

In-situ PTRF-XAFS study on Pt_{subML}/Au(111) model catalyst

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1 Introduction

Platinum possesses an outstanding performance in oxygen reduction reaction (ORR) occurring at the cathode side of polymer electrolyte membrane fuel cell (PEMFCs) systems. Nevertheless, the high price of the Pt has tremendously limited the wide spread of PEMFCs. The PtM (M=other metals than Pt) bimetallic catalysts have shown great potential since better utilization of Pt and higher ORR catalytic activity can be achieved [1]. The discussion on Pt-Pt bond distance effect on ORR activity in PtAu bimetallic system, whether the longer or shorter bond distance contributes to the ORR activity are still controversial. In order to investigate how the Pt-Pt bond distance affects the ORR activity, we used a model catalyst in this work, where a flat Pt submonolayer (ML) was deposited on a well-defined Au (111) surface and carried out the structure investigation by an *in-situ* electrochemical polarization dependent total reflection fluorescence X-ray absorption fine structure (EC-PTRF-XAFS) spectroscopy [2] as shown in Fig.1.

2 Experiment

A well-defined Au(111) substrate was used for the preparation of the model catalyst. A subML Pt was deposited via surface limited redox replacement (SLRR) reaction with UPD Cu ML. The freshly prepared Pt_{subML}/Au(111) sample was set on the home-made *in situ* cell as shown in Fig.1 The *in-situ* EC-PTRF-XAFS measurement was carried out in BL-12C using a Si(111) double crystal monochromator. The total reflection condition was adjusted by a 5-axis goniometer. The fluorescence signal was detected by a 7-channel SDD. Before XAFS measurement started, the sample was reduced in the *in situ* cell.

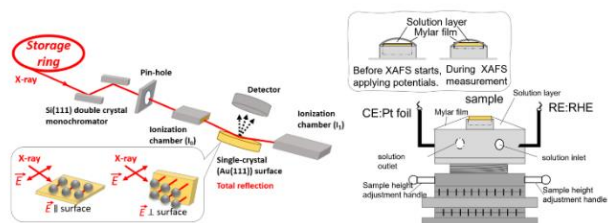


Fig.1 (Left) *In-situ* EC-PTRF-XAFS apparatus. (Right) details of *in-situ* EC cell.

3 Result and Discussion

Figure 2 shows the EXAFS oscillation ($\chi(k)$) in the two polarization directions (electric vector \vec{E} || surface called as

s-pol and $\vec{E} \perp$ surface called as p-pol). The $\chi(k)$ for both directions showed a more comparable wavelength to that of Au foil instead of Pt foil, which indicated the Pt-Pt bond distance might be expanded in this model catalyst system. A constrained thorough search (CTS)^[3,4] and Feff8 theoretical simulation were carried out to precisely determine the Pt-Pt bond distance using a model structure of Au(111) supported Pt sub-monolayer model, the fitting parameters such as Pt-Pt bond distance as well as the Pt sub-monolayer size (Pt₇, Pt₁₉, Pt₃₇, etc) were changed. Figure 3 shows the best simulation result at Pt₁₉/Au (111) model by setting the Pt-Pt bond distance at 2.88 Å, which well reproduced the experimental simulation feature. The Pt-Pt bond distance was proved to be expanded to that of Au-Au bond distance in Au foils. This is due to the lattice constant difference between the Pt and Au, the strain effect induced by the underlying Au(111) substrate.

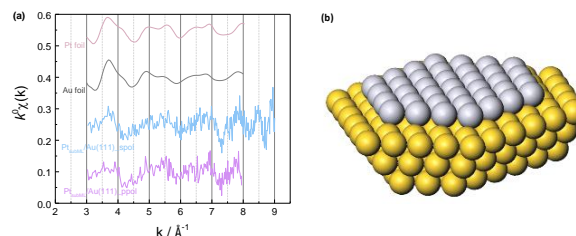


Fig.2 (a)EXAFS oscillation for Pt_{subML}/Au(111) model catalyst at different polarization directions compared to Pt foil and Au foils. (b)Pt₁₉/Au(111) model.

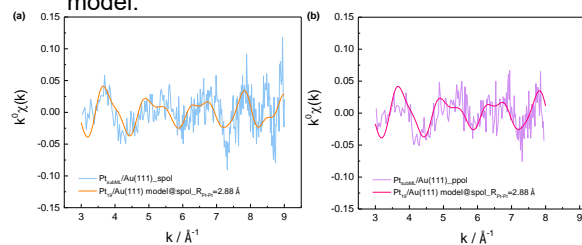


Fig.3 Model simulation using Pt₁₉/Au(111) model at (a)-s-polarization and (b)p-polarization, Pt-Pt bond distance = 2.88 Å.

Related ORR catalytic activity measurements for this model catalyst system are under preparation. It is possible to elucidate how the Pt-Pt bond distance affects the ORR activity.

Acknowledgment

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