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Effect of Additives on the Direct Electrodeposition of Copper From Acid Solution Containing 20 g/L Copper(II)

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The effect of 3-mercapto-1-propanesulfonate sodium salt (MPS), polyethylene glycol (PEG), thiourea (TU) and ethylenethiourea (ETU) on copper electrodeposition from acidic sulfate electrolyte with low Cu^{2+} concentration was investigated by linear sweep voltammetry (LSV), and chronoamperometric and electrochemical impedance spectroscopy (EIS) measurements. The LSV experimental results showed that all additives have inhibitory effects on copper electrodeposition. The results of the chronoamperometric experiments suggested that copper electrodeposition was related to three-dimensional instantaneous nucleation in the diffusion-controlled regime regardless of the presence of the additives. In agreement with the LSV results, EIS experiments revealed the influence of the additives on the electrodeposition of copper through direct adsorption on the cathode surface, while TU and ETU produce stronger inhibition through complex intermediate reactions. Scanning electron microscopy images showed that the addition of TU and ETU resulted in flatter and finer-grained copper electrodeposition at low copper ion concentration.

Keywords: electrodeposition; low Cu²⁺ concentration; additives; nucleation; electrodeposit analysis

1. INTRODUCTION

In recent years, with the extensive application of copper in the manufacturing of electronic equipment, particularly printed circuit boards (PCBs) and GMR hard disk read heads [1–3], a large amount of electroplating wastewater and other industrial wastewater with low Cu^{2+} concentration has been produced.

Unfortunately, conventional treatments of dilute metal ionic solutions such as chemical precipitation [4–6], ion exchange [7,8] and solvent extraction [9,10] usually require multiple processing steps, giving rise to loss of metal, environmental problems and low treatment efficiency. By contrast, when used for the treatment of dilute metal ionic solutions, electrodeposition [11,12] can directly recover metal in a single step which is highly beneficial for reducing the cost and increasing the economic efficiency of the treatment process. However, the mass transfer process of copper ions is limited in the electrodeposition at low Cu^{2+} concentration, so that the copper ions cannot reach the cathode surface and be reduced at a sufficiently high rate.

Three-dimensional fluidized bed electrodes [13,14] and rotating electrodes [15,16] have been widely employed to improve the mass transfer conditions in electrodeposition at low Cu^{2+} concentration. While the use of these electrodes improves the mass transfer efficiency, it is difficult to recover the electrodeposited metal on these electrodes. In addition, the complex structure and large dimensions of these electrodes limit the practical application of this approach.

In addition to the equipment, additives [17-32] also play an important role in electrodeposition. The most commonly used additives in Cu²⁺ electrodeposition are 3-mercapto-1-propanesulfonate sodium salt (MPS) [17-20], polyethylene glycol (PEG) [21-24,31], thiourea (TU) [25-30] and TU derivatives [32]. While MPS and Cl⁻ are often used as accelerators in copper electrodeposition, the addition of MPS without Cl⁻, shows an inhibitory effect on copper electrodeposition, due to the adsorption of MPS at the cathode interface [17-20]. PEG is a polymer with strong surface active properties and is often used as an inhibitor in copper electrodeposition [21-24,31]. TU and derivatives of TU are often used as grain refiner and leveling agent because they inhibits the coarsening of crystal grains [25-30,32]. Nevertheless, since most studies have focused on the commonly used concentration of copper ions (\geq 40 g·L⁻¹), the kinetic behavior and mechanism of the effects of these additives in electrodeposition at low metal ion concentration of metal ions has been studied [33], the kinetic behavior and mechanism of deposition have not been explored. Since the Cu²⁺ concentration of 20 g·L⁻¹ is only one half of the limit concentration of industrial electrolysis, we used this concentration as the example of "low concentration" for this work.

In this work, to obtain high-quality cathode copper directly from an acid solution with low Cu^{2+} concentration, MPS, PEG, TU, and ethylenethiourea (ETU) were used as additives to systematically study the effects of the additives on the electrochemical behavior, nucleation mechanism and quality of the deposit in electrodeposition at low Cu^{2+} concentration by electrochemical techniques.

2. EXPERIMENTAL

The blank electrolyte contained 120 $g \cdot L^{-1}$ H₂SO₄ and 20 $g \cdot L^{-1}$ Cu²⁺ in the form of CuSO₄·5H₂O. The Cu²⁺ concentration of the solution used in this work is equal to a half of the limit concentration of the solution used in industrial electrolysis. For the solutions containing the additives, the concentration of the additive in the solution was 10 mg·L⁻¹. All of the chemicals used in this work were of analytical grade and were purchased from Macklin Biochemical Co., Ltd, China.

All of the experiments were performed using an electrochemical workstation (Modulab XM ECS, Solartron-Analytical, UK) and a 250 mL standard three-electrode cell. The working electrode was a glassy carbon disk electrode (Φ 3 mm). A platinum wire (Φ 1 mm, 5 mm) was used as the counter electrode and all potentials were recorded with respect to the saturated calomel electrode (SCE) at room temperature. Prior to each experiment, high-purity nitrogen was used to remove dissolved oxygen from the solution. The working electrode was polished with emery papers (4000 grit), 0.5 and 0.1 µm alumina slurry respectively, rinsed with acetone and deionized water after ultrasonic cleaning, and finally dried.

Linear sweep voltammetry (LSV) experiments were carried out by applying a linear potential varying in the range from +0.20 V to -0.60 V (vs. SCE) at a scan rate of 20 mV·s⁻¹. In chronoamperometric experiments, the applied cathode potential was held at the nucleation region. Electrochemical impedance spectroscopy (EIS) experiments were carried out at -0.20 V using a sine wave perturbation with an amplitude of 10 mV a.c. at frequencies between 10^5 and 10^{-1} Hz. Electrodeposit analysis experiments were carried out at the current density of 280 A·m⁻² for 1 hour. The elemental and surface morphology analyses of the copper electrodeposits were carried out using a JXA-8230 scanning electron microscope (SEM, JEOL, Japan). All copper electrodeposits were rinsed thoroughly with deionized water and then were used for analysis without any prior surface treatment.

3. RESULTS AND DISCUSSION

3.1 Linear sweep voltammetry curves

Figure 1 shows the result of the LSV experiments. A pronounced increase in the current density with increasing cathode potential with a peak current density of approximately $32 \text{ mA} \cdot \text{cm}^{-2}$ is observed due to the electrocrystallization of copper ions, suggesting that the electrodeposition process is controlled by mass transfer [34]. For the Cu²⁺ electrodeposition from acid sulfate solutions without additives, Mattson and Bockris proposed the following mechanism [35]:

$$Cu^{2+}+e^{-} = Cu^{+}$$
 (1)
 $Cu^{+}+e^{-} = Cu^{0}$ (2)

Generally, the reaction described by Eq. 1 is the slow, rate-determining reaction while the Eq. 2 is considered to be the fast one.



Figure 1. Linear scan voltammograms for copper electrodeposition with low Cu²⁺ concentration at scan rate of 20 mV s⁻¹ in the absence and presence of different additives

The addition of MPS negatively shifted the initial deposition potential by approximately 0.60 V, demonstrating the inhibitory effect of MPS on Cu^{2+} electrodeposition. Such an inhibitory effect has also been reported at other copper ion concentrations [17] and may be due to the adsorption of copper ions by the thiol group in MPS [19]. Interestingly, when MPS and chloride ions are present in the electrolyte, the chloride ions weaken the binding of the copper atoms to sulfonate. The decrease of the binding energy of this substance may cause more copper ions to move to the surface, accelerating the electrodeposition process [18,19].

The addition of PEG negatively shifted the initial deposition potential by approximately 0.70 V, while the peak current density was reduced and a broader curve was observed, revealing the sluggish kinetics of Cu^{2+} electrodeposition. PEG is a polymer with strong surface activity that contains O atoms that allow the PEG molecules to directly adsorb on the copper layer of the electrode surface, forming a single-layer or multi-layer film coating the surface that prevents the electrons from reducing the copper ions [21,22]. It is observed from Figure. 1 that the inhibition effect of PEG on copper electrodeposition is slightly stronger than that of MPS.

In the presence of TU, the peak current density was observed at a more negative potential and the limiting current density was also significantly reduced, suggesting that electrodeposition was inhibited. Furthermore, the appearance of a tiny shoulder (point I) indicated that a complex intermediate reaction occurred during the electroreduction of Cu^{2+} , corresponding to the generation of Cu^{+} species. TU is known to form stable complexes with both cupric and cuprous ions in acidic solution and can also be oxidized in the presence of Cu^{2+} to produce Cu^{+} and formamidine disulfide (FDS). The complexes with strong surface activity block the active sites and hinder the nucleation process. The formation of the intermediate and its discharge are described by the following reactions [32]:

$$Cu^{+} + nFDS = [Cu(FDS)_{n}]^{+}$$
(3)

$$Cu^{+} + nTU = [Cu(TU)_{n}]^{+}$$
(4)

$$Cu^{2+} + nTU = [Cu(TU)_{n}]^{2+}$$
(5)

$$[Cu(FDS)_n]^+ + e^{-} = Cu + nFDS$$

$$[Cu(TU)_n]^+ + e^{-} = Cu + nTU$$

$$[Cu(TU)_n]^{2+} + 2e^{-} = Cu + nTU$$
(8)

Among the additives, ETU showed the strongest polarization effect. Similarly, a shoulder (point II) also appeared in the LSV curve at -0.25 V, indicating that intermediates were produced during electrodeposition. Lesage et al. found that ETU is unstable in the acidic copper sulfate system, and undergoes a decomposition reaction [34]; thus, the mechanism of action of ETU appears to be consistent with that of TU. As a derivative of TU, ETU has a stronger polarization effect than TU, most likely because the molecular structure of ETU is more polar than that of TU, and the complex generated in the electrolyte also has a higher electron affinity, so that it is more strongly adsorbed on the electrode surface, resulting in a stronger polarization effect.

3.2 Chronoamperometric experiments

Chronoamperometric experiments were carried out to analyze the effect of different additives on the nucleation kinetics of Cu^{2+} electrodeposition at low Cu^{2+} concentration.

Figure 2 shows the experimental current-time transient curves in the absence and presence of the additive at different potentials; here, for the comparison of the theoretical nucleation curve and transient data, the experimental results are converted into dimensionless values. Such transient currents are typical of a diffusion-controlled three-dimensional (3D) nucleation process. The dimensionless theoretical 3D instantaneous nucleation (Eq. 9) and progressive nucleation (Eq. 10) curves proposed by Scharifker and Hills [37–40] are given by:

$$i_{ins}/i_m = 1.9542 \{1 - \exp[-1.2564(t/t_m)]\}^2 (t/t_m)^{-1}$$
(9)

$$i_{pro}/i_m = 1.2254\{1 - \exp[-2.3367(t/t_m)^2]\} (t/t_m)^{-1}$$
 (10)

where *i* and *t* are the current density and the corresponding time recorded by the experiment, respectively, and i_m and t_m are the peak current density and the corresponding time, respectively. A comparison of the experimental and theoretical data indicates that the Cu²⁺ electrodeposition follows a 3D instantaneous nucleation mechanism in the absence of additives, and the addition of these four additives did not change the nucleation mechanism of Cu²⁺ electrodeposition. The transient nucleation mechanism is equivalent to the slow growth of atomic nuclei over a certain number of active sites, and the resulting crystal grains are usually relatively coarse and display cracks.

The diffusion coefficient of Cu^{2+} in solution in the absence and presence of different additives was estimated by linearizing the instantaneous process descent stage according to the Cottrell equation [40]:

$$i = nFAc(D/\pi)^{1/2}t^{-1/2}$$
 (11)

where A and *c* are the electrode area and ion bulk concentration, respectively, *n* and F are the number of electrons and Faraday's constant, respectively, and all other symbols have their usual meaning. The same method was also used in other studies reported in the literature [37,40] and the diffusion coefficient values obtained under different applied potentials are shown in Figure 3. As the cathode potential increases, the diffusion coefficient for the Cu²⁺ of the blank solution finally stabilizes

after converted into a dimensionless value (**a'** blank, **b'** MPS, **c'** PEG, **d'** TU, **e'** ETU) at approximately 4.63×10^{-6} cm²·s⁻¹, close to the 4.83×10^{-6} cm²·s⁻¹ value reported in a similar system [41]. Upon the introduction of the additives, the diffusion coefficient of Cu²⁺ decreases significantly, and different additives lead to different degrees of decrease. This may be due to the different strengths of the additive adsorption on the cathode surface, resulting in different increases in the interfacial viscosity.



Figure 2. Current–time transient curves at different potentials with or without additives (**a** blank, **b** MPS, **c** PEG, **d** TU, **e** ETU), and the comparison with the theoretical curve and transient data



Figure 3. The diffusion coefficient of Cu²⁺ at different applied potentials in the absence and presence of different additives

3.3 EIS experiments

Figure 4 shows the Nyquist plot of the copper electrodeposition system in the absence and presence of additives. The charge transfer process gives rise to a high-frequency capacitive loop that appears as the circular are in Figure 4. The diameters of the semicircles in the high-frequency regions of TU and ETU are clearly larger than those obtained for the samples with TU and ETU additives are clearly larger than those obtained for the blank sample and the samples with the MPS and PEG additives, suggesting that the changes in the charge transfer resistance values due to the presence of TU and ETU are relatively large.



Figure 4. Nyquist plots of Cu^{2+} electrodeposition in the absence and presence of different additives in the frequency range of 10^5 to 10^{-1} Hz disturbed with amplitude of 10 mV a.c. sine wave at -0.2V vs. SCE





In the low-frequency region, in the absence and presence of MPS, PEG shows the characteristic of diffusion control at E = -0.2 V, that is, approximately a sloped line. The addition of TU and ETU results in the appearance of a second capacitor loop in the low-frequency region that may be caused by the adsorption layer on the cathode surface. Furthermore, because the presence of either TU or ETU significantly inhibits the electrodeposition, it is almost unaffected by mass transfer at E = -0.2 V, which is different from the results obtained with the addition of MPS or PEG.

The two equivalent circuit models shown in Figure 5 are used to explain these two different phenomena. Here, R_s , R_{ct} , R_{sf} , C_{dl} , C_{sf} and W represent the solution resistance, charge transfer resistance, surface layer resistance, double layer capacitance, surface layer capacitance and Warburg impedance, respectively. For a more accurate simulation of the equivalent circuit model and experimental data, the constant phase element (*CPE*) was used for mathematical modeling.

Additive	R_s	R_{ct}	C_{dl}
	$\Omega~{ m cm}^2$	$\Omega~{ m cm}^2$	F cm ²
Blank	4.023	21.93	2.631×10 ⁻⁶
MPS	3.904	26.90	2.535×10 ⁻⁶
PEG	4.103	34.39	4.416×10 ⁻⁶
TU	3.669	63.39	5.099×10 ⁻⁵
ETU	3.643	68.62	1.772×10 ⁻⁵

Table 1. EIS parameters for copper electrodeposition in the absence and presence of different additives at -0.2V vs. SCE

The calculated EIS parameters are presented in Table 1. In the presence of an additive, the change in the solution resistance R_s can be ignored, but the changes in the charge transfer resistance R_{ct} and double layer capacitance C_{dl} are significant, indicating that the additives hinder copper electrodeposition. Among the additives, the largest R_{ct} value is obtained in the presence of ETU,

indicating that ETU has the strongest inhibition effect on copper electrodeposition. These results are consistent with the results discussed above. In summary, during electrodeposition, TU and ETU directly influence charge transfer rather than mass transfer.





Figure 6. SEM images (**a** blank, **b** MPS, **c** PEG, **d** TU, **e** ETU) and EDS analysis (**a**' blank, **b**' MPS, **c**' PEG, **d**' TU, **e**' ETU) of electrodeposits in the absence and presence of different additives

Figure 6 shows the SEM images, elemental analysis results and the contents of the deposit obtained from the solutions without and with the additives at the current density of 280 $A \cdot m^{-2}$ for 1 hour. The deposit obtained from the blank solution (Figure 6a) had a coarse structure with hemispherical grains and cracks that were oriented almost perpendicular to the substrate surface, consistent with the typical characteristics of instantaneous nucleation mentioned above. The addition of either MPS or PEG (Figures 6b,c) slightly improves the surface roughness of the electrodeposits, while the addition of either TU or ETU results in a flat surface of the electrodeposits with a reduction in the roughness and grain size (Figures 6d,e) showing good resistance to grain growth.

Since the granularity of the deposit is determined by the competition between growth and nucleation and the addition of TU and ETU results in strong adsorption on the electrode surface that suppresses the growth of the crystallites in the vertical direction, the introduction of these additives reduces the grain size. More importantly, upon the addition of TU and ETU, trace amounts of sulfur (S) were found in the electrodeposits (Figures 6d',e'). The presence of the S originating from TU and ETU in the deposit in some form indicates that the inhibitory mechanism of these two additives is more complicated than that of MPS and PEG. MPS and PEG give rise to inhibition through their direct adsorption on the copper layer, while TU and ETU produce stronger inhibition through complex intermediate reactions. Other researchers [27,29] have found that S exists in the deposit as a CuS-based species when TU is added separately. This may be due to the decomposition of TU into H₂S that then reacts with Cu^{2+} to form insoluble CuS. CuS is believed to be tightly bonded to the copper surface and is trapped in the deposit during the formation of each layer [29], which is also the reason for the increase in the resistivity and decrease in the grain size of the deposits. Such insoluble CuS will preferentially cover the rapidly growing copper electrocrystallization surface, preventing the crystal surface from growing in the vertical direction, and finally resulting in the flat crystal surface.

4. CONCLUSIONS

The effect of four additives, namely MPS, PEG, TU and ETU on the linear sweep voltammetry behavior and the nucleation mechanism of Cu^{2+} electrodeposition as well as the morphology and the elemental composition of the deposited copper with low Cu^{2+} concentration bath were studied. The LSV studies showed that all additives have a polarizing effect on Cu^{2+} electroreduction, with the strengths of the effect following the order of the polarity of the additives, that is ETU>TU>PEG> MPS. In addition, intermediate products appear during Cu^{2+} electrodeposition in the presence of TU and ETU.

The chronoamperometric experiments showed that the four additives do not change the nucleation mechanism of Cu^{2+} electrodeposition, but rather reduce the copper ion diffusion coefficient. The addition of TU or ETU resulted in a substantial decrease in the estimated diffusion coefficient, suggesting that the complex electrodeposition process significantly slows down the diffusion of copper ions.

An examination of the electrodeposit morphology indicated that the addition of MPS or PEG slightly improves the surface roughness of the electrodeposits, while the addition of TU or ETU

induced the formation of flatter and finer-grained copper electrodeposits. TU and its derivatives are considered to be suitable additives for direct copper electrodeposition at low copper ion concentration.

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