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Sonochemical Synthesis of Non-platinum Nanoparticles and Their Electrocatalytic Activity for Oxygen Reduction

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Received January 10, 2009 ; Accepted April 6, 2009

Non-platinum nanoparticles (Pd, Au, PdAu) have been prepared by sonochemical synthesis. The nanoparticle-modified electrodes showed improved catalytic activity for oxygen reduction compared with Pt nanoparticles in alkaline solution even in the presence of methanol.

Key Words : Sonochemistry, Nanoparticle, Non-Pt Catalyst, Oxygen Reduction Reaction

1 Introduction

Pt is widely used as the electrocatalyst for oxygen reduction reaction (ORR) in fuel cell due to its high electrocatalytic activity, while the high cost of Pt and its instability in cathode catalysts pose serious issues. When binary catalysts, replaced of some Pt with less expensive metal,¹⁾ the cost is still rather prohibitive for full exploitation of fuel cell. Therefore, the development of Pt-free electrocatalysts for oxygen reduction will be one of the key engines for widespread commercialization of fuel cells. Many studies for Pt-free catalysts have been performed such as inorganic and organometallic complexes,²⁾ transition metal oxide,³⁾ chalcogenides,⁴⁾ non-Pt binary metal,⁵⁾ and so on. Although, several non-Pt metallic combination electrocatalysts have been investigated for ORR, but their activities were inferior to those of Pt. In addition, Pt catalyst has a problem of fuel tolerance comes from the fuel crossover.

On the other hand, sonochemical synthesis is an interesting method to develop metallic nanoparticles (NPs).^{6,7)} Sonochemically prepared NPs were reported to have features of narrow distribution in particle size and variation of bimetallic structures. These features are comes from its unique preparation condition of low temperature in the solution without annealing. Only few works have been reported on the alloy catalysts for fuel cells prepared by sonochemistry. PtRu NPs has been reported as potential candidate for fuel cell catalyst by Grieser *et al.*⁸⁾

Herein, preparation of Pd-based NPs (PdAu, PdCo) by ultrasound irradiation to aqueous solution containing each metal salt and citric acid was reported and the ORR activity of the resulting NPs was evaluated.

2 Experimental

(NH₄)₂PdCl₄, NaAuCl₄·2H₂O, H₂PtCl₆·6H₂O, CoSO₄·7H₂O, and citric acid were purchased from Aldrich and Wako, respectively. 3-aminopropyltriethoxysilane (APS)

and ITO (indium-tin oxide; surface resistance 10 Ω/cm²) electrode were purchased from Kanto. Water used throughout the experiments was purified by a Milli Q system (Millipore). All the chemicals were analytical grade and used without further purification.

The citrate stabilized Pd, Pt, Au, PdAu, and PdCo-NPs are prepared with ultrasonic irradiation using below solution. A solution containing 0.2 mM (NH₄)₂PdCl₄, 10 mM citric acid, 10 vol% ethanol and either 0.2 mM CoSO₄·7H₂O or 0.2 mM NaAuCl₄·2H₂O was used as the initial solution for sonication. Temperature of the solution was kept constant at 278 ± 0.5 K in a cooling bath. Ultrasonic irradiation was performed with a collimated 20 kHz beam from a ceramic transducer with a titanium amplifying horn (13 mmΦ, Branson Sonifier 450D) directly immersed in the solution and operated with an input power of 42 W cm⁻², unless otherwise stated. The horn was vertically positioned 5.0 cm above the cell bottom.

Transmission electron microscopy (TEM) images were recorded operating at 200 kV. Samples were prepared by placing a drop of the each nanoparticles dispersing solution onto a carbon-coated grid followed by drying. The electronic state of the prepared NPs were characterized by XPS. With the integration of photoelectron intensity for each atom, the composition was estimated.

The NPs immobilized electrodes were prepared using self-assembly of APS primer monolayer onto ITO electrodes. Nanoparticles s were immobilized The ITO electrodes are washed with ethanol and distilled water for 30 min with ultrasonic bath and then transferred in 1 M KOH solution for 30 min to clean the surface and make the OH terminated surface and rinsed with distilled water, followed by drying. After cleaning, a self-assembled- monolayer of APS was formed on ITO by immersion in dehydrated toluene containing 2.5 wt% of APS at room temperature for 6 hour. Subsequently, the ITO was washed in methanol solution and then dried at 100 °C for

10 min. Finally, the APS modified ITO electrode was performed by immersion in 30 mL of citrate stabilized NPs solution for 24 hour. The value of current in electrochemical characterization was shown as the one in the current density form calculated with the electrode area of ITO substrate. Onset potential for ORR was determined as the potential at which the reduction current density leached to $-50 \mu\text{A cm}^{-2}$.

3 Results and Discussion

The formation of spherical NPs was observed as shown in Fig. 1. In the synthesizing solution, under the ultrasonic irradiation, hydrogen radicals and hydroxyl radicals are generated. Some amount of hydroxyl radicals react with ethanol to generate organic radicals. These radicals reduce the metal ions into metal nanoparticles, whose surface is stabilized by the existing citrate adsorption maintaining nano-size particles.⁹⁾ The particles sizes of Pd-NPs and PdAu-NPs were 4~6 and 5~7 nm, respectively. The Au-NPs are identical in size (5-10 nm). Also, the PdCo-NPs having an average particle size of 30 nm with size distribution of 25~40 nm were observed.

XPS spectra are shown in Fig. 2. The metallic state of

Fig. 1 TEM images of (a) Pd, (b) Au, (c) PdAu, and (d) PdCo nanoparticles prepared with ultrasonic irradiation (20 kHz, 42 W cm^{-2} , 2 h).

Fig. 2 XPS spectra of Pd $3d_{5/2}$ level for the surface of Pd, PdAu, and PdCo nanoparticles immobilized APS monolayer on ITO.

Pd 3d region is characterized by $3d_{5/2}$ (335.2 eV) and $3d_{3/2}$ (340.5 eV).¹⁰⁾ The Pd and PdCo-NPs exhibited the binding energy of 335.2 eV for the Pd $3d_{5/2}$ peak. It indicated that Pd is mostly in the metallic state because this value is lower than that of Pd oxide (PdO, 336.6 eV).¹⁰⁾ On the other hand, Pd $3d_{5/2}$ peak of the PdAu-NPs shifts from 335.2 to 334.9 eV (*ca.* -0.28 eV). The slight shift to lower binding energy values compared with those of Pd metal can be assigned to interaction between Pd and Au. The Au $4f_{7/2}$ peak of the PdAu-NPs exhibited the binding energy at 83.1 eV which shift to lower binding energy compared with pure Au metal (84.0 eV). The Au 4f region of the PdAu-NPs indicates the formation of PdAu alloy. The atomic ratio of Pd/Au and Pd/Co was 85/15 and 95/5, respectively.

The activities of Pd, Au, PdAu, and PdCo-NPs for oxygen reduction in alkaline solution were evaluated with the NPs immobilized ITO electrode prepared with the procedure reported in literature.¹¹⁾ From atomic force microscopy (Fig. 3), we found that assembled nanoparticles was not layered, but rather an alternating pile-up of these metal nanoparticles. Thus, electrostatic and covalent interactions could be the driving forces for the formation of 3-D superstructure of these nanoparticles on ITO electrode. The ITO and APS/ITO electrodes were confirmed to have no activity for oxygen reduction in alkaline media. As shown in Fig. 4A, the Pd-NPs and PdCo-NPs electrodes show catalytic activity towards oxygen reduction at higher overpotential and onset potential is -84 mV and -98 mV vs. Ag/AgCl, respectively. In the case of PdAu-NPs, the onset potential is shifted to more positive potential (53 mV vs. Ag/AgCl). It is clear that the PdAu-NPs electrocatalysts have high performance for oxygen reduction comparing with that

Fig. 3 A typical AFM image of PdAu-NPs immobilized on ITO. The image was taken for $1 \mu\text{m} \times 1 \mu\text{m}$ area.

Fig. 4 Linear sweep curves of oxygen reduction on Pd, Au, Pt, PdAu, and PdCo nanoparticles immobilized on ITO in O_2 saturated 0.5 M KOH solution in the absence A) and the presence B) of 2 M CH_3OH at 25°C ; scan rate: 100 mV s^{-1} .

of Pt-NPs catalysts (Fig. 4A). Pd-Au NPs which form alloy of Pd and Au shows the better ORR activity than that of Pd NPs. On the other hand, Pd-Co NPs which the PdCo alloy formation was not detected in XPS result do not exhibit higher ORR activity than that of Pd NPs. From these results, PdCo NPs was judged to be consisting of Pd metal with some impurity of Co, and Pd Co alloy was not formed in this experiment. Ota *et al.*¹²⁾ reported that decrease of the density of states (DOS) by alloying inhibited the formation of Pd oxide and contribute to the improvement of the ORR activity. These indicate that the alloys effect of Pd and other metal is important factor to improve their ORR activity.

To evaluate the ORR activity in methanol containing electrolyte, the change in the ORR on sonochemically prepared Pd, Au, Pt, and PdAu-NPs in the presence of 2 M CH₃OH is shown in Fig. 4B. As compared to the ORR in pure KOH solution (Fig. 4A), all the catalysts for the ORR showed an increase in overpotential in the presence of CH₃OH. ORR activity of the prepared NPs decreases in the presence of methanol, because the oxygen molecules are in competition with methanol molecules for the adsorption sites on catalyst surface during the process of ORR.¹³⁾ The onset potential for oxygen reduction at Pt NPs catalyst shift cathodically by ca. 350 mV. This is due to the formation of a mixed potential on the surface of the Pt NPs catalysts. Such a mixed potential at the cathode should negatively affect the cathode performance of the DMFC. The onset potential for oxygen reduction at Au-NPs catalyst shift cathodically by ca. 200 mV. ORR activity of PdAu NPs largely decreases in the presence of methanol than that of Pd catalyst. Gold is known to have a weak coordination ability towards CO due to fully occupied d-orbitals.¹⁴⁾ The presence of methanol have effect on ORR activity of PdAu NPs because Pd surface released by oxidation of CO-like species on Au surface increase.

Although the onset potential of these NPs catalysts shift cathodically (less than 100 mV), the Pd and PdAu-NPs electrocatalysts showed superior ORR activities to the Pt-NPs in the presence of high methanol concentration (2 M). It is clear that the PdAu-NPs electrocatalyst has high performance for oxygen reduction comparing with that of Pt-NPs catalysts in the absence and presence of methanol. The results are interesting since the PdAu NPs electrocatalyst prepared by ultrasonic irradiation are totally Pt-free and the cost would be much less than that Pt-based electrocatalysts. Moreover, among them, PdAu has high inactivity toward methanol oxidation, which should positively affect the cathode performance of the DMFC.

4 Conclusion

Pd-based nanoparticles were prepared by ultrasonic irradiation and examined for the electroreduction of oxygen in alkaline media. PdAu-NPs immobilized on ITO electrode exhibited an enhanced oxygen reduction reac-

tion activity compared to Pt in the presence of methanol. The results revealed that both of them showed a synergic effect to improve the activity for oxygen reduction and reduced significantly the overpotential of oxygen reduction in alkaline media in the presence of methanol. The oxygen reduction reactivity increased in the following order in alkaline solution: Au < Pd, Pt < PdAu (without methanol), Pt < Au < Pd, PdAu (with methanol). The unique properties of the selectivity and immunity to methanol of the PdAu-NPs catalyst favour them for potential applications in anion exchange membrane hydrogen or alcohol fuel cells, and metal-air batteries.

Acknowledgement

This work was partly supported by Encouraging Development Strategic Research Centers Program "Establishment of Consolidated Research Institute for Advanced Science and Medical Care", 21st Century COE Program "Practical Nano-Chemistry", and the Grant-in-Aid for Specially Promoted Research "Establishment of Electrochemical Device Engineering" from MEXT, Japan.

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