

In Situ XAFS Observation of Platinum Nanoparticle Thin Layer Formed on HOPG Surface: A New Approach to the Carbon Electrode/Electrolyte Interface

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1 Introduction

Platinum are widely used as electrocatalyst of polymer electrolyte fuel cells (PEFCs) because of their high catalytic activity for hydrogen evolution reaction and oxygen reduction reaction. The durability of PEFCs is highly depended on the degradation process of electrocatalysts, although their stabilizing interaction among PtNPs, carbon support and polymer electrolyte are still unclear. Polarization dependent total reflection fluorescence X-ray absorption fine structure (PTRF-XAFS) is the most appropriate technique for the investigation of the local interaction between metal and support. However, the thin electrolyte layer prevents the effective mass transport to the electrode surface and also decreases the incident X-ray intensity. In this study, we carried out a new XAFS set-up where X-ray irradiates the PtNPs from the back side of the highly oriented pyrolytic graphite (HOPG) substrate and fluorescence X-ray was detected at the same side in order to minimize the X-ray absorption by electrolyte (Figure 1). Here we use a bent crystal Laue analyzer (BCLA) to extract desired X-ray energy from the large scattering X-ray generated by light element matrix such as electrolyte and HOPG. We also tested PILATUS detector which has large detection area and low noise to accumulate tiny fluorescence X-ray signal through BCLA.

2 Experiment

Well-defined dodecanethiol-protected PtNPs were

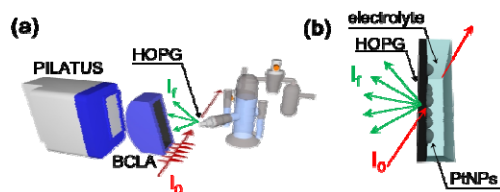


Figure 1. (a),(b) Schematic illustration of backside irradiation configuration under electrochemical condition.

prepared^[1] and deposited on HOPG by spin coating. After spin coating, dodecanethiol layers were removed by electrochemical oxidation-reduction cycles (ORC) treatment in 0.1 M HClO₄ aqueous solution. For XAFS experiment, freshly cleaved HOPG sheet was used as an X-ray window (Figure 1b). The fluorescence signal was extracted from scattering X-ray using BCLA (8.4 keV) and detected by a Ge detector and/or an area detector, PILATUS.

3 Results and Discussion

According to the electrochemical and AFM image, the number of loading platinum atom on the HOPG can be calculated as 3×10^{14} atom·cm⁻², which is well consistent with the concentration derived from PTRF-

XAFS experiment. When the XANES spectrum was measured without BCLA, a background signal caused by scattering from the electrolyte was too strong. Hence it did not give an absorption edge. On the other hand, when BCLA was inserted before the Ge detector, the background signal was remarkably decreased so that good S/B ratio spectra was obtained, although total count was reduced to ca. 1/100 (Figure 2a). In order to increase the number of photon count, we conducted the experiment at high flux undulator beam line with PILATUS. When we used 0.01 mg PtO₂ diluted into 1 mg BN pellet as test sample, we could reconstruct a nice fluorescent XANES spectrum from PILATUS images. However it was found that the intensity of monochromatized X-ray through the BCLA had inhomogeneous distribution. (Figure 2b, inset) due to some defects in BCLA. Improvement of throughput of BCLA is currently in progress.

Acknowledgement

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References

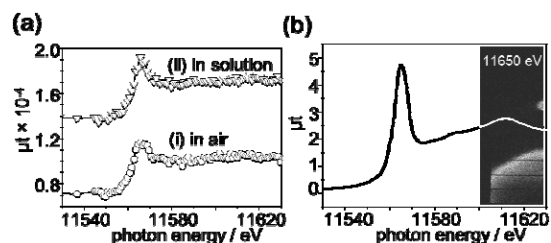


Figure 2. (a) XANES spectra of PtNPs using Ge detector with BCLA. (i) In air and (ii) in electrolyte solution. (b) XANES spectrum of PtO₂ test sample obtained by PILATUS. (inset) fluorescent X-ray intensity images through BCLA obtained at 11650 eV.

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