

In-situ PTRF-XAFS study on ultrathin layer Pt on Au(111)

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1 Introduction

Platinum has been proved to possess an outstanding catalytic property in fuel cell technology, especially in Oxygen Reduction Reaction (ORR) occurring at the cathode of the fuel cell system. However, the high price of Pt has greatly limited the wide spreading of PEMFCs. Some reports have revealed that the core-shell (Pt@M) structure not only increases the utilization of Pt even up to 100%, but also enhances the specific activity^[1]. In Pt@Au core-shell nanocluster, shorter Pt-Pt distances were found^[2] though the Pt-Pt distance was suggested to be elongated and to have the same as Au-Au on Pt on Au(111) single crystal surface in our previous studies.^[3] But the Pt on Au(111) system was the mixture of Pt monolayer and [PtCl₂]_n structures so that the Pt-Pt distance was not so clearly determined in the previous work. In order to confirm the Pt-Pt distances were really longer on Au(111) surface we prepared flat sub monolayer Pt on Au(111) and we carried out *in-situ* electrochemical polarization dependent total reflection fluorescence X-ray absorption fine structure spectroscopy (*in-situ* EC-PTRF-XAFS) for model catalyst system of Pt/Au(111) with a well-defined surface.^[4]

2 Experiment

Before Pt deposition experiment, Au(111) was annealed by butane gas to reveal the characteristic surface. A sub monolayer (subML) Pt species was deposited by a so-called Cu underpotential deposition (Cu UPD) and Surface Limited Redox Replacement (SLRR)^[3]. The freshly prepared Pt_{subML}/Au(111) sample was set on a homemade electrochemical (EC) cell with 0.1 M HClO₄ filled. All above-mentioned operation was carried out in a N₂-filled glovebox. The *in-situ* EC-PTRF-XAFS of Pt L₃ edge was measured at BL12C using a Si(111) double crystal monochromator. Total reflection condition was adjusted by a 5-axis goniometer. The fluorescence signal was detected by a 7 channel SDD. Due to the interference coming from the Au L₃ edge, the measurement had to stop at $k = 7 \text{ \AA}^{-1}$.

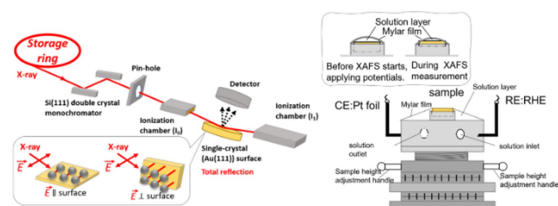


Fig.1 (Left) *In-situ* EC-PTRF-XAFS apparatus. (Right) details of *in-situ* EC cell.

3 Results and Discussion

Figure 2 shows Pt L₃ edge XANES spectra at reduced condition (+0.4 V vs RHE) which had a slightly higher white line (WL) compared to that of Pt foil. Pt 4f XPS suggested the main species was metallic species as shown in Fig.3. To determine the Pt-Pt bond distance, the constrained thorough search analysis(CTS) was carried out for both s- and p-polarization^[5-7] using the model structure of monolayer Pt on Au (111) as shown in Fig.4. Figure 5 shows the CTS results and experimental data. The Pt-Pt bond distance was confirmed to be 2.88 Å. This is due to the epitaxial growth of Pt monolayer on Au.

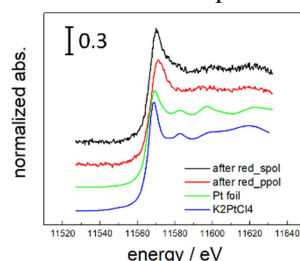


Fig.2 Pt L₃ edge XANES spectra.

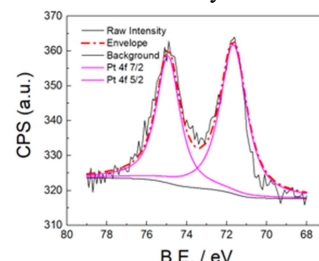


Fig.3 XPS for subML Pt/Au(111) sample.

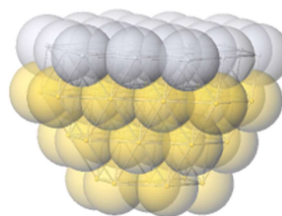


Fig.4 Pt₁₉/Au(111) model.

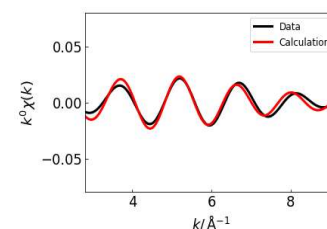


Fig.5 thorough-search result in s-pol.

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References

- [1] Oezaslan *et al.*, *J. Phys. Chem. Lett.* **4**, 3273(2013).
- [2] B.Hu *et al.*, *J.Phys.Chem.C* **126**, 1006-1016 (2022).
- [3] Q. Yuan *et al.* *J. Phys. Chem. C* **122**, 16664 (2018).
- [4] S. Takakusagi *et al.*, *Top. Catal.* **56**, 1 (2013).
- [5] D. Kido *et al.* *Acc. Mater.Surf. Res.*, **5**, 148(2020).
- [6] D.Kido *et al.* *e-J Surf.Sci.Nanotech.* **18**, 249(2020).
- [7] D.Kido *et al.* *Chem.Lett.*, **51**, 538(2022).

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