Influence of Supporting Materials on Catalytic Activities of Gold Nanoparticles as CO-Tolerant Catalysts in DMFC

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Gold nanoparticles supported on Pt-Sn/C and Pt/C (nano-Au/Pt-Sn/C and nano-Au/Pt/C, respectively) were prepared by the gas-phase grafting method and their catalytic activities for methanol oxidation were evaluated by steady-state polarization measurement. X-ray diffraction measurement revealed that gold nanoparticles had a diameter of *ca.* 4 nm, and X-ray photoelectron spectroscopy revealed that gold nanoparticles deposited on Pt-Sn/C and Pt/C were in the zero-oxidation state. Electrochemical measurements performed in an aqueous solution of 1 M (M = mol dm⁻³) HClO₄ and 1 M CH₃OH demonstrated that the addition of gold nanoparticles to Pt-Sn/C catalyst gave higher catalytic activities for methanol oxidation than Pt-Sn/C catalyst without gold nanoparticles. In contrast, nano-Au/Pt/C and Pt/C showed almost identical catalytic activities. These results showed that the catalytic activities of gold nanoparticles were influenced by the supporting materials.

Key Words : Gold Nanoparticles, Pt-Sn Alloy, DMFC, CO-tolerance

1 Introduction

The urgent need to identify new materials for polymer electrolyte fuel cells (PEFCs) to reduce their cost has led to recent investigations of electrocatalysts for the anode and cathode. Over the past few decades, numerous studies have been conducted on the development of electrocatalysts for the anode in PEFCs and direct methanol fuel cells (DMFCs). Pt-Ru/C is often used as a benchmark catalyst for the anode.¹⁾ Although there have been many studies to enhance catalytic activities, further improvement of catalytic activity at the anode is still an important issue. One of the main problems concerning anode catalysts is so-called CO-poisoning, which involves strongly adsorbed carbon monoxide on Pt in the catalyst.²⁾ In PEFCs, CO, which is inevitably contained in the reformed H₂ fuel gas, occupies the active sites of Pt in the anode catalyst and deactivates its catalytic activities. CO-poisoning is also a serious problem in DMFCs, since CO is produced as an intermediate through methanol oxidation.

In the early 1980s, Haruta and his co-workers prepared gold nanoparticles supported on transition-metal oxides and found that gold nanoparticles exhibited remarkable catalytic activities toward CO oxidation.³⁾ Although gold was thought to be inert, gold nanoparticles exhibit attractive activities for CO oxidation, with high selectivity and high conversion to CO₂ in a gas-phase reaction even at temperatures below 273 K. The high catalytic activities of gold nanoparticles for CO oxidation motivated us to investigate the nature of gold nanoparticles in aqueous solution.

In our previous studies, we reported that gold

nanoparticles accompanied by Pt and transition-metal oxides improved CO-tolerance during methanol oxidation in both acid and alkaline solutions.⁴⁾ However, very little information is currently available on the behavior of gold nanoparticles in aqueous solutions, which could help us to understand the catalytic mechanism of gold nanoparticles systematically. In particular, the influence of supporting materials on the catalytic activities of gold nanoparticles requires additional study. The aim of the present work was to evaluate the electro-catalytic activities of Pt-Sn/C with gold nanoparticles in acidic solution, and the effect of the supporting materials on these catalytic activities is discussed.

2 Experimental

Gold nanoparticles supported on Pt-Sn/C and Pt/C (nano-Au/Pt-Sn/C and nano-Au/Pt/C, respectively) were prepared by the gas-phase grafting method as described in the literature.^{4,5)} (CH₃)₂Au(CH₃COCHCOCH₃) (Me₂Au(acac), Tri Chemical Laboratory) was used as a gold precursor, which was vaporized and adsorbed onto the settled catalysts in a vacuum chamber. Deposition was conducted for 2 h, followed by calcination in an (Ar+H₂) atmosphere. Pt/C (E-TEK, 40 wt% Pt) and Pt-Sn/C (E-TEK, 40 wt% Pt-Sn) were used for supporting materials. The resulting catalysts were characterized by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI Model 5500) and X-ray diffraction (XRD, Rigaku RINT2500). The amount of gold nanoparticles in the catalyst was measured by atomic adsorption spectroscopy (Hitachi A-1000).

To evaluate the catalytic activities of the prepared cat-

alysts and as-received catalysts, steady-state polarization was performed using a conventional three-electrode cell, which consisted of Pt wire and a reversible hydrogen electrode as counter and reference electrodes, respectively. To prepare working electrodes, a suspension of catalysts in ultra-pure water was pipetted onto the glassy carbon electrode in a manner similar to that reported by Schmidt *et al.*⁶⁾ An electrolyte of 1 M ($M = \text{mol dm}^{-3}$) HClO_4 and 1 M CH_3OH was used.

3 Results and Discussion

XPS spectra of Pt/C before and after the deposition of gold are shown in Figs. 1(a) (Au 4f) and 1(b) (Pt 4f). After gas-phase grafting, Au was deposited on Pt/C, and its valence was in an almost zero-oxidation state. This indicates that the gold complex was almost completely decomposed by calcination. Similar spectra for Pt 4f peaks of both nano-Au/Pt/C and Pt/C were observed, indicating that the addition of gold did not change the oxidation state of Pt. Figure 2 shows the results of XPS measurement for nano-Au/Pt-Sn/C and Pt-Sn/C. Au was also deposited on Pt-Sn/C in metallic form as with nano-Au/Pt/C. Notably, the peaks of Sn 3d were shifted more positively by *ca.* 2 eV relative to the position corresponding to the binding energy of Sn metal. Within the escape depth of electrons for XPS measurement, Sn was oxidized on the surface of Pt-Sn/C catalysts. The existence of Sn oxide caused by exposure to air has been reported

in the literature.^{7,8)} The metal complex used as a gold precursor was reported to be adsorbed on oxygen species of the supporting materials by hydrogen bonding.⁹⁾ In the case of Pt/C, the gold complex was probably deposited on the functional groups on carbon. On the other hand, Pt-Sn/C has Sn oxide on its surface, and therefore the gold complex can also be deposited on Sn oxide.

Figures 3 and 4 show the XRD patterns of the Pt-Sn/C and Pt/C catalysts before and after gas-phase grafting.

Fig. 1 (a) Au 4f, (b) Pt 4f photoelectron spectra of Pt/C and nano-Au/Pt/C.

Fig. 2 (a) Au 4f, (b) Pt 4f, (c) Sn 3d photoelectron spectra of Pt-Sn/C and Au/Pt-Sn/C.

After the deposition of gold nanoparticles, Pt-Sn/C showed almost the same XRD pattern as Pt₃Sn (JCPDS 35-1360). The strongest peak was seen at around $2\theta = 39^\circ$, corresponding to Pt₃Sn(111). A closer look enabled us to deconvolute the peak into two different peaks at 38.3 and 38.9° for Au(111) and Pt₃Sn(111), respectively. Based on the full width at half-maximum (FWHM) of the deconvoluted peak for Au(111), the crystalline size of gold was about 4 nm using the Scherrer equation, which was almost the same value as that of gold nanoparticles supported on molybdenum oxide in our previous report.⁴⁾ In a similar manner, the crystalline size of gold was about 4 nm for nano-Au/Pt/C. The amount of gold nanoparticles determined by atomic adsorption spectroscopy was 2.5 and 3.3 wt% for nano-Au/Pt/C and nano-Au/Pt-Sn/C, respectively.

The catalytic activities for methanol oxidation were

Fig. 3 X-ray diffraction pattern of Au deposited on Pt-Sn/C. Inset : Deconvoluted patterns for Au(111) and Pt₃Sn(111).

Fig. 4 X-ray diffraction pattern of Au deposited on Pt/C. Inset : Deconvoluted patterns for Au(111) and Pt(111).

evaluated by steady-state polarizations. After the beginning of polarization at a certain potential, oxidation currents decreased gradually and showed an almost steady value at 1000 s. Therefore, the currents at 1000 s were regarded as the steady-state values for methanol oxidation. The current densities of Pt/C and nano-Au/Pt/C were almost identical at all potentials, as shown in Fig. 5. Oxidative current was obtained at potentials exceeding 450 mV for both Pt/C and nano-Au/Pt/C. Steady-state polarization curves of Pt-Sn/C and nano-Au/Pt-Sn/C are shown in Fig. 6. At potentials greater than 550 mV, Pt-

Fig. 5 Steady state polarization curves for methanol electro-oxidation on (a) Pt/C (broken line) and (b) Au nanoparticles deposited on Pt/C (solid line) in 1 M HClO₄ + 1 M methanol at 303 K. Time : 1000 s.

Fig. 6 Steady state polarization curves for methanol electro-oxidation on (a) Pt-Sn/C (broken line) and (b) Au nanoparticles deposited on Pt-Sn/C (solid line) in 1 M HClO₄ + 1 M methanol at 303 K. Time : 1000 s.

Sn/C and nano-Au/Pt-Sn/C showed almost the same current densities. However, the difference in the current densities of Pt-Sn/C and nano-Au/Pt-Sn/C increased as the electrode potential decreased. The fact that Pt-Sn/C and nano-Au/Pt-Sn/C had the same current densities at more than 550 mV, at which the catalysts were thought to be free from CO poisoning, indicated that the number of catalytic sites for methanol oxidation should be the same for both catalysts. Compared to Pt-Sn/C, nano-Au/Pt-Sn/C was more active for methanol oxidation at potentials below 500 mV. Since CO poisoning becomes dominant at lower potentials, gold nanoparticles improved the resistance toward CO poisoning in Pt-Sn/C electrocatalyst, resulting in the activation of methanol oxidation.

The suppression of CO poisoning by Pt-Sn alloy catalyst has been reported previously.^{10,11)} In this catalyst, atomic oxygen or -OH bound to the surface of Sn is thought to promote the oxidation of CO adsorbed on Pt sites. This mechanism is called the Langmuir-Hinshelwood mechanism.^{10,11)} This mechanism is also applicable to the case of Ru in Pt-Ru alloy. While the addition of Ru promotes CO oxidation and methanol oxidation in Pt-Ru catalyst, the addition of Sn showed little or no enhancement of methanol oxidation,^{10,12)} principally due to the suppression of methanol dissociation on Pt. In our results, the addition of gold nanoparticles enhanced the electrocatalytic activity of Pt-Sn/C for methanol oxidation. Therefore, gold nanoparticles improved catalytic activities for methanol oxidation without retarding methanol dissociation on Pt. Moreover, by comparing the activities of nano-Au/Pt/C and nano-Au/Pt-Sn/C for methanol oxidation, gold nanoparticles required a secondary element (such as Sn) in addition to Pt to enhance the resistance to CO poisoning. To oxidize CO to CO₂, some oxygen species must be present in the catalyst. In the case of nano-Au/Pt/C, the oxygen species exist on the surface of carbon. However, the oxygen species on carbon are not enough to continue oxidizing CO formed as an intermediate through methanol oxidation. Therefore, the secondary element should serve as an oxygen supplier. As mentioned above, Sn is such a preferable element for dissociating water that the oxygen species of -OH is easily formed on Sn, leading to the conclusion that Pt-Sn alloy is suitable as a supporting material for gold nanoparticles. The importance of secondary elements revealed in this study is in good agreement with our previous reports (Au/Pt/MoO_x/C,⁴⁾ Au/Pt-Ru/C,⁵⁾ Pt/Au/ α -Fe₂O₃/C¹³⁾). For catalysts containing nano-Au, the interaction between gold nanoparticles and supporting metal oxides appears to play a key role in the catalytic activities of gold nanoparticles.

4 Conclusion

Nano-Au/Pt-Sn/C and nano-Au/Pt/C were prepared by a gas-phase grafting method and their catalytic activi-

ties for methanol oxidation were estimated by steady-state polarization measurement. The results of XRD and XPS revealed that gold nanoparticles were deposited with a diameter of *ca.* 4 nm and with a zero-oxidation state. Electrochemical measurements were performed in an aqueous solution of 1 M HClO₄ and 1 M CH₃OH and demonstrated that the addition of gold nanoparticles to Pt-Sn/C catalyst gave higher catalytic activities for methanol oxidation compared with Pt-Sn/C alone. In contrast, nano-Au/Pt/C and Pt/C showed almost identical catalytic activities regardless of the addition of gold nanoparticles. The results showed that the catalytic activities of gold nanoparticles depended on the existence of a supporting material, which has the potential to provide oxygen species for gold nanoparticles.

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