

The effect of copper on zinc electrowinning from industrial acid sulphate electrolyte

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The effect of copper on the electrowinning of zinc from industrial acid sulphate electrolyte was studied using X-ray diffraction, scanning electron microscopy and cyclic voltammetry techniques. Concentrations of copper as high as 50 mg l^{-1} had no effect on the zinc deposition current efficiency for 1-h deposits. Copper co-deposited with zinc and reduced the deposit grain size. The copper content of the zinc deposits increased with increasing copper concentration in the electrolyte and with decreasing current density. The cyclic voltammogram for copper-containing electrolyte was characterized by an appreciable cathodic current in the reverse scan after zinc dissolution indicating the presence of previously deposited copper on the cathode.

1. Introduction

The presence of impurities in the electrolyte is a major problem for the zinc electrowinning industry. Decreases in zinc current efficiency and changes in deposit morphology [1, 2] and cathodic polarization [2, 3] occur for electrolytes containing small concentrations of certain impurities. The work described in this paper is part of an overall programme to develop a better understanding of the factors which influence zinc deposition in order to gain closer control over the process. Specifically, the objective of this work is to determine if a characteristic behaviour pattern exists for the effect of various impurities on the current efficiency and polarization for zinc deposition and on the morphology and orientation of the zinc deposits.

Recently, reports have been published which characterized the effects of antimony [1-3], germanium [4-7] and tin [8] on zinc deposition current efficiency and polarization behaviour as well as their effects on deposit morphology and orientation. Although small concentrations of these impurities drastically reduce zinc deposition current efficiency, their effect on deposit morphology and orientation and on zinc deposition polarization is quite different. Since very

low concentrations of copper, like germanium antimony and tin, are detrimental to zinc electrowinning, it was felt that a detailed study of its effect might provide insight into the general mechanism of impurity behaviour.

Copper, although readily removed from zinc electrolyte by conventional zinc dust cementation purification, can re-enter the electrolyte during electrolysis via corrosion of bus bars, etc. It is known that copper will co-deposit with zinc and thus reduce metal quality; however, little is known about the effects of this impurity on zinc deposit structure or on zinc deposition polarization. Maja *et al.* [9] reported that low concentrations of copper produced a zinc deposit morphology consisting of groups of column-like growths; at higher copper concentrations the deposits were spongy and dendritic.

The present study was undertaken to examine the effect of copper on the morphology and orientation of 1-h zinc deposits electrowon from industrial acid sulphate electrolyte under conditions normally applied in the zinc industry. The effect of copper on zinc deposition current efficiency and the quantity of addition agent required to counteract this effect were also determined. Cyclic voltammetry experiments were conducted to characterize the effect of copper on

zinc deposition polarization and to assess the interaction of copper with antimony and organic additives such as glue.

2. Experimental procedure

2.1. Electrolyte and apparatus

The electrolyte was an industrial zinc sulphate solution prepared from hot zinc dust purified neutral zinc electrolyte obtained from Cominco Ltd., Trail, British Columbia. The average analysis was in g l^{-1} : Zn 150, MgSO_4 38, Mn 1.6; in mg l^{-1} : Cd 0.2, Sb 0.02, Co 0.3, Ge 0.01, Ni 0.1, Cu 0.1, Fe 0.9, Pb 0.2, Cl 80 and F 3.

Cell solutions were prepared by adding H_2SO_4 , redistilled water and impurities to the electrolyte to give final concentrations of 55 g l^{-1} zinc and 150 g l^{-1} H_2SO_4 . Animal glue additions were made as concentrated solutions. Copper was added as sulphate solution and anti-mony additions were made as a potassium antimony tartrate solution.

The electrolysis cell consisted of a one-litre beaker fitted with a Lucite cover which had slots cut in it to mount the electrodes [2]. A three

electrode assemblage consisting of a central aluminium cathode and two platinum anodes was used. The cathode was fashioned from 4.7 mm thick aluminium sheet (purity 99.6%) obtained from Cominco. It measured $31.8 \text{ mm} \times 136.3 \text{ mm}$ and was mounted so that zinc deposited on both sides onto a total area of 12.9 cm^2 . The anodes were cut from a 0.3 mm thick platinum sheet and measured $17.9 \text{ mm} \times 109.7 \text{ mm}$. The platinum anodes were used to avoid lead contamination on the zinc deposits from conventional Pb–Ag anodes [10].

2.2. Electrolysis

The electrolysis experiments were run in a constant temperature bath at 35°C with stirring, and at a cathode current density of 430 A m^{-2} for a period of one hour. Additional tests were run at current densities of 323 and 215 A m^{-2} and for times of four hours.

2.3. Examination of deposits

Sections of the zinc deposits were examined by scanning electron microscopy to determine the surface morphology of the deposit and by X-ray

Table 1. Current efficiency, crystallographic orientation and copper content of zinc deposits as a function of copper concentration and current density

Current density (A m^{-2})	Copper (mg l^{-1})	CE (%)	Cathode Copper (%)	Crystallographic orientation*
430	0	93.6	—	(112) (103) (102)
	5	93.0	0.025	(112) (110)
	10	95.3	0.060	(112) (101)
	20	95.1	0.095	(112)
	30	92.3	0.157	(114) (112)
	50	92.5	0.254	(002) (101)
323	0	96.0	—	(112)
	10	94.0	0.041	(112)
	20	92.4	0.129	(101) (103)
	30	94.8	0.240	(002) (101)
	50	93.0	0.399	(002)
215	0	94.3	—	(112)
	10	92.1	0.065	(101) (102) (103)
	20	93.9	0.161	(101) (002) (103)
	30	90.7	0.232	(101) (002)
	50	88.5	0.393	(101)

*Relative to ASTM Standard for zinc powder. Electrolysis conditions: 55 g l^{-1} Zn; 150 g l^{-1} H_2SO_4 ; 35°C .

diffraction to determine the preferred crystal orientation relative to the ASTM standard for zinc powder. One side of the deposits electrowon from copper contaminated electrolyte was dissolved in HNO_3 for chemical analysis to determine the copper content of the deposits by atomic absorption spectrophotometry.

2.4. Cyclic voltammetry

Cyclic voltammograms were obtained using a voltage scan generator, a potentiostat and a x - y recorder for recording current versus applied potential plots. The voltage scan generator was used to cycle the potential from -0.7 V to about -1.12 V versus a saturated calomel electrode. The latter limit was determined to give a maximum current of approximately 65 mA on the forward scan; hence there is some variation in the potential scan range. The scan was done at a rate of 1 or 2 mV s^{-1} .

The same cell was used for both the cyclic voltammetry and the electrowinning; however, the electrode assembly differed. The working electrode was an aluminum cathode measuring 15.4 mm by 109.5 mm by 0.8 mm thick. It was mounted so that the surface area was approximately 3.2 cm^2 . The counter electrode was one of the platinum anodes used in electrowinning. A

saturated calomel electrode mounted adjacent to the cathode was used as the reference electrode.

Prior to each test the cathode was conditioned by polishing with 600 grit paper, washing with acetone followed by redistilled water, and patting dry with a tissue. The cathode was then put into the cell while the electrolyte was stirred. Once a steady rest potential was established, the stirrer was turned off and the scan was initiated.

3. Results and discussion

3.1. Current efficiency and deposit orientation

The current efficiencies for 1-h zinc deposits electrowon at current densities of 215 , 323 and 430 A m^{-2} from electrolytes containing up to 50 mg l^{-1} copper are summarized in Table 1. The CE remained $>90\%$ in all cases except for the deposit electrowon at 215 A m^{-2} from an electrolyte containing 50 mg l^{-1} copper. At high current density and low copper concentration, the preferred deposit orientation remained unchanged at (112) . However, as the current density decreased and the copper concentration increased, the preferred deposit orientation changed to predominantly (002) , Table 1.

The data in Table 1 also show that the copper content of the zinc deposit increased with

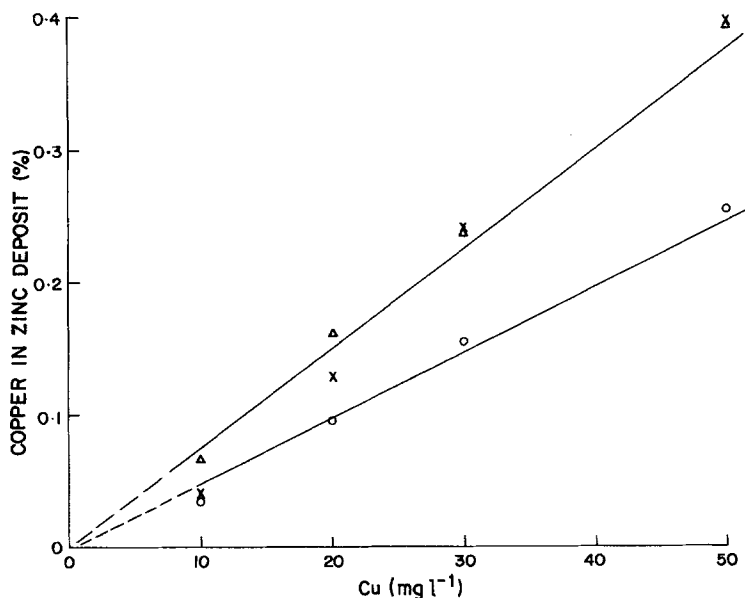


Fig. 1. Plots showing the correlation between percent copper in the 1-h zinc deposits and the concentration of copper in the electrolyte at various current densities. ○ 430 A m^{-2} , × 320 A m^{-2} , △ 215 A m^{-2} .

Table 2. Current efficiency, crystallographic orientation and copper content of zinc deposits as a function of Cu–Sb interactions

Copper (mg l ⁻¹)	Antimony (mg l ⁻¹)	CE (%)	Cathode Copper (%)	Crystallographic orientation*
10	0	95.3	0.060	(1 1 2) (1 0 1)
10	0.04	90.4	0.068	(1 1 2) (1 1 0)
10	0.08	85.4	0.066	(1 0 1) (1 0 2) (1 1 2)
10	0.10	83.2	0.072	(1 0 2) (1 0 3) (1 0 1)
10	0.15	74.6	0.144	(1 0 2) (1 0 3) (1 0 1)

*Relative to ASTM Standard for zinc powder. Electrolysis conditions: 55 g l⁻¹ Zn; 150 g l⁻¹ H₂SO₄; 35° C; 430 A m⁻².

increasing copper concentration in the electrolyte and with decreasing current density. Fig. 1 indicates a correlation between copper concentration in the electrolyte and the copper content of the zinc deposit. At 430 A m⁻², for each mg l⁻¹ copper in the electrolyte, the copper content of the zinc deposits increased by 0.0075%.

Interactions among impurities are important particularly because impurities which do not exhibit an effect when present alone become intolerable when small amounts of another impurity are introduced. Antimony is frequently added to the electrolyte in small concentrations with glue in order to control deposit growth [1]. The effect of increasing antimony concentrations in combination with a fixed amount of copper on the current efficiency (CE), orientation and percent copper in the 1-h zinc deposits electrowon at 430 A m⁻² is shown in Table 2. Increasing the antimony concentration from 0 to 15 mg l⁻¹ in an electrolyte containing 10 mg l⁻¹ copper, decreases the CE from 95.3 to 74.6% and increases the copper content of the zinc deposit from 0.06 to 0.114%, presumably because less zinc is deposited from antimony-containing electrolyte. The preferred deposit orientation

changes from (1 1 2) (1 0 1) to (1 0 2) (1 0 3) (1 0 1).

The addition of glue to the electrolyte counteracts the effect of Cu–Sb interactions to some extent as indicated in Table 3. The CE is increased and the copper content of the zinc deposit remains unchanged; the preferred deposit orientation changes from (1 1 2) to (1 0 1) in the presence of 30 mg l⁻¹ glue.

3.2. Deposit morphology

The effect of copper on the zinc deposit morphology is shown in Fig. 2. Fig. 2a shows the morphology of a 1-h zinc deposit electrowon from a solution containing 10 mg l⁻¹ copper. The morphology is very similar to that for the deposit electrowon from an addition-free electrolyte [2, 10] except that the platelet size is reduced. Increasing the electrolysis time to 4 h results in a further reduction in the deposit grain size, Fig. 2b. The presence of 10 mg l⁻¹ copper in the electrolyte did not alter the preferred (1 1 2) deposition orientation, Table 1.

The morphology of the deposit electrowon from a solution containing 10 mg l⁻¹ copper

Table 3. Current efficiency, crystallographic orientation and copper content of zinc deposits as a function of Cu–Sb–Glue interactions

Copper (mg l ⁻¹)	Antimony (mg l ⁻¹)	Glue (mg l ⁻¹)	Ce (%)	Cathode Copper (%)	Crystallographic orientation*
10	0	0	95.3	0.060	(1 1 2) (1 0 1)
10	0.04	15	91.5	0.062	(1 1 2)
10	0.08	30	88.5	0.067	(1 0 1)
10	0.10	30	88.5	0.062	(1 0 1)

*Relative to ASTM Standard for zinc powder. Electrolysis conditions: 55 g l⁻¹ Zn; 150 g l⁻¹ H₂SO₄; 35° C; 430 A m⁻².

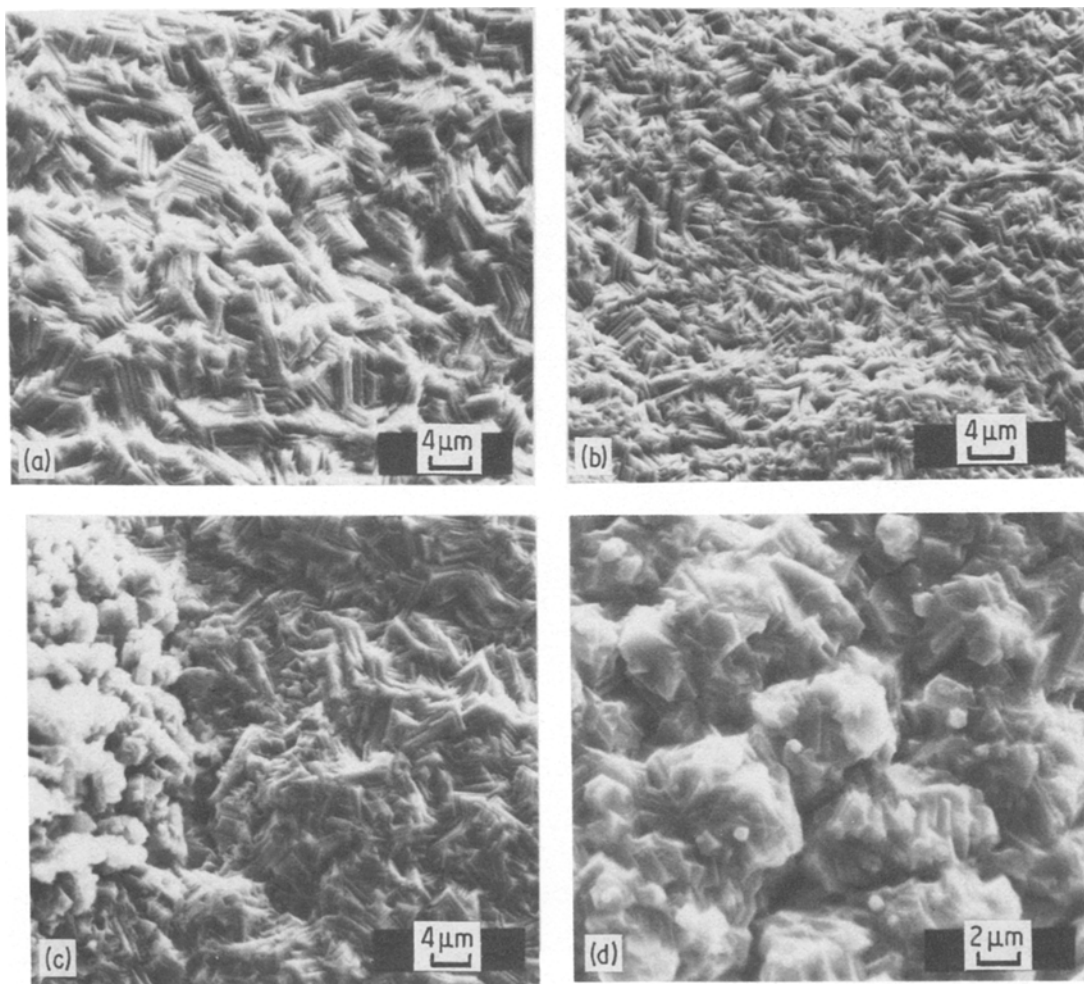


Fig. 2. SEM photomicrographs showing the effect of copper and copper + glue on the morphology of 1-h and 4-h zinc deposits electrowon at 430 A m^{-2} . (a) $10 \text{ mg l}^{-1} \text{ Cu}$; 1 h, (b) $10 \text{ mg l}^{-1} \text{ Cu}$; 4 h, (c) $10 \text{ mg l}^{-1} \text{ Cu} + 15 \text{ mg l}^{-1} \text{ glue}$; 1 h and (d) $50 \text{ mg l}^{-1} \text{ Cu}$; 1 h.

+ 15 mg l^{-1} glue is shown in Fig. 2c. The morphology is essentially similar to that shown in Fig. 2a except that part of the surface contains crystals of irregular form, probably copper. The preferred orientation of this deposit (Fig. 2c) was (1 0 1) that is characteristic of glue-containing electrolytes [1, 2].

The morphology of the deposit electrowon from a solution containing 50 mg l^{-1} copper is shown in Fig. 2d. In this case, the crystals grew in small clusters which were composed of small, ill-defined, hexagonal platelets. The deposit was nodular and had a preferred (0 0 2) orientation.

The effect of lower current density, 215 A m^{-2} , on the morphology of 1-h zinc deposits elec-

trowon from electrolytes containing 10 and 30 mg l^{-1} copper is shown in Fig. 3a and b, respectively. At 10 mg l^{-1} copper, the deposit surface was uneven and the photomicrograph, Fig. 3a, reveals voids between clusters of platelets. The morphology of the deposit electrowon at 430 A m^{-2} consisted of better defined crystals with no voids, Fig. 2a. At 30 mg l^{-1} copper, Fig. 3b, the growth of isolated clusters was enhanced and the preferred orientation had a significant (0 0 2) component; this deposit morphology was similar to that electrowon at 430 A m^{-2} from a solution containing 50 mg l^{-1} copper, Fig. 2d.

The combined presence of 10 mg l^{-1} copper

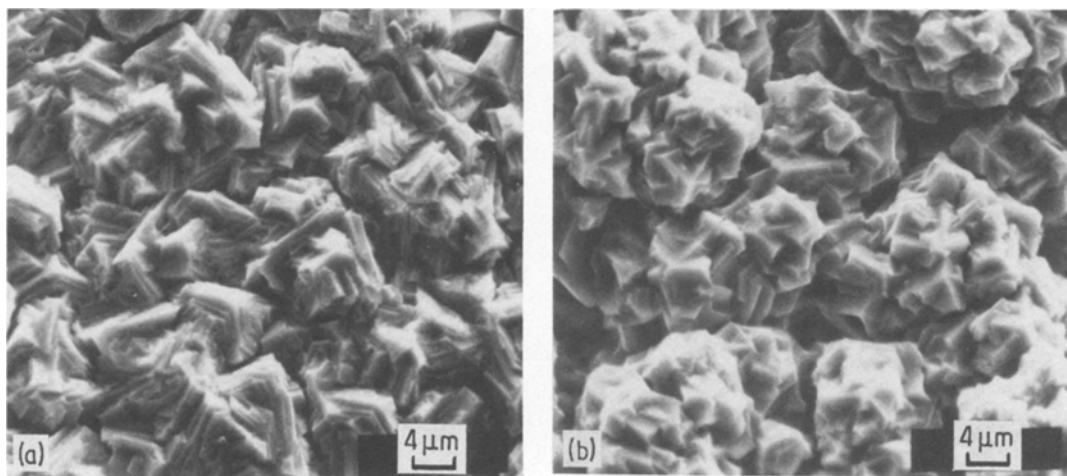


Fig. 3. SEM photomicrographs showing the effect of copper on the morphology of 1-h zinc deposits electroplated at 215 A m^{-2} . (a) 10 mg l^{-1} Cu, (b) 30 mg l^{-1} Cu.

and 0.08 mg l^{-1} antimony in the electrolyte resulted in a deposit morphology which was characteristically 'antimony-like' [1, 2]; i.e. consisting of large, flat, poorly defined hexagonal platelets, Fig. 4a. The addition of 30 mg l^{-1} glue to the electrolyte changed the deposit morphology from the antimony-like structure to the addition-free structure, Fig. 4b.

3.3. Polarization studies

The cyclic voltammograms obtained for zinc deposition from electrolytes containing 1 and

5 mg l^{-1} copper are compared to that obtained from the addition-free electrolyte, Fig. 5. With reference to Fig. 5, a cycle starting from Point A (-0.85 V versus SCE) goes through a region of low current until Point B where zinc deposition commences. The current increases to Point C where the scan is reversed. The current then decreases, reaches zero at Point D where it becomes anodic corresponding to the dissolution of deposited zinc. The anodic peak is reached at E and dissolution is complete on return to A.

A significant difference between the cyclic vol-

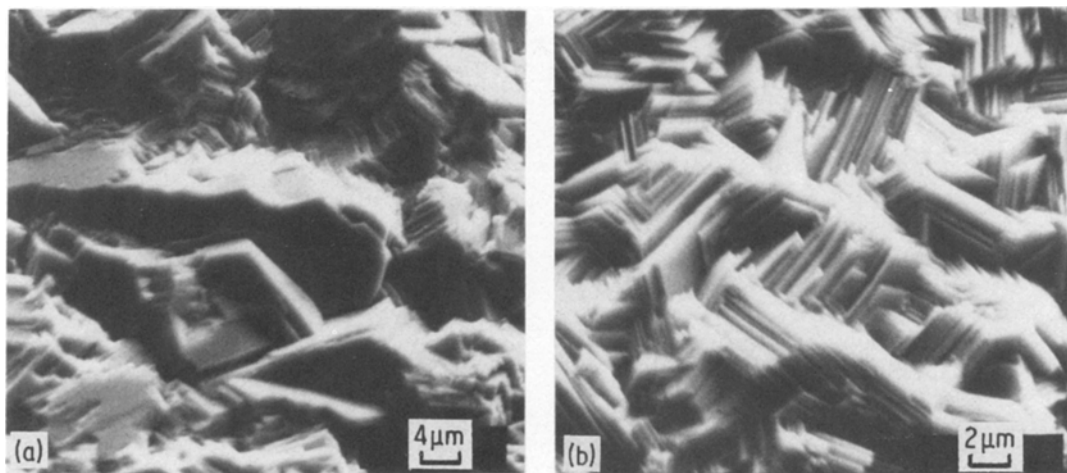


Fig. 4. SEM photomicrographs showing the effect of (a) 10 mg l^{-1} copper + 0.08 mg l^{-1} antimony and (b) 10 mg l^{-1} copper + 0.08 mg l^{-1} antimony + 30 mg l^{-1} glue on the morphology of 1-h zinc deposits electroplated at 430 A m^{-2} .

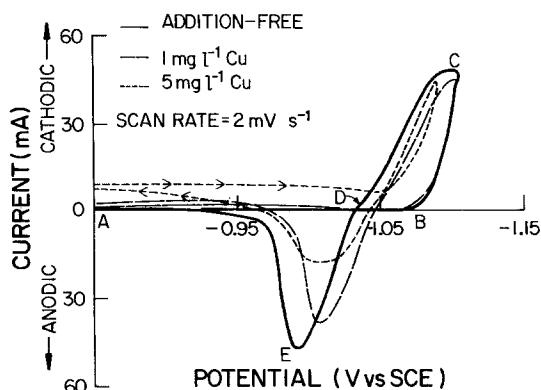


Fig. 5. Cyclic voltammograms showing the effect of copper on zinc deposition polarization.

tammograms for the addition-free and copper-containing electrolytes is the potential at which the descending branch crosses the zero-current axis (crossover potential). The crossover potential occurs at or near the reversible potential of the system so that any departure is generally caused by impurity currents, side reactions such as hydrogen evolution or perhaps the dissolution of an alloy phase; e.g. Zn–Cu alloy. Analysis of the zinc deposits confirmed that copper co-deposited with zinc, Tables 1 to 3.

At the higher copper concentration; i.e. 5 mg l^{-1} , the voltammogram was characterized by higher current in the potential region prior to zinc deposition; i.e. prior to the decomposition potential, Point B, Fig. 5. At this concentration, copper strongly depolarized the zinc deposition reaction as the decomposition potential for zinc occurred at a less negative cathode potential compared to the copper-free electrolyte. The reverse scan was characterized by an increasing cathodic current (> 0) that occurred after the anodic peak for zinc dissolution.

This feature was investigated in more detail by initiating the potential scan at a less negative potential; i.e. -0.7 V versus SCE. The results are presented in Fig. 6. As indicated in Fig. 6, there is an appreciable cathodic current peak in the reverse scan following the anodic dissolution of zinc. This may be attributed to hydrogen evolution on copper which remains on the cathode surface after the zinc has been dissolved. The dashed curve, Fig. 6, was obtained by initiating a second potential scan immediately

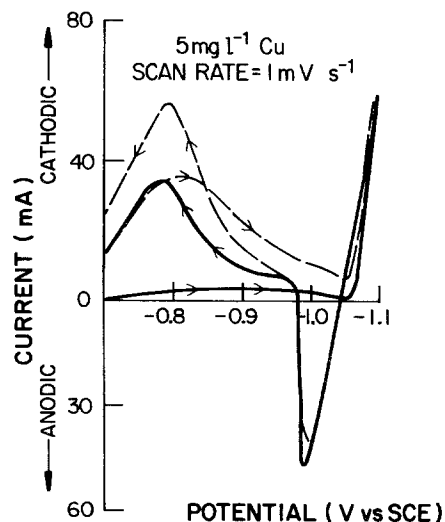


Fig. 6. Cyclic voltammogram showing the effect of 5 mg l^{-1} copper on zinc deposition polarization; (---) 2nd scan.

after the initial reverse scan returned to -0.7 V versus SCE. This curve is characterized by an appreciable cathodic current during the forward scan prior to zinc deposition, probably due to hydrogen evolution at copper sites on the cathode surface. If the cathode is removed from the cell, wiped and rinsed between scans, then the first scan, heavy black line, is reproduced.

4. Conclusions

The copper content of electrodeposited zinc increased with increasing copper concentration in the electrolyte and with decreasing current density. Although copper co-deposited with zinc, it did not result in a drastic decrease in the current efficiency for 1-h zinc deposits; co-deposited copper did reduce the grain size of the zinc deposits. The presence of increasing concentrations of antimony together with copper resulted in a significant decrease in the current efficiency for 1-h zinc deposits and an increase in the copper content of the zinc deposits. The presence of glue in the electrolyte counteracted the effect of Cu–Sb interaction on zinc deposition.

The cyclic voltammogram for copper-containing electrolyte was characterized by a substantial cathodic current in the reverse scan after zinc dissolution. This current was attributed to hydrogen evolution on previously co-deposited

copper which remained on the surface after zinc dissolution.

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References

- [1] D. J. Robinson and T. J. O'Keefe, *J. Appl. Electrochem.* **6** (1976) 1.
- [2] D. J. MacKinnon and J. M. Brannen, *ibid.* **7** (1977) 451.
- [3] B. A. Lamping and T. J. O'Keefe, *Metall. Trans.* **7B** (1976) 551.
- [4] D. R. Fosnacht and T. J. O'Keefe, *J. Appl. Electrochem.* **10** (1980) 495.
- [5] D. R. Fosnacht, PhD Thesis, University of Missouri-Rolla, 1979.
- [6] M. Maja, N. Pennazzi, R. Fratesi and G. Roventi, *J. Electrochem. Soc.* **129** (1982) 2695.
- [7] D. J. MacKinnon and P. L. Fenn *J. Appl. Electrochem.* **14** (1984) 467.
- [8] D. J. MacKinnon and P. L. Fenn, *ibid.*, **14** (1984) 701.
- [9] M. Maja, N. Penazzi, R. Fratesi and G. Roventi, *J. Electrochem. Soc.* **129** (1982) 2695.
- [10] D. J. MacKinnon, J. M. Brannen and R. C. Kerby, *J. Appl. Electrochem.* **9** (1979) 55.