

## *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 nanoparticles (PtNPs) are widely used as the fuel cell catalyst because of their high electrocatalytic activity such as hydrogen evolution reaction (HER), oxygen reduction reaction (ORR) or methanol oxidation reaction (MOR). However its degradation process and the interaction among carbon substrate, PtNPs and polymer electrolyte are still unclear.

Polarization dependent total reflection fluorescence X-ray absorption fine structure (PTRF-XAFS) shown in Figure 1a is the most appropriate technique for the investigation of interface structure and 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 XAFS was detected in the fluorescence X-ray mode at the same side (Figure 1b) in order to minimize the X-ray absorption by electrolyte and enhance interface effect.

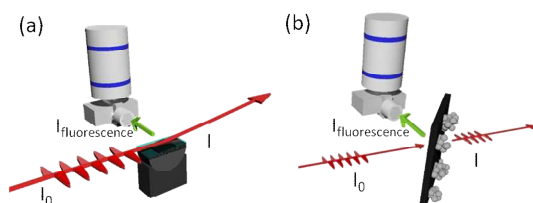


Figure 1 Schematic illustration of (a) PTRF-XAFS configuration and (b) backside irradiation in this study.

### 2 Experiment

Well-defined dodecanethiol-protected PtNPs were prepared according to the literature<sup>[1]</sup> and deposited on the atomically flat HOPG ( $S = 1.44 \text{ cm}^2$ ) by spin coating. After spin coating, dodecanethiol layers were removed by electrochemical oxidation-reduction cycles (ORC) treatment in 0.1 M  $\text{HClO}_4$  aqueous solution. For XAFS experiment, freshly cleaved HOPG sheet was used as an X-ray window (Figure 2a). The fluorescence signal was extracted from scattering X-ray using a BCLA (Bent Crystal Laue Analyzer designed for 8.4 keV) and detected by a 19 elements Ge-detector (Figure 2b).

### 3 Results and Discussion

According to the electrochemical measurement, the electrocatalytic activity of PtNPs for HER was increased with increasing the number of potential cycles (Figure 3a)

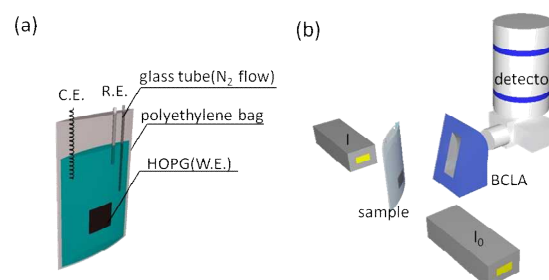


Figure 2 Schematic illustration of (a) sample for *in situ* XAFS measurement and (b) optical configuration with BCLA. C.E. and R.E. are a counter electrode and a reference electrode, respectively.

because of desorption of dodecanethiol layer coated on PtNPs surface. From the cyclic voltamogram (CV), platinum active surface area was calculated as  $0.074 \text{ cm}^2$ . XANES spectra of Pt  $L_3$ -edge were obtained at various electrode potential although background signal caused by scattering from the electrolyte was increased (Figure 3b). However, BCLA reduced the most of the undesired scattering X-ray and we could get good S/B ratio spectra. The result indicated that the thin HOPG sheet could be

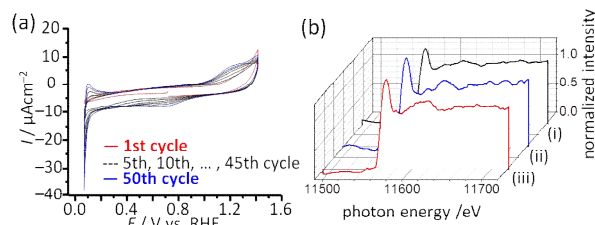


Figure 3. (a) CVs of PtNPs on HOPG in 0.1 M  $\text{HClO}_4$ . (b) XANES spectra recorded at various electrode potential; (i)  $E = 0.2 \text{ V}$  (before ORC treatment), (ii)  $E = 0.2 \text{ V}$  (after ORC treatment), (iii)  $E = 0.05 \text{ V}$  (after ORC treatment).

used for an X-ray window and polarization technique was applicable to the studies of PtNPs on HOPG.

#### Acknowledgement

The work is supported by NEDO project of PEFC project.

#### References

- [1] C. Dablenmont, P. Lang, C. Mangeney, J.-Y. Piquemal, V. Petkov, F. Herbst, and G. Viau, *Langmuir* **24** (2008) 5832.

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