

Electrical double layer structure that activates the oxygen reduction reaction

The reduction of electrocatalyst usage in polymer electrolyte fuel cells (PEFCs) is an urgent issue for realizing the widespread use of fuel cell vehicles. Currently, mainstream research on PEFC catalysts is aimed at reducing the overpotential of the oxygen reduction reaction (ORR) using Pt alloy electrocatalysts such as PtNi [1]. However, nonprecious metals in the catalyst are easily dissolved by the fluctuations of electrode potential during the start-stop operation of the fuel cell. Therefore, the catalytic durability of commercial fuel cell vehicles is maintained by the overloading of Pt alloy catalyst. Recently, we have focused on the properties of the ionic species in the electrical double layer (EDL) formed at the solid electrode-electrolyte solution interface [2]. We found that the hydrophobicity of organic cations in the EDL extraordinarily enhances the ORR activity in acidic solutions, which is the same as the condition in the PEFC. The high hydrophobicity of the tetraalkylammonium cation with a longer alkyl chain enhances the ORR activity. The activity on Pt(111) in the presence of the tetra-n-hexylammonium cation is eight times as high as that without this cation, and is comparable to the activities on Pt₃Co(111) and Pt₃Ni(111) electrodes [3]. Although this study was performed using well-defined model surfaces of singlecrystal electrodes, the modification by organic cations on fuel cell catalysts for practical use can be easily introduced into the process of catalyst preparation. Determination of the detailed interfacial structure is important for the elucidation of the appropriate reaction field in the EDL of a fuel cell catalyst. In this study, three-dimensional structural determination at the atomic level using in situ X-ray diffraction revealed the activation factor of the ORR and the abnormal structural displacement of substrate Pt atoms.

X-ray diffraction was measured using SPring-8 **BL13XU** with an X-ray energy of 20 keV. Structural analyses along the surface normal direction were performed using X-ray specular crystal truncation rod (CTR) scattering. The CTR profiles were obtained at 0.9 V vs RHE where the ORR activity was estimated. Figure 1 shows the specular CTR and normalized CTR profiles of Pt(111) in 0.1 M HCIO₄ with and without 10⁻⁶ M THA⁺. The CTR clearly changes with the electrode potential and the addition of THA⁺. Since THA⁺ is composed of nitrogen, carbon, and hydrogen, the electron density at the interface is significantly lower than that of Pt. Therefore, the main origin of this change in the CTR is the structural change in the substrate Pt. The initial model used for structural optimization comprises three Pt layers and one layer of oxygen of water molecules or an OH_{ad} layer. The vertical atomic position, occupancy factor, and Debye-Waller factors for the Pt and oxygen layers were optimized by the least-squares method. The electron density profiles and schematic models of the interfacial structure are shown in Fig. 2.

Compared with the structural data at the double layer potential of 0.50 V at which water adsorbed on the Pt(111) surface, the distance between the layers of oxygen and the first Pt (d_{O-1stPt}) in 0.1 M HClO₄ without THA⁺ decreased from 2.47 to 2.14 Å. This distance of 2.14 Å corresponds to the Pt-O bond length of OH_{ad} on Pt(111) proposed on the basis of low-energy electron diffraction and in situ X-ray diffraction measurements. Potential-dependent coadsorbed structures of water and OH_{ad} were also suggested to exist from the results of DFT calculations and Monte Carlo simulations. Previous XPS measurements indicate the coadsorption of water and OH_{ad}, hence the oxygen coverage at 0.90 V ($\theta_{\rm O}$ = 0.78) includes adsorbed water and OH species. The surface relaxation of the Pt layer is promoted by electron donation from an oxygen



Fig. 1. (a) Specular crystal truncation rod (CTR) profiles of Pt(111) in 0.1 M HClO₄ with and without 10^{-6} M tetra-*n*-hexylammonium cation (THA⁺) saturated with Ar at 0.90 V *vs* RHE. The dots are the data points and the solid lines are the structure factors calculated using the optimized model. (b) Specular CTR profiles at 0.90 V normalized to the data at 0.50 V.



Fig. 2. (a) Electron density profiles of the optimized model at 0.90 V. (b) Schematic models estimated from structural optimization.

lone pair of the OH_{ad} as well as adsorbed water. Therefore, the distance between the first and second Pt ($d_{1stPt-2ndPt}$) layers does not change compared with that at the double layer potential of 0.50 V. Conversely, in the presence of THA⁺, $d_{O-1stPt}$ was 2.38 Å, which indicates that adsorbed water is dominant instead of OH_{ad} . It is notable that the surface relaxation was eliminated ($d_{1stPt-2ndPt} = 2.29$ Å) even though the water and OH_{ad} were adsorbed on Pt. This result indicates that the interaction between the oxygen species and Pt is decreased by the presence of THA⁺.

In acidic solution, the hydration water around H^+ is linked with OH_{ad} through a hydrogen bond, as shown in Fig. 3(a). $H^+-H_2O-OH_{ad}$ formation stabilizes the OH_{ad} layer and inhibits the ORR. According to studies on the Pt(111) surface under an ultrahigh vacuum condition, the coadsorption of OH_{ad} and H_2O forms a well-defined 3×3 honeycomb structure because the symmetry and OH···O distance in the coadsorbed layer fit well with the Pt(111) lattice. The approach of the hydration shell around THA⁺ to the Pt surface disrupts the stabilization effect between the hydration water and the OH_{ad} layer (Fig. 3(b)). The coverage of OH_{ad} is decreased by this destabilization effect, inducing the disruption of the stable hydrogen bonding network in the coadsorbed layer. These multiple effects are enhanced by the hydrophobicity of the cation and promote the access of oxygen molecules to the Pt(111) surface.



Fig. 3. Schematic model of interfacial hydrated cations and adsorbed hydroxide species on Pt(111): (a) hydrophilic cation and (b) hydrophobic cation. Arrows indicate the direction of the water dipole within the hydration shell.

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