Effects of the Alkane on the Oxygen Reduction Reaction on Well-Defined Pt Surfaces

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ABSTRACT

Previous study shows that tetra-*n*-hexylammonium cation (THA⁺), which is composed of one nitrogen atom and four alkyl chains, increases the activity of the oxygen reduction reaction (ORR) on Pt(111) eight times as high as that of bare Pt(111). We have studied the ORR on Pt single crystal electrodes modified with alkane to elucidate which part of THA⁺ contributes to the enhancement of the activity for the ORR. The ORR activity is increased only twice by the modification of Pt(111) with dodecane and hexadecane. Combination of a nitrogen atom and alkyl chains of THA⁺ plays an important role in enhancing the ORR on Pt electrodes. Dodecane and hexadecane increases the ORR activity on Pt(111) and Pt(110), but they deactivate the ORR on Pt(100) and the high index planes.

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Keywords : High Index Planes, Pt Single-crystal Electrodes, Alkane, Enhancement of the Oxygen Reduction Reaction

1. Introduction

Pt is generally used for an electrocatalyst of polymer electrochemical fuel cells (PEFC). Nonetheless, due to the high overpotential, the oxygen reduction reaction (ORR), which occurs in the air electrode, is considerably sluggish, and the wide use of PEFCs is prevented by the limited supply of Pt. Owing to these reasons, it is necessary to invent the electrocatalysts which have higher ORR activity for the decrease of Pt loading.

One of the strategies to enhance the ORR activity of Pt is the control of the atomic arrangement of the surface at atomic level. According to Marković et al., the order of ORR activity is Pt(100) < Pt(111) < Pt(110) in 0.1 M HClO₄, showing that the ORR activity is strongly dependent on the surface structure of Pt.¹ Structural effects on the well-defined Pt surfaces were also investigated using the high-index planes of Pt. High-index planes are written as *n*(*hkl*)-(*mno*), where *n*, (*hkl*), and (*mno*) mean the number of terrace atomic rows, the structure of the terrace and step, respectively. Feliu et al. examined the structural effects on the ORR on the high-index planes of Pt and elucidated that the introduction of step structure is the dominant cause to enhance the ORR with the use of an exchange current density and a half-wave potential.^{2,3} We appraised the ORR activity on Pt high-index planes with the use of a current density at 0.9 V (RHE), elucidating that the (111) terrace edge plays an important role in enhancing the ORR on Pt.^{4,5} Moreover, by the use of DFT calculations, the change of the structure of adsorbed water is caused by (111) terrace edge on *n*(111)-(111) Pt series.⁶ The change of the water structure prevents the production of Pt oxides that is known as blocking species of the ORR. The study also showed that the ORR is enhanced by the structural change of water due to the presence of the terrace edge.

The adsorbed water structure on an electrode will be changed by modifying the electrode with hydrophobic organic molecules. The ORR activity is enhanced by the modification of hydrophobic organic molecules.^{7–12} According to Miyabayashi et al., the ORR activity of Pt nanoparticles was increased by modifying them with alkyl amines, such as octylamine (OA) and an alkyl amine with a

pyrene ring (PA). After the modification, the Pt nanoparticles become more durable than bare nanoparticles.^{8,10} Study using Pt single-crystal electrodes shows that the ORR activity is enhanced dramatically by OA/PA on the surfaces with wide (111) terrace.¹³

We also investigated the effects on the ORR using hydrophobic tetra-alkyl ammonium cations with longer alkyl chains, elucidating that the ORR activity on Pt(111) modified with tetra-*n*-hexylammonium cation is eight times as high as that of bare Pt(111). The longer the alkyl chains enhance the hydrophobicity, resulting in the higher ORR activity.¹⁴ The adsorbed hydroxide and adsorbed water are destabilized by the hydrophobic cations and their hydration shells. A tetra-alkyl ammonium cation is composed of a nitrogen atom and four alkyl chains. We need to identify the main factor of the enhancement of ORR activity by alkyl-ammonium cations. In this paper, we used hydrophobic alkanes with various alkyl chain length (Fig. 1(a)) to examine the effect of alkanes on the ORR on the single-crystal electrodes of Pt. Hard-sphere models of the single-crystal electrodes are summarized in Fig. 1(b).

2. Experimental

2.1 Reagents

We purchased alkanes from Sigma-Aldrich. Perchloric acid (ultrapure) was purchased from Kanto Chemical Co., Inc. We made all the solutions using ultrapure water produced from a Milli-Q Advantage A10 (Millipore).

2.2 Preparation of single-crystal electrodes

A single-crystal bead of Pt was created by Clavilier's method.¹⁵ We oriented the crystal with the use of He-Ne laser and polished the crystal surface mechanically using a diamond slurry. The polished single-crystal surface needs annealing in an H₂/O₂ flame at approximately 1300°C to get rid of the distortion caused by the mechanical polishing. After the annealing, we cooled down the single-crystal to room temperature in an Ar (99.9999% purity) atmosphere. The annealed surface was immersed in ultrapure water and then moved to a cell.

Figure 1. (a) Structural formula of alkanes examined. (b) Hard-sphere models of Pt single-crystal electrodes.

2.3 Modification with alkane

An acetone solution of alkane (10 mM) was prepared. We protected the surface of single-crystal electrode with ultrapure water and dipped it in the alkane solution for 10 min. We rinsed the electrode surface with ultrapure water before electrochemical measurements.

2.4 Electrochemical measurement

We measured linear sweep voltammograms (LSV) of the ORR in the hanging meniscus rotating disk electrode (HMRDE) configuration by using an electrochemical analyzer (ALS 700C) and a rotating ring disk electrode (RRDE-3, BAS).¹⁶ LSVs were measured in the range of 0.05 V (RHE) to 1.0 V (RHE) in the positive direction. Scanning rate was 0.010 V s⁻¹ and a rotation speed was 1600 rpm. The ORR activity was estimated with a kinetic current density at 0.90 V (RHE) j_K obtained from the Koutecky–Levich equation:^{17,18}

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L},$$

where j , j_K , and j_L represent the total current density, kinetic current density, and limiting current density, respectively. All the potentials were represented with respect to RHE.

3. Results and Discussion

Figure 2(a) illustrates voltammograms of single crystal electrodes of Pt measured with and without dodecane (C12) in 0.1 M HClO₄ in Ar atmosphere.

The amount of electricity of adsorbed hydrogen (Q_H) and oxide formation regions (Q_{OX}) decrease slightly with dodecane. Sharp redox peaks at 0.12 V(RHE), which is due to the adsorption of hydrogen at (110) step site, shrink after the modification with alkane. This result indicates that dodecane is adsorbed at the (110)

Figure 2. (a) Voltammograms of Pt with and without dodecane (C12) in 0.1 M HClO₄ saturated with Ar. Scanning rate: 0.050 V s⁻¹. (b) Linear sweep voltammograms of single-crystal electrodes of Pt with and without dodecane (C12) in 0.1 M HClO₄ saturated with O₂. Scanning rate: 0.010 V s⁻¹. Red broken lines show the potential at which the ORR activity is estimated.

step site. We estimated Q_H and Q_{OX} with the use of the anodic peaks within the potential ranges of 0.05–0.4 V(RHE) and 0.5–0.9 V(RHE), respectively. We also modified Pt(111) and Pt(110) with hexadecane (C16). The results were similar to those of dodecane.

We also measured linear sweep voltammograms of the ORR with and without dodecane (C12) modification in 0.1 M HClO₄ saturated with O₂ (Fig. 2(b)). The ORR activity of Pt(111) and Pt(110) increases after the modification, but those of Pt(331) = 3(111)-(111) and Pt(775) = 7(111)-(111) decrease. The difference of the limiting current density is found on Pt(111) and Pt(331) before and after the modification. This difference might be caused by the change of hanging meniscus shape. Figure 3(a) summarizes the ORR activities on Pt electrodes with and without alkanes. In particular, the ORR activity on Pt(111) increases about twofold after the modification of dodecane and hexadecane. The ORR activity on Pt(110) also increases after the modification. The activity of other high-index planes decrease after the modification. On Pt(111) and Pt(110), the longer the alkyl chain length is, the higher the ORR activity is. However, Pt(331) $n = 3$, of which activity is the highest in Pt single-crystal electrodes,⁵ decreases after the modification of alkanes. Dependence of the alkyl chain length of alkanes on the ORR activity is less remarkable than that of tetra-alkyl ammonium cations.

Previous studies show that Pt oxides are blocking species of the ORR on Pt electrodes.^{19–21} Voltammograms in Fig. 2(a) show that the charge of Pt oxide formation (Q_{OX}) decreases on all the surfaces examined. However, the ORR is deactivated on Pt(331) = 3(111)-(111) and Pt(775) = 7(111)-(111) after alkane modification even though Q_{OX} decreases. These results indicate that factors other than Pt oxides determine the ORR activity after the alkane modification.

Figure 3. (a) Specific activities of the ORR (j_K) at 0.90 V(RHE) of the single-crystal electrodes of Pt with and without dodecane (C12) or hexadecane (C16). (b) Increase ratio of the ORR activity plotted against the terrace atom density d_T . Red: dodecane (C12) Blue: hexadecane (C16).

We plotted the increase ratio of the ORR activity against the terrace atom density d_T in Fig. 3(b). Pt(110) gives unreconstructed (1×1) or reconstructed (1×2) structures, of which structures depend on the annealing and cooling conditions.^{22,23} Our annealing and cooling conditions are similar to those giving the (1×2) structure of Pt(110). The plots of dodecane are similar to those of hexadecane except Pt(110) (1×2). We revealed that alkane modification is effective especially against Pt(111) surface.

We employed eicosane (C20) to achieve higher ORR activity. However, the activity of Pt(111) and Pt(110) (1×2) decreased markedly after the modification with eicosane. The difference of physical property (melting point, solubility in acetone) among eicosane and dodecane and hexadecane may cause this result. We changed the concentration of the solution to optimize the condition, however, we could not enhance the ORR activity by eicosane.

Alkanes are not very effective against the improvement for the ORR activity compared with tetra-alkyl ammonium cations that have both a nitrogen atom and alkyl chains. Similar phenomenon is found in the case of the modification with aromatic molecule such as melamine increases the ORR activity of Pt nanoparticles and Pt(111) significantly.^{24,25} However, 1,3,5-triazine and aniline (benzenamine) have no effect on the increase of the ORR activity of Pt nanoparticles.²⁴ Combination of a nitrogen atom and alkyl chains in tetra-alkyl ammonium cation plays a key role to improve the ORR activity.

Hexadecane (C16) molecules form ordered structure with the chain axis parallel to the surface on Au(111) in 0.1 M HClO₄ at the potential near pzc, but they are aggregated at more positive potentials than pzc.²⁶ The physically adsorbed alkanes may block some activated sites for the ORR. On the other hand, THA⁺ is not adsorbed on the electrode surface at 0.90 V(RHE) at which the ORR activity is estimated because the cation is positively charged, not blocking the activated sites.¹⁴ Difference of the adsorption characteristics of organic molecules may also influence the ORR activity.

Study using infrared spectroscopy reveals that the significant decrease of the coverage of PtOH increases the ORR activity on Pt(111) after THA⁺ modification.¹⁴ Also, we investigated the mechanism of the activation of ORR on Pt single-crystal electrodes using infrared spectroscopy. According to the study, the change of water structure on Pt surface was observed and smaller icelike water is formed on Pt(111), resulting in achieving the increasement of ORR activity.²⁷ The change of electronic structure might also promote ORR. XPS measurement needs to be done to know the state of electrons. Study on the mechanism of the improvement of the ORR activity by alkane and melamine is now on progress using infrared spectroscopy in our laboratory.

4. Concluding Remarks

Dodecane and hexadecane increase the ORR activity on Pt(111) and Pt(100). The activity on Pt(111) is doubled after the modification with dodecane and hexadecane. Pt(110) is also enhanced by dodecane and hexadecane. However, high-index planes, such as Pt(331) = 3(111)-(111) and Pt(775) = 7(111)-(111), is deactivated by alkanes. Combination of a nitrogen atom and alkyl chains in tetra-alkyl ammonium cations play a key role to enhance the ORR on Pt electrodes.

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References

1. N. M. Marković, R. R. Adžić, B. D. Cahan, and E. B. Yeager, *J. Electroanal. Chem.*, **377**, 249 (1994).
2. M. D. Maciá, J. M. Campiña, E. Herrero, and J. M. Feliu, *J. Electroanal. Chem.*, **564**, 141 (2004).
3. A. Kuzume, E. Herrero, and J. M. Feliu, *J. Electroanal. Chem.*, **599**, 333 (2007).
4. A. Hitotsuyanagi, M. Nakamura, and N. Hoshi, *Electrochim. Acta*, **82**, 512 (2012).
5. N. Hoshi, M. Nakamura, and A. Hitotsuyanagi, *Electrochim. Acta*, **112**, 899 (2013).
6. R. Jinnouchi, K. Kodama, and Y. Morimoto, *J. Electroanal. Chem.*, **716**, 31 (2014).
7. Z.-Y. Zhou, X. Kang, Y. Song, and S. Chen, *J. Phys. Chem. C*, **116**, 10592 (2012).
8. Y.-H. Chung, D. Y. Chung, N. Jung, and Y.-E. Sung, *J. Phys. Chem. Lett.*, **4**, 1304 (2013).
9. Z.-Y. Zhou, X. Kang, Y. Song, and S. Chen, *Chem. Commun.*, **48**, 3391 (2012).
10. K. Miyabayashi, H. Nishihara, and M. Miyake, *Langmuir*, **30**, 2936 (2014).
11. N. Jung, S. Bhattacharjee, S. Gautam, H.-Y. Park, J. Ryu, Y.-H. Chung, S.-Y. Lee, I. Jang, J. H. Jang, S. H. Park, D. Y. Chung, Y.-E. Sung, K.-H. Chae, U. V. Waghmare, S.-C. Lee, and S. J. Yoo, *NPG Asia Mater.*, **8**, e237 (2016).
12. Y.-Y. Wang, D.-J. Chen, and Y. J. Tong, *ACS Catal.*, **6**, 5000 (2016).
13. K. Saikawa, M. Nakamura, and N. Hoshi, *Electrochem. Commun.*, **87**, 5 (2018).
14. T. Kumeda, H. Tajiri, O. Sakata, N. Hoshi, and M. Nakamura, *Nat. Commun.*, **9**, 4378 (2018).
15. J. Clavilier, R. Faure, G. Guinet, and R. Durand, *J. Electroanal. Chem.*, **107**, 205 (1980).
16. B. D. Cahan and H. M. Villullas, *J. Electroanal. Chem.*, **307**, 263 (1991).
17. H. M. Villullas and M. Lopez Teijelo, *J. Electroanal. Chem.*, **384**, 25 (1995).
18. H. M. Villullas and M. Lopez Teijelo, *J. Electroanal. Chem.*, **385**, 39 (1995).
19. N. M. Marković, H. A. Gasteiger, B. N. Grgur, and P. N. Ross, *J. Electroanal. Chem.*, **467**, 157 (1999).
20. H. Tanaka, S. Sugawara, K. Shinohara, T. Ueno, S. Suzuki, N. Hoshi, and M. Nakamura, *Electrocatalysis*, **6**, 295 (2015).
21. T. Ueno, H. Tanaka, S. Sugawara, K. Shinohara, A. Ohma, N. Hoshi, and M. Nakamura, *J. Electroanal. Chem.*, **800**, 162 (2017).
22. C. A. Lucas, N. M. Marković, and P. N. Ross, *Phys. Rev. Lett.*, **77**, 4922 (1996).
23. N. M. Marković, B. N. Grgur, C. A. Lucas, and P. N. Ross, *Surf. Sci.*, **384**, L805 (1997).
24. M. Asahi, S. Yamazaki, N. Taguchi, and T. Ioroi, *J. Electrochem. Soc.*, **166**, F498 (2019).
25. N. Wada, M. Nakamura, and N. Hoshi, *Electrocatalysis*, **11**, 275 (2020).
26. Y. He, T. Ye, and E. Borguet, *J. Phys. Chem. B*, **106**, 11264 (2002).
27. N. Hoshi, K. Saikawa, and M. Nakamura, *Electrochem. Commun.*, **106**, 106536 (2019).