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.

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. 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. 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. Moreover, by the use of DFT calculations, 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 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. We oriented the crystal with the use of He-Ne laser and polished the 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.
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). 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:

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_l},
\]

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 HClO\(_4\) in Ar atmosphere. Figure 2(b) shows that the charge of Pt oxide formation \(Q_{\text{OX}}\) decreases on all the surfaces examined. However, the ORR is deactivated on Pt(331) = 3(111)-(111) and Pt(775) = 7(111)-(111) after modification. 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. Voltammograms in Fig. 2(a) show that the charge of Pt oxide formation \(Q_{\text{OX}}\) decreases on all the surfaces examined. However, the ORR is deactivated on Pt(331) = 3(111)-(111) and Pt(775) = 7(111)-(111) after modification even though \(Q_{\text{OX}}\) decreases. These results indicate that factors other than Pt oxides determine the ORR activity after the alkane modification.

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We employed eicosane (C20) to achieve higher ORR activity. However, the activity of Pt(111) and Pt(10) (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 (1,3,5-triazine-2,4,6-triamine). Modification with melamine increases the ORR activity of Pt nanoparticles and Pt(111) significantly. However, 1,3,5-triazine and aniline (benzene-amine) have no effect on the increase of the ORR activity of Pt nanoparticles. Combination of a nitrogen atom and alkyl chains in tetra-alkyl ammonium cations plays a key role to enhance the ORR on Pt electrodes.

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References

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