Influence of thiourea and thiourea ageing on the electrodeposition of copper from acid sulfate solutions studied by the ring-disc technique

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The influence of the additive thiourea in freshly made and aged solutions on copper deposition from acid sulfate solutions was studied using a Pt/Pt rotating ring-disc electrode. In fresh thiourea solutions copper deposition is retarded, but the most distinct effect of thiourea is seen during dissolution of the deposits. The intermediate in copper dissolution, Cu^+, is partly complexed with adsorbed thiourea. Thus Cu^+ is adsorbed at the electrode surface and the current peak at the ring due to dissolving Cu^+ becomes very small. The small peak indicates that active additive is present in the deposit. Thiourea containing solutions aged for only a few days have a distinct effect on the electrode reactions. At low concentrations of thiourea ($1\,mg\,dm^{-3}$) a correlation between ageing and growth of the Cu^+ peak at the ring is clearly seen. At high thiourea concentrations ($100\,mg\,dm^{-3}$) a small growth of the Cu^+ peak is seen during the first few days but upon further ageing of the thiourea solution copper deposition becomes strongly inhibited. The ring current can be used as a qualitative diagnostic criterion for the concentration and state of thiourea in copper sulfate solutions.

1. Introduction

Electrolytic production of copper is carried out in aqueous copper sulfate–sulfuric acid baths. During electrolysis metallic copper is deposited on the cathode. Organic additives, such as thiourea, are added to the bath since they improve the smoothness and brightness of the deposit. In solution thiourea is oxidized by Cu^{2+}. The final products of this reaction are formamidine disulfide and Cu^+ ion which is stabilized by complex formation with thiourea and formamidine disulfide [1–4]. Thiourea [5] and the copper complexes [2, 3] can also be adsorbed on the electrode surface. Additionally thiourea can react with metallic copper forming copper sulfides [6–8]. It is well known that the quality of the deposit in copper electrorefining depends on maintaining an optimum level of additive in the electrolyte bath. Thiourea, however, undergoes slow hydrolysis in the presence of acids [3, 8] and therefore the concentration of thiourea is constantly lowered in acid solutions. A good control of thiourea concentration and a better knowledge of the effects of ageing is therefore very important.

It was the purpose of this work to study the effects of thiourea on the electrode surface using the ring-disc technique, to especially focus on the effects of ageing of acidic thiourea solutions and to find criteria for detecting such effects.

2. Experimental details

A conventional three-electrode cell equipped with a platinum counter electrode and a saturated calomel reference electrode (SCE) was used. The rotating ring-disc electrode (RRDE) was a Tacussel EAD 4000 Pt/Pt with the following dimensions: Pt disc radius $r_1 = 2.0\,mm$, Pt ring inner radius $r_2 = 2.2\,mm$ and outer radius $r_3 = 2.4\,mm$. The theoretical collection efficiency was calculated to be 0.212 [9]. The electrode was mechanically polished with graded alumina powders (5–$0.05\,\mu m$) before each measurement.

The electrolyte solutions consisted of $0.70\,M$ $CuSO_4$ and $1.8\,M$ H_2SO_4 including thiourea at various concentrations (0, 1, $100\,mg\,dm^{-3}$) and of various age (0–13 days). The thiourea containing solutions were allowed to age at room temperature without contact with metallic copper. The cell was deoxygenated with nitrogen before each measurement. All measurements were made at room temperature.

Measurements were made using a Tacussel BI-PAD bipotentiostat together with a Tacussel GSTP 3 function generator. Cyclic voltammograms were recorded using a slow potential scan rate, $2.5\,mV\,s^{-1}$. The potential of the disc was swept from $+200\,mV$ vs SCE down to $-50\,mV$ and back again to $+200\,mV$. The ring electrode was kept at $+400\,mV$ vs SCE. This is anodic enough to reoxidize Cu^+ reaching the

ring to Cu^{2+}. The rotation rate of the RRDE was 1500 rpm and 300 rpm.

XPS spectra were measured using a Perkin–Elmer 3057 SCA-based ESCA. SIMS spectra were measured using a VG IX70S system.

3. Results and discussion

Deposition of copper is usually explained in terms of a consecutive mechanism

$$Cu^{2+} + e^- \rightleftharpoons Cu^+ \quad \text{(slow step)}$$
$$Cu^+ + e^- \rightleftharpoons Cu \quad \text{(fast step)}$$
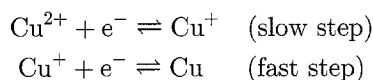
The intermediate Cu^+ can be detected using a rotating ring-disc electrode (RRDE) even in solutions not containing a ligand to stabilize Cu^+ [9]. Thiourea affects the occurrence of Cu^+ in solution. Hence the effects of thiourea and thiourea ageing can conveniently be studied by analyzing RRDE data measured in copper sulfate solutions without thiourea, in solutions containing fresh thiourea and in thiourea containing solutions of various age.

In solutions without thiourea (see Fig. 1) copper is deposited on a Pt disc at potentials below $+75$ mV vs SCE. The reverse scan of the voltammogram shows an anodic stripping peak at $+150$ mV vs SCE for the dissolution of copper. The cathodic/anodic charge ratio $Q_{d,c}/Q_{d,a}$ at the disc measured at the rotation rate of 1500 rpm is 1.1. The same ratio was obtained for copper deposition on glassy carbon [10]. Since

$Q_{d,c}/Q_{d,a} > 1$ all the deposited copper is not readily anodically stripped and the nucleation takes place more easily in subsequent cycles (the hump at $+30$ mV vs SCE will vanish). At the ring the Cu^+ ions swept over from the disc can be detected by reoxidizing them to Cu^{2+}. It is seen that the intermediate in copper deposition, Cu^+, is observed at very low reducing potentials (peaks A and B). At more cathodic potentials no Cu^+ is observed at the ring; it is all consumed at the disc. During copper dissolution Cu^+ is again observed at the ring (peak C) since it is also an intermediate in copper dissolution.

The inhibiting effects of fresh thiourea are shown in Figs 2 and 3. The second step in copper deposition, the reduction of Cu^+, is retarded due to adsorbed thiourea, and the Cu^+ ions thus generated can be stabilized in solution as thiourea complexes. Consequently more Cu^+ escapes from the disc into solution at low reducing potentials. This is seen as a growth of the relative amount of Cu^+ detected at the ring (peaks A and B) and as a growth of the cathodic ring/disc charge ratio $Q_{r,c}/Q_{d,c}$. The values of $Q_{r,c}/Q_{d,c}$ for fresh thiourea solutions are included in Table 1. All values are calculated from the first scan. On subsequent scans the ratio tends to become smaller. The growth of the Cu^+ peaks seen at the ring during deposition depends on the scan rate used. In steady-state measurements no growth of the Cu^+ peaks were observed at a Pt/Pt RRDE at low thiourea concentrations [11]. This is because the reduction of
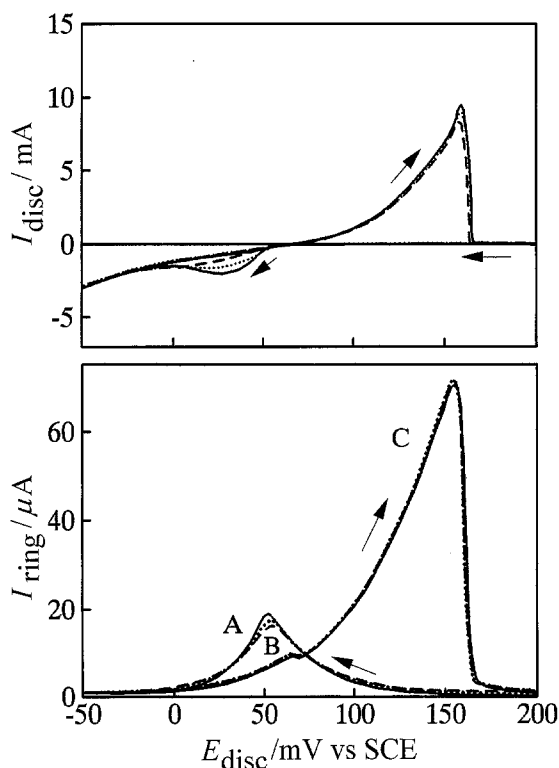

Fig. 1. Current–potential curves at a Pt/Pt RRDE in an aqueous 0.7 M CuSO$_4$ – 1.8 M H$_2$SO$_4$ solution. $A_{disc} = 0.126$ cm^2, $A_{ring} = 0.029$ cm^2, rotation rate 1500 rpm. $E_{ring} = +400$ mV vs SCE. Scan rate: 2.5 mV s^{-1}, subsequent scans: (—) 1st, (···) 2nd and (- - -) nth.
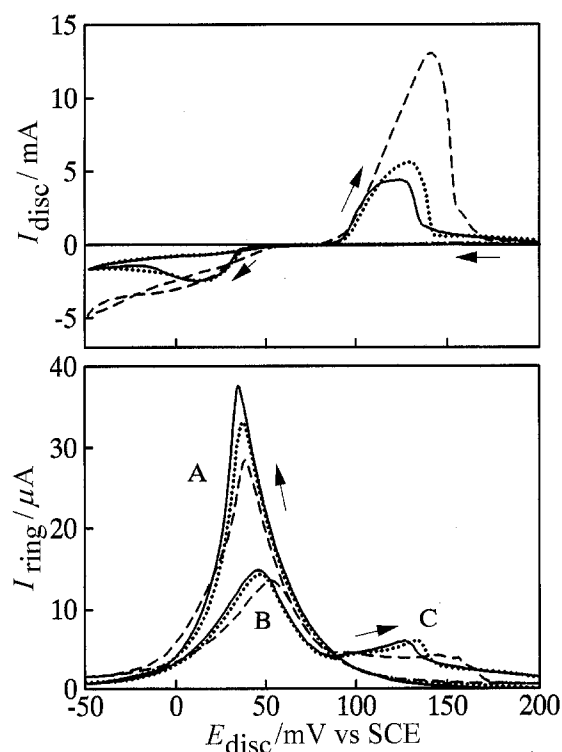
Fig. 2. Influence of 1 mg dm^{-3} fresh thiourea on the current–potential curves at a Pt/Pt RRDE. The freshly made aqueous solution contained 0.7 M CuSO$_4$, 1.8 M H$_2$SO$_4$ and 1 mg dm^{-3} thiourea. $A_{disc} = 0.126$ cm^2, $A_{ring} = 0.029$ cm^2, rotation rate 1500 rpm. $E_{ring} = +400$ mV vs SCE. Scan rate: 2.5 mV s^{-1}, subsequent scans: (—) 1st, (···) 2nd and (- - -) nth.
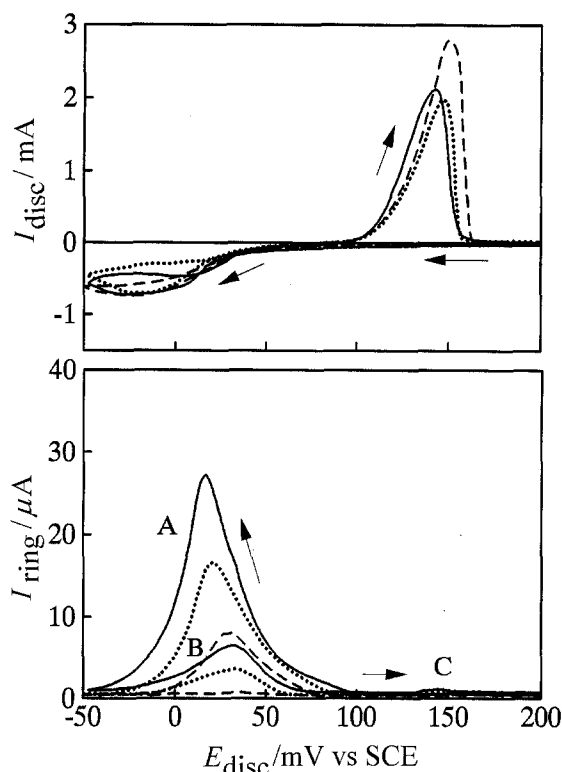
Fig. 3. Influence of $100 \, mg \, dm^{-3}$ fresh thiourea on the current–potential curves at a Pt/Pt RRDE. The freshly made aqueous solution containing $0.7 M$ $CuSO_4$, $1.8 M$ H_2SO_4 and $100 \, mg \, dm^{-3}$ thiourea. $A_{disc} = 0.126 \, cm^2$, $A_{ring} = 0.029 \, cm^2$, rotation rate 1500 rpm. $E_{ring} = +400 \, mV$ vs SCE. Scan rate: $2.5 \, mV \, s^{-1}$, subsequent scans: (—) 1st, (···) 2nd and (- - -) nth.

Cu^+ is always slow at a foreign substrate, such as Pt, and in steady state no further inhibition by thiourea is seen.

The most remarkable effect of thiourea appears, however, during dissolution of copper. Even if the disc voltammograms show that copper is dissolved the corresponding Cu^+ peak observed at the ring is very small (peak C in Figs 2 and 3). The value of the anodic ring/disc charge ratio $Q_{r,a}/Q_{d,a}$ is very low in fresh thiourea solutions (see Table 1) and it tends to

Table 1. Influence of thiourea and thiourea ageing on the cathodic and anodic ring/disc charge ratios $Q_{r,c}/Q_{d,c}$ and $Q_{r,a}/Q_{d,a}$, respectively. Values calculated from current–potential curves measured at a Pt/Pt RRDE in solutions containing $0.7 M$ $CuSO_4$, $1.8 M$ H_2SO_4 and thiourea of various concentration and age. Rotation rate of the RRDE was 1500 rpm or 300 rpm

| | $Q_{r,c}/Q_{d,c}$ | | $Q_{r,a}/Q_{d,a}$ | |
	1500 rpm	300 rpm	1500 rpm	300 rpm
No thiourea	0.0041	0.0028	0.011	0.0052
$1 \, mg \, dm^{-3}$ thiourea				
fresh	0.010	0.0034	0.0023	0.0006
3 days old	0.010	0.0040	0.0023	0.0009
7 days old	0.0024	0.0012	0.0043	0.0028
13 days old	0.0023	0.0010	0.0043	0.0026
$100 \, mg \, dm^{-3}$ thiourea				
fresh	0.018	0.010	0.0014	0.0017
3 days old	0.026	0.010	0.0091	0.0029
7 days old	0.027	0.013	0.0068	0.0022
13 days old	0.039	0.017	0.026	0.0052

be further lowered on subsequent scans. It seems that the intermediate in copper dissolution, Cu^+, is complexed with adsorbed thiourea at the disc surface. The complexes most probably also contain solvated sulfate ions [12]. Probably the adsorption/desorption equilibrium of the intermediate is shifted strongly towards the adsorbed state due to the presence of adsorbed thiourea. The small Cu^+ peak at the ring therefore indicates that active additive was incorporated into the deposit. Even if most of the deposit is dissolved during the reverse scan a small fraction of the deposit remains undissolved. A thin brownish coating is visible at the disc after subsequent scans and the charge ratio $Q_{d,c}/Q_{d,a}$ at the disc increases slightly due to thiourea. It is 1.2 and 1.5 measured at 1500 rpm in solutions containing $1 \, mg \, dm^{-3}$ and $100 \, mg \, dm^{-3}$ fresh thiourea, respectively. Obviously a reverse scan to $+200 \, mV$ is not sufficiently anodic to dissolve all the deposit formed. Surface analysis using XPS showed that the undissolved residue contained sulfur as SO_4^{2-} and S^{2-}, nitrogen and metallic copper, together with minor amounts of copper ions. Since the intensity ratio of nitrogen to S^{2-} was small, decomposition products of thiourea rather than thiourea molecules existed on the surface. A SIMS analysis confirmed that the residue contained only very small amounts of thiourea. These residual surface compounds are probably oxidized at more anodic potentials in agreement with the experimental results on glassy carbon [10] where the anodic stripping peak at high concentrations of thiourea is split into two peaks associated with copper dissolution, the ordinary stripping peak at $+150 \, mV$ and a smaller, more anodic peak at $+500 \, mV$ vs SCE.

The acidic thiourea solutions were allowed to age at room temperature without contact with metallic copper. Thus hydrolysis of thiourea and complex formation in solution could take place but no reactions between thiourea and metallic copper were possible during storage. Cyclic voltammograms were then measured in 3, 7 and 13 days old solutions. It was clearly seen that the thiourea concentration is stable for only a few days. According to the literature [13] the decay would be even faster if the solutions were ageing in contact with metallic copper. Measurements made in solutions containing $1 \, mg \, dm^{-3}$ thiourea show that a three days old solution still behaves similarly to a fresh one, but already after seven days ageing of thiourea is obvious (see Fig. 4). A higher reduction current at the disc is induced while the cathodic ring/disc charge ratio $Q_{r,c}/Q_{d,c}$ is lowered as shown in Table 1. This indicates that thiourea now promotes the deposition reaction and very little Cu^+ is transported to the ring. The charge ratio $Q_{d,c}/Q_{d,a}$ at the disc is 1.1 as for a solution without thiourea. Peak C, observed at the ring during dissolution, is growing. A corresponding growth of the anodic ring/disc charge ratio $Q_{r,a}/Q_{d,a}$ is best seen at low rotation rates. Thus the complexing effect of adsorbed thiourea is relaxed, i.e. the Cu^+ ions

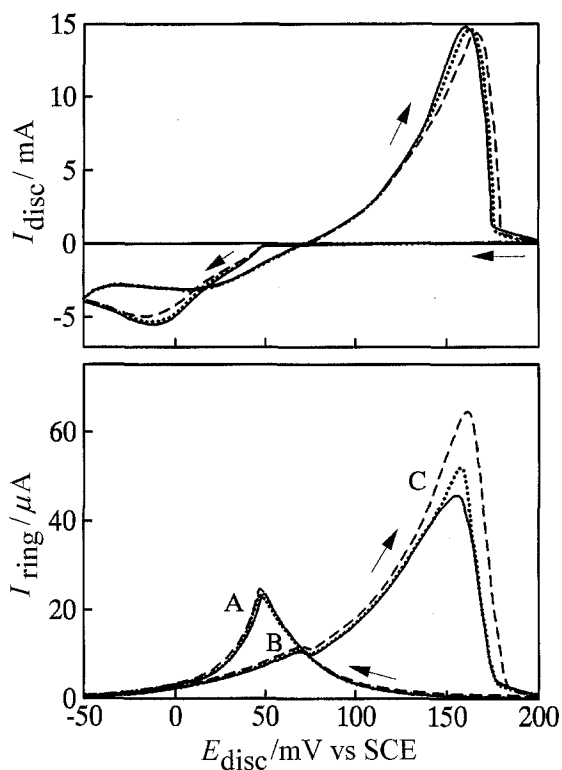Fig. 4. Influence of ageing of $1\,mg\,dm^{-3}$ thiourea on the current–potential curves at a Pt/Pt RRDE. The aqueous $0.7\,M$ $CuSO_4$–$1.8\,M$ H_2SO_4 and $1\,mg\,dm^{-3}$ thiourea solution was seven days old. $A_{disc} = 0.126\,cm^2$, $A_{ring} = 0.029\,cm^2$, rotation rate $1500\,rpm$. $E_{ring} = +400\,mV$ vs SCE. Scan rate: $2.5\,mV\,s^{-1}$, subsequent scans: (—) 1st, (···) 2nd and (- - -) nth.

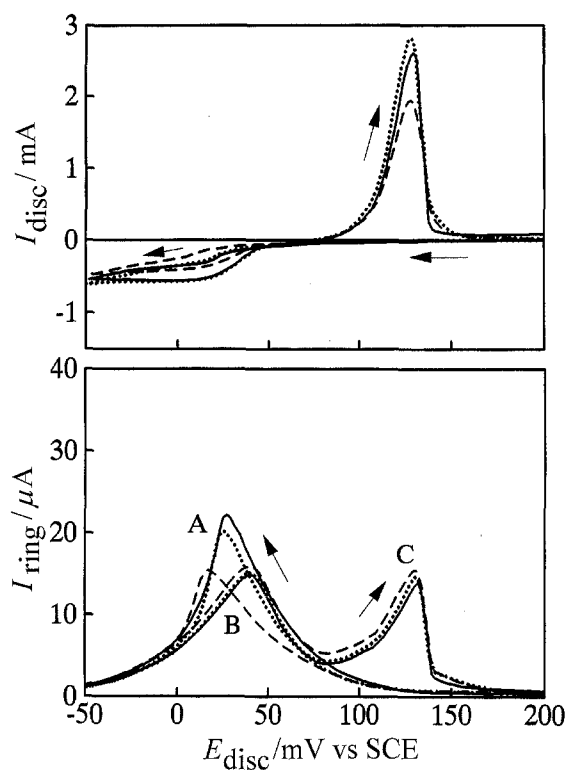Fig. 5. Influence of ageing of $100\,mg\,dm^{-3}$ thiourea on the current–potential curves at a Pt/Pt RRDE. The aqueous $0.7\,M$ $CuSO_4$–$1.8\,M$ H_2SO_4 and $100\,mg\,dm^{-3}$ thiourea solution was 3 days old. $A_{disc} = 0.126\,cm^2$, $A_{ring} = 0.029\,cm^2$, rotation rate $1500\,rpm$. $E_{ring} = +400\,mV$ vs SCE. Scan rate: $2.5\,mV\,s^{-1}$, subsequent scans: (—) 1st, (···) 2nd and (- - -) nth.

generated during dissolution can now be transported to the ring either as free Cu^+ or as dissolving Cu^+ complexes.

In a $100\,mg\,dm^{-3}$ thiourea solution the deposition of copper on the disc is further inhibited upon ageing and thus the cathodic ring/disc charge ratio $Q_{r,c}/Q_{d,c}$ increases (see Table 1). Already in a three day old solution a small amount of Cu^+ is allowed to escape to the ring during copper dissolution (peak C in Fig. 5) in contrast to the fresh solution where almost no Cu^+ peak is seen during dissolution (peak C in Fig. 3). In a solution aged for 13 days the deposition reaction on the disc is strongly inhibited. This means that very little copper is deposited and very little Cu^+ is observed at the ring (see Fig. 6).

4. Conclusions

Thiourea is used in copper electrorefining to promote smooth and bright copper deposits. Measurements using a Pt/Pt rotating ring-disc electrode show that in a freshly made, acidic thiourea solution the deposition reaction is retarded. The most distinct effect of thiourea is, however, seen during dissolution of the deposits formed in thiourea containing solutions. The intermediate in copper dissolution, Cu^+, is partly complexed with adsorbed thiourea. Probably the adsorption/desorption equilibrium of the intermediate is strongly shifted towards the adsorbed state due to the presence of adsorbed thiourea. Hence
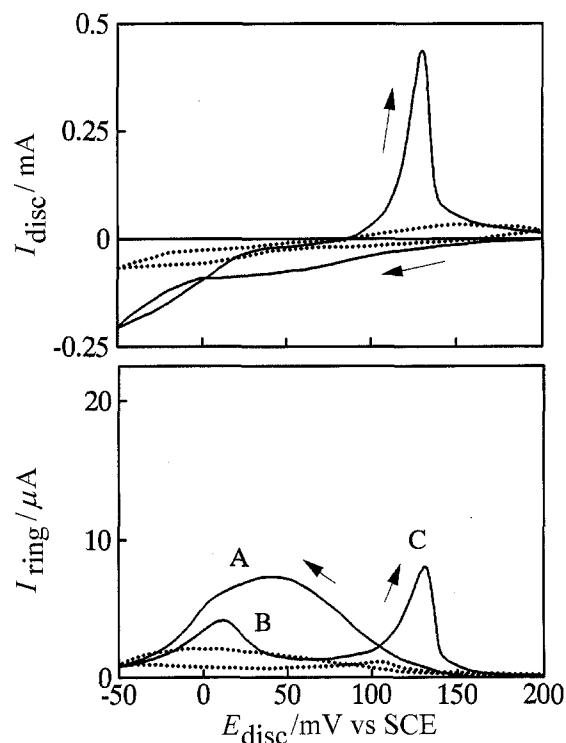

Fig. 6. Influence of ageing of $100\,mg\,dm^{-3}$ thiourea on the current–potential curves at a Pt/Pt RRDE. The aqueous $0.7\,M$ $CuSO_4$–$1.8\,M$ H_2SO_4 and $100\,mg\,dm^{-3}$ thiourea solution was 13 days old. $A_{disc} = 0.126\,cm^2$, $A_{ring} = 0.029\,cm^2$, rotation rate $1500\,rpm$. $E_{ring} = +400\,mV$ vs SCE. Scan rate: $2.5\,mV\,s^{-1}$, subsequent scans: (—) 1st and (···) 2nd.

Cu^+ is adsorbed at the electrode surface and the Cu^+ peak at the ring, corresponding to the amount of Cu^+ swept over from the disc to the ring, becomes very small. The small Cu^+ peak indicates that active additive, necessary for the formation of a smooth surface, was incorporated into the deposit.

Acidic thiourea solutions are not very stable since thiourea decomposes in the solution. Measurements using a rotating ring-disc electrode showed that thiourea containing solutions aged for only a few days have a distinct effect on the electrode reactions. It was found that the Cu^+ peak observed at the ring during dissolution can be used as a qualitative diagnostic criterion for thiourea ageing. At low concentrations of thiourea ($1\,mg\,dm^{-3}$, used in commercial electrorefining) a correlation between ageing and growth of the Cu^+ peak at the ring is clearly seen. At high thiourea concentrations ($100\,mg\,dm^{-3}$) a small growth of the Cu^+ peak is seen during the first few days. Upon further ageing of the thiourea solution the deposition reaction becomes strongly inhibited. Thus very little copper will be deposited and very little Cu^+ will reach the ring.

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