

In situ Structural Studies on Ag/AgCl Reaction at the Underpotentially Deposited on the Au(111) Electrode Surface

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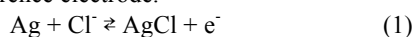
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Introduction

To fully understand the mechanisms of electrochemical reactions and to apply these reactions to modern nanotechnology such as fuel cells, sensors, and molecular devices, it is very important to know the structures at the electrode/electrolyte interfaces in situ in real time with an atomic resolution. It is also well-known that physical and chemical properties of an ultrathin metal layer on a foreign substrate are different from those of the bulk metal [1,2]. The establishment of preparation methods of ultrathin metal films with ordered structures and understanding of the origin of their unique physical and chemical properties are very important for both fundamental science and industrial applications. For example, we have studied the structure of an underpotentially deposited (UPD) Ag ultrathin layer on a Au(111) surface using in situ surface X-ray scattering (SXS) technique and proved that the UPD Ag layer on Au(111) is pseudomorphic mono- and bi-layers at 50 and 10 mV (vs. Ag/Ag⁺), respectively [3], and the structure of the Ag bilayer is intact even after the circuit was disconnected and the surface exposed to ambient atmosphere [4].

Ag/AgCl reaction (Eq. (1)) is one of the most fundamental reactions in electrochemistry and is a basis for a Ag/AgCl reference electrode.



Moreover, the silver halides have been playing an important role in photography. There are, however, no reports about Ag/AgCl reaction at an atomic level, although several structural studies on a Cl monolayer on a Ag single crystal surface with an atomic dimension are available. This is because when potential is made positive so that the chlorination reaction (forward reaction of Eq. (1)) proceeds at the Ag single crystal electrode, the reaction takes place not only at the surface but also at the bulk, and the aggregates of AgCl clusters, in which atomic arrangements should be random, are formed. Furthermore, the electrochemical reduction of AgCl does not result in an atomically flat single crystalline Ag surface.

Here, we were able to investigate the Ag/AgCl reaction at an atomic level for the first time by using the Ag bilayer prepared by UPD on Au(111) (Ag(2ML)/Au(111)) as a substrate. Electrochemical quartz crystal microbalance (EQCM), scanning tunneling microscopy (STM), SXS, and electrochemical techniques were used [5].

Experimentals

Prior to Ag UPD, the Au(111) disk electrode was annealed using a Bunsen burner and quenched in ultrapure water. Only the (111) face was contacted to a deaerated 50

mM H₂SO₄ containing 1 mM Ag₂SO₄ while keeping the potential at +700 mV (vs. Ag/Ag⁺). The Ag UPD bilayer on the Au(111) electrode was electrochemically prepared by scanning the potential from +700 to +10 mV with a scan rate of 5 mV s⁻¹. After that, the surface was rinsed and set to the SXS cell. In situ SXS measurements were carried out in 50 mM H₂SO₄ containing a given amount of NaCl at a several electrode potentials in BL4C at Photon Factory.

Results and Discussion

From the results of EQCM, STM, and SXS, we concluded as follows; Ag bilayer was anodically converted to AgCl when the potential more positive than +230 mV (vs. Ag/AgCl), at which the anodic current peak due to the chlorination was observed, was applied. The formation of AgCl clusters and the AgCl monolayer of ($\sqrt{13} \times \sqrt{13}$)R13.9° structure, although the former and the latter were formed slowly and very slowly, respectively. The AgCl monolayer of ($\sqrt{13} \times \sqrt{13}$)R13.9° structure was transformed to the AgCl monolayer of (4×4) structure when the potential more positive than +480 mV, at which a very broad anodic current peak was observed, was applied for prolonged time. The AgCl monolayer of (4×4) structure was returned to the AgCl monolayer of ($\sqrt{13} \times \sqrt{13}$)R13.9° structure when the potential became more negative than +330 mV, at which a sharp cathodic current peak was observed. Both AgCl clusters and the AgCl monolayer of the ($\sqrt{13} \times \sqrt{13}$)R13.9° structure disappeared, and the Ag monolayer, not bilayer, was formed on the Au(111) surface when the potential became more negative than +180 mV, where a very large cathodic peak was observed.

In the sequent potential cycling between 0 and +600 mV, the conversion of Ag monolayer \rightleftharpoons AgCl cluster + AgCl monolayer of ($\sqrt{13} \times \sqrt{13}$)R13.9° \rightleftharpoons AgCl cluster + AgCl monolayer of (4×4) took place repeatedly.

References

- [1] G. A. Somorjai, "Surface Chemistry and Catalysis", Wiley, New York (1994).
- [2] H. Naohara et al., J. Electroanal. Chem., 500, 435 (2001).
- [3] T. Kondo et al., J. Electroanal. Chem., 532, 201 (2002).
- [4] T. Kondo et al., Electrochem. Commun., 11, 804 (2009).
- [5] K. Uosaki et al., J. Phys. Chem. C, 115, 12471 (2011).

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