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The effect of additives on the electrodeposition of copper studied by the impedance technique

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The impedance technique has been used to study the effects of NaCl, glue, thiourea and 'Avitone' on the elctrodeposition of copper in a 0.71 M $CuSO_4$–1.80 M H_2SO_4 solution. NaCl affects the rate of the two-step reaction and glue is a polarizer due to adsorption on the surface. The degradation of glue by hydrolysis can be followed using impedance measurements. No significant effects of thiourea and Avitone could be detected in the concentration and potential range used in electrorefining.

1. Introduction

The organic additives used in copper refining are very important in achieving good cathode copper quality. The effect of such additives has therefore been studied in numerous works [1–9].

Ordinary steady-state measurements, however, do not seem to give enough information about the influence of additives on the deposition reaction. The impedance technique has been used for investigations of the copper depositing reaction from pure acidic sulphate solutions [10–13] but only Glarum and Marshall [14] have included an additive, chloride.

Using the impedance technique it should be possible to gain new information about the effects of additives and it might also be possible to find a way of controlling the concentrations of active additives in the electrolyte. It is well known that too high or too low a concentration may be very detrimental to the quality of cathode copper and therefore better control of additive concentrations is important.

In the present work the effects of the most commonly used additives glue, thiourea, Avitone* and also chloride have been investigated in a 0.71 M $CuSO_4$–1.80M H_2SO_4 solution using the impedance technique. The effect of combinations of these additives is under investigation.

2. Experimental details

2.1. *Apparatus*

The impedance measurements were performed using a potentiostat (HiTek DT 2101) and a frequency response analyser (Solartron 1174) controlled by a microcomputer (Hewlett-Packard 85).

2.2. *Electrolytic cell*

A conventional three-electrode cell was used containing a copper reference electrode (99.999%, Koch Light Labs) in conjunction with a Luggin capillary. All potentials in this work are given against this reference electrode. The secondary electrode was made of platinum. The copper rotating disc electrode (99.999%, $A = 0.071$ cm^2, Koch Light Labs) was embedded in a Teflon holder and mechanically polished with graded alumina powders before each measurement.

The electrolyte used consisted of 0.71 M $CuSO_4$ (pa Merck) and 1.80 M H_2SO_4 (pa Merck) in triply-distilled water. Stock solutions of NaCl, glue, thiourea and Avitone were made so that desired concentrations of additive could be prepared by adding small amounts of the respective stock solution to the test solution without diluting the latter significantly.

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* Avitone is a sulphonated petroleum product described in US Patent 2 660 555.

All measurements were made at room temperature (22 ± 1)° C.

2.3. *Experimental procedure*

After electrode polishing, the cell was assembled and deoxygenated using nitrogen. A flow of nitrogen was maintained over the surface of the solution during the experiments.

The rotation rate of the working electrode was 300 rpm. The frequency sweeps were measured on a logarithmic scale (10 points decade^{-1}) from 10 mHz to 30 kHz using a sinusoidal perturbance signal of 5 mV rms.

The electrode impedance is well defined for all frequencies only when the response is independent of time. In a concentrated copper solution the growth of the electrode surface is, however, very rapid and will inevitably affect the measurements to some extent at least at low frequencies and large overpotentials. To minimize the time effects impedance values at a low frequency (10 mHz) were measured before each frequency sweep until a time-independent value (± 5%), indicating a stable growth, was obtained. During one sweep the change of the steady-state cell current was less than 5%.

The validity of the impedance measurements were confirmed by checking that the resistance obtained by extrapolating to zero frequency was equal to the reverse of the slope of the corresponding steady-state current-potential curve.

The effects of additives were investigated by successive frequency sweeps and additions of additive. Dummy measurements without additives were performed to reveal the effects of surface growth and measuring technique. The decrease in impedance because of growth effects during a series of measurements was found to be less than 7% at the lowest potential used (− 50 mV) and less than 23% at the highest potential used (− 250 mV). The measurements at − 250 mV were in all cases seriously affected by surface growth and thus the results measured at that potential are only indicative.

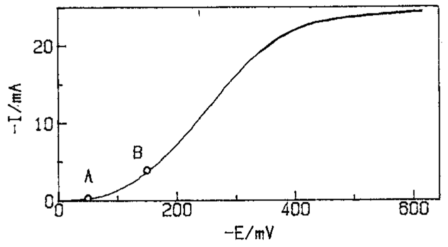

Fig. 1. Current–voltage curve for a pure 0.71 M $CuSO_4$–1.80 M H_2SO_4 solution. Sweep rate 5 mV s^{-1}, electrode area 0.071 cm^2.

3. Results

3.1. *Pure $CuSO_4$–H_2SO_4 solution*

The current–potential curve for the 0.71 M $CuSO_4$–1.80 M H_2SO_4-solution is shown in Fig. 1. The impedance measured at two potentials is shown in the complex impedance plane ($Z = Re - jIm$) in Fig. 2. In the impedance diagrams a high frequency feature due to double layer capacitance, C_{dl}, and to charge transfer resistance, R_{ct}, can be seen. R_{ct} is proportional to the rate of the electrode reaction. The high frequency feature in the diagrams obtained at low overpotentials (e.g. − 50 mV) are flattened and distorted. In both diagrams also, a low frequency feature due to mass transport can be seen.

The resistance at zero frequency, R_{dc}, is related

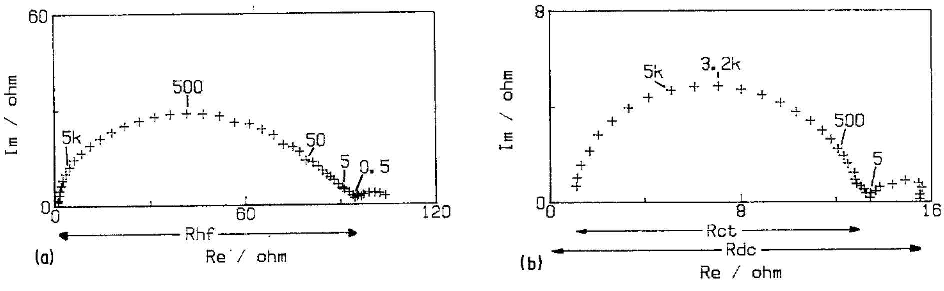

Fig. 2. Impedance diagrams obtained for a pure 0.71 M $CuSO_4$–1.80 M H_2SO_4 solution: (a) at − 50 mV, Point A in Fig. 1; (b) at − 150 mV, Point B in Fig. 1. Frequencies are expressed in Hz.

Table 1. Parameters obtained for a 0.71 M $CuSO_4$–1.80 M H_2SO_4 solution from impedance measurements (R^A_{ct}, R^A_{dc}) and I–E curve (R^B_{ct}, R^B_{dc}). The area of the electrode was 0.071 cm²

Potential (mV)	R^A_{ct} *(Ω)*	R^B_{ct} *(Ω)*	R^A_{dc} *(Ω)*	R^B_{dc} *(Ω)*
− 50	–	–	100	96
−100	–	–	29	28
−150	12.6	14.3	16.4	16.5
−250	6.2	4.8	11.4	11.0

to the reverse of the slope of the steady-state *I–E* curve at the potential of measurement by the relationship:

$$R_{dc} = dE/dI \qquad (1)$$

The charge transfer resistance, R_{ct}, is related to the Tafel slope corrected for mass transport according to

$$R_{ct} = \frac{1}{2.303I}\,\frac{dE}{d\log[I/(I_d - I)]} \qquad (2)$$

where I_d is the limiting current.

In Table 1 R_{dc} and R_{ct} estimated from the *I–E* curve using Equations 1 and 2 are shown together with R_{dc} and R_{ct} obtained from the impedance measurements. The latter are means of graphical determinations from five separate measurements and their reproducibility was estimated to be ± 14%.

3.2. *The effect of NaCl*

Chloride concentrations of 5–50 mg l^{-1} are common in electrorefining solutions. In Figs. 3 and 4 impedance diagrams obtained for 1–100 mg l^{-1} NaCl (0.6–60 mg l^{-1} Cl^-) at − 50 and − 150 mV are shown.

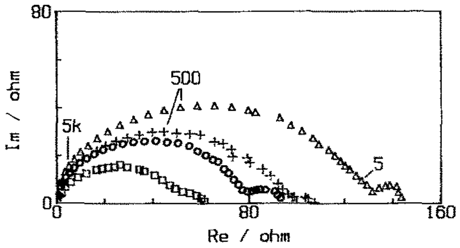

Fig. 3. The effect of NaCl at − 50 mV: + – 0 mg l^{-1} NaCl; △ – 1 mg l^{-1} NaCl; ○ 10 mg l^{-1} NaCl; □ – 100 mg l^{-1} NaCl. Frequencies are expressed in Hz.

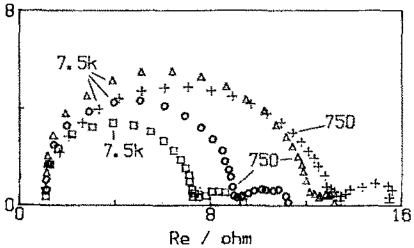

Fig. 4. The effect of NaCl at − 150 mV: + – 0 mg l^{-1} NaCl; △ – 1 mg l^{-1} NaCl; ○ 10 mg l^{-1} NaCl; □ – 100 mg l^{-1} NaCl. Frequencies are expressed in Hz.

For 1 mg l^{-1} NaCl a polarizing effect, i.e. an increase in impedance, was found at overpotentials smaller than − 100 mV. In all other cases a small depolarization, i.e. a decrease in impedance, was evident. These results are in accordance with earlier investigations using different techniques [1, 3–6]. The shapes of the impedance spectra are not affected by NaCl. The only effect seen is the change in rate of reaction due to formation of insoluble CuCl at the electrode surface at low NaCl concentrations and soluble cuprous complexes at higher concentrations. In Table 2 this is shown as a change in R_{ct} (for − 50 mV, R_{hf}, the resistance of the high frequency feature, is taken as a parameter according to Fig. 2a).

3.3. *The effect of glue*

Glue is the most commonly used levelling agent and the concentrations of glue in the electrolyte are typically 1–10 mg l^{-1}. In Figs. 5 and 6 impedance diagrams measured for 1–100 mg l^{-1} glue at − 50 and − 150 mV are shown.

Glue has a polarizing effect at all concentrations and potentials investigated. This is evidently due to adsorption of glue on the electrode surface.

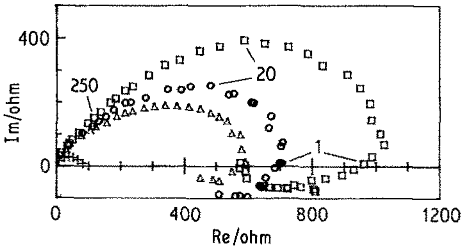

Fig. 5. The effect of glue at − 50 mV: + – 0 mg l^{-1} glue; △ – 1 mg l^{-1} glue; ○ 10 mg l^{-1} glue; □ – 100 mg l^{-1} glue. Frequencies are expressed in Hz.

Table 2. The effect of NaCl on the rate of reaction

NaCl concentration *(mg l^{-1})*	R_{hf} *(Ω)*	R_{ct} *(Ω)*		
	− 50 mV	− 100 mV	− 150 mV	− 250 mV
0	93	25	12.6	6.3
1	133	34	11.0	4.5
10	79	23	8.0	4.0
100	50	18	6.2	2.2

At small overpotentials this effect is very strong. In the impedance diagrams at − 50 mV the adsorption is seen as a large capacitive feature at low frequencies (a few hundred Hz to about 1 Hz). Below 1 Hz an inductive feature is visible. No diffusional mass transport is seen at this low overpotential, i.e. the impedance is independent of the rotation rate of the working electrode. At more negative potentials the adsorption effect of glue diminishes.

It is well known that glue is hydrolysed when heated, thus losing its polarizing effect. In commercial refining good control of the active glue concentration is therefore very important [15, 16]. The impedance technique could provide a new method to follow the degradation of glue. This is based on the fact that the impedance is decreasing as glue is being hydrolysed and thus the degradation can be followed by measuring the impedance at a properly chosen frequency. Fig. 7 shows an example of the effect of heating a $CuSO_4$–H_2SO_4 solution containing 10 mg l^{-1} glue and in Table 3 values for the real and imaginary components of the impedance are given to show the decrease due to hydrolysis.

3.4. *The effect of thiourea and Avitone*

Table 3. The effect of heating a 0.71 M $CuSO_4$–1.80 M H_2SO_4 solution containing glue at 90° C for 45 min (measured at − 50 mV)

Glue	9.7 *Hz*		120 *Hz*	
	Z_{Re}*(Ω)*	Z_{Im}*(Ω)*	Z_{Re}*(Ω)*	Z_{Im}*(Ω)*
10 mg l^{-1} fresh	603	200	177	176
10 mg l^{-1} heated	134	20	77	43
0 mg l^{-1}	82	6	66	19

In commercial electrorefining the thiourea concentration is kept low (< 1 mg l^{-1}) to avoid incorporation of sulphur in the cathode. In Figs. 8 and 9 impedance diagrams measured for 0.1–100 mg l^{-1} thiourea at − 50 and − 150 mV are shown.

Only at very low overpotentials (less than − 100 mV) thiourea was found to have a depolarizing effect on copper deposition. The same effect was seen in the steady-state *I–E* curves as a steeper slope close to equilibrium. At more negative potentials no significant additive effects could be detected for concentrations lower than 10 mg l^{-1} thiourea. At higher concentrations the impedance increased enormously due to a deposit almost blocking the surface.

Thus it must be concluded that, surprisingly enough, no effects of thiourea during copper deposition could be detected in the concentration and potential range which has been found useful in electrorefining. Lahousse and Heerman [9]

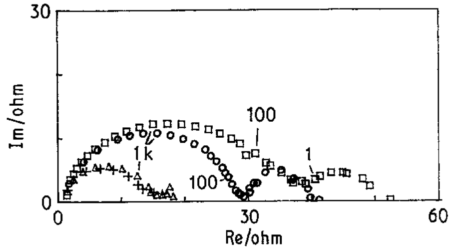

Fig. 6. The effect of glue at − 150 mV: + − 0 mg l^{-1} glue; △ − 1 mg l^{-1} glue; ○ − 10 mg l^{-1} glue; □ − 100 mg l^{-1} glue. Frequencies are expressed in Hz.

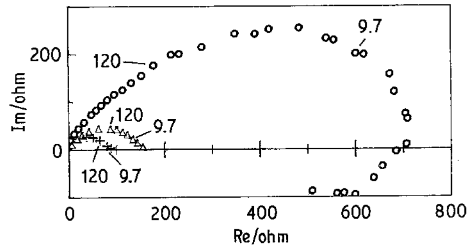

Fig. 7. The effect of heating a 0.71 M $CuSO_4$–1.80 M H_2SO_4 solution containing 10 mg l^{-1} glue (at − 50 mV): + − 0 mg l^{-1} glue; △ − 10 mg l^{-1} glue, solution heated at 90° C for 45 min; ○ 10 mg l^{-1} fresh glue. Frequencies are expressed in Hz.

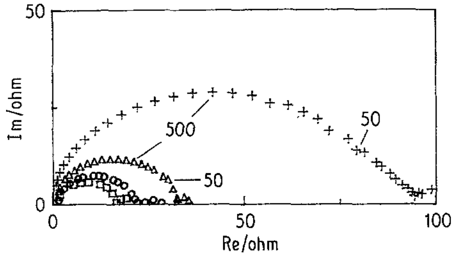

Fig. 8. The effect of thiourea at — 50 mV: + – 0 mg l^{-1} thiourea; △ – 0.1 mg l^{-1} thiourea; ○ – 1 mg l^{-1} thiourea; □ – 10 mg l^{-1} thiourea. Frequencies are expressed in Hz.

found a small depolarization at low concentrations (0.15 mg l^{-1} thiourea) and a polarization at higher concentrations, but often results are reported only for relatively high concentrations (> 10 mg l^{-1} thiourea).

It may be mentioned that the behaviour of thiourea in sulphate solutions has been studied on silver and copper electrodes using surface enhanced Raman spectroscopy [17], and it was found that the detection of thiourea at the surface was possible only at concentrations far higher than can be used in the copper electrorefining process.

Avitone was investigated in the concentration range 0.1–10 mg l^{-1}. Only at 10 mg l^{-1} was a polarizing effect evident at potentials smaller than — 100 mV but at lower concentrations no significant effects were found.

4. Conclusions

NaCl has a depolarizing effect, except at low concentrations and overpotentials where a polarizing effect is evident. This is due to changes in the rate of the two step reaction.

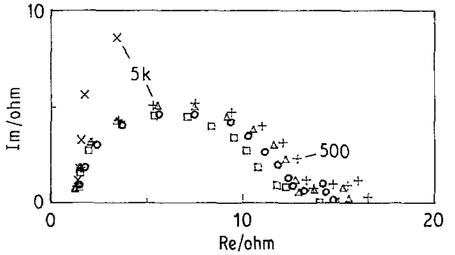

Fig. 9. The effect of thiourea at — 150 mV: + – 0 mg l^{-1} thiourea; △ – 0.1 mg l^{-1} thiourea; ○ – 1 mg l^{-1} thiourea; □ – 10 mg l^{-1} thiourea; X – 100 mg l^{-1} thiourea. Frequencies are expressed in Hz.

Glue has a polarizing effect due to adsorption on the surface. The degradation of glue by hydrolysis can conveniently be followed using the impedance technique.

No effects of thiourea during copper deposition could be found in the concentration and potential range used in copper refining. At higher concentrations a blocking of the electrode was evident.

Only minor effects of Avitone could be detected, which is in accordance with the well-known fact that this additive is beneficial only if used in connection with additives such as glue.

In commercial electrorefining combinations of additives are always used. The effect of combinations of additives is therefore of interest and is now under investigation using the same technique.

Acknowledgement

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