

XAFS Study of Structure of Pt Monolayer Prepared by Galvanic Displacement Reaction

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1 Introduction

Pt is a material of fundamental importance in the electrocatalyst design for polymer electrolyte fuel cells (PEFCs). Electrodeposition advances other varieties of methods for Pt thin film deposition, such as MBE, PVD and so on in the standpoint of view of its simple process, no requirement of UHV environment and lower cost. Moreover, electrochemical atomic layer deposition (E-ALD) [1] was one of the most promising electrodeposition methods to achieve 2D growth of Pt though 3D Pt clusters were created by the other method. E-ALD could be applied in growth of a wide range of materials not only Pt but also other metals like Ru, Ag, Cu etc.[2] However, as the fundamental step in E-ALD growth of Pt, galvanic displacement using underpotentially deposited Cu or Pd as the sacrificial layer, has not been fully understood regarding the structure and the electronic state of the Pt monolayer, which plays important role in their application as electrocatalyst. Polarization dependent total reflection fluorescence X-ray absorption fine structure (PTRF-XAFS) is ideal for atomic flat, low coverage surface[3].

2 Experimental

A $\phi 15$ mm Au(111)(5 mm thick) single crystal (SPL) was used as substrate. The Au(111) was electrochemically polished and flame-annealed and then transferred into an Ar filled glovebox for further deposition. A monolayer of Cu was underpotentially deposited and then replaced with Pt by immersing the sample into 0.1 M HClO₄ + 1 mM H₂PtCl₆ for 30 s. Sample was then transferred to the in-situ XAFS cell [4]. 6 μ m Mylar film was used as X-ray window. The XAFS cell was assembled inside the glovebox, and then transferred to a 5-axis goniometer for total reflection adjustment. XAFS spectra were measured at BL12C and BL9A, PF. A 19-element Ge solid state detector (MSSD; Canberra) was used as the fluorescence detector. A Zn filter ($\mu t = 3$) was placed in front of the MSSD to remove the elastic scattering from the solution and Au substrate.

3 Results and Discussion

Figure 1 showed the EXAFS of Pt monolayer obtained from displacement reaction in both s- and p-polarizations. FEFF analyses showed that [PtCl₄] was the main species

as shown in Fig.2. Moreover, electrochemical measurement revealed that the surface was a mixture of Pt metal and Pt complex. Electrochemical analysis gave the percentage of 70 %. The XAFS spectrum could fit well when a small amount of Pt metal was present with the PtCl₄²⁻. Setting significance level to 0.05, the acceptable lower percentage of complex was 70%. Thus we concluded that 70% was PtCl₄²⁻ with 30 % Pt metal.

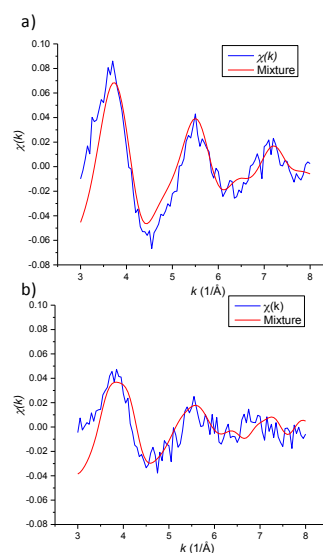


Figure 1: EXAFS comparison between experimental data and FEFF calculation the mixture model. a) s-polarization b) p-polarization.

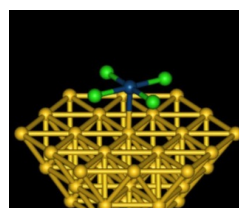


Figure 2: [PtCl₄] with square planar structure that parallel to the Au(111) surface, with Pt adsorbed on top on Au.

References

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