form.

2.2. Evaluation of Materials and Catalytic Properties

The chemical compositions of the product powders were analyzed by inductively couple plasma atomic emission spectroscopy (ICP-AES, Shimadzu, ICPE-9000) and their microstructures were examined via TEM (Hitachi, H-8100, 200 kV). The nanoscale distributions of Sn and Pt in the samples were investigated by spherical aberration corrected STEM instrumentation (FEI, Titan³ G2 60-300) equipped with units allowing energy dispersive X-ray (EDX) spectroscopy and high angle annular dark field (HAADF) observations. Crystallographic analyses were performed by X-ray diffraction (XRD, Rigaku, RINT2100 Ultima) using Cu-K α radiation. The chemical states of the Pt and Sn in the catalysts were examined by assessing the X-ray absorption near edge structure (XANES) around the Pt *L*_{III}- and Sn *K*-edges at the BL14B2 beamline at SPring-8 (Hyogo, Japan) at room temperature. The Sn-*K* edges of the samples synthesized under dissolved air conditions were examined using the fluorescence method and all other edges were examined using the transparent method. The EOR activities were evaluated using the linear sweep voltammetry (LSV) technique in a three electrode-type beaker cell, employing a gold wire with a 0.5 mm diameter as the counter electrode and an Ag/AgCl electrode (BAS, RE-1B) as the reference electrode. Each sample was sandwiched between two carbon papers (Chemix, TGP-H-060), which served as the working electrode. Potential-current curves were obtained with an electrochemical analyzer (BAS, ALS630B) by sweeping the potential from 0.1 to 0.7 V *ver.* a reversible hydrogen electrode (RHE) at a rate of 5 mV/sec. The LSV was performed in a solution containing 1.5 M H₂SO₄ and 20 vol.% C₂H₅OH under a nitrogen atmosphere, maintaining the temperature at 35 °C using a heated magnetic stir plate.

3. Results and discussion

3.1. Structural Characterization

The chemical analyses indicated that, in each case, almost all of the Pt precursor material had been reduced and was contained in the powdered product, although a significant portion of the initial Sn was not found. In addition, the supernatants after the irradiation included significant amounts of Sn ions. Table 1 shows

the Sn/Pt molar ratios in the catalyst powders. The Sn/Pt molar ratios in the products were less than those applied when initially charging the reaction vessels, which reflects the fact that Sn is a base metal and not easily reduced.

Table 1 Sn/Pt ratios in precursors and products, average particle sizes, and standard deviations of particle sizes of catalyst specimens.

Sample ID	Sn/Pt molar ratio		Average particle size (nm)	Standard deviation (nm)
	Precursor	Product		
Pt_air	--	--	4.0	1.0
Pt1Sn1_air	1	0.13	4.6	2.4
Pt1Sn2_air	2	0.18	5.0	2.2
Pt1Sn3_air	3	0.49	5.6	2.4
Pt1Sn4_air	4	0.67	4.6	1.6
Pt_Ar	--	--	3.1	1.1
Pt1Sn1_Ar	1	0.19	4.0	1.5
Pt1Sn2_Ar	2	0.62	4.0	1.4
Pt1Sn3_Ar	3	0.99	4.5	1.6
Pt1Sn4_Ar	4	1.3	4.2	1.6

The XRD patterns of the samples are shown in Figs. 1(a) and (b) and exhibit two broad peaks at $2\theta = 39.8^\circ$ and 46.2° that are associated with the fcc (111) and (200) planes of Pt metal, respectively. These peaks did not shift when significant quantities of Sn were added, indicating that no alloying occurred between the Pt and Sn. Another two peaks are evident at $2\theta = 33.9^\circ$ and 51.8° , and these are consistent with the peak positions of the (101) and (211) planes of SnO_2 . These peaks increased in intensity with higher Sn concentrations, demonstrating that SnO_2 was generated. Figures 2(a) and (b) show typical Pt- L_{III} and Sn- K edge XANES spectra obtained for the Pt1Sn4_air and Pt1Sn4_Ar samples, along with the spectra of reference materials for comparison purposes. All the other samples exhibited quite similar spectra. The Sn- K spectra are in good agreement with the reference SnO_2 spectrum, which is in accordance with the above XRD results. In contrast, the Pt- L_{III} spectra were intermediate between those of Pt and PtO_2 , and appear to represent a linear combination of approximately 80% Pt and 20% PtO_2 based on the respective reference spectra. This is characteristic of Pt metallic nanoparticles with an oxidized surface layer, and is similar to the results reported by Tanaka *et al.* (1999). Thus no significant Pt-Sn direct bonding occurred in the present samples.

Fig. 1 X-ray diffraction patterns of catalyst samples with various Sn/Pt ratios: (a) air exposed samples and (b) samples with Ar gas purge.

Fig. 2 (a) Pt-L_{III} and (b) Sn-K XANES spectra of catalyst samples and various reference materials.

Figure 3(a) presents a typical TEM micrograph of the sample synthesized using solely Pt, designated as Pt_air, while Figs. 3(b) and (c) show micrographs of the Pt-SnO₂ samples Pt1Sn2_air and Pt1Sn2_Ar, respectively. It is evident that the 5 nm metal nanoparticles are both dispersed over and immobilized on the carbon support. Although the SnO₂ phase must be present, it is essentially invisible by TEM because of its low loading, as well as the low atomic weight of Sn and the poor crystallinity of the phase. Quite similar morphologies were observed with the other Sn-containing samples. The sizes of one hundred Pt particles were measured to obtain average particle sizes and the size distributions. The distributions for the Pt_air, Pt1Sn2_air, and Pt1Sn2_Ar samples are shown in Fig. 3(d), while the average sizes and the standard deviations of the samples are listed in Table 1.

Fig. 3 Typical TEM images of metallic nanoparticles on the carbon support and histograms of their particle sizes: (a) without Sn addition (Pt_air), (b) dissolved air sample (Pt1Sn2_air), (c) dissolved Ar sample (Pt1Sn2_Ar), and (d) histograms obtained from these images.

Figure 4 shows typical HAADF and elemental distribution maps obtained with EDX for the Pt1Sn1_air and Pt1Sn1_Ar samples. The micrographs clearly show that, in the case of the dissolved air sample (Pt1Sn1_air), an Sn-rich phase is surrounded by Pt

particles several nanometers in size. This kind of morphology, involving intimate contact on the 1 nm scale, would be very difficult to generate in processes in which the Pt metal and the SnO₂ are precipitated separately. The microstructures observed in these images are therefore characteristic of the materials synthesized by the present process. In contrast, the dissolved Ar sample (Pt1Sn1_Ar) exhibits only minimal instances of close contact between the Pt and the SnO₂, and these tend to exist as individual phases.

Fig. 4 Typical HAADF micrographs of (a) a dissolved air sample (Pt1Sn1_air), (b) its elemental distribution map, (c) a dissolved Ar sample (Pt1Sn1_Ar), and (d) its elemental distribution map. (Pt: red, Sn: green)

3.2. Enhanced Catalysis through Pt-SnO₂ Contact

As evident in Fig. 5, the catalytic activity was enhanced by Sn addition. Here the anode currents at 0.5 V vs. NHE, normalized to the Pt weight contained in the sample, are plotted against the Sn/Pt ratios in the catalyst powders. The enhancement obtained from the Sn was dependent on the Sn/Pt ratio and the samples also exhibit different trends depending on the dissolved gas. The highest current was obtained from the dissolved air samples at Sn/Pt = 0.13 (Pt1Sn1_air), while lower activities were evident at higher Sn/Pt ratios. In contrast, the samples that had been treated with an Ar purge showed higher activity levels at higher Sn/Pt ratios.

Fig. 5 Ethanol oxidation currents measured as the anode currents at 0.5 V, plotted against Sn/Pt ratios in the catalysts. Legend: (●) dissolved air catalysts, (■) dissolved Ar samples. The above current values were normalized to the mass of Pt contained in each sample.

As noted, in the case of the dissolved air samples, the Sn and Pt were present in respective SnO_2 and Pt metal phases and thus were not alloyed. As such, the EOR current was considerably enhanced by the coexistence of SnO_2 . It is worth comparing these results with those reported by Xin's group (Jiang et al., 2004, Jiang et al., 2005, Zhou et al., 2003) so as to better understand the enhancement provided by the Sn addition. They observed the formation of both a Pt-Sn alloy and SnO_2 on the carbon support, and also reported enhanced EOR catalysis. They postulated the importance of adequate lattice dilatation caused by the alloying and the coexistence of multi-valence Sn atoms around active sites in the Pt-containing alloy particles. In our samples, however, enhanced EOR catalysis was evident even though the Pt was not alloyed with the Sn. Our present results thus make it clear that alloying is not necessary for catalytic enhancement, and also show that catalysis is not suppressed by the small amount of alloying that inevitably occurs. Xin's group employed a polyol method using ethylene glycol at 130 °C or higher for several hours, which tends to favor alloying in comparison with our method, that proceeds at room temperature only for several seconds.

The decrease in activity seen at higher Sn/Pt ratios in the dissolved air samples may be explained as the result of coverage of metallic Pt particles by an excess of the SnO_2 phase. Since the active sites were presumably associated with the three phase interface consisting of the electrolyte, the Pt metal, and the SnO_2 , there should be

adequate coverage at Sn/Pt = 0.13 (Pt1Sn1). A ratio of 0.13 is remarkably small compared to the optimum ratio of about Sn/Pt = 1 reported by Li *et al.* (2010). This can be attributed to the nature of the present radiolytic method, in which SnO₂ is formed in such a manner that it undergoes intimate contact with the Pt surfaces.

3.3. Radiolytic Formation Process of Pt-SnO₂ Nanoparticles

The results obtained thus far are in good agreement with previous literature reports with respect to the importance of the coexistence of SnO₂, and more specifically the contact between phases, to the catalysis enhancement. It should be pointed out here that our radiolytic method has the inherent ability to introduce such intimate contact between components of the catalyst. Belloni (2006) has already reported the reduction process of this radiochemical method, as shown below. In this mechanism, electron beam irradiation of a water solution causes the ionization and excitation of water molecules, thus generating active species (Belloni et al., 1998). When 2-propanol is added to the precursor solution, it scavenges both H· and OH· radicals to produce reducing radicals.

The primary reducing agents are the hydrated electrons, e_{aq}^- , which are strong enough to reduce Sn ions to the zero-valence state, even though Sn is considered a base metal. This is possible since the e_{aq}^- species generate a redox potential of -2.6 V, while the standard redox potential of Sn is -0.14 V (CRC, 2010). Pt ions are also reduced by radicals originating from the alcohol, leading to lower Sn/Pt ratios in the catalyst powders than in the original precursor solutions, as shown in Table 1.

In this paper, we took the approach of changing the dissolved gas in the precursor solution in an attempt to control the resulting nanostructure. It has been reported that hydrated electrons (Woods and Pikaev, 1993) are scavenged in the presence of oxygen, as shown in the reaction equation below. Thus, in the case of the dissolved air samples, the hydrated electrons were scavenged and fewer reducing agents were available to react with the Sn ions, which led to smaller Sn/Pt ratios compared to the dissolved Ar samples.

The Sn^0 atoms generated in the equation shown above are in a nascent state and are unstable and thus very likely to be oxidized back to ions and/or the oxide state in the dissolved air samples. In contrast, the nascent Pt atoms are not as susceptible to oxidation and thus combine in a stepwise manner to form particles. When Sn clusters encounter these nascent Pt atoms, it is reasonable to expect that some quantity of the Sn^0 atoms reduce Pt^{4+} , and are oxidized in the process, according to the order of the redox potentials, as in the reaction equation below. This redox reaction forms structures in which Pt particles are surrounded by SnO_2 , as seen in Fig. 3(b).

In contrast, in the case of the samples synthesized applying an Ar gas purge, the Pt^{4+} ions were reduced by both hydrated electrons and other radicals. A greater number of the Pt atoms were thus present in a more mature state and were unlikely to undergo redox reactions with Sn^0 . This variation in the reduction pathways explains some of the nanostructure differences observed when changing the dissolved gas. The differences in the standard deviations and the size distributions shown in Fig. 2 and Table 1 are also explained by considering the uniformity of the reaction field. Typically, a more uniform reaction field generates smaller particles and a narrower size distribution when synthesizing nanoparticles. In the present synthesis method, the particle size uniformity increased when an Ar gas purge was applied since fewer substitution reactions occurred

and the majority of the ions were reduced by either hydrated electrons or radicals originating from the alcohol. Following irradiation, the Sn atoms would have been readily oxidized to form SnO₂ by reacting with dissolved O₂, since the oxygen potential of SnO₂ is low (Samsonov, 1982). The observed differences between the samples as a result of changing the dissolved gas are thus explained by variations in the amount of hydrated electrons reacting with the precursors.

4. Conclusion

By employing electron beam irradiation we were able to synthesize Pt-SnO₂/C electrocatalysts. The nanostructures of these catalysts were found to differ depending on the dissolved gas in the original reactant solution. In the case of the dissolved air samples, SnO₂ was surrounded by Pt particles approximately 5 nm in size and thus intimate contact on the nanoscale was achieved. Conversely, Ar purged samples consisted of individual Pt and SnO₂ particles. Ethanol oxidation catalysis was assessed using these samples and was found to be enhanced by the coexistence of SnO₂ in the materials. The EOR activity of the dissolved air samples was maximized with a composition in which the molar Sn/Pt ratio was 0.13, a value far smaller than the previously reported optimal ratio. It was concluded that contact between nascent Pt atoms and Sn⁰ clusters formed this unique structure. This report suggests that the concentration of dissolved oxygen in the precursor solution is the key factor controlling the nanoparticle structure during radiochemical synthesis.

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