

In situ Structural Study on Ag/AgCl Reaction at Ag UPD Layer Formed on Au(111) Using EQCM, STM, and SXS Techniques

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Introduction

Ultra-thin layer of a metal formed on a foreign metal substrate is one of the most important materials not only for fundamental surface science but also for various industrial applications. Thus, underpotential deposited (UPD) layer has been one of the central issues of surface electrochemistry in the last two decades. We have also investigated the Pd, Pt, and Ag UPD layers on Au single crystal electrodes using electrochemical quartz crystal microbalance (EQCM), scanning tunneling microscopy (STM), and surface X-ray scattering (SXS) [1-3]. In this report, Ag/AgCl reaction at the UPD Ag layer on Au(111) was structurally investigated using *in situ* EQCM, STM, and SXS.

Results and Discussion

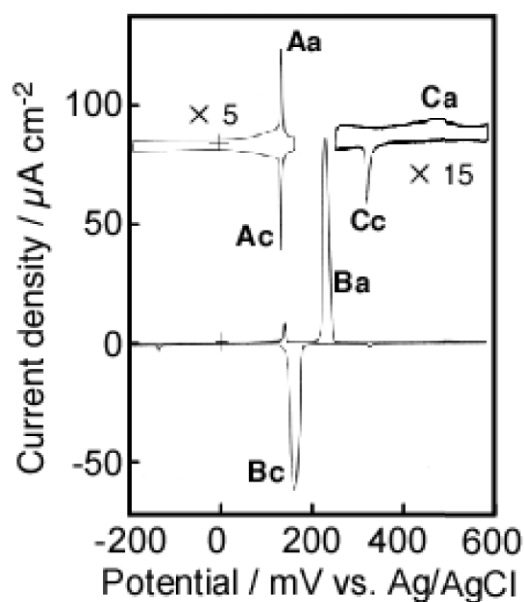


Figure 1. CVs of Ag UPD ultra-thin layer formed on Au(111) measured in 2 mM NaCl + 50 mM H₂SO₄ with a scan rate of 5 mV s⁻¹.

Figure 1 shows a cyclic voltammogram (CV) of the UPD Ag layer prepared on the Au(111) electrode measured in the electrolyte solution containing 2 mM Cl⁻. Relatively sharp and large anodic and cathodic peaks (**Ba/Bc**) were observed at 230 mV and 180 mV (vs. Ag/AgCl), respectively. Because these peak potentials

linearly depended on the concentration of Cl⁻ in the electrolyte solution, these anodic and cathodic peaks (**Ba/Bc**) can be assigned to be due to chlorination and dechlorination reactions, respectively. Small spikes (**Aa/Ac**) observed around 100 mV were assigned to be due to Cl⁻ physisorption by EQCM data and previous reports. Relatively small and broad peaks (**Ca/Cc**) observed around 450 mV were assigned to be due to the change of the surface atomic arrangements by the followings.

SXS data shows that the pseudomorphic Ag bilayer was still remained on Au(111) just after dipping the electrode at -200 mV. At 350 mV, which was slightly more positive than that of **Ba/Bc**, STM and SXS (Fig. 2) data showed that AgCl monolayer with a ($\sqrt{13} \times \sqrt{13}$)R13.9° structure was formed on Au(111).

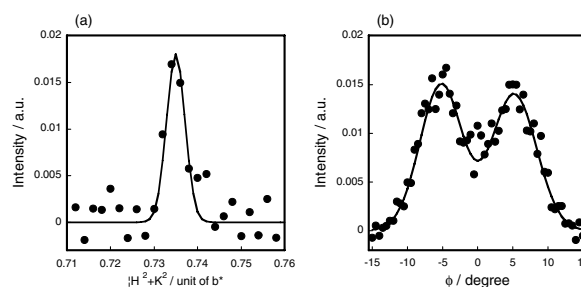


Figure 2. In plane diffraction profiles of Ag UPD on Au(111) measured in 2 mM NaCl + 50 mM H₂SO₄ at 350 mV along (a) the direction of K (at H = 0 and L = 0.2) and (b) the φ direction (φ = 0° at (H K L) = (0 0.735 0.2)). Solid lines represent the curves fitted by Gaussian.

At 500 mV, which was more positive potential, in plane structure of AgCl monolayer was changed to be a (4×4). When the potential was made more negative than **Ba/Bc**, the Ag monolayer was observed by SXS and then these structural changes were reversibly observed. Dynamic of these structural changes were also investigated.

References

- [1] K. Uosaki et al., J. Phys. Chem. 101, 7566 (1997).
- [2] M. Takahashi et al., Surf. Sci. 461, 213 (2000).
- [3] T. Kondo et al., J. Electroanal. Chem. 532, 201 (2002).

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