The Oxygen Reduction Reaction on Pt Single Crystal Electrodes Modified with Aromatic Organic Molecules

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ABSTRACT

Structural effects on the activity for the oxygen reduction reaction (ORR) have been studied on single crystal electrodes of Pt modified with six aromatic organic molecules (AOMs). The AOMs examined affect the ORR activity slightly. However, the activity of the sites uncovered by AOMs increases after the modification: the ORR activity of uncovered Pt(111) area after the modification of phthalocyanine is 2.5 times as high as that of bare Pt(111). *t*-BuTAP and iron (II) phthalocyanine also enhance the ORR on Pt(997). These facts show that adsorbed AOMs can enhance the ORR activity of the uncovered active sites on Pt electrodes.

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1. Introduction

Pt has the highest ORR activity among pure metals, and has been widely used for electrocatalysts such as polymer electrolyte fuel cells (PEFC). However, limitation of the natural resource, higher cost of Pt and higher overpotential of the oxygen reduction reaction (ORR) hinder the wide spread of fuel cells. It is indispensable to reduce the Pt loading by development of electrocatalysts that have higher activity for the ORR.

One of the strategies for the increase of the ORR activity is the structural regulation of the surface of a catalyst. Markovic et al. reported that the ORR activity on the low index plane of Pt increases as Pt (100) < Pt (111) < Pt (110) in 0.1 M HClO₄, showing that the ORR activity depends on surface structure significantly.¹

Feliu et al. studied the ORR on the high index planes of Pt. They found that introduction of step structures is a major factor improving the ORR activity using an exchange current density and a half wave potential as a measure of the ORR activity.^{2,3} We evaluated the ORR activity on the high index planes using a current density at 0.9 V (RHE) as a common measure, and found that (111) terrace edge enhances the ORR on Pt electrodes.^{4,5} DFT calculation attributed the high ORR activity of Pt single crystal electrodes with (111) terrace edge to the change of adsorbed water structure by the terrace edge. The change of water structure results in the hindrance of Pt oxides formation that deactivates the ORR.⁶

Modification of Pt electrodes by organic molecules can also change adsorbed water structure. The ORR activity of Pt nanoparticles is enhanced by the modification with octylamine (OA) and amine with a pyrene ring (PA) remarkably.⁷ We extended the study to the high index planes of Pt, and found that OA/PA enhances the ORR on Pt electrodes with more than 7 atomic rows of (111) terrace.⁸

Modification by organic molecules can alter the vacancy density of the d-band, changing the adsorption force of O₂.⁹ This effect can improve the ORR activity. Aromatic organic molecules (AOM) such as CoTPP and C₆₀ affect the d-band vacancy due to the charge transfer from the adsorbed molecules.^{10,11} In this study, we have studied the ORR on single crystal electrodes of Pt modified with various AOMs as shown in Fig. 1(a).

Figure 1. (a) Aromatic organic molecules examined. (b) Hard sphere models of surfaces of Pt electrodes.

2. Experimental

CoTPP (5,10,15,20-tetraphenyl porphyrinato Cobalt(II)) and Pc (phthalocyanine) were purchased from Wako Pure Chemicals Co., Ltd. C₆₀ (Fullerene), CoPc (Cobalt(II) phthalocyanine), *t*-BuTAP (2,7,12,17-Tetra-tert-butyl-5,10,15,20-tetraaza-21H,23H-porphine) and FePc (Iron(II) phthalocyanine) were purchased from Sigma-Aldrich Co., Ltd. Perchloric acid (ultrapure) and N,N-Dimethylformamide were purchased from Kanto Chemical Co., Inc.

A single crystal bead of Pt was prepared by Clavilier's method.¹² The crystal was oriented using a reflection beam of a He-Ne laser¹³ and then mechanically polished with diamond slurries. Hard sphere models of the prepared electrodes are shown in Fig. 1(b). Pt(553) = 5(111)–(111) and Pt(322) = 5(111)–(100) have terrace widths that almost coincides with the size of AOMs examined.

Terrace widths of Pt(997) = 9(111)–(111) and Pt(544) = 9(111)–(100) are larger than those of Pt(553) and Pt(322), but they accommodate only one AOM on the (111) terraces, giving more uncovered active sites.

A single crystal electrode of Pt was annealed in H₂/O₂ flame about 1300°C for the removal of distortions caused by the mechanical polishing, and then cooled to room temperature in Ar/H₂ atmosphere (Ar/H₂ = 8/2). The annealed surface was protected with ultrapure water before the modification of AOM.

Modification of AOM was carried out as follows.

1. DMF (N,N-Dimethylformamide) solution of AOM (0.07 mM) was prepared.
2. An annealed single crystal electrode was immersed in the solution for 0.5–2.0 h.
3. The electrode was rinsed with ultrapure water.

Electrolytic solution was prepared from ultrapure water treated with Milli-Q Advantage A10 (Millipore) and perchloric acid (ultrapure, Kanto Kagaku).

Linear sweep voltammograms of the ORR were measured in the hanging meniscus rotating disk electrode (HMRDE) configuration¹⁴ using an electrochemical analyzer (ALS 701 C) and a rotating ring disk electrode apparatus (BAS: RRDE–3). The potential was scanned from 0.05 to 1.0 V (RHE) at scanning rate 0.010 V s^{−1} and rotation rate 1600 rpm. We estimated the ORR activity using kinetic current density at 0.90 V (RHE) j_k calculated from the Koutecky-Levich equation.^{15,16}

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L}$$

where j , j_k and j_L are the total current density, kinetic current density and limiting current density, respectively. All the potentials were referred to RHE.

3. Results and Discussion

Figure 2(a) shows voltammograms of single crystal electrodes of Pt before and after Pc modification as a representative. The single crystal surfaces were modified with Pc successfully because the charge of the adsorbed hydrogen region decreases. The charges of the oxide formation regions also decrease on Pt(111) and Pt(110) after the modification. Sharp redox peaks at 0.12 V (RHE) on $n(111)$ –(111) and 0.27 V (RHE) on $n(111)$ –(100) originate from the adsorption/desorption of hydrogen at (111) and (100) steps, respectively.^{17,18} Broad redox peaks between 0.05 and 0.4 V (RHE) are due to the adsorption/desorption of hydrogen at (111) terrace. Only the peaks due to the steps shrink after the modification, showing that Pc molecules are preferentially adsorbed at the steps. Coverage of Pc is estimated from the charge density of adsorbed hydrogen after the modification. Table 1 summarizes coverages of Pc at terraces and steps. Other organic aromatic molecules gave the similar results.

Figure 2(b) shows linear sweep voltammograms before and after the modification by Pc. Limiting current decreases after the modification on the high index planes, but the cause is unclear. The value of j_k at 0.90 V (RHE) is calculated using geometrical surface area of a single crystal electrode. Geometric surface area of a single crystal electrode gives real surface area because single crystal surface of Pt is atomically flat. Figure 3(a) shows the values of j_k and the ORR activity normalized to that of bare Pt single crystal electrode. Surprisingly, all the AOMs except Pc and C₆₀ enhance the ORR activity on Pt(111) slightly, although nearly 40% of the surface area is covered by the AOMs. On the other hand, the ORR on the other surfaces are deactivated by AOMs except the cases of *t*-BuTAP on Pt(110) and Pt(997).

The slight enhancement of the ORR activity after the modification indicates that the ORR activity of uncovered active

Figure 2. (a) Cyclic voltammograms of Pt electrodes before and after the modification with Pc in 0.1 M HClO₄ saturated with Ar (Scanning rate: 0.050 V s^{−1}). (b) Linear sweep voltammograms of Pt electrodes before and after the modification with Pc in 0.1 M HClO₄ saturated with O₂ (Scanning rate: 0.010 V s^{−1}, Scanning direction: Positive, Rotation rate: 1600 rpm).

Table 1. Coverage of Pc at terrace (θ_{terrace}) and step (θ_{step}).

	θ_{terrace}	θ_{step}
Pt(111)	0.61	—
Pt(110)	—	0.12
Pt(553)	0.12	0.86
Pt(322)	0.02	0.54
Pt(544)	0.24	0.88

sites is enhanced compared with a Pt electrode without modification. We calculate the ORR activity of uncovered active sites using the electrochemically active surface area (ECSA) after the modification. We calculated ECSA by the division of the charge of hydrogen desorption (0.05–0.4 V) by 210 mC cm^{−2}.¹⁹ Figure 3(b) shows the normalized ORR activity of uncovered active sites. The ORR activity of uncovered active sites is enhanced on Pt(111) by the modification of all the AOMs. Pc enhances the ORR on Pt(111) most remarkably: the ORR activity of the uncovered active sites on Pc modified Pt(111) is 2.5 times as high as that of bare Pt(111). The following combinations also enhance the ORR activity of uncovered active sites after the modification slightly: (CoTPP, Pc, CoPc)/Pt(110), (Pc, CoPc)/Pt(553), (*t*-BuTAP, FePc)/Pt(322), (*t*-BuTAP, FePc)/Pt(997) and FePc/Pt(544). The ORR activity of FePc on glassy carbon is negligible compared with those of FePc covered

Figure 3. (a) The ORR activity after the modification with aromatic organic molecules (evaluated by geometrical surface area) normalized to that before the modification. (b) The ORR activity of the sites uncovered by aromatic molecule normalized to that before the modification.

single crystal electrodes of Pt at 0.9 V (RHE).^{20,21} In ultra-high vacuum, electron transfer is induced between FePc and a metal substrate, resulting in a change of electronic state of FePc.²² The same phenomenon might occur in electrochemical environments, and the ORR activity of FePc might be enhanced. However, we cannot evaluate the ORR activity of FePc adsorbed on Pt electrodes because we cannot increase the coverage of FePc more than 0.4. Thus we assume that the ORR activities of AOMs are negligible at 0.90 V (RHE) on Pt electrodes. Based on this assumption, the ORR activity of AOM/Pt(*hkl*) originates from Pt surface uncovered by AOM.

Control experiment was done after a Pt single crystal electrode was immersed in DMF solution without AOM. The charge of the adsorbed hydrogen region decreased slightly, but the change was small compared with that after AOMs modification. The ORR activity was slightly decreased after the modification of DMF. These facts show that DMF has no effect on the enhancement of the ORR activity.

There are several reasons for the improvement of the ORR activity. The first one is the shift of the d-band center by the electron attractive force of AOMs. The second one is the change of the adsorbed water structure due to the modification that prevents Pt oxide formation. However, modification of C₆₀ does not improve the ORR activity on all the surfaces, although C₆₀ has strong electron attractive property.¹¹ Shift of d-band center prevents the formation of Pt oxides that block the ORR. AOMs inhibit the Pt oxides formation as shown in the voltammograms of Pt(111) in Fig. 2(a). However, the decrease of Pt oxide formation is too small

to cause the remarkable enhancement of the ORR activity of the surface uncovered by AOMs. IR spectroscopy shows that ice-like water structure is formed on Pt single crystal electrodes after the modification of amines. The ice-like structure may stabilize water, resulting in the prevention of the formation of Pt oxides that block the ORR.⁸ Pt(111) has a wider (111) terrace structure that is appropriate for the ice-like structure (hexamer) formation. Therefore, the ORR activity may be enhanced most significantly. It is possible that ice-like structure formation is one of the factors of the enhancement of the ORR.

Study of the vibrational spectroscopy of the adsorbed water is necessary to reveal the enhancement mechanism, and is now on progress in our laboratory.

4. Conclusion

Adsorbed aromatic organic molecules (AOMs) enhance the ORR activity of uncovered active sites on Pt(111): the ORR activity of the uncovered active sites on phthalocyanine modified Pt(111) is 2.5 times as high as that of bare Pt(111). The following combinations also enhance the ORR activity of uncovered active sites after the modification slightly: (5,10,15,20-tetraphenyl porphyrinato Cobalt(II), phthalocyanine, Cobalt(II) phthalocyanine)/Pt(110), (phthalocyanine, Cobalt(II) phthalocyanine)/Pt(553), (2,7,12,17-Tetra-tert-butyl-5,10,15,20-tetraaza-21H,23H-porphine, iron(II) phthalocyanine)/Pt(322), (2,7,12,17-Tetra-tert-butyl-5,10,15,20-tetraaza-21H,23H-porphine, iron(II) phthalocyanine)/Pt(997) and iron(II) phthalocyanine/Pt(544).

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