

Fundamental Studies of Copper Anode Passivation during Electrorefining: Part III. The Effect of Thiourea

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Thiourea has been extensively used as a grain refiner in industrial copper electrorefining processes. The influence of thiourea on deposit structure and morphology has received considerable study; however, the effect of thiourea and its degradation chemistry on the passivation behavior of commercial copper anodes is still not fully understood. This study was conducted to provide useful information regarding the electrochemical response of a commercial copper anode in the absence and presence of thiourea. Chronopotentiometry measurements were performed in synthetic electrolytes containing different thiourea concentrations and in industrial electrolytes obtained directly from a commercial tank house. Passivation time (t_p) and periodic passivation phenomena were found to be closely associated with thiourea concentration and degradation.

I. INTRODUCTION

CATHODE deposits obtained from acidified copper sulfate solutions without additives are often soft and coarsely crystalline or nodular. In copper electrorefining, such deposits tend to entrain electrolyte and anode residues, resulting in cathodes of less-than-desirable purity. Organic additives are widely used in industrial operations to modify deposit structure and morphology and to improve cathode quality.^[1-5] Thiourea and glue are common organic additives used in modern tank houses to produce smooth, dense, coherent deposits. In addition, the chloride ion is an essential member of the normal suite of addition agents. These additives influence the electrocrystallization of copper in various ways: glue (protein colloid) serves as a leveling agent, and thiourea and chloride ions serve as grain refiners. The need for these and possibly other additives (*i.e.*, Avitone A, Tembind, Orzan, and Magnafloc) with regard to the cathodic deposition is clearly established. However, the role of these electrolyte constituents on the anodic dissolution of impure copper anodes is not so well understood.

Anode passivation is an important problem in many commercial copper electrorefineries. In general, anode passivation is believed to be related to a number of chemical, physical, and operational factors (including the nature of adherent slime layers, composition of the anode and electrolyte, current density and temperature, and the chemical and electrochemical formation of anodic surface films). Very little is known about the influence of organic additives on the passivation behavior of impure copper anodes. Commercial tank houses commonly use glue in the range of 1 to 10 ppm, thiourea in the range of 0.5 to 3 ppm, and chloride in the range of 20 to 60 ppm. Jin and Ghali^[6] examined the influence of glue, thiourea, Avitone (surfactant), and Percol 351 (nonionic flocculating agent) on anode passivation behavior. With an electrolyte containing 42 g/L Cu, 160 g/L H₂SO₄,

17 g/L Ni, and 12 ppm Cl at 65 °C, they found that the time to passivation of impure anodes was almost independent of thiourea in the range of 0 to 30 ppm. However, the effect of thiourea concentration and its degradation chemistry on anode passivation remains unclear.

Galvanostatic (chronopotentiometry) potential-time curves are extremely useful in helping to identify the formation of a passive surface layer. In Part I of this article, it was demonstrated that chronopotentiograms generated at high current density (3820 A/m²) are a convenient method of producing potential-time ($E-t$) responses in about 1 hour.^[7] Anode passivation phenomena as examined by this method yield a time to passivation (t_p) parameter and four distinct electrochemical regions in the chronopotentiograms. A typical chronopotentiogram for a commercial copper anode is depicted in Figure 1. Indicated on this pattern are the passivation time (t_p) and the four characteristic regions: active dissolution (region I), prepassivation (region II), passivation onset (region III), and passivation (region IV).

The primary objective of this research is to examine the effect of thiourea on copper anode passivation using high current density chronopotentiometry. Two different series of chronopotentiometry measurements were carried out. One employed synthetic electrolytes containing varying initial Tu concentrations. To determine the specific role of thiourea, other additives and impurities were purposely avoided. The second electrolyte was an industrial electrolyte, tested fresh and for different periods of aging. Detailed analysis of the chronopotentiograms for a commercial copper anode in industrial electrolytes is presented. Passivation time (t_p) and passivation behavior are explained in terms of initial Tu concentration and degradation.

II. EXPERIMENTAL

A. Materials

The pure electrowon copper cathode, high-purity copper rod, and commercial copper anode (sample A5) were the same as those previously described.^[7,8] The chemical analyses of these copper samples are provided in Table I. The synthetic electrolyte, simulating the primary constituents for industrial operating conditions, contained 40 g/L Cu²⁺

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Table I. Chemical Analyses of Copper Samples

Sample	Element (Ppm)												
	Se	Te	Bi	Sb	As	Pb	S	Sn	Ni	Fe	Ag	Au	O
EW Cu cathode	0.4	—	<0.1	<1	<1	0.3	3	<1	<1	7	<1	—	—
ER Cu rod	0.5	<1	0.4	<1	<1	0.5	4	<1	<1	2	9	—	—
Anode A5	375	75	73	107	393	38	32	1	125	14	343	—	—

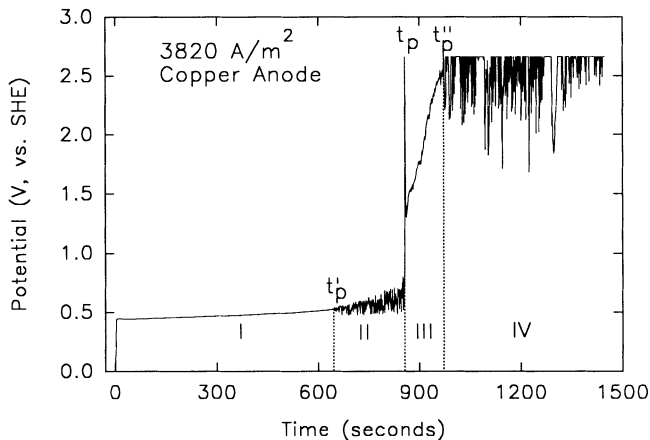


Fig. 1—Typical chronopotentiogram for a commercial copper anode (sample A5) at 3820 A/m² showing four distinctive regions and passivation time (t_p).

and 160 g/L H₂SO₄. Cupric sulfate (CuSO₄·5H₂O), sulfuric acid (H₂SO₄), and thiourea (CS(NH₂)₂), all of analytical reagent grade, as well as distilled deionized water of 18 MΩ/cm purity were used for the preparation of the electrolyte. Analysis of the electrolyte indicated <3 ppm chloride. (Note: the chloride ion is known to be electroactive in the copper electrorefining system, especially with regard to cathodic deposition. However, this research intentionally overlooked any role that chloride might have on anodic dissolution.) The chronopotentiometry measurements were carried out in the synthetic electrolyte at initial thiourea concentrations of 1, 5, 15, 50, and 100 ppm. Some tests were performed in an industrial electrolyte obtained directly from an operating tank house. Aging of this electrolyte was studied by allowing a solution to remain at 65 °C and then periodically making chronopotentiometry measurements. The composition of this electrolyte is shown in Table II. It should be noted that this research did not involve the identification and analysis of degradation products. A complete investigation of the role of glue and its decomposition products on anode passivation will be the subject of future research.

B. Methods and Instruments

A conventional three-electrode cell and a model 273 potentiostat/galvanostat, controlled by HEADSTART software (provided by EG&G Instruments, Inc., Princeton, NJ), were used to perform chronopotentiometry measurements. The working electrode was a pure copper or a commercial copper anode (sample A5). The preparation and assembly of the working electrodes was described in Part I of this article.^[7] The counter electrode was a high-purity copper rod measuring 1 cm in diam and 19.3 cm in length, prepared from a high-purity electrorefined rod. The exposed areas of working and counter electrodes were 1 and 22.8

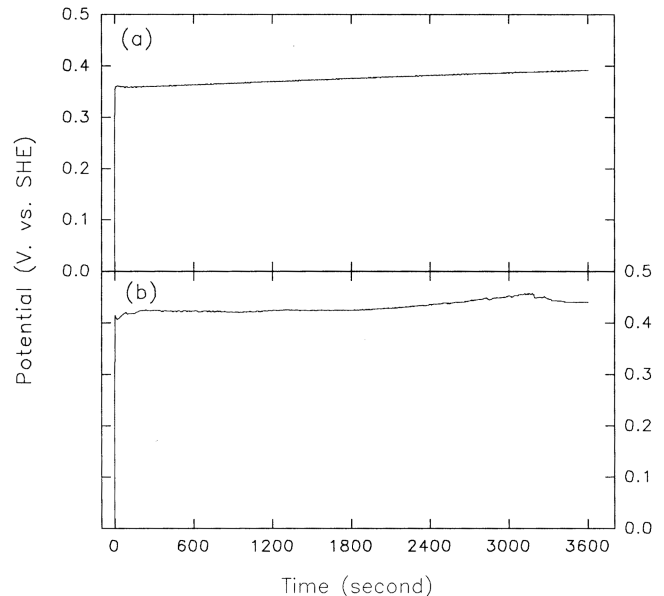


Fig. 2—Chronopotentiograms for pure copper at 3820 A/m²: (a) synthetic electrolyte and (b) industrial electrolyte.

cm², respectively. The reference electrode was a mercurous sulfate electrode (0.62 V vs SHE), which was also obtained from EG&G Instruments, Inc. The preparation of the working and auxiliary electrodes and the experimental procedures for the chronopotentiometry measurements were the same as those reported earlier.^[7]

III. RESULTS

A. Pure Copper

Chronopotentiograms for a pure copper electrode in the synthetic and industrial electrolytes at 3820 A/m² are presented in Figure 2. The industrial electrolyte was tested about 45 minutes after sampling at the plant and is referred to as the fresh sample. A pure copper anode shows no apparent passivation in either the synthetic electrolyte (Figure 2(a)) or the industrial electrolyte (Figure 2(b)). However, the anodic potentials for active dissolution obtained in the industrial electrolyte are about 50 mV higher than those in the synthetic electrolyte. The slight increase in potential is mainly attributed to the presence of other species in the industrial electrolyte. As shown in Table II, the industrial electrolyte contains notable amounts of chloride ions and other metal ions such as Ni, As, Sb, Bi, and Fe. In addition, the plant electrolyte contains organic additives such as Tu and glue not reported in Table II. The tank house electrolyte where this sample was collected typically contains 10 ppm glue and 5 ppm Tu.

The overall effect of electrolyte impurities and additives

Table II. Industrial Electrolyte Composition

Element	Concentration (g/L)
Cu	42.6
H ₂ SO ₄	166
SO ₄ ⁼	232
As	0.74
Sb	0.12
Bi	0.195
Se	<0.1
Te	<0.002
Fe	0.148
Ni	0.55
Zn	0.015
Pb	0.008
Ca	0.103
Cl ⁻	0.036

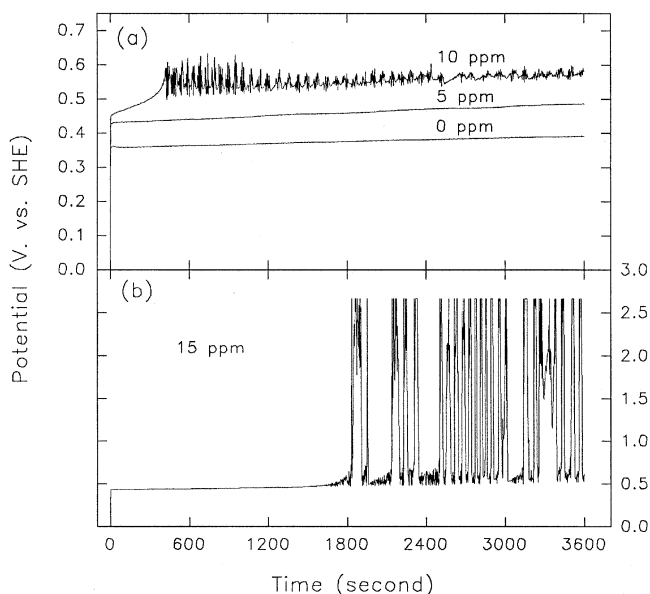


Fig. 3—Chronopotentiograms for pure copper at 3820 A/m² in the absence and presence of thiourea. The concentrations of thiourea are (a) 0, 5, and 10 ppm; and (b) 15 ppm.

on the anodic dissolution of pure copper is to polarize the electrode. As with the cathodic deposition of copper, the effect of individual species is rather complex. For instance, Sun and O'Keefe^[9] have shown that the chloride ion at 40 ppm produces a depolarizing effect, glue at 5 ppm causes a polarizing effect, and thiourea at 0.5 ppm exhibits a strong polarizing effect.

Chronopotentiograms for a pure copper electrode in the synthetic electrolyte for different initial Tu concentrations are shown in Figure 3. As can be seen in Figure 3(a), the addition of 5 ppm Tu causes an increase in the anodic potentials by approximately 100 mV. Aside from the slight polarizing effect, thiourea at an initial concentration of 5 ppm does not seem to influence the anodic dissolution of pure copper. The addition of 10 ppm Tu increased the anodic potential further and resulted in noticeable potential oscillation after approximately 420 seconds. However, the pure copper electrode did not show any apparent passivation. Upon the addition of 15 ppm Tu, the electrode exhibited characteristically strong passivation commencing at about 1800 seconds, as shown in Figure 3(b). The chron-

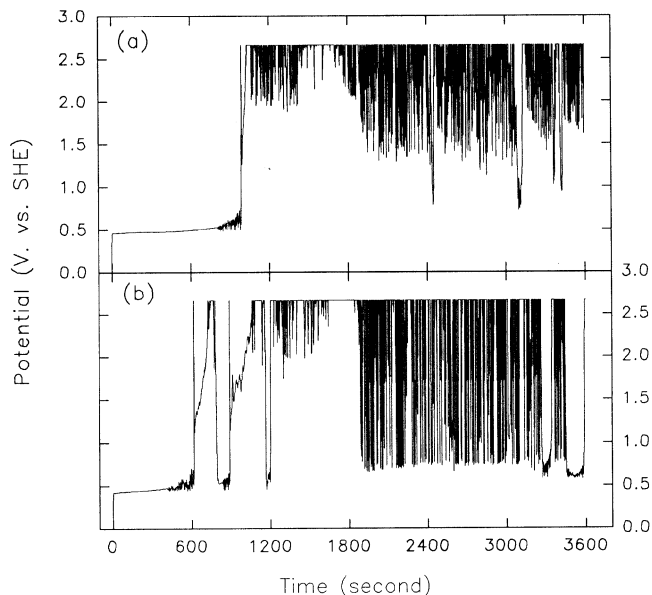


Fig. 4—Typical chronopotentiograms for a commercial copper anode (sample A5) at 3820 A/m². (a) synthetic electrolyte and (b) industrial electrolyte.

opotentiogram shows some evidence of erratic depassivation between 1800 and 3600 seconds. This indicates instability of the passivating layer in this region. It is apparent that high Tu concentrations strongly influence the electrochemical response of pure copper during anodic dissolution. Thiourea at an initial concentration of 15 ppm causes passivation of pure copper at conditions where it normally does not passivate.

B. Commercial Copper Anode

Typical chronopotentiograms for a commercial copper anode (sample A5) in the synthetic and fresh industrial electrolytes at 3820 A/m² are shown in Figure 4. In the synthetic electrolyte (Figure 4(a)), anode A5 exhibited four distinctive regions in the chronopotentiogram, as previously discussed: (1) active dissolution, (2) prepassivation, (3) passivation onset, and (4) passivation. The time to passivation (t_p) for this sample was observed to be 990 seconds. In the fresh industrial electrolyte, sample A5 was found to have a t_p value of about 600 seconds and displayed a cyclic passivation-depassivation response in region IV. Periods of reactivation were observed between the times of 800 to 900, 1160 to 1200, 3250 to 3320, and 3430 to 3560 seconds. Similar periodic passivation behavior of impure copper anodes has also been reported by Winand and Harlet,^[10] but the effect was not explained.

To investigate the effect of Tu concentration on anode passivation, chronopotentiograms were obtained with anode A5 in synthetic electrolytes at initial Tu values of 1, 5, 15, 50, and 100 ppm. The results of these experiments are shown in Figure 5. It appears that Tu concentrations higher than 15 ppm promote a passivation and depassivation response, especially in the portion of the chronopotentiogram immediately following t_p . The passivation time (t_p) in this case should be taken as the time at which the first sudden jump in potential occurs. The passivation times occurring subsequent to t_p are defined as the cyclic passivation time

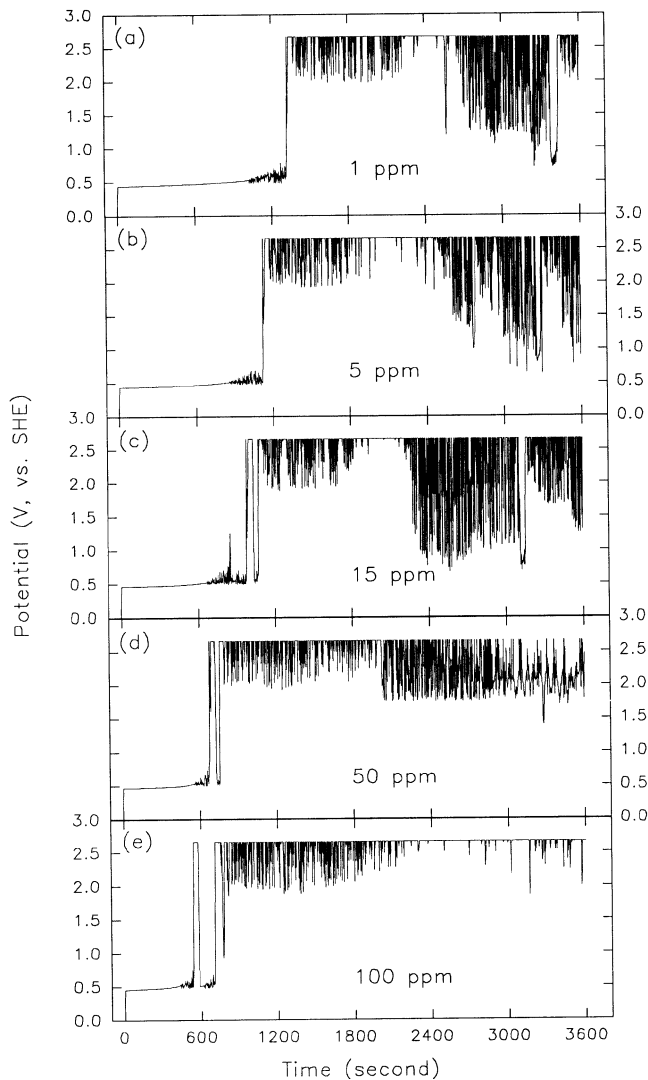


Fig. 5—Chronopotentiograms for a commercial copper anode (A5) at 3820 A/m² in synthetic electrolytes containing different concentrations of thiourea: (a) 1 ppm, (b) 5 ppm, (c) 15 ppm, (d) 50 ppm, and (e) 100 ppm.

Table III. Effect of Thiourea Concentration on Passivation Time for Anode A5

Thiourea Concentration (Ppm)	Cyclic Passivation Time (s)		Passivation Time (s)
	t_1	t_2	t_p
0	—	—	990
1	—	—	1324
5	—	—	1126
15	1076	—	982
50	752	—	678
100	708	—	540
50 (24 h)	1242	1582	700

t_n (where n indicates the passivation cycles). The values of passivation time (t_p) and of cyclic passivation times (t_1 and t_2) are listed in Table III for anode A5 at different initial Tu concentrations. It is obvious that the t_p values of this sample are strongly effected by Tu concentration. Small additions of thiourea (1 and 5 ppm) resulted in an increase in the time to passivation. These results suggest that thio-

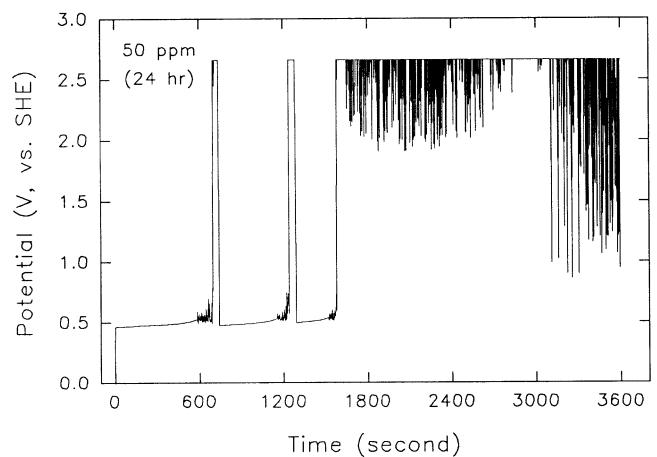


Fig. 6—Typical chronopotentiogram for a commercial copper anode (A5) at 3820 A/m² after 24 h of 50 ppm thiourea addition in a synthetic electrolyte.

urea concentrations near those used in commercial copper tank house operations delay anode passivation. The addition of 15 ppm Tu resulted in a cyclic passivation-depassivation response, as depicted in Figure 5(c); however, the t_p values remained approximately the same as those in the synthetic electrolyte (990 seconds). Thiourea concentrations of 50 and 100 ppm promoted anode passivation and also produced passivation-depassivation cycles (Figures 5(d) and (e), respectively). It is possible that the cyclic passivation-depassivation response observed in the synthetic electrolyte with higher Tu values is related to thiourea decomposition products.

The effect of Tu degradation on the electrochemical response of a commercial copper anode can be seen in Figure 6. In this chronopotentiogram, the passivation response of anode A5 was measured in synthetic electrolyte containing an initial Tu concentration of 50 ppm after 24 hours. The passivation times are included in Table III. A comparison of chronopotentiograms for fresh (Figure 5(d)) and aged (Figure 6) electrolytes containing 50 ppm Tu shows distinctly different electrochemical responses. Although the t_p value remained essentially unchanged, more passivation cycles were observed in the electrolyte aged for 24 hours, and the periodic passivation pattern was very similar to that observed in the industrial electrolyte (Figure 4(b)).

To further examine whether this cyclic passivation phenomenon is related to the aging of the industrial electrolyte, a series of chronopotentiometry tests were performed with anode A5 in a commercial tank house electrolyte at different aging times (in each case, the electrolyte was maintained at 65 °C). The chronopotentiograms for these experiments are compared in Figure 6. A cyclic passivation-depassivation response was observed in all cases. The values for passivation time (t_p) and cyclic passivation time ($t_1, t_2, t_3, t_4, etc.$) are summarized in Table IV.

The value of t_p in a synthetic electrolyte for A5 was measured to be 990 seconds. As can be seen in Table IV, the values of t_p with the aged commercial electrolytes were nearly constant, but were shorter than t_p with the synthetic electrolyte. The values of t_1 were approximately the same as those for t_p in the synthetic electrolyte, except the 2- and 30-hour samples. However, more passivation cycles were observed and the continuous potential oscillation of region

Table IV. Effect of Electrolyte Age on Passivation Time

Electrolyte Age (H)	Cyclic Passivation Time (s)						Passivation Time (s)
	t_1	t_2	t_3	t_4	t_5	t_6	
Fresh	1024	1350	1630	1860	—	—	612
2	1262	1836	2361	2635	2829	—	712
4	1062	1400	1636	1718	—	—	714
24	1008	1646	2113	2507	2871	3241	664
30	1334	1796	2173	2683	3307	—	730

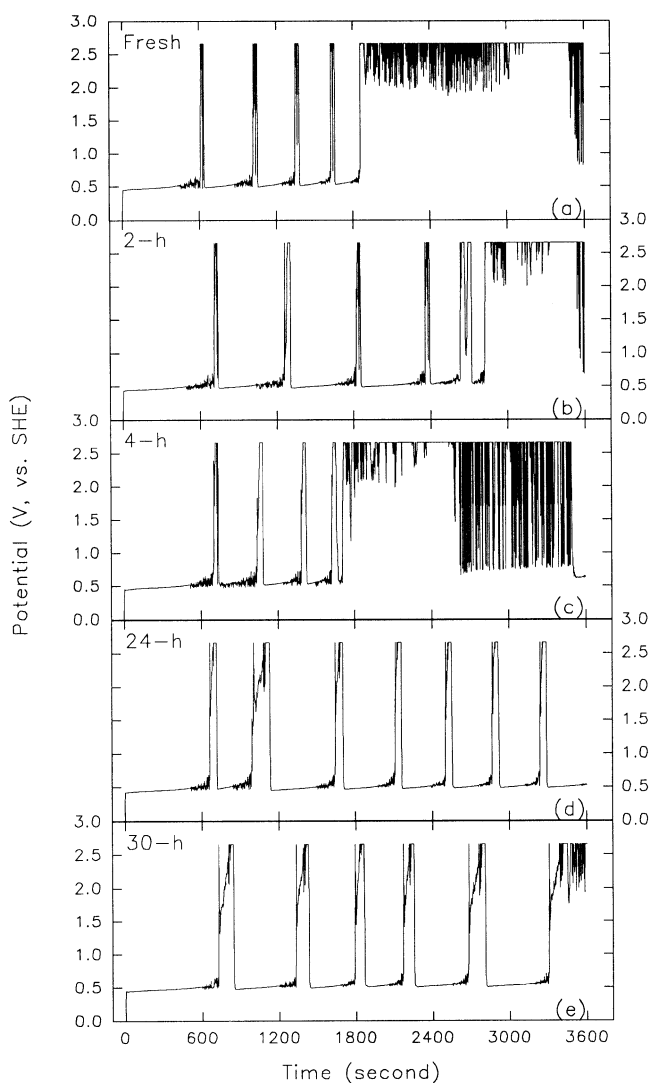


Fig. 7—Chronopotentiograms for a commercial copper anode (A5) at 3820 A/m² in aged industrial electrolytes: (a) fresh, (b) 2 h, (c) 4 h, (d) 24 h, and (e) 30 h.

IV was significantly delayed in the industrial electrolyte. Importantly, commercial electrolyte aged for 24 hours never exhibited continuous potential oscillation (region IV) during the duration of the test. The data for 30 hours were similar, but appeared to indicate passivation near the end of the test. These data suggest that the cyclic passivation-depassivation phenomena and potential oscillation are directly related to the aging and decomposition chemistry of the electrolyte.

IV. DISCUSSION

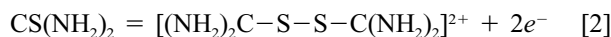
Organic molecules added during copper electrorefining mainly influence deposit brightness, hardness, grain size, ductility, and surface smoothness. The exact mechanism by which these agents affect these properties is rather complex; however, glue, thiourea, and the chloride ion all affect cathode polarization. Thiourea is widely used in copper electrorefining in the ppm range as a grain-refining agent for copper cathodes. The effect of thiourea with regard to the anodic processes, including anode passivation, has not been elucidated.

Thiourea has a chemical structure equivalent to CS(NH₂)₂. It is believed that the potential across the double layer can be influenced by the S = C < dipole, because Tu molecules are oriented *via* adsorption and change the dipole configuration of the double layer.^[11] Thiourea molecules may undergo decomposition through a number of possible reactions, including^[3,12-14] hydrolysis, oxidation, complexation, and redox.

Thiourea hydrolyzes to form urea and H₂S according to the following reaction:



Alternately, thiourea can be oxidized in successive stages to form a number of products, the first of which is formamidine disulfide (FDS). Oxidation reactions are important in this study because they would be associated with anodic processes. In an acid solution, the oxidation of Tu to FDS occurs at anodic potentials greater than approximately 0.50 V^[15]. The following reaction illustrates the first stage of thiourea oxidation:

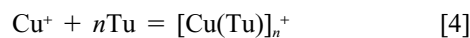


The FDS, as shown in Eq. [2], is in the protonated form. Subsequent disproportionation of FDS produces thiourea and a sulfinic acid which reacts further to yield cyanamide and elemental sulfur.

The main redox reaction in copper electrolytes involving Tu is where Cu²⁺ is reduced to Cu⁺ and Tu is partially oxidized to form FDS, according to the following reaction:



This reaction is followed by complexation of the Cu⁺ with thiourea according to the following complexation equilibrium:^[16]



The research of Onstott and Laitinen^[17] confirmed that the cuprous species is coordinated with four thiourea molecules. They found the stability constant for formation of the tetrathiourea copper (I) ion to be 2.44 x 10¹⁵, which indicates that the complex is very stable.

A typical chronopotentiogram for anode A5 in the industrial electrolyte is shown in Figure 8. The electrochemical features of this chronopotentiogram are similar to those observed for commercial copper anodes in the synthetic electrolyte (*i.e.*, four distinctive regions can be identified). However, the periodic passivation phenomenon is evident in the industrial electrolyte and also in the synthetic elec-

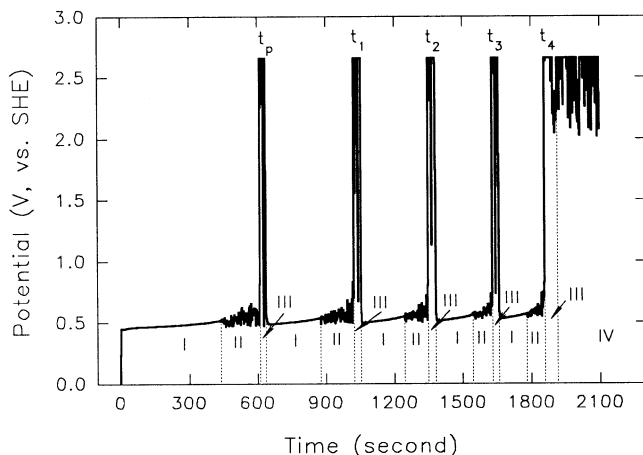


Fig. 8—Chronopotentiogram for a commercial copper anode (A5) at 3820 A/m² in an industrial electrolyte. Four distinct electrochemical features are shown for each cycle.

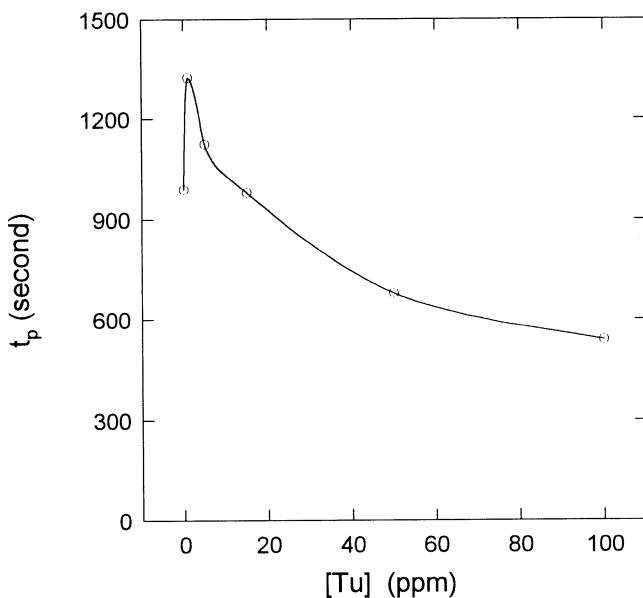


Fig. 9—Passivation time (t_p) as a function of thiourea concentration for a commercial copper anode (A5) at 3820 A/m² in synthetic electrolytes.

trolite containing Tu concentrations greater than 15 ppm. Each cycle displays active dissolution, prepassivation, passivation onset, and reactivation. Complete passivation commences after a series of these cycles. Reactivation of the electrode surface is believed to correspond to the detachment and sloughing of the slimes layer. Thiourea, or possibly its decomposition products, seems to affect the tenacity by which slimes adhere to the electrode surface.

Time to passivation (t_p) values for a commercial anode (A5) are plotted as a function of Tu concentration in Figure 9. The data indicate that t_p increases at low Tu concentrations up to about 1 ppm. As the Tu concentration increases above this value, t_p decreases markedly. The beneficial effect of thiourea at low concentrations may be the result of the complexation equilibrium involving the cuprous ion. This would have a direct influence on the chemical formation of Cu₂O passivating films on the electrode surface:



The detrimental effect of thiourea at high concentrations is believed to be the result of passivating films of elemental sulfur that form during the decomposition of thiourea.

V. SUMMARY AND CONCLUSIONS

A series of chronopotentiometry measurements were performed using pure copper and a commercial copper anode (sample A5) to study the effects of initial Tu concentration on passivation behavior. Pure copper does not passivate in a fresh tank house electrolyte. Pure copper shows no apparent passivation in a synthetic electrolyte containing 5 ppm Tu. At 10 ppm Tu, the pure copper reveals minor oscillations in potential, but no passivation. Passivation is observed in the synthetic electrolyte containing 15 ppm Tu. For the impure copper anode A5, periodic passivation response was characteristic in industrial electrolytes. In synthetic electrolytes, high Tu concentrations (>15 ppm) caused cyclic passivation-depassivation. In particular, after 24 hours with 50 ppm Tu addition, the similar periodic passivation phenomenon as appeared in industrial electrolytes was noticed.

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