Electrochemical STM Observation of Well-ordered Adsorbate on Cu(111) Electrode Surfaces in an Alkaline Electrolyte

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(Received June 1, 1998; CL-980417)

Electrochemical scanning tunneling microscopy revealed two kinds of periodical structure of bright spot on Cu(111) electrode surfaces in NaOH aqueous solutions. These structures show the arrangement of the CuOH surface species formed by the reduction of subsurface oxygens.

Redox behavior of copper surfaces in aqueous solution is of great interest in many industrial fields, such as energy, catalytic, and microelectronic applications. The vital importance of the chemistry of immersed copper surfaces has resulted in many characterization studies of copper surfaces in solutions using a variety of techniques, such as electrochemisty[1,2] and spectroscopy.[3-5] Such studies revealed that surface oxygen is not entirely removed from copper electrode surfaces even at the potential corresponding to the onset of hydrogen evolution.[3-5] These oxygen-containing adlayers on metal surfaces were previously considered active for catalytic reactions in both gas and liquid phases. For example, subsurface oxygen is catalytically active site for the formation of formaldehyde from methanol and oxygen on Ag catalysts.[6] Furthermore, subsurface oxygen is necessary for the epoxidation of ethylene over the surface of a Ag catalyst.[7] The mediating hydrous oxide species are considered active species for oxidation of organic molecules on Cu and Pt surfaces.[1,8] Thus, the structure of this overlayer is very interesting from the catalytical point of view.

Compared with the information about copper surfaces in gas phase, however, that in liquid phase is scarce. Subsurface oxygen on copper surfaces in liquid was characterized as a three-fold hollow site by in-situ X-ray standing-wave analysis.[9] Wong et al.[4] revealed by using surface second harmonic generation (SHG) method that oxygen containing species on Cu(111) surface formed ordered overlayer.[4] The recent development of electrochemical STM (EC-STM) and electrochemical AFM allowed real space characterization of copper electrode surface at atomic resolution.[10-12] In this study, we investigated the structure of Cu(111) electrode surfaces that have an oxygen-containing adlayer by using electrochemical STM (EC-STM).

A single crystal of Cu(111) (99.999%, ca. 8 mm in diameter and 1 mm in thickness) was used as the working electrode. The crystal was mechanically polished with Al_2O_3 powder and then electropolished in a HNO_3/CH_3OH solution (30 ml HNO_3 +70 ml CH_3OH) at about 500 mA for 3 min at room temperature. Both the electropolishing and transfer of the samples into the STM cell were done in a nitrogen atmosphere in a glove box. The EC-STM measurements were done using a PicoSPM (Molecular Imaging Co.) and Nanoscope IIIa control station (Digital Instruments, Santa Barbara, CA). Both the reference and counter electrodes were Pt wires. The electrolyte was a 0.01mol dm^{-3} NaOH aqueous solution. The potential of the Pt quasi-reference electrode was calibrated against an Ag/AgCl (saturated NaCl) electrode. All potentials are reported with respect to an Ag/AgCl electrode. Before the EC-STM measurements, flat terraces on the electrode surface were attained by cycling the potential sweep between -0.50 V and -1.10 V (3 times) and then holding the potential at a level more negative than -0.90 V. To minimize surface roughness, the potential of the electrode was always kept below that for Cu_2O and $Cu(OH)_2$ formation.[11] The STM tip was made of Pt-Ir wire, and its side-walls were coated with an apiezon wax.

A cyclic voltammogram (Figure 1) showed cathodic peaks at around -0.58 V and -0.90 V, and their anodic counterparts at -0.53 V and -0.68 V, respectively. An anodic peak at -0.53 V was considered either metal dissolution or dissolution of mediating Cu(I) hydrous oxide species at the metal/solution interface.[1] The top layer of the flat terraces (the height of a terrace was 0.21 ± 0.01nm.) dissolved when the potential exceeded -0.53 V and reproduced when it fell below -0.58 V. A cathodic peak at -0.90 V was considered as the formation of CuOH surface species ($CuOH_{surf}$), according to a study that used in-situ surface-enhanced Raman spectroscopy (SERS).[3] Burk et al.[3] proposed that the process leading to $CuOH_{surf}$ formation is proton (water) reduction on oxygenated copper according to

$$Cu^*(O)_{ad} + H^+ + e^- = CuOH_{surf} \quad (1)$$
$$Cu^*(O)_{ad} + H_2O + e^- = CuOH_{surf} + OH^- \quad (2)$$

where $Cu^*(O)_{ad}$ is oxygenated copper characterized as subsurface oxygen. Regrowth of a subsurface oxygen must occurred at an anodic peak of -0.68V .

Figure 2 shows an EC-STM image of a Cu(111) surface in 0.01mol dm^{-3} NaOH aqueous solution at a potential of -0.95 V where $CuOH_{surf}$ is formed according to equetion (1) or (2). This image shows two kinds of periodical structure of bright spot:

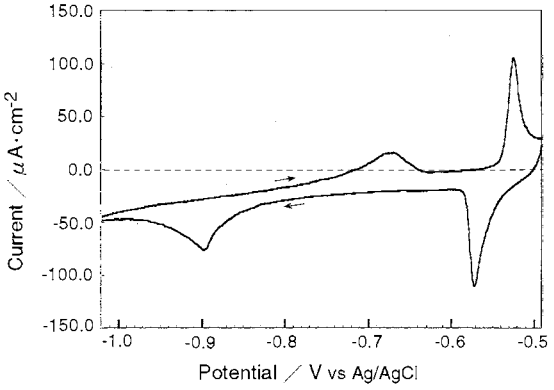

Figure 1. Cyclic voltammogram (-1.2 V to -0.5 V vs Ag/AgCl, 20 mV s^{-1}, commencing at cathod limit.) of a Cu(111) electrode in a 0.01mol dm^{-3} NaOH aqueous solution.

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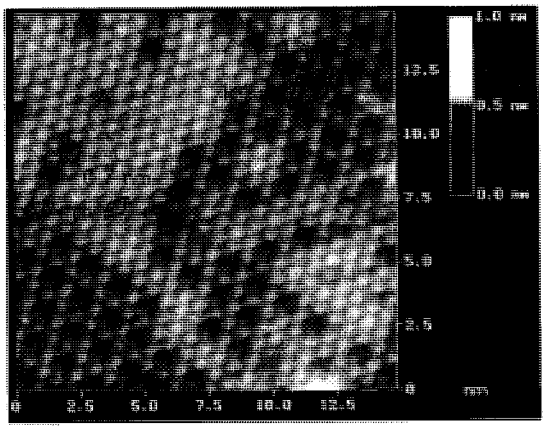

Figure 2. EC-STM image of a Cu(111) surface at a potential of -0.95 V vs.Ag/AgCl. The voltage bias of the tip is +0.67 V and the tunnelling current is 560 mA. The unit cell of structure B is twice as large as that of structure A.

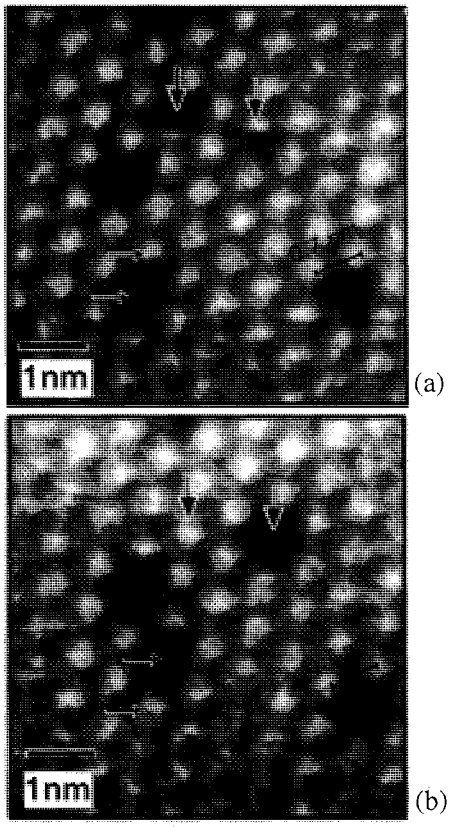

Figure 3. EC-STM images of a Cu(111) surface at a potential of -0.95 V vs.Ag/AgCl. The voltage bias of the tip is +0.67 V and the tunnelling current is 560 mA. The tip was moved from left to right for each scan and downward for another line-scan. Image (b) was recorded at 53 s after the image (a). Translation of a dark spot occurred during a line-scan (indicated by large arrows). An another dark spot shifted during the image (a) and (b) (indicated by small arrows).

hexagonal lattice with spacing of 0.70±0.03 nm ("structure A" indicated by A in Figure 2) and rhombic lattice with spacing of 1.40±0.03 nm ("structure B" indicated by B in Figure 2). The unit cell of structure B is twice as large as that of structure A. The value of 0.70 nm is about 2.9 times lager than the spacing of bare Cu(111) surface (0.26nm).[10,11] Both structures disappeared immediately when the potential was swept to -0.65 V where subsurface oxygen are formed, but reappeared when the potential returned to -0.95 V. Diffuse spots could be seen in the structure B. Because these diffuse spots change their position dependent on the direction of a line-scan of the tip on the surface, we consider these are an artifact caused by the tip.

Based on a previous SERS study,[3] these ordered surface species revealed by the EC-STM images are assigned to $CuOH_{surf}$. Figure 3 shows the shift of the dark spots in structure A. The shift of the dark spot during a line-scan was clearly imaged in figure 3(a) (indicated by large arrows). An another dark spot at the lower left also shifted (indicated by small arrows of figure 3). The shifts of the dark spots seem to suggest that structure B is formed by the extraction of $CuOH_{surf}$ or the adsorption of water molecules in structure A under the condition not to extract or adsorb nearest two sites. More detailed analyses about both structures is in progress in our laboratory.

This work was performed by Mitsui Chemicals Inc. as a part of a research and development joint project on civil industrial technology consigned by the New Energy and Industrial Technology Development Organization (NEDO).

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