

A XAFS Investigation into the Pt Monolayer deposited from Surface-Limited Redox Reaction

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1 Introduction

The 2D monolayer catalysts obtained by surface-limited redox replacement (SLRR) reaction have found wide applications in fuel cell technology [1]. Their properties are very dependent on the morphology of the catalyst monolayers, i.e., the size/shape and structure of 2D nanoclusters constituents of the catalyst monolayer [2]. This renders the need for better understanding of all processes involved in catalyst synthesis via SLRR including underpotential deposition (UPD) and catalyst nucleation. In order to characterize the surface morphology we carried out PTRF-XAFS (Polarization dependent total reflection XAFS) and found a new structure different from that previously reported.

2 Experiment

Pt L3 edge PTRF-XAFS measurements were performed at BL12C in Photon Factory, IMSS (Institute for Material Structure Science)-KEK (High Energy Accelerator Research Organization), with Si(111) as monochromator and a 19-element Ge solid state detector (SSD) as fluorescence detector. A homemade polychlorotrifluoroethylene (PCTFE) cell, with a 0.6 μm Mylar film as an X-ray window was used for the in-situ PTRF-XAFS measurement. The cell was mounted on a six-axis goniometer to allow fine adjustment for the total reflection conditions. The sample was retraced away from the Mylar film and kept at desired potential to allow electrochemical treatment. For XAFS measurement, sample was pushed against the Mylar film to minimize solution amount between the sample and Mylar film since the irradiation of the solution causes the elastic scattering to reduce S/N. When changing the electrochemical condition, the sample was retracted from the Mylar window to allow enough electrolytes for the electrochemical reaction. A Zn filter ($\mu\text{t}=3$) was placed in front of the SSD to cut the elastic scattering. The electrolyte was deaerated with N_2 in a sealed bottle outside of the cell and circulated during the whole measurement. A 99.999% Pt wire (Nilaco) and RHE (Reversible hydrogen electrode) was used as CE (counter electrode) and RE (reference electrode), respectively. CE and RE are set in separated holders and shield with Pb plates to remove Pt fluorescence of the CE and RE.

3 Results and Discussion

Fig.1 shows the XANES white line (WL) intensity of s and p polarized Pt/Au(111) and its comparison with Pt

foil, K_2PtCl_4 and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ measured at transmission mode. WL intensity was calculated by subtracting an arctangent background and fitting WL with Gaussian shape. The intensity of s-polarization at 0.3 V are in between of Pt(II) and Pt(IV), showing that the Pt monolayer was not reduced to Pt^0 . This is quite a surprising result, that Cu_{UPD} should be oxidized while $\{\text{PtCl}_6\}^{2-}$ being reduced to Pt^0 according to the stoichiometry of galvanic replacement reaction.

k^3 -weighted EXAFS oscillations and their Fourier transform for the 0.3 V sample are shown in Fig. 2. For s-polarization at 0.3 V, Curve fitting analysis showed the presence of Pt-Cl at $2.25 \pm 0.02 \text{ \AA}$ with the 95% confidence interval, indicating the Pt-Cl complexes on the surface. Preliminary fitting for p-pol EXAFS indicated the presence of Au. Further details are now being analyzed. $\pm 0.02 \text{ \AA}$

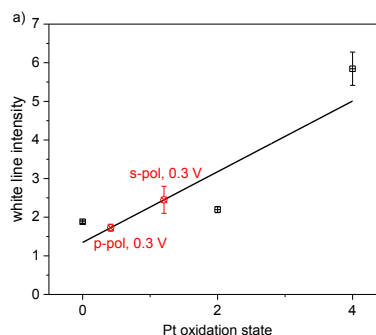


Fig.1 XANES WL intensity comparison between the Pt monolayer at $E=0.3 \text{ V}$ (s- and p-polarization) with standard reference Pt foil and Pt complex (K_2PtCl_4 and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$).

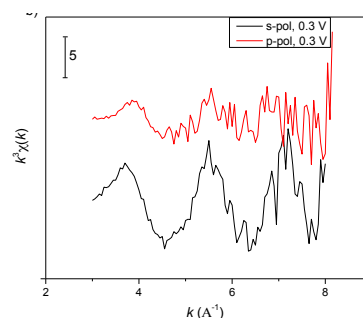


Fig.2 Pt L3 edge EXAFS comparison of s and p polarization of Pt monolayer at 0.3 V with k weight = 3

References

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