



Electrocrystallizations of copper on glassy carbon in CuCl_2 silica sol and aqueous solutions

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Abstract

Electrocrystallizations of copper from both CuCl_2 silica sol and aqueous solutions were studied by the chronoamperometry technique. It was found that current density contributions of the double-layer charging (i_{DL}) in current-time transients (CTTs) from both of the solutions were large. An adsorption-nucleation based model was proposed to analyze quantitatively the CTTs, by which copper electrocrystallization mechanism was characterized as progressive nucleation with 3D growth (3DP) under diffusion control. The diffusion coefficient of copper ions and the AN_∞ products in aqueous solutions were larger than that in silica sols, which indicated that copper nucleation was inhibited in sol solution. The large i_{DL} may be resulted from the adsorption of chloride ions on the electrode surface.

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Electrochemical sol–gel methodology is a novel approach for various thin films preparation [1–7], which is introduced first by David Avnir's research group in 1999 [1]. Recently, sol–gel/copper (Cu/SiO_2) nanocomposite thin film was prepared by electrochemical co-deposition sol–gel [8]. It was thought that the chemical and physical properties of metal/polymer composites were very sensitive to small changes in the amount, size, and shape of the metal particles [8]. Electrocrystallization process, including nucleation and nuclei growth, of metal is the initial stage of the electrochemical deposition, which determines the properties of the metal particles. Therefore, it is important to study the electrocrystallization of metal in the case of co-deposition of sol–gel.

Although a lot of studies of copper nucleation have been carried out in sulfate salt aqueous solutions [9–11], there are few studies concerning copper nucleation in CuCl_2 aqueous solution, much less in CuCl_2 sol. In this paper, we reported the copper electrocrystallizations both in CuCl_2 sol and aqueous solutions by using chronoamperometry (CA) for the first time.

1. Experimental

A conventional three-electrode cell, equipped with a big area platinum foil counter electrode and a saturated calomel electrode (SCE), was used. All the potentials were quoted with respect to the SCE. The glass carbon electrode

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was a rod, 3 mm in diameter. It was carefully polished using successively three grades of alumina slurry (1, 0.3 and 0.05 μm respectively), and then cleaned ultrasonically in distilled water to remove any residues from the polishing process. It was then rinsed with distilled water before each experiment.

The CuCl_2 silica sol consisted of 4 mL of TEOS, 16 mL of 1 mmol/L phthalate buffer (pH 3.5) containing 0.2 mol/L KNO_3 , and 5 mmol/L CuCl_2 , which was similar to that reported in Ref. [8]. A stable CuCl_2 silica sol was obtained by stirring this sol for 7 h at room temperature. 5 mmol/L CuCl_2 aqueous contained the same phthalate buffer as that in the CuCl_2 silica sol. All solutions were prepared from analytical grade reagents using triply distilled water.

The current-time transients (CTTs) were obtained from chronoamperometry (CA) experiments. CA was performed from the open-circuit potential to the potentials that Cu electrodeposition would occur. CA experiments were carried out on a CHI660 electrochemical analysis equipment (Shanghai Chenhua, China) under quiescent condition at ambient temperature.

2. Results and discussion

Fig. 1a and b shows a family of CTTs obtained from silica sol and aqueous solutions at different potentials, respectively. During the initial period of the CTTs, a sharp decline in the current density, which is related to the electrode double-layer charging effect initiated by the potential pulse employed [12,13]. Then the CTTs exhibit an arising current density, and a peak (t_{max} , i_{max}) appears, which is usually associated with the formation and growth of copper nuclei. The current density contribution of charging of the double layer (i_{DL}) is usually small in comparison with the current density of the nucleation for sulfate salt systems [9–11]. Therefore, its influence is usually disregarded. However, i_{DL} and the current density contribution of nucleation ($i_{\text{nucleation}}$) are overlapping. The characterization of copper electrocrystallization process by $i_{\text{nucleation}}$ is strongly influenced by the double-layer charging effect in CuCl_2 solutions. Therefore, $i_{\text{nucleation}}$ should be separated from i_{DL} .

The current density consists of two contributions, i_{DL} and $i_{\text{nucleation}}$,

$$i = i_{\text{DL}} + i_{\text{nucleation}} \quad (1)$$

There have been two primary classes of models for electrochemical phase formation on smooth surfaces, based on adsorption and nucleation growth, respectively [14]. i_{DL} can be correlated quantitatively to the adsorption process of ions on the electrode surface. Among the adsorption models, Eq. (2) based on a Langmuir-type adsorption-desorption equilibrium is usually used to quantify the double-layer charging effect [12,15,16].

$$i_{\text{DL}} = k_1 \exp(-k_2 t) \quad (2)$$

where $k_1 = k_2 Q_{\text{ads}}$ and k_1 is related to the total charge of the adsorption process Q_{ads} [12].

After testing various models for treating CTTs, it is found the adsorption-nucleation-based model which is expressed in Eq. (3) can satisfactorily reproduce the experimental current density of CTTs,

$$i = k_1 \exp(-k_2 t) + p_1 t^{-1/2} [1 - \exp(-p_2 t^2)] \quad (3)$$

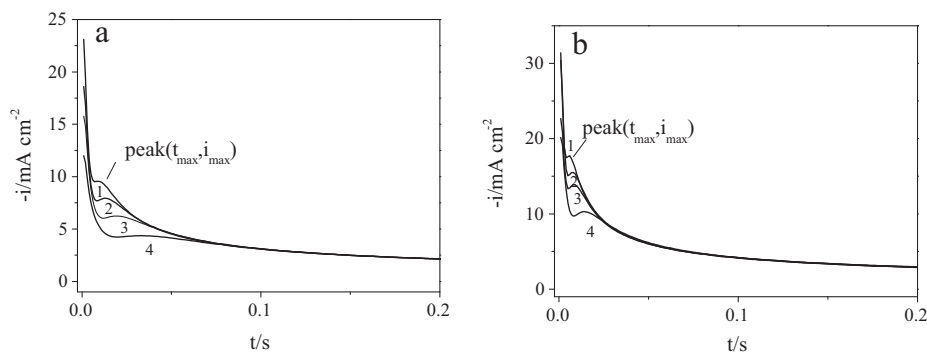


Fig. 1. A family of CTTs from silica sol (a) and aqueous solutions (b): 1, -0.45 V; 2, -0.40 V; 3, -0.35 V; 4, -0.30 V.

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