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Voltammetric behaviour of the copper(II)–thiourea system in sulphuric acid medium at platinum and glassy carbon electrodes

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Thiourea, a levelling agent used in copper electrorefining baths, is the focus of a cyclic and rotating disc or ring-disc electrode voltammetric study. Thiourea adsorption, its interaction with Cu^{2+} and formation of $Cu(Tu)_n^+$ complexes are part of the multistep electrode mechanism proposed. Results at platinum and glassy carbon electrodes are applicable to copper electrodes in electrorefining.

1. Introduction

Copper electrorefining is carried out in acidic ($200\,g\,dm^{-3}$ H_2SO_4) copper (II) sulphate ($45\,g\,dm^{-3}$ as Cu) solutions [1] with additives to obtain smooth copper deposits.

Thiourea (Tu) is used as levelling agent, with 10 to 30 g consumption per metric ton of refined copper [2]. While cathode and anode potentials are kept close to the equilibrium potential (about +0.050 V vs SCE) in electrorefining, the anode in electrowinning can reach +1.8 to +2.0 V vs SCE. This produces a thiourea oxidation to dithioformamidine through a mechanism studied by different electrochemical techniques [4]. Cupric ion can slowly oxidize thiourea and form copper (I) complexes $Cu(Tu)_n^+$ ($n = 1$, 2, 3 or 4) of known stability [5].

Thiourea adsorption on platinum [4, 8, 9] mercury [8, 11] and copper [7] has been described. The focus of the present work is the understanding of how thiourea affects the voltammetric behaviour of both the cathode, where copper is deposited, and the anode, where copper dissolution occurs in electrorefining. Participation of thiourea in the electrode mechanism is proposed, based on results obtained at platinum and glassy carbon electrodes.

2. Experimental details

Rotating disc and ring-disc electrode experiments were performed with a Pine Instruments Co. model ASRE rotator with either a Pt–Pt or a GC–GC ring-disc electrode. The parameters of the electrodes were as follows: Pt–Pt electrode, $r_1 = 0.250\,cm$, $r_2 = 0.276\,cm$, $r_3 = 0.358\,cm$; GC–GC electrode, $r_1 = 0.382\,cm$, $r_2 = 0.416\,cm$, $r_3 = 0.556\,cm$. Potential control was provided by a Pine Instruments Co. model RDE 3 dual potentiostat and measured with respect to a saturated calomel electrode (SCE) with a Tacussel Aries 20000 digital millivoltmeter. Current/potential curves were recorded on a Hewlett-Packard HP-7004B XY recorder or on a Hewlett-Packard HP-7090A measurement plotting system.

The same setup was used for the cyclic voltammetry experiments except that the working electrode was not rotated.

Electrode conditioning before each experiment consisted of polishing with Buehler No. 3 (0.05 μm) alumina for the glassy carbon electrode and an electrochemical treatment [12] for the platinum electrode. Temperature control was achieved using a Haake D3-G refrigerated bath and circulator connected to a jacketed cell. All chemicals were of analytical reagent grade.

3. Results and discussion

3.1. *Rotating disc electrode voltammetry*

A 10^{-3} M Cu^{2+} solution in 0.6 M H_2SO_4 with thiourea concentrations from 4×10^{-5} to 4×10^{-4} M was scanned between −0.4 and +1.2 V (Fig. 1). In the region between +0.4 and +1.2 V two anodic waves are observed, corresponding to the electrochemically irreversible oxidation of thiourea [4].

Both waves increase proportionally to thiourea concentration. The Cu^{2+}–Tu interaction [5] is not evident at these concentration levels. Cathodic processes are observed between +0.3 and −0.4 V, which lead to a copper deposit. Increasing thiourea concentration does not affect the foot at −0.25 V but decreases the current at −0.4 V as a result of increasing the copper deposition overpotential. On the reverse scan a significant effect is observed between −0.4 and +0.2 V.

The anodic copper dissolution peak at +0.5 V decreases, shifts positively initially and negatively later. The onset of a new anodic peak (−0.1 V) occurs simultaneously. This strong effect of small thiourea concentrations suggests adsorption of thiourea at the electrode solution interface. The

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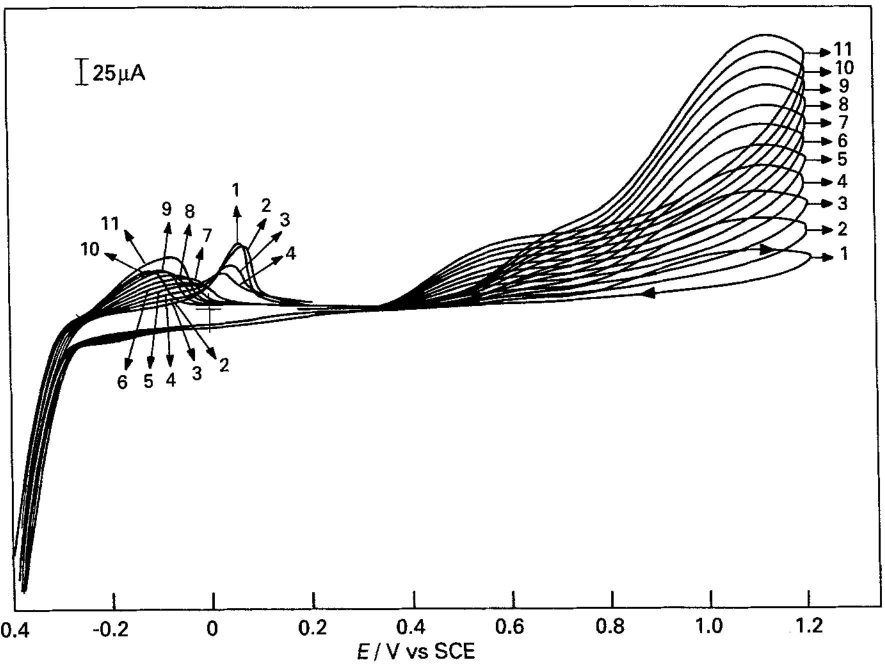

Fig. 1. Rotating platinum disc electrode voltammetry. Area: 0.2 cm^2. [Cu^{2+}] = 10^{-3} M; [H$_2$SO$_4$] = 0.6 M; [Tu] × 10^5/M = (1) 4; (2) 8; (3) 12; (4) 16; (5) 20; (6) 24; (7) 28; (8) 32; (9) 36; (10) 40; (11) 44. ω = 2500 r.p.m.; v = 1 V min^{-1}.

negative shift of the anodic copper dissolution indicates complexation of the Cu(I) product [5] by adsorbed thiourea.

Next, an 8 × 10^{-4} M thiourea solution in 0.6 M H$_2$SO$_4$ with Cu^{2+} concentrations from 1 × 10^{-3} M to 4.3 × 10^{-3} M was scanned between −0.4 and +1.2 V (Fig. 2). The thiourea oxidation waves (+0.4 to +1.2 V) are not affected, meaning that the Cu^{2+}–Tu interaction [5] is not present at these concentration levels. The cathodic currents between +0.3 and −0.4 V increase proportionally to Cu^{2+} concentration. On the reverse scan the −0.15 V peak (copper dissolution facilitated by thiourea) gradually shifts positively while the +0.05 V peak (normal copper dissolution) grows. A small post-peak develops which may be ascribed to a Cu(Tu)$_n^+$ species oxidation at +0.2 V.

3.2. *Cyclic voltammetry*

Since the solution was not stirred, the reaction products and intermediates stayed at the electrode/solution interface as in contrast to rotating electrode voltammetry. This facilitates their detection on the reverse scan.

A 4 × 10^{-3} M Cu^{2+} + 3.2 × 10^{-4} M thiourea in 0.6 M H$_2$SO$_4$ solution was scanned between +0.3 and −0.45 V with scan rates (v) from 2 to 9 V min^{-1} (Fig. 3). The −0.35 V peak grows proportionally to v rather than $v^{1/2}$, suggesting the reduction of an

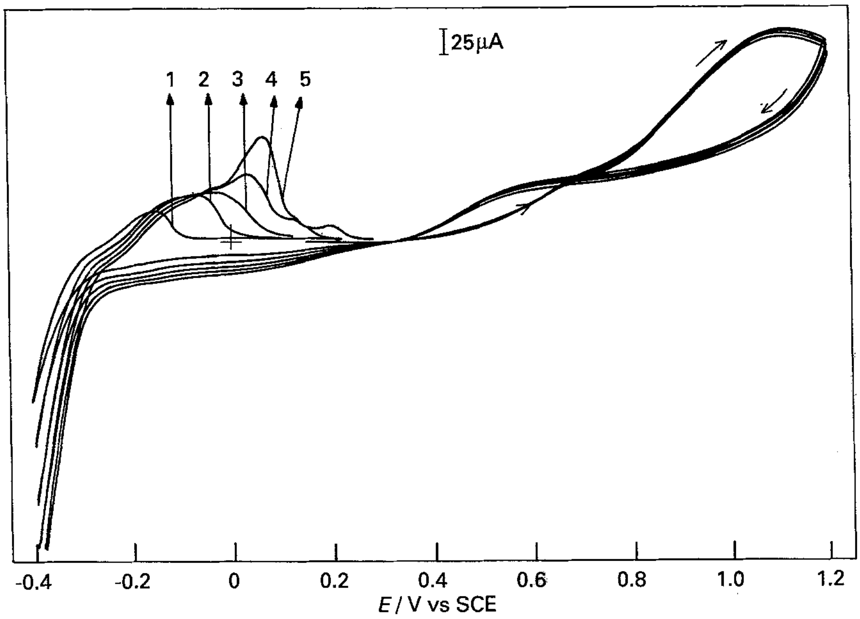

Fig. 2. Rotating platinum disc electrode voltammetry. Area: 0.2 cm^2. [Tu] = 8 × 10^{-4} M; [H$_2$SO$_4$] = 0.6 M; [Cu^{2+}] × 10^{-3}/M = (1) 1; (2) 1.92; (3) 2.78; (4) 3.57; (5) 4.31. ω = 2500 r.p.m.; v = 1 V min^{-1}.

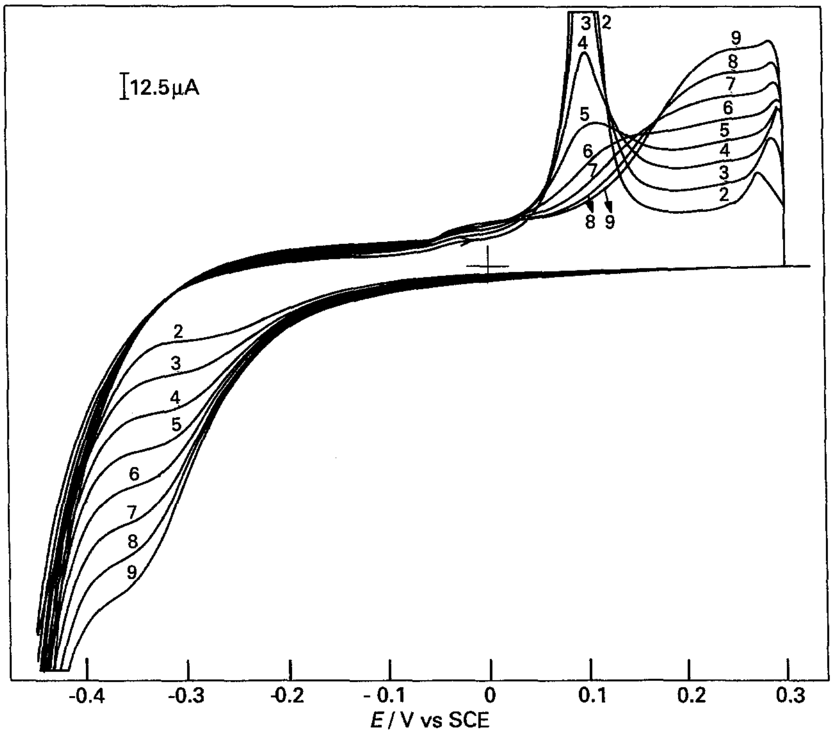

Fig. 3. Cyclic voltammetry with a platinum disc electrode. Area: 0.2 cm^2. [Cu^{2+}] = 4 × 10^{-3} M; [H_2SO_4] = 0.6 M; [Tu] = 3.2 × 10^{-4} M. v = 2; 3; 4; 5; 6; 7; 8; 9 V min^{-1}.

adsorbed $Cu(Tu)_n^+$ species. On the reverse scan a large anodic peak (+0.1 V) followed by a small one (+0.27 V) are observed at 2 V min^{-1}. The +0.1 V peak gradually vanishes while an anodic wave between +0.15 and +0.30 V develops with increasing scan rate. Since copper dissolution in the presence of thiourea involves complexation between Cu(I) and adsorbed Tu, the results in Fig. 3 may be interpreted as a consequence of a relatively slow interaction. This shows up with slow scans facilitating copper dissolution (observed at more negative potentials). In contrast, with fast scans, it does not show up such that copper dissolution is observed at more positive potentials. The wave shape suggests a sequence of multiple consecutive steps occurring at different potentials involving different $Cu(Tu)_n^+$ species.

In a further experiment a constant ratio [Cu^{2+}]/[Tu] = 100 was used with [Cu^{2+}] between 4 × 10^{-4} to 4 × 10^{-3} M (Fig. 4). The −0.32 V cathodic peak corresponding to copper deposition, increases with Cu^{2+} concentration as an adsorption isotherm. This confirms that the reactive species involved are ad-

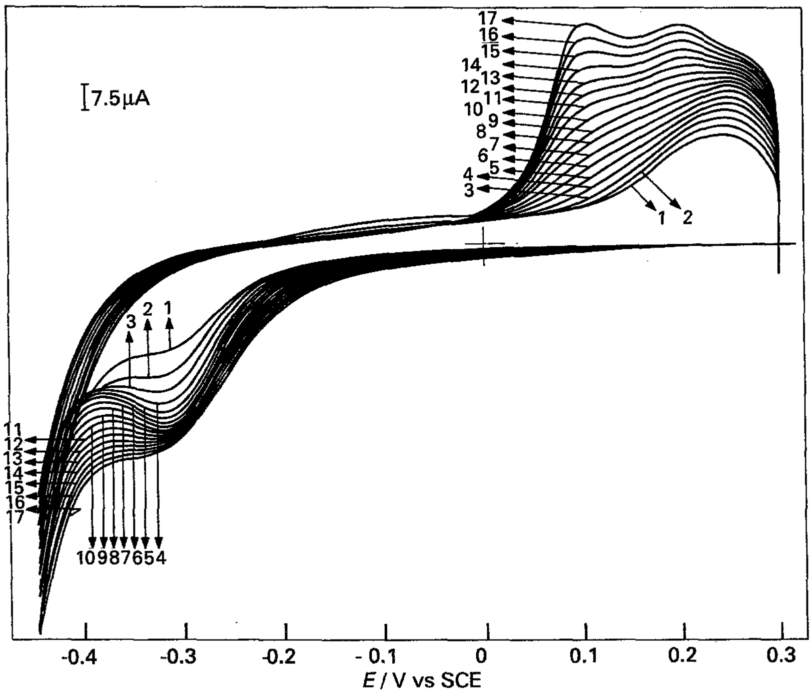

Fig. 4. Cyclic voltammetry with a platinum disc electrode. Area: 0.2 cm^2. [Cu^{2+}]/[Tu] = 100; [H_2SO_4] = 0.6 M. [Cu^{2+}] × 10^4/M = (1) 6; (2) 8; (3) 10; (4) 12; (5) 14; (6) 16; (7) 18; (8) 20; (9) 22; (10) 24; (11) 26; (12) 28; (13) 30; (14) 32; (15) 34; (16) 36; (17) 38.

sorbed species. On the reverse scan the initial +0.24 V peak is gradually covered by two (+0.1 and +0.2 V) new peaks.

The ratio $[Cu^{2+}]/[Tu] = 100$ does not favour Cu(I)–Tu complex formation in the bulk solution, but thiourea adsorption can lead to adsorbed species on the electrode surface. Thiourea adsorption in the first scan ($[Tu] = 4 \times 10^{-6}$ M) is too low to facilitate copper dissolution which is observed at +0.24 V. In contrast, thiourea adsorption in the last scan ($[Tu] = 4 \times 10^{-5}$ M) is high as to produce copper dissolution at more negative potentials (+0.1 and +0.2 V).

3.3. *Rotating ring-disc electrode voltammetry*

Figure 5 shows collection efficiency experiments run in the absence (curve 0) and in the presence (curves 1 to 3) of thiourea with a 10^{-4} M Cu^{2+} solution in 0.6 M H_2SO_4, on glassy carbon electrodes. The disc potential was scanned from +0.4 to −0.6 V while the ring potential was kept constant at +0.4 V.

The two step nature of Cu^{2+} reduction to Cu^0 in the absence of thiourea is clearly illustrated through the detection of Cu(I) at the ring ($Cu(I) \rightarrow Cu^{2+} + e^-$). The disc current after addition of thiourea changes little in the region between +0.4 and −0.3 V, indicating no Cu^{2+}–Tu interaction. However, it drops to approximately one half at −0.5 V while the ring current increases and divides in two peaks. This can be interpreted as stabilization of Cu(I) by complexation to give $Cu(Tu)_n^+$ species.

The disc current drop is due to the lower number of electrons involved ($n = 1$ instead of $n = 2$). The ring current increase is due to larger $Cu(Tu)_n^+$ concentrations as compared to Cu(I), reaching the ring. Whereas the ring peak current split indicates two different sources of $Cu(Tu)_n^+$ species.

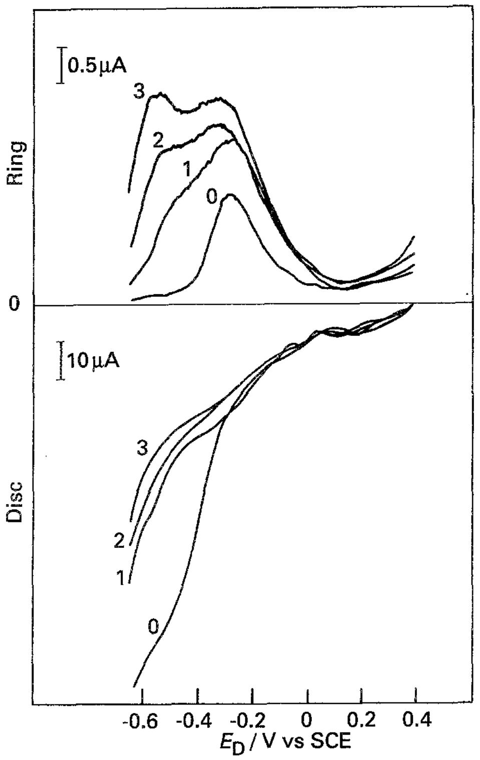

Fig. 5. Rotating ring-disc (glassy carbon–glassy carbon) electrode voltammetry. $[Cu^{2+}] = 10^{-4}$ M; $[H_2SO_4] = 0.6$ M; $[Tu] \times 10^5$/M = 0; 1; 2; 3. $v = 1\ V\,min^{-1}$. $\omega = 2500$ r.p.m. $E_R = +0.4$ V vs SCE.

3.4. *Proposed mechanism*

The electrode surface becomes partially covered by adsorbed thiourea. The adsorbed thiourea may complex with copper(I), generated as an intermediate, giving adsorbed $Cu(Tu)_n^+$ species. A different reaction path may apply to the covered and uncovered electrode surfaces.

On the covered electrode:

(a) $nTu_{(ads)} + Cu^{2+}(sol) + e^- \rightarrow [Cu(Tu)_n^+]_{ads}$
(b) $[Cu(Tu)_n^+]_{(ads)} + e^- \rightarrow Cu^0 + nTu_{(ads)}$
(c) $[Cu(Tu)_n^+]_{(ads)} \rightarrow [Cu(Tu)_n^+]_{(sol)}$

On the uncovered electrode:

(d) $Cu^{2+}_{(sol)} + e^- \rightarrow Cu^+_{(sol)}$
(e) $Cu^+_{(sol)} + e^- \rightarrow Cu^0$

With low thiourea concentrations and, therefore, low electrode coverage, the reaction path (d) and (e) prevails. With increasing thiourea concentrations the more complex reaction path (a) through (c) gradually becomes more important.

4. Conclusions

The voltammetric experiments clearly show the action of thiourea on both cathodic copper deposition and anodic copper dissolution processes. While small amounts of Tu (10^{-5} to 10^{-4} M) in the copper electrorefining electrolyte increase the cathode overpotential as a consequence of Cu(I) complexation as $[Cu(Tu)_n^+]$, anodic copper dissolution is facilitated, so that the cell voltage may not be affected. No signs of thiourea consumption through anodic oxidation in a copper electrorefining process is predicted from the voltammetric behaviour.

A slow Cu^{2+}–Tu interaction at room temperature is predicted, which may become more important at higher electrolyte temperatures. Stabilization of Cu(I) through formation of complex species with thiourea has been demonstrated by rotating ring-disc electrode voltammetry.

The adsorption of Tu and $[Cu(Tu)_n^+]$ complex species plays a fundamental role. Blockage of active electrode sites and slow copper availability from $Cu(Tu)_n^+$ dissociation, are the most probable mechanism of thiourea levelling action. This can be finely tuned by adjusting the thiourea concentration, which sets the optimum contribution of each reaction path.

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