Understanding the copper underpotential deposition process at strained gold surface

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ARTICLE INFO

ABSTRACT

Copper underpotential deposition (UPD) on a gold surface is investigated by cyclic voltammetry coupled with *in situ* cyclic strain to understand the strain-modulated electrodeposition. Our work emphasizes quantification of an electrocapillary coupling coefficient ς, which relates the response of Cu electrodeposition potential, E, to applied strain, ε. The different responses to the strain are observed at two Cu UPD stages. The data indicate that tensile strain could enhance the formation of a Cu monolayer on the Au surface. The typical electrodeposition process could be modulated by an external mechanical strain.

1. Introduction

The past decades have seen a great interest in the electrocapillary coupling of electrochemistry and surface mechanics at the metal-electrolyte interface [1–4]. Recent studies suggest that mechanical stress or strain could modulate conventional electrode processes of interest [5–8]. For example, mechanical strain has been experimentally demonstrated as a tool to tune the reactivity and selectivity of electrode surfaces [9–11]. The tension or compression at a surface layer could increase the (electro)-catalytic activity of the active component [12–14]. The coupling strength between the mechanical strain and the electrode process is generally described and quantified by a coupling coefficient, ς, which is defined *via* $\varsigma = \mathrm{d}E/\mathrm{d}\varepsilon|q$ [15–17], where E denotes electrode potential, q is superficial charge density, and ε is a tangential strain variable. The determination of ς could reflect the impact of surface strain on electrode processes. The magnitude and sign of ς strongly depends on electrode materials and electrochemical processes [7–9,18–20].

A lock-in technique, dynamic electro-chemo-mechanical analysis (DECMA), has been recently explored to probe ς values during different electrode processes, *e.g.*, during the pseudo-capacitive charging process [19,21], as well as the electrosorption of oxygen and hydrogen species [7–9]. During the electrosorption process for hydrogen and/or oxygen species, surface expansion (tensile strain) is favorable for the adsorption [7,11,22]. However, there is no direct ς data available during the metal underpotential deposition (UPD) process, which is one of the most

important and interesting topics in electrochemistry. Cu UPD on Au (111), a model UPD system, has been investigated and characterized by many modern analytical techniques in surface science [23–42]. Herein, we report the investigation Cu UPD on a cyclically strained Au surface, with emphasis on the quantification of the coefficient ς.

2. Material and methods

The working electrode is 50 nm thin Au layer, sputtered unto the polyimide substrate (Upilex, UBE), with 2 nm Ti layer for better adhesion. A platinum wire is used as the counter electrode. The electrode potential is measured *versus* the commercial Ag/AgCl reference electrode (World Precision Instruments) and converted *versus* the standard hydrogen electrode (SHE). The electrolyte is prepared from H_2SO_4 (Suprapur, Merck) and $CuSO_4$ (Suprapur, Alfa Aesar).

The wetted area of the electrode is determined by analyzing the footprint of the meniscus on the sample after the experiments. A typical value of the geometrical area is 1.5 ± 0.2 cm^2. The roughness factor, defined as the ratio between the real and projected surface area, is estimated at ~ 1.15, which is quantified by AFM measurement. The Cu coverage, θ_{Cu}, is calculated by dividing the charge density by a value of 445 μC/cm^2, which is the theoretical charge for the formation of a Cu monolayer [43].

DECMA measures the potential variation during conventional cyclic voltammetry while a small strain is cyclically imposed on the electrode surface. Experimental details for DECMA measurements were described

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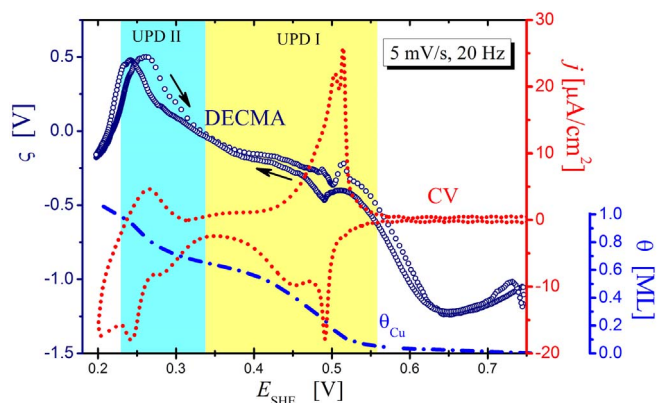 E-mail address: qibodeng@tjut.edu.cn (Q. Deng).

Fig. 1. Experimental results of DECMA on 111-textured Au electrode in 100 mM H_2SO_4 + 5 mM $CuSO_4$. The coefficient, ς, is measured at cyclic strain frequency of 20 Hz. The right Y-axes show the *in situ* CV and the Cu coverage, associated with the plot of ς.

in refs [7,9,19,21]. The central difference is the focus on Cu UPD on Au (111) textured surfaces from sulfate containing electrolytes.

3. Results and discussion

Fig. 1 shows an *in situ* cyclic voltammogram (CV) for a 111-textured clean Au surface in 100 mM H_2SO_4 + 5 mM $CuSO_4$ electrolyte, which is consistent with previous reports [41,42]. Cu atoms restructure from random to an ordered adlayer on the electrode surface, starting with the first UPD peak in cathodic sweep. Upon the completion of the first stage (UPD I), a 2/3 Cu monolayer (ML) is formed, covered by a well-known $(\sqrt{3} \times \sqrt{3})R30°$ structure of sulfate. These sulfate ions are adsorbed in the centers of the Cu honeycomb lattice. Such a honeycomb structure has been confirmed by scanning tunneling microscopy (STM) [23–25,36–38] and other surface science techniques [26–29].

At the UPD II stage, a complete Cu monolayer is formed on the Au (111) surface, near the second UPD peak [30]. The sulfate ions are adsorbed on top of the Cu layer to stabilize the monolayer [31,32,35–38]. However, the detailed structure of the sulfate layer that adsorbs on top of the pseudomorphic Cu monolayer is still a topic of debate. For instance, Lee et al. proposed a $(\sqrt{3} \times \sqrt{3})R30°$ structure [31], while Vasiljevic et al. observed the co-existence of $(\sqrt{3} \times \sqrt{3})R30°$ and $p(2 \times 2)$ structures by STM [32]. On the reverse potential sweep, the deposited copper is electrochemically stripped from electrode surface.

Consistent with previous reports on the pseudo-capacitive process on a clean gold surface [7,19,21], the observed value of ς is negative in Fig. 1. When E approaches the region of interest for Cu UPD, $\varsigma(E)$ increases with decreasing E. At the first Cu UPD peak ($E = \sim 0.5$ V), $\varsigma(E)$ exhibits a slight drop and reaches a local minimum. Then, $\varsigma(E)$ continues increasing, followed by a sign-inversion of ς at $E = 0.33$ V where

θ_{Cu} is about 2/3 ML. As θ_{Cu} approaches 1 ML (near $E = 0.24$ V), $\varsigma(E)$ attains a maximum coupling value of $+0.5$ V. Just after the formation of a Cu monolayer on the surface, $\varsigma(E)$ starts decreasing. This may be attributed to the adsorbed sulfate layer on top of the $Cu(1 \times 1)$ monolayer, which has been reported using SEXAFS [33,34] and STM [36–38]. At more negative potentials in the overpotential deposition (OPD) region, $\varsigma(E)$ once again exhibits a negative value.

Because the E of an electrosorption (electrodeposition) process measures the free energy of adsorption, ΔG^{ad} [8], and provided that the entropy of adsorption is not significantly strain-dependent, ς could then be linked to the variation of ΔG^{ad} with surface strain, using the relationship: $d\Delta G^{ad}/d\varepsilon = -zF\varsigma$ (where z is ionic valency and F is Faraday's constant) [7–9,11]. The sign of ς is therefore of great importance to reflect the impact of strain. Because the opposite signs are obtained at different UPD stages, it raises the question: does tensile strain enhance or inhibit the Cu UPD process?

The sign of ς was examined after relatively long periods at the first and second UPD peaks in the CV. In Fig. 2a, ς values were recorded with the time during potential hold experiments. Prior to each potential hold, the electrode surface was cleaned using a CV at 100 mV/s, with a 0.8 V positive potential limit. The electrode was first equilibrated by holding $E = 0.6$ V for 600 s, and ς exhibited a stable value of -0.9 V during the capacitive process. After 600 s at $E = 0.5$ V, which is associated with the first UPD peak, ς saturates at a negative value. Subsequently, after 600 s at $E = 0.25$ V, which is associated with the second UPD peak, the value of ς is positive. The data in Fig. 2a clearly show that for a given potential, ς reaches a steady-state value, which is consistent with those obtained from the potentiodynamic scans in Fig. 1.

Fig. 2b and c show the dependence of ς on the potential sweep rate. Prior to the Cu UPD process, ς is independent of sweep rate during the capacitive process. The contribution from capacitive charging is constant. At the UPD I stage, the ς value increases slightly with decreasing sweep rate around the first UPD peak, corresponding to the intermediate structure combined with Cu deposition and sulfate adsorption. The coverage of Cu is dependent on the electrode potential, not the sweep rate (see Fig. 2d). The phenomenon of sweep rate dependence can then be attributed to some sort of surface rearrangement, which is associated with a phase transition into the ordered adlayer around the first UPD peak.

ς returns to its sweep rate independence at the UPD II stage, where the sulfate ions, which occupy the hollow sites in honeycomb structure of 2/3 Cu ML, are substituted by Cu atoms. At the end of UPD II stage, the first Cu monolayer occurs by additional adsorption of 1/3 Cu ML. This stage is dominated by the Cu deposition. The positive value of ς at the UPD II stage indicates that tensile strain could decrease Cu adsorption enthalpy and enhance the Cu deposition, similar to the observation in the study of hydrogen UPD on Pt surface [7,9].

The ς value at the UPD I stage represents a superposition of signals
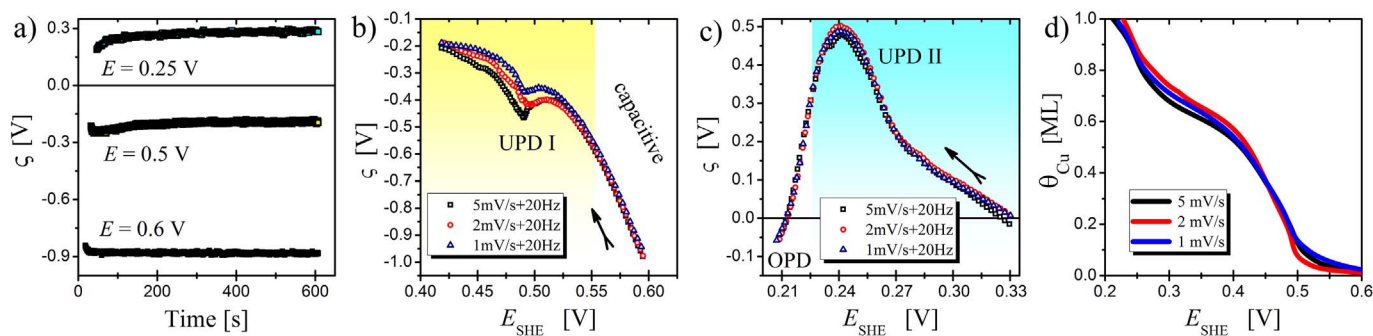
Fig. 2. a) Time-dependence of ς within the capacitive ($E = 0.6$ V) and two Cu UPD regions ($E = 0.25$ V and 0.5 V), obtained by holding a constant potential. b) Potential sweep rate dependence of ς during the capacitive process and the UPD I stage. c) Potential sweep rate dependence of ς at the UPD II stage and the initial stage of OPD process. Strain frequency is 20 Hz. d) The Cu coverage at different sweep rates.