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Electrocatalytic Activity for Oxygen Reduction Reaction of Pseudomorphic Pt Monolayer Prepared Electrochemically on a Au(111) Surface

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Electrocatalytic activity for oxygen reduction reaction (ORR) of pseudomorphic Pt monolayer prepared electrochemically on a Au(111) surface was investigated and compared with that of a single-crystal Pt(111) electrode.

Ultrathin metal layers deposited on foreign metal substrates have been expected to be attractive electrocatalytic materials not only in basic surface science but also in industrial applications, because of their unique physical and chemical properties, particularly their high electrocatalytic activities.[1–4] Such special catalytic activity is due to the surface atomic arrangements and their induced surface electronic energy.

Pt is the best catalyst for the oxygen reduction reaction (ORR) particularly used in polymer-electrolyte fuel cells (PEFC), which is expected to be an attractive energy-conversion device in the near future. However, the Pt resources are limited and Pt is also very expensive. Thus, reduction of the quantity of Pt used as a catalyst for PEFC has been paid much attention in developing PEFC and many studies such as Pt monolayers on other metals[4,5] and/or other metal-core–Pt-shell nanoparticles[6] have been reported in the last decade.

Adzic et al. investigated electrocatalytic activity for ORR of a Pt monolayer formed on various single-crystal metal surfaces, which were prepared by the galvanostatic replacement of underpotential deposited (UPD) Cu monolayer, and examined the relationship between the experimentally observed electrocatalytic activity and surface electric energy theoretically estimated by density functional theory (DFT) calculation.[4] However, their AFM observations[7] showed that the constructed Pt monolayers consisted of a monoatomic height island but the Pt atoms were not arranged in order, indicating that the atomic arrangement of Pt was not pseudomorphic on the single-crystal surfaces. On the other hand, DFT calculation was carried out based on the optimized structure of the Pt monolayer, which means that the atomic arrangement of Pt should be pseudomorphic, thus the value of the discussion based on the different structures is quite low.

Recently, we succeeded in electrochemically constructing a pseudomorphic Pt monolayer on a single-crystal Au(111) surface, and its atomic arrangement was precisely confirmed by resonance surface X-ray scattering (RSXS) measurements, which is one of the best methods to analyze interfacial structures with an atomic dimension.[8] In this paper, electrocatalytic activity for ORR of the electrochemically constructed pseudomorphic Pt monolayer on the Au(111) was investigated using a rotating ring disk electrode (RRDE) system, and the relationship between the electrocatalytic activity and calculated surface energy is discussed to obtain fundamental understanding of the origin of the ORR enhancement.

Single-crystal Au(111) and Pt(111) disks were purchased from MaTeck, and mechanically processed to connect the RRDE system. Ultrapure reagent grade H_2SO_4 and $HClO_4$ and reagent grade H_2PtCl_6 were purchased from Wako Pure Chemicals, Kanto Kagaku, and Sigma, respectively, and were used without further purification. Water was purified using a Milli-Q system (Yamato, WQ-500). Ultrapure N_2 (99.9995%), O_2 (99.99%), and mixed gas ($Ar:H_2 = 97:3$) were purchased from Kotobuki Sangyo.

Before using, the Au(111) disk was annealed using a Bunsen burner, cooled in a quartz vessel for a few minutes, and then quenched in ultrapure water.[8,9] Before using, the Pt(111) disk was annealed by using an induction heater (HOTSHOT-2 kW, Ameritherm) under mixed gas ($Ar:H_2 = 97:3$) atmosphere at 1600 °C for 1 h and quenched in ultrapure water.[10a] A Pt wire and Hg/Hg_2SO_4 (sat. Na_2SO_4) electrode were used as the counter and reference electrodes, respectively. The potential values were referred to a reversible hydrogen electrode (RHE). The electrode potential was controlled with a potentiostat (CompactStat, Ivium) and the rotation of the Pt ring single-crystal disk electrode was controlled by an RRDE system (AFMSRCE, Pine). Pseudomorphic Pt monolayer deposition on the Au(111) surface, which is abbreviated here as Pt/Au(111), was carried out in 0.1 M $HClO_4$ electrolyte solution containing 0.05 mM H_2PtCl_6 by negative potential scanning from open-circuit potential (OCP) to 0.90 V (vs. RHE) and kept at this potential for 2000 s.[8] Before the electrochemical measurements of the Pt/Au(111) electrode, it was rinsed with concd $HClO_4$ and ultrapure water and then dried with flowing N_2 gas. ORR measurements were performed in an oxygen-saturated 0.1 M $HClO_4$ solution by positive potential scanning from 0.15 to 1.05 V at a scan rate of $10\,mV\,s^{-1}$ with various rotating rates. Potential of the Pt ring electrode was kept at 1.30 V, which is more positive than the oxidation potential of H_2O_2, during the ORR measurements. Cyclic voltammograms (CVs) were measured in 0.05 M deaerated H_2SO_4 before and after the ORR measurements in order to determine the real electrode area and to confirm the atomic arrangements of the surface.[9,10]

Figure 1 shows CVs of the Pt(111) and Pt/Au(111) measured in 0.05 M deaerated H_2SO_4 solution with a scan rate of $20\,mV\,s^{-1}$. It was noted that these CVs were measured by the electrodes, which were set in the handmade holder of the RRDE system without rotation. Potential scan negatively started from 0.70 V, and the first scan in each case is shown in the figure. Shapes of the CVs were in good agreement with those in literatures,[10] so that the atomic arrangement of Pt on the electrode surface seemed to be maintained after setting it to the present system. Interestingly, while the waves due to the hydrogen adsorption and desorption were observed between 0.05 and 0.35 V in both cases, the peaks due to the sulfate anion

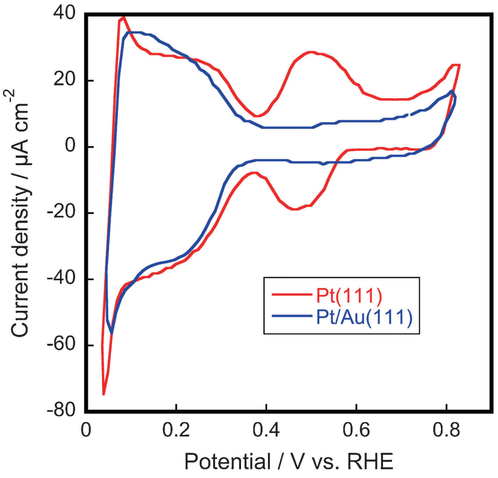

Figure 1. CVs of Pt(111) (red line) and Pt/Au(111) (blue line) measured in 0.05 M deaerated H_2SO_4 solution with a scan rate of 20 mV s^{-1}.

adsorption/desorption around 0.5 V were observed in the Pt(111) electrode but not observed in the Pt/Au(111) electrode. This revealed that the adsorption of the sulfate anion is easier on the Pt(111) surface than on the Pt/Au(111) electrode.

Figure 2a shows a set of linear sweep voltammograms (LSVs) for ORR of the Pt/Au(111) disk–Pt ring electrodes measured in 0.1 M oxygen-saturated $HClO_4$ at room temperature. Direction of potential scanning in these LSVs was positive. Cathodic current for ORR at the disk was observed at potential more negative than 1.0 V. These LSVs have the following two characteristic regions similar to those of the literatures;[4,10,11] the well-defined diffusion-limiting currents ($\boldsymbol{J}_\mathbf{D}$) region between 0.2–0.7 V and the mixed diffusion-kinetic control region between 0.7–1.0 V. The ring current density showed the formation of H_2O_2 at a more negative potential than 0.4 V, where the hydrogen adsorption/desorption was observed in the CV (Figure 1). Similar results were obtained in the single-crystal Pt(111) electrode,[10,11] indicating that adsorbed hydrogen inhibits ORR to H_2O with 4 electrons and/or accelarates ORR to H_2O_2 with 2 electrons.

Figure 2b shows the Koutecky–Levich plots whose linearity and parallelism suggest first-order kinetics with respect to molecular oxygen.[12] Based on these plots, the number of electrons for ORR and kinetic current density ($\boldsymbol{J}_\mathbf{k}$) were obtained from the slopes and the intercepts, respectively, of the plots, where following values are used for the analyses; the diffusion coefficient of O_2 (1.93×10^{-5} cm^2 s^{-1}), the kinetic viscosity of the solution (1.009×10^{-2} cm^2 s^{-1}), and the concentration of dissolved O_2 in solution (1.26×10^{-3} mol L^{-1}).[10c,12] The number of electrons for ORR was obtained from the slopes of the plots in Figure 2b to be 3.8, which is matched well with one of the Pt(111) electrode.[10] $\boldsymbol{J}_\mathbf{k}$ value obtained from the intercept of the plots in Figure 2b at 0.90 V was 0.81 mA cm^{-2}.

Figure 2c shows the diffusion–current-corrected Tafel plot, where $\boldsymbol{J}_\mathbf{k}$ values at various potentials were obtained from either the following eq 1 or the intercepts of Koutecky–Levich plots (Figure 2b),

$$1/\boldsymbol{J} = 1/\boldsymbol{J}_\mathbf{k} + 1/\boldsymbol{J}_\mathbf{D} \qquad (1)$$

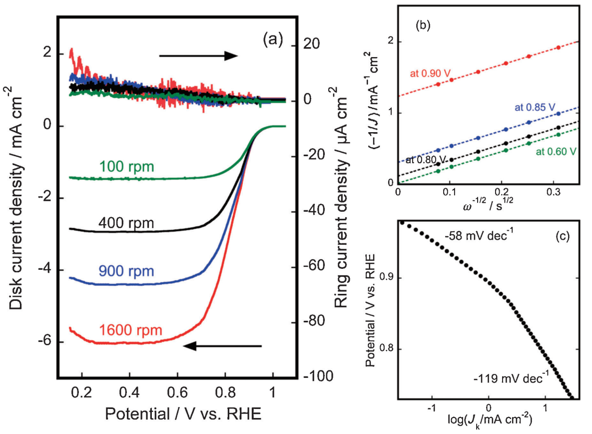

Figure 2. (a) LSVs for ORR of Pt/Au(111) electrode measured in 0.1 M oxygen-saturated $HClO_4$ at a scan rate of 10 mV s^{-1} with various rotation rates. Pt ring potential was fixed at 1.30 V. Potential of the Pt/Au(111) disk electrode was positively scanned from 0.15 to 1.05 V. (b) Koutecky–Levich plots of Pt/Au(111) electrode. (c) Diffusion-corrected Tafel plot of Pt/Au(111) electrode obtained with a rotation rate of 1600 rpm.

where $\boldsymbol{J}$ is the observed total current density. Two Tafel slopes were observed to be −58 mV dec^{-1} in the potential range of 0.89–0.97 V and −119 mV dec^{-1} in the potential range of 0.76–0.86 V. Two Tafel slopes were also reported for the Pt(111), $Pd_3Fe(111)$, and $Pt_3Ni(111)$ electrodes measured in 0.1 M $HClO_4$.[11] Wang et al.[11a] ascribed the two Tafel slopes for the Pt(111) electrode to the blocking and/or the electronic effect caused by a change in the coverage of the adsorbed oxygen-containing species with alterations in the potential.

Figure 3 shows LSVs for ORR of the Pt(111) and Pt/Au(111) electrodes measured in 0.1 M oxygen-saturated $HClO_4$ with a rotation rate of 1600 rpm. As clearly seen in Figure 3, although the potential, where cathodic current started to flow, of the Pt/Au(111) electrode was more positive than that of the Pt(111) electrode, the potential, where the diffusion-limited current flowed, of the former was more negative than that of the latter. This indicates that the Tafel slope of the former was different from that of the latter. Two Tafel slopes were also obtained in the Pt(111) electrode (inset of Figure 3) to be −51 mV dec^{-1} in the potential range of 0.89–0.93 V and −101 mV dec^{-1} in the potential range of 0.76–0.83 V. As described before, two Tafel slopes caused by the blocking and/or the electronic effects due to the adsorbed oxygen species suggested by Wang et al.[11a] In the CVs (Figure 1), on the Pt/Au(111) surface, sulfate anion was not adsorbed while it was adsorbed on the Pt(111) surface. Thus, on these surfaces, coverage of the adsorbed oxygen species in these potential ranges should be different from each other, and then the Tafel slopes should be different.

$\boldsymbol{J}_\mathbf{k}$ value obtained from the intercept of Koutecky–Levich plot of the Pt(111) electrode was 0.60 mA cm^{-2} at 0.90 V. This value is in good agreement with the literature value.[10] However, $\boldsymbol{J}_\mathbf{k}$ of the Pt/Au(111) electrode at the same potential (0.81 mA cm^{-2}) was much larger than that of the Pt(111) electrode (0.60 mA cm^{-2}), in other words, the electrocatalytic activity of the Pt/Au(111) electrode is better than that of the Pt(111) electrode.

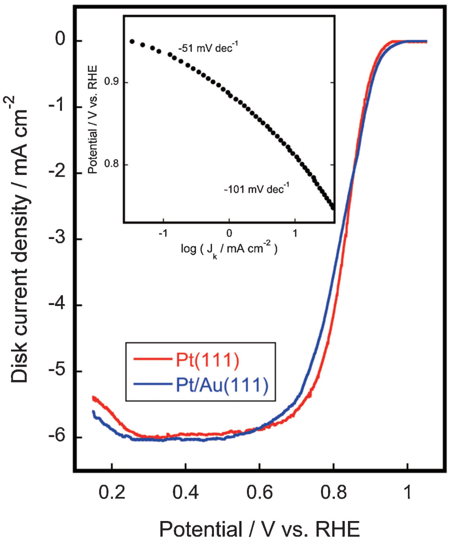

Figure 3. LSVs for ORR of Pt/Au(111) (red line) and Pt(111) (blue line) electrodes measured in 0.1 M oxygen-saturated $HClO_4$ at a scan rate of 10 mV s^{-1} with a rotation rate of 1600 rpm. Inset: Diffusion-corrected Tafel plot of the Pt(111) electrode obtained with a rotation rate of 1600 rpm.

Adzic et al. reported that the electrocatalytic activity, i.e., $\boldsymbol{J}_\mathrm{k}$, of the Pt(111) electrode measured in 0.1 M oxygen-saturated $HClO_4$ was better than that of the Pt-monolayer-coated Au(111).[4d] This discrepancy between our and their results could be caused by the atomic arrangement of Pt on the electrode surface. They constructed Pt monolayer by the galvanostatic replacement of the UPD Cu. Atomic arrangement of Pt on the surface may be at random. On the other hand, we prepared Pt monolayer by electrochemical deposition, and atomic arrangement was confirmed to be pseudomorphic by RSXS measurements.[8] Difference of atomic arrangement of Pt on the electrode surface must affect the surface electronic structure and, therefore, the electrocatalytic activity should be different.

More quantitative analysis including the surface electronic energy calculation is now under investigation.

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