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Extracting the surface states of Pt films under electrochemical environments using total reflection fluorescence X-ray absorption fine structure spectroscopy

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1 Introduction

Improvements in catalytic performances of fuel cells is essential for their widespread application and realizing a clean energy society. In fuel cells, Pt nanoparticles covered with ionomer play a crucial role for the catalytic reactions. It is, therefore, of great importance to elucidate the fundamental surface structures of ionomer-coated Pt under electrochemical environments. In this respect, a model system of Nafion-coated Pt polycrystalline film with 30 nm thickness was investigated by in-situ total reflection fluorescence X-ray absorption fine structure spectroscopy (TRF-XAFS). The possibility of extracting the local adsorption states of Pt films is presented in this report.

2 Experiment

A 30-nm-thick Pt polycrystalline film was grown by a sputter deposition on a 1-inch-diameter Si (100) wafer, followed by ultraviolet-ozone cleaning. This Pt film sample was coated by a 15-nm-thick Nafion by spin coating.

TRF-XAFS spectra were measured at BL-9A. The fluorescence X-ray signal was measured by using a 19-element Ge solid-state detector placed perpendicular to the X-ray beam direction. A 400-μm pinhole was used to regulate the size of the incident X-ray to reduce elastic scatterings. A 5-axis goniometer was used to adjust the total reflection conditions. An X-ray CCD was placed most downstream from the cell to monitor the X-ray incident angle which was adjusted as 3.5 mrad, approximately half of the theoretically-calculated critical angle of Pt. Transmission spectra of Pt foil were taken simultaneously using the total reflected X-ray for energy calibration.

The sample was inserted in an in-situ electrochemical XAFS cell made of polychlorotrifluoroethylene (PCTFE) with a 2.5-μm-thick polyester membrane as an X-ray window. The electrolyte solution,the counter and reference electrodes were 0.1 M $HClO_4$,a Pt coil, and a reversible hydrogen electrode, respectively. While changing the sample potential, the membrane window was inflated by applying a high enough pressure of the solution to assure ion diffusion. During the XAFS measurements, in contrast, the window was deflated by applying a slightly negative pressure to make the solution layer sufficiently thin between the sample surface and the membrane window. Thus, the sample was not mechanically moved between measurements at different potentials once the total-reflection condition was fixed. The X-ray window was placed under humid N_2 gas using an X-ray transparent cup. The X-ray reflectivity was constantly checked that it only varies within about ±5% at a certain energy.

3 Results and Discussion

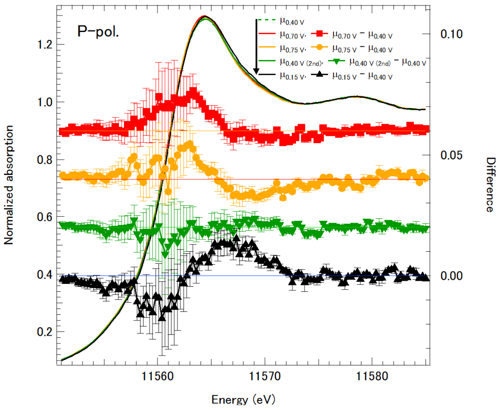

Fig. 1: Normalized XANES spectra at different potentials. The difference spectra $\Delta\mu=\mu_X-\mu_{0.40\ V}$ are also shown with vertical shifts.

Figure 1 shows the potential dependence of the normalized Pt L_3 X-ray absorption near edge structure (XANES) spectra at P polarization with their difference spectra ($\Delta\mu=\mu_X-\mu_{0.40\ V}$) overlaid. The potentials were applied starting from 0.40 V to 0. 70 V, 0.75 V, 0.40 V, and 0.15 V. The Pt surface states at 0.15, 0.40 V, and 0.70-0.75 V correspond to adsorption of hydrogen, double-layer, and adsorption of oxygen species, respectively. Compared to the double-layer potential (0.40 V), an increase in the spectral intensity at around 11564 eV for 0.70 and 0.75 V, and a slight decrease at around 11568 eV for 0.75 V are observe clearly. On the other hand, a broad increase in the spectral intensity centered at 11567 eV is observed for 0.15 V. These characteristics are consistent to the previous XANES spectra observed in Pt nanoparticles [1, 2]. Therefore, it is confirmed that the XAFS information from metal/solution interface in Pt films having limited surface/bulk ratio can be captured by using TRF-XAFS. The feasibility of TRF-XAFS for capturing the surface states of Pt films enables us to directly compare XAFS information with other surface-sensitive measurements, which will help us understand the surface or interface structures comprehensively.

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References

[1] M. Teliska *et al*., *J. Phys. Chem. B* **109**, 8076 (2005).
[2] K. Asakura *et al*., *J. Synchrotron. Radiat.* **6**, 439 (1999).

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