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Influence of thiourea on the nucleation of copper on polycrystalline platinum

A. TARALLO and L. HEERMAN
Departement Scheikunde, Afdeling Coördinatiechemie, K.U. Leuven, Celestijnenlaan 200G, B-3001 Heverlee, Belgium

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Abstract

The influence of thiourea on the nucleation of copper from a 0.30 M $CuSO_4$–1 M H_2SO_4 solution on polycrystalline platinum electrodes covered by a copper adlayer was investigated. In the case of diffusion controlled nucleation and growth the conditioning potential, that is, the potential of the electrode prior to the application of a large negative potential step, has a strong influence on the nucleation transients. This can result in either a promotion or an inhibition of the nucleation (which is characterized by a change in the nucleation rate constant and/or the site density) depending on the applied potential and the concentration of thiourea. In the region of mixed kinetics and for a fixed value of the conditioning potential (0.175 V vs $Cu^{2+}|Cu$, that is, in the region of strongest inhibition), a new and rather unexpected effect was observed. Thus, after an induction period, which is proportional to the concentration of thiourea, the current increases sharply to a much higher value, but after reaching a maximum drops again to its original value. At present there is no ready explanation for this phenomenon, which has been called 'nucleation outbursts', but it deserves more investigation because the linearity between the induction time and the concentration of thiourea might have practical applications.

1. Introduction

Thiourea is widely used as an addition agent in copper electrorefining and as a brightener in copper plating, usually in combination with other organic and inorganic addition agents. In practical copper electrorefining, thiourea is used in combination with gelatine, with small additions of chloride ions (which are believed to promote nucleation) and other organic additives.

The general philosophy behind the use of a combination of several addition agents has been reviewed by Plieth [1] who considers such a combination as a necessary prerequisite for optimal process control. An inhibitor is needed to slow down the rate of electrocrystallization but there must also be some possibility to reactivate the process, for example by nucleation. Overall control of the electrodeposition process is thus achieved by the use of two counteractive regulators. Along these lines Plieth [1] developed a 'local perforation' model to explain the synergistic action of brightener and surfactant in the case of copper plating. We believe that this concept can also be used to explain the successful use of the combination thiourea/gelatine in copper electrorefining. However, before this concept can be really applied to this particular case, it is necessary to obtain a better understanding of the action of thiourea *in the absence* of other addition agents. In fact, despite a very large number of investigations [2–7], the basics of how thiourea influences the electrocrystallization of copper is still poorly understood.

Generally, it is believed that addition agents in electrodeposition do not really take part in the electrode reaction itself: addition agents can adsorb on the electrode, block active sites, promote nucleation etc., but they merely act as catalysts (either positive or negative) of the electrocrystallization process. The influence of thiourea on the electrodeposition of copper is certainly more complicated; in $CuSO_4/H_2SO_4$ solutions the following equilibria must be considered [8–17]:

$$2\,Cu^{2+} + 2\,TU = 2\,Cu^{+} + FDS + 2\,H^{+} \tag{1}$$

$$Cu^{+} + q\,TU = Cu(TU)_q^{+} \tag{2}$$

$$Cu^{+} + p\,FDS = Cu(FDS)_p^{+} \tag{3}$$

Thus, thiourea (TU) is readily oxidized by cupric ions to form formamidinedisulphide (FDS) and both thiourea and formamidinedisulphide can form complexes with cuprous ions; as a matter of fact, it has been stated that there is no free thiourea in a copper electrorefining bath [2]. All these species can eventually adsorb on the electrode surface [4, 5, 7, 10, 14, 18–20] and/or participate in redox reactions, so that the overall picture can be expected to be very complex, as shown by the wide variety of experimental results reported in the literature.

This paper reports a study of the influence of thiourea on the electrochemical nucleation of copper on polycrystalline platinum electrodes, with special attention to the effect of the conditioning potential and the measuring potential on the nucleation transients.

2. Experimental details

Solutions were prepared with reagent grade chemicals and doubly distilled water. Fresh stock solutions of thiourea in 1 M H_2SO_4 were prepared on a daily basis to prevent the deterioration of this organic compound.

Experiments were performed at room temperature with an Autolab Pstat10 potentiostat (ECO Chemie, Utrecht, The Netherlands) provided with the low current module ECD specially designed for voltammetric work with microelectrodes. This computer controlled instrument was used with the software package GPES3 (General Purpose Electroanalytical System, vers. 3). Nucleation experiments were performed at room temperature with a conventional two-electrode cell using a large copper plate as both the counter and the reference electrode. The working electrode was a platinum microelectrode (100 μm diameter), purchased from BAS (Bioanalytical Systems Inc.); the size and shape of the electrode was controlled by SEM and voltammetric measurements using the $Fe(CN)_6^{4/3-}$ system and these measurements fully confirmed factory specifications. Before each series of experiments, the working electrode was polished on a nylon disc using 1 μm diamond paste. Immediately after polishing, the electrode was placed in a 0.30 M $CuSO_4$–1 M H_2SO_4 solution containing no organic additive. The electrode was held at -0.450 V vs the $Cu^{2+}|Cu$ equilibrium potential for 1 min. The deposited bulk copper was subsequently stripped at a potential of 0.050 V until the current dropped below 1 nA (after about 30 min) and this deposition/stripping sequence was repeated . This pretreatment results in the formation of an underpotential deposition layer of copper on the platinum substrate [21]. This pretreatment was carried out before the addition of thiourea to the solution to ensure that the *upd* characteristics of the copper/polycrystalline platinum system were the same at the start of each experiment [22].

Unless noted otherwise, all potentials in this paper are given vs the $Cu^{2+}|Cu$ equilibrium potential.

3. Results and discussion

Transients for the nucleation of copper on a polycrystalline platinum microelectrode from a 0.30 M $CuSO_4$–1 M H_2SO_4 solution in the absence of thiourea were recorded as a function of the conditioning potential, which was varied over the range 0.005–0.300 V (the conditioning time was 180 sec for all experiments); a typical transient is shown in Figure 1.

These experiments clearly show that a variation of the conditioning potential has little, if any, effect on the nucleation of copper under conditions where the growth is controlled by diffusion. Analysis of the experimental

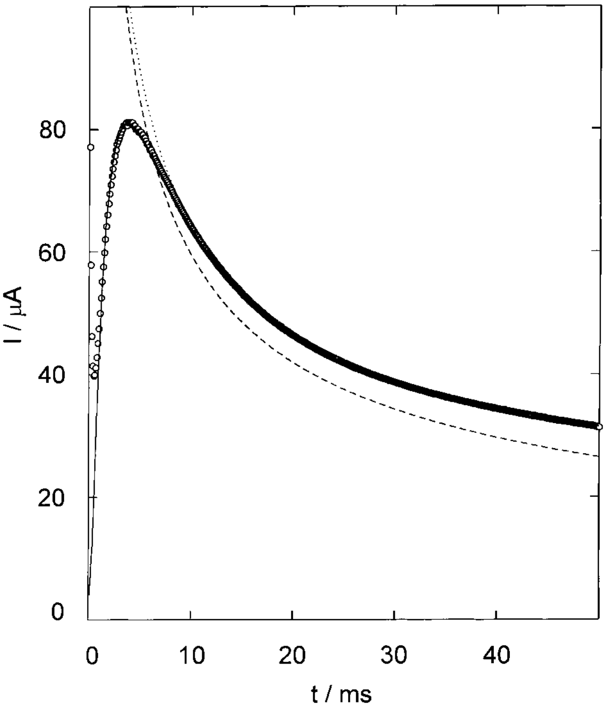

Fig. 1. Transient for the nucleation of copper from a 0.30 M $CuSO_4$–1 M H_2SO_4 solution in the absence of thiourea on an *upd* copper layer formed on a platinum microelectrode (100 μm dia.). Conditioning potential: 0.025 V. Measuring potential: -0.450 V. Key: (○) experimental points; (——) theoretical model using the values of N_0 and the nucleation rate constant obtained from the fitting procedure [23]. Also shown are the transients for the diffusion controlled currents calculated for this microelectrode (······) and for a planar electrode (- - - -; Cottrell).

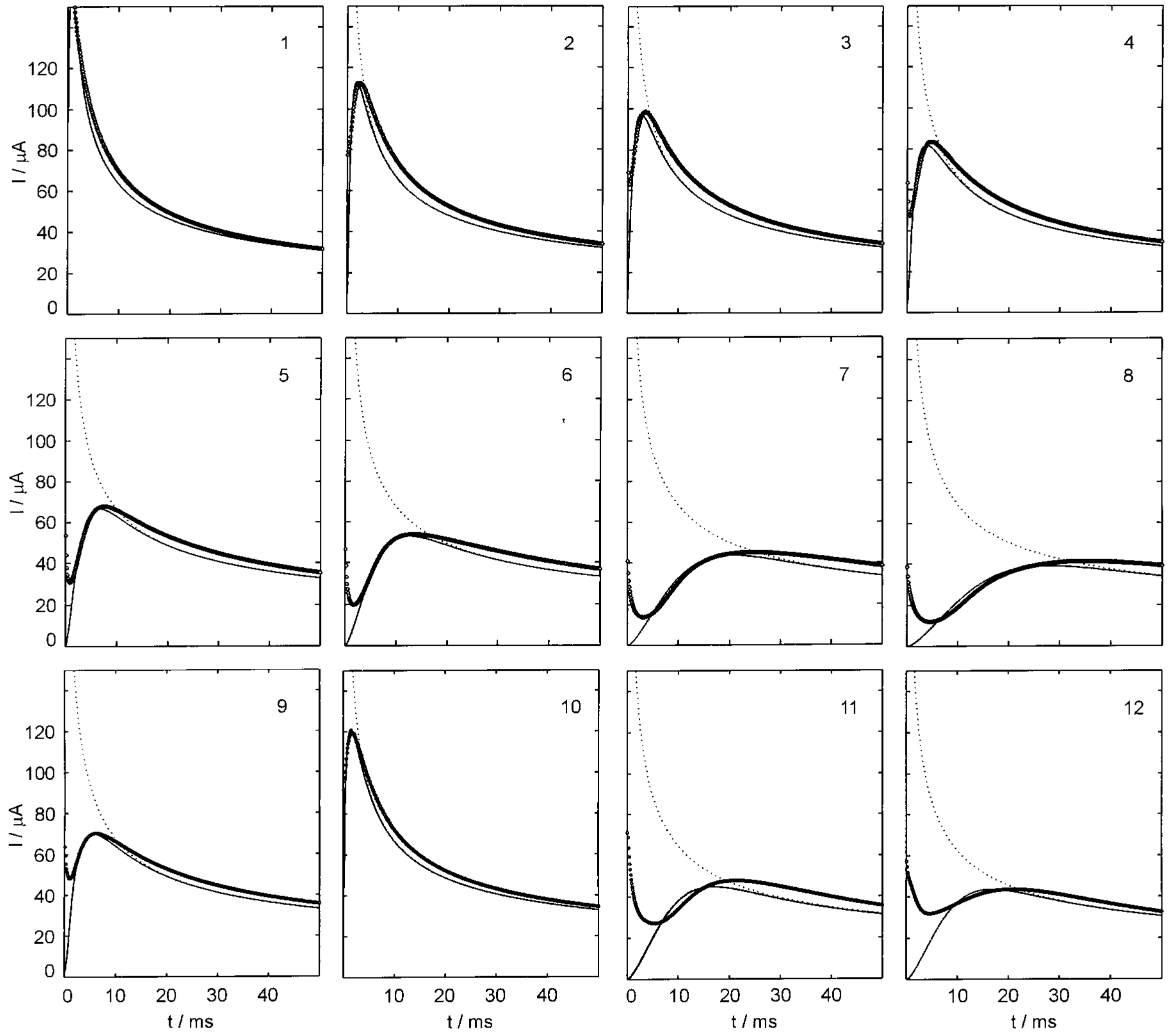

Fig. 2. Transients for the nucleation of copper from a 0.30 M $CuSO_4$–1 M H_2SO_4 solution with 0.5 mg dm^{-3} thiourea on an upd copper layer formed on a platinum microelectrode (100 μm dia.). Conditioning potential: (1) 0.005, (2) 0.025, (3) 0.050, (4) 0.075, (5) 0.100, (6) 0.125, (7) 0.150, (8) 0.175, (9) 0.200, (10) 0.225, (11) 0.250 and (12) 0.275 V. Measuring potential: −0.450 V. Key: (○) experimental points; (——) theoretical model using the values of N_0 and the nucleation rate constant obtained from the fitting procedure [23]. Also shown are the transients for the diffusion controlled currents calculated for this microelectrode (······).

transients was performed using a nonlinear least square fitting procedure based on the Levenberg–Marquardt algorithm with the nucleation site density, N_0, and the nucleation rate constant, A, as fitting parameters [23]. The results of this analysis indicate that nucleation in this case is almost instantaneous (the nucleation rate constant $A = 1151 \pm 18\ \mathrm{s}^{-1}$; the nucleation site density $N_0 = 1.32 \times 10^8 \pm 0.01 \times 10^8\ \mathrm{cm}^{-2}$). The value of the diffusion coefficient of cupric ions, $D = 5.5 \times 10^{-6}$ cm^2 s^{-1}, was determined from the long time limit of the experimental transient and is in good agreement with values reported earlier [24].

The addition of a small quantity of thiourea (0.5 mg dm^{-3}) has a pronounced effect, as shown in Figure 2, and the nucleation transients become strongly dependent on the conditioning potential. The values of A and N_0 obtained from the experimental transients are summarized in Table 1. The agreement between the experimental and the calculated transients is in many cases not very satisfactory, and certainly not as good as in the absence of the organic additive. It is important to note that the same value of the diffusion coefficient, $D = 5.5 \times 10^{-6}$ cm^2 s^{-1} (i.e., the value measured for pure solutions containing no additive), was used for the fitting of all the transients.

A much better agreement between the experimental and the calculated transients can be obtained if a much higher value of the diffusion coefficient, $D = 7.3 \times$

Table 1. Influence of conditioning potential, E_c on nucleation site density and nucleation rate constant for the nucleation of copper on an upd copper layer on a platinum microelectrode (100 μm dia.) from a 0.30 M $CuSO_4$–1 M H_2SO_4 solution with 0.5 mg dm^{-3} thiourea

E_c/V	$N_0/10^8\,cm^{-2}$	A/s^{-1}
0.005	4.51 ± 1.30	> 10^6
0.025	2.29 ± 0.13	3200 ± 711
0.050	1.67 ± 0.08	2209 ± 373
0.075	1.16 ± 0.04	1306 ± 186
0.100	0.87 ± 0.03	412 ± 29
0.125	0.71 ± 0.05	115 ± 12
0.150	0.50 ± 0.05	60 ± 7
0.175	0.44 ± 0.04	36 ± 4
0.200	0.79 ± 0.02	807 ± 59
0.225	2.23 ± 0.05	18547 ± 10829
0.250	0.86 ± 0.30	53 ± 22
0.275	0.76 ± 0.07	66 ± 7

Measuring potential: always −0.450 V.

10^{-6} cm^2 s^{-1}, is used for the fitting of the transients in the presence of thiourea. However, this is physically not meaningful because it is evident that such a large change in the value of the diffusion coefficient can not be caused by the addition of such small quantities of thiourea (of the order of 5×10^{-6} mol dm^{-3}). Such an apparent increase in the value of the diffusion coefficient of cupric ions was already made by Hölzle et al. [15] in a study of copper deposition on Au(111) in the presence of thiourea. At present there seems no ready explanation for this phenomenon but it seems to indicate that the usual models to describe diffusion controlled growth and nucleation [25–27] do not work very well in the present case. Therefore, the numerical data in Table 1 must be regarded with due caution, although qualitatively they correspond well with the changes in the morphology of the experimental transients.

For conditioning potentials slightly more positive than the $Cu^{2+}|Cu$ equilibrium potential (0.005–0.050 V), the addition of thiourea results in a promotion of the nucleation, which is reflected by an increase of both nucleation site density and the nucleation rate constant (Table 1). For conditioning potentials more positive than 0.075 V and up to 0.275 V, the nucleation is more and more inhibited which is not unexpected since it has been reported that thiourea strongly adsorbs on the copper adlayer [15]. However, in a narrow range of the conditioning potential, 0.200–0.225V, a sharp and rather unexpected increase in A and N_0 is observed.

An increase in the concentration of thiourea to 1 mg dm^{-3} essentially gives the same overall picture, although in this case the initial promotion of the nucleation is much less pronounced. The nucleation of copper is increasingly inhibited with increasingly positive conditioning potentials but, here again, a strong increase of A and N_0 is observed at $E_c = 0.200$–0.225 V. The transients in Figure 3 can not be fitted anymore using the usual models for electrochemical nucleation and diffusion controlled growth and the interpretation of these results is therefore only qualitative.

It seems to be generally accepted that free thiourea does not exist in the bath at the low levels used in this work (which are characteristic for copper electrorefining) [2]. Thus, in the bulk of the solution thiourea is only present as $Cu(TU)_q^+$ or $Cu(FDS)_p^+$ complexes, but this does not exclude the possibility that free thiourea or, eventually, formamidinedisulphide can exist as adsorbates on the copper adlayer. Furthermore, it has been reported by several authors that very low levels of thiourea (less than 1 mg dm^{-3}) have a depolarizing effect on the electrodeposition of copper during copper electrorefining [2, 6]. This last effect may be correlated with the promotion of the nucleation observed in this work for solutions containing 0.5 mg dm^{-3} and for conditioning potentials close to the $Cu^{2+}|Cu$-equilibrium potential. In fact, it has been demonstrated by Loo by means of SERS investigations [28] that coordination of thiourea at the copper surface occurs via the sulphur atom and not through the nitrogen atom, which implies that thiourea is adsorbed perpendicularly on the electrode surface. Since these studies were conducted with bulk copper electrodes, these conclusions are strictly valid only for potentials negative enough to prevent dissolution of the electrode, but are probably also valid for potentials slightly positive of the equilibrium potential. Then, for low levels of thiourea, and thus low coverage of the electrode, it is conceivable that the adsorbed molecules hinder the surface diffusion of adatoms and that the resulting local build-up of adatoms leads to a higher nucleation rate. Also, it can be considered that an adsorbed molecule can create around itself a kind of ‘free island’ which would increase the number of available nucleation sites. These mechanisms can be operative only at low surface coverage and will not be observed at higher concentrations of thiourea (then, clearly, thiourea itself will block the nucleation sites).

At potentials positive enough vs the $Cu^{2+}|Cu$ equilibrium potential, it can be expected that thiourea at low surface coverage will adsorb in a lateral position on the electrode to maximize the interaction between the free electron pair of the nitrogen atoms and the positive charge of the electrode (at high thiourea concentrations, and thus high surface coverage, adsorption is always perpendicular since this allows a much higher packing density of adsorbed molecules). As a consequence, it can be expected that the inhibition of the nucleation will increase as the conditioning potential becomes more

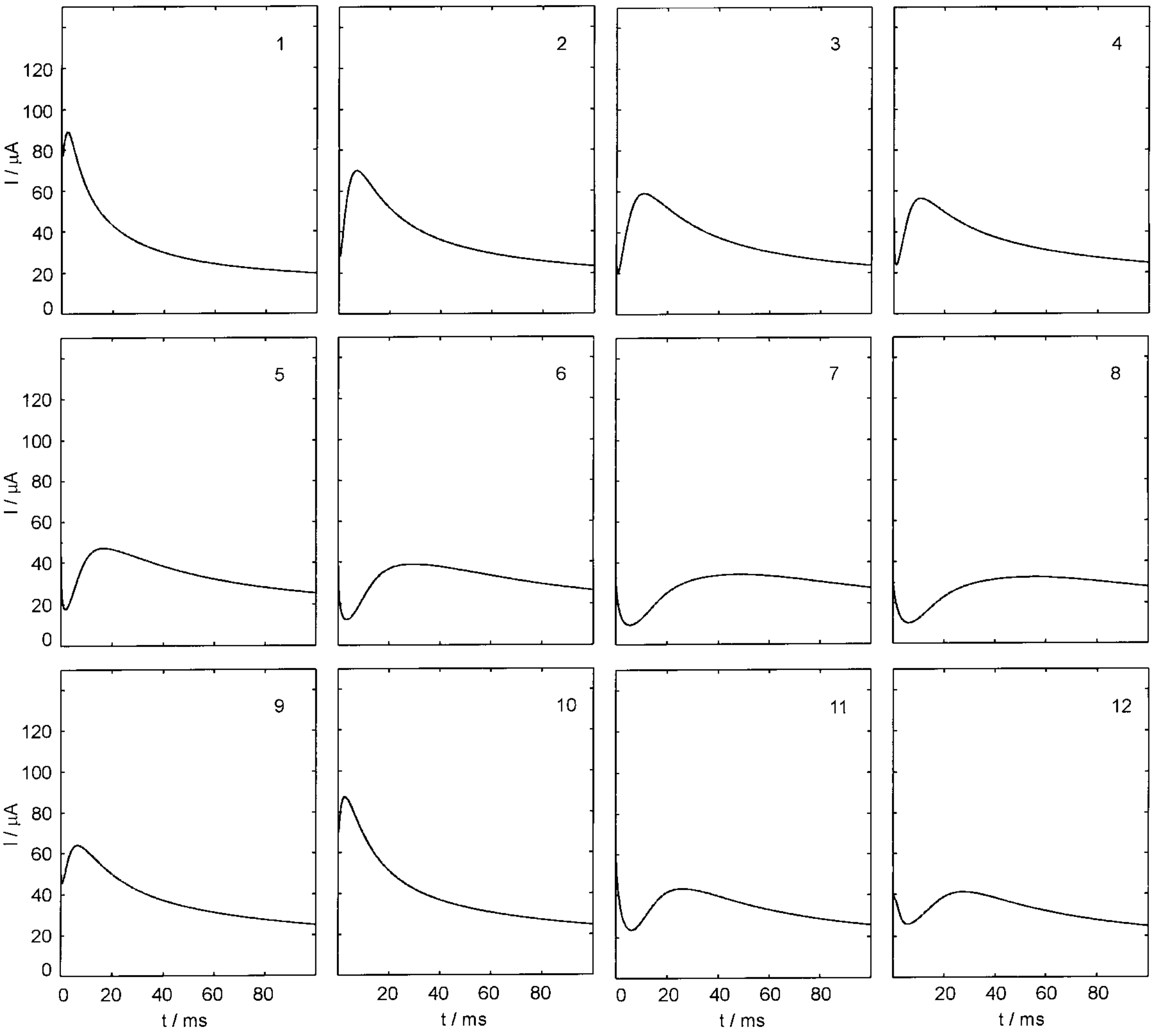

Fig. 3. Experimental transients for the nucleation of copper from a 0.30 M $CuSO_4$–1 M H_2SO_4 solution with 1 mg dm^{-3} thiourea on an upd copper layer formed on a platinum microelectrode (100 μm dia.). Conditioning potential: (1) 0.005, (2) 0.025, (3) 0.050, (4) 0.075, (5) 0.100, (6) 0.125, (7) 0.150, (8) 0.175, (9) 0.200, (10) 0.225, (11) 0.250 and (12) 0.275 V. Measuring potential: −0.450 V.

positive, as is indeed observed in the experiments. However, there is no ready explanation for the very pronounced increase of A and N_0 at a conditioning potential of 0.225 V. The standard electrode potential of the redox couple FDS/TU,

$$\mathrm{FDS} + 2\,\mathrm{H}^+ + 2\mathrm{e}^- = 2\,\mathrm{TU} \qquad (4)$$

is in the range 0.420–0.450 V (vs NHE) [2, 16, 29] and this value is confirmed by a cyclic voltammogram for the oxidation/reduction of thiourea on a bare platinum electrode (Fig. 4).

The increase of A and N_0 at 0.225 V may be associated with the oxidation of adsorbed thiourea to formamidinedisulphide. Even so, it has been reported that dissolution of a copper adlayer on polycrystalline platinum starts in this potential region [21] (although it can be expected that the adlayer is stabilized to some degree by adsorbed thiourea and/or formamidinedisulphide). At this stage, any attempt to explain this experimental result is simply speculative. Therefore, it is intended to complement, in the near future, the results of this work by experiments using in situ methods, for example, EQCM and AFM.

Finally, some results are given about the influence of the measuring potential for a fixed value of the conditioning potential. In these experiments the measuring potential is in the region of mixed diffusion/kinetic control and again a marked influence of the thiourea concentration is observed. The most striking results obtained are shown in Figures 5 and 6.

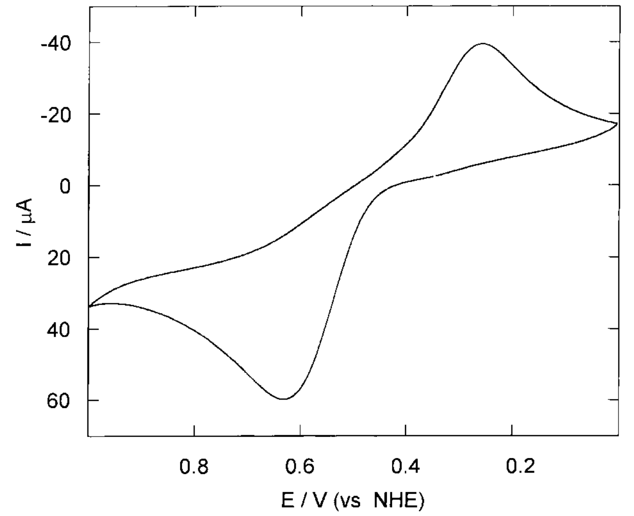

Fig. 4. Cyclic sweep voltammogram for the oxidation/reduction of the FDS/TU couple. The working electrode is a polished platinum macroelectrode (2 mm dia.). The thiourea concentration is 0.01 M in 1 M H_2SO_4. Conditioning potential 0.150 V vs AgCl/Ag (sat.). Scan-rate 100 mV s^{-1}.

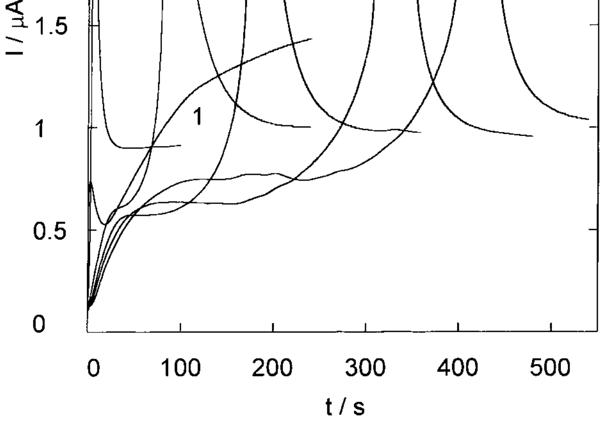

Fig. 5. Experimental transients for the nucleation of copper from a 0.30 M $CuSO_4$–1 M H_2SO_4 solution on an upd copper layer formed on a platinum microelectrode (100 μm dia.). Conditioning and measuring potential: 0.175 and −0.125 V, respectively. Thiourea concentration: (1) 0, (2) 0.5, (3) 1, (4) 1.5, (5) 2 and (6) 2.5 mg dm^{-3}.

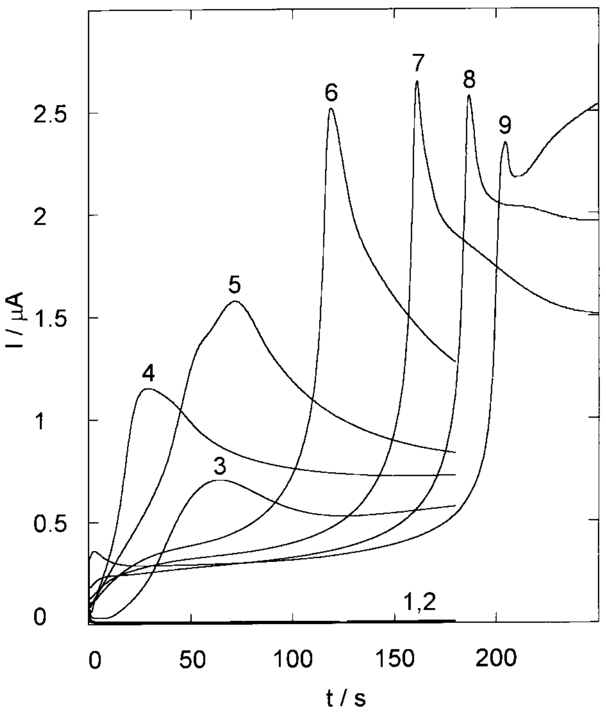

Fig. 6. Experimental transients for the nucleation of copper from a 0.30 M $CuSO_4$–1 M H_2SO_4 solution with 1 mg dm^{-3} thiourea on an upd copper layer formed on a platinum microelectrode (100 μm dia.). Measuring potential: (1) −0.005, (2) −0.025, (3) −0.050, (4) −0.075, (5) −0.100, (6) −0.125, (7) −0.150, (8) −0.175 and (9) −0.200 V. Conditioning potential: 0.175 V.

For all the transients in Figure 5, both the conditioning potential and the measuring potential were kept constant, $E_C = 0.175$ V (i.e., in the region of strongest inhibition) and $E_M = -0.125$ V. In a pure solution (no thiourea added) a current maximum is observed at a relatively short time after the start of the nucleation pulse and, after this maximum, the current steadily increases, presumably indicating a coarsening of the surface of the deposit. Addition of thiourea has a spectacular and rather unexpected effect. Thus, after addition of 0.5 mg dm^{-3}, the current maximum appears at a slightly longer time (hardly visible in the drawing) but the most important feature observed is the more than fivefold increase of the maximum. After the maximum the current drops to a constant value, that is, the coarsening of the surface observed in the absence of thiourea now has disappeared. On increasing the concentration of thiourea, nucleation becomes more and more progressive, in agreement with the fact that the organic additive initially inhibits the nucleation of copper. However, after kind of an induction period which increases almost linearly with the amount of thiourea, there appears suddenly what rightly may be called a 'nucleation burst'. The height and width of these peaks is apparently almost independent of the concentration of thiourea and the current always returns to the same constant value. Finally, Figure 6 shows a series of transients recorded with $E_C = 0.175\,\mathrm{V}$ for a constant concentration of thiourea ($1\,\mathrm{mg\,dm^{-3}}$) with a systematic variation of the measuring potential. Here again these 'nucleation bursts' are observed but now a roughening of the surface is observed for the more negative measuring potentials. At present there is no ready explanation for the origin of these 'nucleation bursts' and more work, including in situ visual observation techniques, is needed for a better understanding of this remarkable phenomenon.

4. Conclusion

The electrochemical nucleation of copper on a copper adlayer on polycrystalline platinum in the presence of thiourea is strongly dependent on the conditioning potential. In the case of diffusion controlled nucleation and growth, thiourea can cause either an increase (promotion) or a decrease (inhibition) of the nucleation rate and the site density. In the case of mixed diffusion/kinetic control, thiourea can cause 'nucleation bursts' after an induction period which is proportional with the concentration of the organic additive.

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