An in-situ PTRF-XAFS Investigation into Self-terminated Pt Deposition on Au(111)

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\textbf{1 Introduction}

It has been proved that core-shell catalyst could be one of the feasible directions in polymer electrolyte fuel cell (PEFC) designs [1]. Many efforts have been made to develop catalysts with uniform core-shell structure with noble metal like Pt as shell to improve the stability as well as activity [2]. Displacement methods were used for a long time as surface decoration method using noble metals [3]. However, it was later found that the Pt shell was not perfectly formed, as multi-layer islands were formed on the core material instead of a homogeneous shell [4]. This would further cause problems including the core material out-leaching and the stability decrease.

In our study, we deposited Pt on Au using self-terminating deposition method [5], which could result in a more uniform 2D Pt coverage on the Au surface. To further understand the catalyst activity of this monolayer Pt covered Au surface, it is necessary to first understand its structure, like Pt-Pt and Pt-Au bond length, and electronic structure change under in-situ condition using model structure like single crystal to exclude other complicating factors like the inhomogeneity of the substrate. Here we used in-situ polarization dependent total reflection fluorescence (PTRF) XAFS, which can provide the three dimensional(3D) structures of metals highly dispersed on the flat surfaces.

\textbf{2 Experiment}

2D Pt layer was deposited on the Au(111) surface following the H-terminated deposition protocol [5]. A -0.7 V vs Ag/AgCl potential was applied on a Φ15mm Au(111) single crystal electrode in 0.5 M NaCl + 3 mM H\textsubscript{2}PtCl\textsubscript{4} for 5 s with RPM of 400, then transferred into the in-situ PTRF-XAFS cell which was described previously [7] for XAFS measurements. Experiment was conducted at BL9A and BL12C, PF. We use a 19-element Ge MSSD (Canberra) as fluorescence detector. A Zn filter (μt=3) was used to remove the elastic scattering from the electrolyte.

\textbf{3 Results and Discussion}

At 0.45 V, where there was no adsorptions of H nor OH on the Pt surface, s- and p-polarization EXAFS spectra were shown by black curves in Fig.1b, c). The oscillation basically followed that of Pt metal, indicating that the Pt deposit on the Au surface mainly existed in the form of Pt metal. Based on the EXAFS spectra, we proposed a 2D Pt layer on Au(111) with the thickness of 2 atomic layer height, as shown in Fig. 1a), with blue atoms indicating Pt and yellow ones of Au. The resulted EXAFS simulation were shown by red curves in Fig.1 b, c). This structure were also consistent with STM results.

Fig. 1: a) proposed model structure. b) EXAFS oscillation of Pt/Au(111) at 0.45 V, s-polarization. c) EXAFS oscillation of Pt/Au(111) at 0.45 V, p-polarization.

\textbf{References}


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