Electrocatalytic Activity of Platinum Nanoparticles Synthesized by Room-Temperature Ionic Liquid–Sputtering Method

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Platinum (Pt) nanoparticles were synthesized with room-temperature ionic liquid (RTIL)–sputtering method under dry N₂ or Ar atmosphere. The resulting Pt nanoparticles were well-dispersed in trimethyl-1-propylammonium bis[(trifluoromethyl)sulfonyl]amide RTIL without any additive like dispersant. Electrocatalytic activity of the Pt nanoparticles embedded on a glassy carbon electrode (GCE) toward oxygen reduction reaction was examined. It was then found that the catalytic activity increases with increment of heat temperature for embedding the Pt nanoparticles onto GCE if the nanoparticles are synthesized under Ar atmosphere.

Key Words: Room-temperature Ionic Liquid, Sputtering, Nanoparticle, Catalyst

1 Introduction

Room-temperature ionic liquid (RTIL) that once considered to be a curious subset of the general class of substances called molten salts have been known to be facile solvents for preparing a variety of functional materials. Electrodeposition in RTIL has taken on an important role in material science.1) Within recent years, however, some non-electrochemical material syntheses2-3) have also been proposed. One of the successful techniques, RTIL-sputtering method,4-5) have opened up a new nanomaterial science area because produced nanoparticles uniformly disperse in RTIL without additive.

In this investigation, we have attempted to synthesize platinum (Pt) nanoparticle, which is well-known as a catalyst for exhaust purification systems and PEM fuel cells. The purpose of this study is to clarify the effects of inert gases, N₂ and Ar, existing during synthesis of Pt nanoparticles by the RTIL-sputtering method and to reveal their electrocatalytic activities toward oxygen reduction reaction (ORR) in aqueous solution.

2 Experimental

Ultrapure RTIL of trimethyl-1-propylammonium bis[(trifluoromethyl)sulfonyl]amide (Me₃PrN⁺TFN⁻) was specially prepared by Kanto Chemical Co., Inc., and was dried in vacuum prior to use. A soda glass plate (2.5 × 2.5 cm), on which Me₃PrN⁺TFN⁻ (0.4 mL) was spread, was set in a Cressington108 auto SE sputter coater. A Pt foil target (Ø5.7 cm, 99.98%) was placed on 4.5 cm above the glass plate. Sputter deposition onto RTIL was conducted with sputter current of 40 mA in dry N₂ (99.999%) or Ar (99.999%) atmosphere whose pressure did not exceed 7 ± 1 Pa. Sputtering was conducted for 300 sec at room temperature (298 ± 2 K). Size distribution of Pt nanoparticle was estimated by a Hitachi H-7650 transmission electron microscope (TEM) operated at 100 kV. Before the TEM observation, a sample grid was prepared by dropping the sputtered RTIL onto a TEM grid (φ3.0 mm, copper, 400 mesh) with amorphous carbon thin layer. Elemental analysis was performed with an EDAX Genesis-XM2 energy dispersive X-ray (EDX) spectrometer and a Rigaku ZSX100e X-ray fluorescence (XRF) spectrometer.

Electrocatalytic activities toward O₂ reduction were examined with an ALS Model 660A and a three-electrode cell. A Pt plate or mesh was used as the counter electrode that was immersed directly in 0.5 M H₂SO₄ aqueous solution. The Ag/AgCl electrode immersed in a KCl-saturated solution was employed as the reference electrode. Pt nanoparticle-embedded glassy carbon electrode (GCE) was prepared under atmospheric conditions by the following procedures; (i) heat treatment of the Pt-sputtered IL on a GCE at various temperatures, (ii) rinsing the GCE with dry acetonitrile, (iii) drying the electrode under vacuum for 30 minutes prior to use. The heat treatment was conducted with a Koyo Thermo Systems REX-C900. The Pt-embedded GCE that was employed as the working electrode was pretreated with multiple potential scans between −0.2 and +1.2 V before the oxygen reduction experiment.

3 Results and Discussion

Figure 1 shows TEM images of Pt nanoparticles prepared by the RTIL-sputtering method under N₂ or Ar
Electrochemistry

Fig. 1 TEM images of Pt nanoparticles synthesized by the RTIL-sputtering method under (a) N₂ and (b) Ar atmosphere. The sputtering time and current were 300 sec and 40 mA, respectively.

Fig. 2 Cyclic voltammograms taken in O₂-saturated 0.5 M H₂SO₄ for GCEs modified with Pt nanoparticle synthesized under (−) Ar and (→) N₂ atmosphere. The scan rates were 50 mV s⁻¹. The Pt-modified GCE was prepared by heating at 423 K for 30 min.

Fig. 3 Cyclic voltammograms taken at 10 mV s⁻¹ in O₂-saturated 0.5 M H₂SO₄ for GCEs modified with Pt nanoparticle synthesized under Ar atmosphere. The Pt-modified GCE was prepared by heating at 373 ~ 573 K for 30 min.

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \Leftrightarrow 2\text{H}_2\text{O} \]  

This reaction is the key to put almost all fuel cell systems to practical use. The electrocatalytic activity of the Pt nanoparticle-embedded GCE prepared in this study was investigated in 0.5 mol L⁻¹ H₂SO₄ aqueous solution. Figure 2 shows cyclic voltammograms taken at GCEs modified with Pt nanoparticles prepared under N₂ or Ar. These electrodes were prepared by heating at 423 K for 30 min to embed Pt nanoparticles. The reduction currents for ORR appear at potentials positive of ca. +0.80 V at the GCE modified with Ar-sputtered Pt nanoparticles, whereas large negative shift of the threshold potential (ca. +0.49 V) was observed in the case of N₂-sputtered Pt nanoparticles. In the latter case, the current densities are much smaller than the former case in all potential region. It is unlikely that such large difference in the electrocatalytic activities is due to difference in the Pt particle size. There seems to be any difference in the Pt surface conditions. One plausible cause is formation of platinum nitride during the sputtering process in N₂ although Pt surface is not yet characterized. Anyhow, the results shown in Fig. 2 indicated clearly that Pt nanoparticles synthesized in Ar are more favoring than those produced in N₂ for the ORR.

Cyclic voltammograms recorded at Pt nanoparticle-modified GCEs prepared at different heat temperatures are shown in Fig. 3. The Pt nanoparticles were synthesized in Ar. In this study, 573 K was chosen as the maximum heat temperature to prevent shape transformation, which is reported to happen at higher than 623 K.¹¹ and to avoid pyrolysis of the Me₃PrN⁺TlN⁻ RTIL. Neither obvious reduction currents due to ORR nor H₂ evolution are observed up to 373 K. But if the temperature is over 423 K, the current flow for ORR appears and eventually
it shows an apparent peak. In order to understand variation in the behavior, we observed the morphology of the GCEs used for the voltammetric experiments. Figures 4 (a) and (b) depict, respectively, a SEM and TEM image of the Pt nanoparticles after heat treatment at 573 K. SEM observation revealed that there are a great number of crystals, which were identified with EDX as pure Pt, on the GCE but they are not uniform deposits. TEM observation for a portion of a crystal part was conducted so as to know detailed morphology of the nanoparticles. Particle size analysis showed the resulting Pt nanoparticles have the mean particle size of 3.69 nm (SD: 0.610). It became slightly larger than the one measured before the heat treatment (see above). In reality, obvious variation in the particle size initiated at 423 K. As shown in Fig. 3, electrocatalytic ability of the Pt-modified GCE increased with an increment of the heat temperature, i.e., increase in the particles size. This anomalous behavior support published article that catalysis efficiency of Pt nanoparticle reaches the maximum at 4.0 nm in diameter.\textsuperscript{12} There is no doubt that heating process if the Pt-modified GCE is fabricated contributes to the improvement of catalytic activity to ORR.

4 Conclusion

Platinum nanoparticle was synthesized with the RTIL-sputtering method. The resulting Pt nanoparticles were ca. 2 ~ 3 nm in diameter and the particle size altered with gaseous species injected into the sputtering apparatus. Prepared Pt nanoparticles aggregated at heat temperature exceeding 423 K, above which the electrocatalytic activity toward ORR was enhanced. Thus, the heating process was an effective way to improve the catalytic ability of the Pt nanoparticle synthesized in this investigation.

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