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Structural and Electronic properties of Platinum Nanoparticle Surface Studied by in situ x-ray Diffraction and in situ x-ray Absorption Spectroscopy

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The electrochemical surface oxidation of platinum and hydrogen chemisorptions on platinum surface has attracted much attention from both fundamental electrochemical researches and for catalyst applications. In particular, for fuel cell applications, the precise understandings of these phenomena at Pt nanoparticle surface, i.e., the surface restructuring and electronic state alternations due to surface oxidation or chemisorptions of hydrogen would give helpful information on developing better catalysts.

In this study, we have investigated structural and electronic properties of Pt nanoparticles supported on various carbon support materials by both in situ x-ray diffraction (XRD), and in situ x-ray absorption spectroscopy (XAS) studies by using synchrotron radiation x-rays.

Pt nanoparticles (ca. 2 nm) were supported on carbon blacks and carbon nanohorns by conventional colloidal methods. The supported nanoparticles were spread on to a carbon electrode. This electrode was placed in an electrochemical cell with 0.5M H_2SO_4 electrolyte. In situ x-ray diffraction and in situ XAS experiments were made on BL16B2 beam line at SPring-8.

X-ray diffraction and XAS studies clearly showed surface restructurings in both surface oxidation and hydrogen adsorption regions. As shown in Fig. 1, above 0.8V vs. RHE (oxide formation region), the peak intensity of XRD decreased upon increasing potential, suggesting that surface restructuring due to surface oxidation. The intensity decrease is about 30 % for each peak, and this corresponds with the nearly mono-layer surface restructuring. And this surface oxidized phase seems to be essentially amorphous, because no additional peak from platinum oxides was found. During the oxidation, the peaks of XRD remain the same position. This indicates the oxidation of Pt nanoparticles is limited within the surface sub-layer in these potential regions.

Similar surface restructuring behaviors due to oxidation were observed by EXAFS also. As shown in Fig. 2, the amplitude of k^3-weighted Fourier transform of the Pt EXAFS significantly decreases above 0.8V, indicating the coordination number for the first nearest neighbor Pt-Pt bonds decreases. This suggests that the Pt nanoparticle surface was roughened by oxidation. Figure 3 shows k^1-weighted Fourier transform of the Pt L_3 EXAFS, which emphasizes low-k region (thus Pt-O bonds), clearly showed the formation of Pt-O bonds above 0.8V. The corresponding Pt-O distance is 1.98 Å, and can be assigned to Pt-OH bonds at atop sites.

In the hydrogen adsorption region (at 0.0 V), on the contrary, the intensity of XRD and the amplitude of k^3-weighted Fourier transform increased. (Figs. 1, 2) This means the surface becomes smooth by hydrogen chemisorptions. Due to strong interaction between SO_4^{2-} anions and Pt surface atoms, platinum surface has a relaxed structure even in the double layer region. Thus, by covered by hydrogen, which has weaker interaction than SO_4^{2-}, the platinum surface may have more ideal structure.

The more detailed results of structure analysis and electronic properties of Pt nanoparticle surface will be presented at the Meeting.

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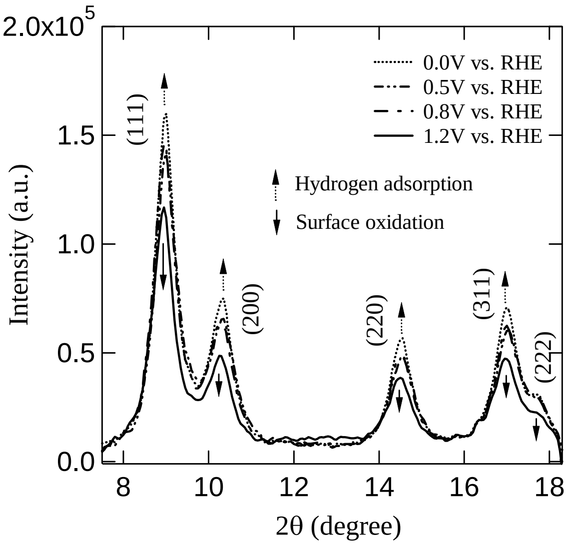

Figure 1 X-ray diffraction patterns of Pt nanoparticles supported on a carbon black obtained by changing the potential from 0.0 V to 1.2 V.

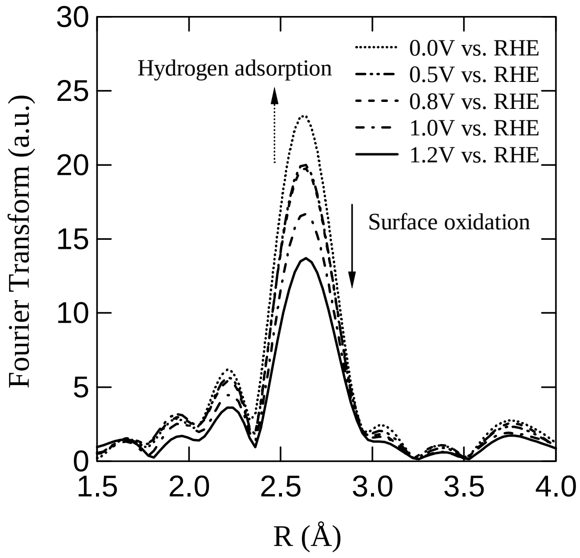

Figure 2 k^3-weighted Fourier transform of the Pt L_3 EXAFS

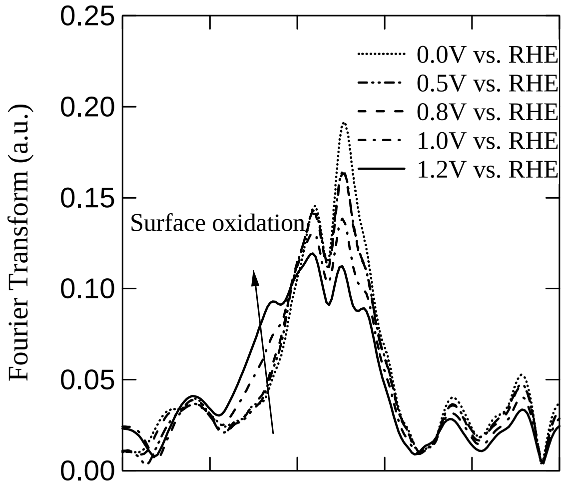

Figure 3 k^1-weighted Fourier transform of the Pt L_3 EXAFS