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Sulphurous acid as anodic depolarizer in copper electrowinning Part II

T. SUBBAIAH [1], P. SINGH [2], G. HEFTER [2], D. MUIR [2] and R.P. DAS [1]

[1] *Regional Research Laboratory (CSIR), Bhubaneswar 751 013, India*

[2] *Department of Chemistry, School of Physical Sciences, Engineering & Technology, Murdoch University, Murdoch, WA 6150, Australia*

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Abstract

The growing interest in the electrowinning of copper has lead to several modifications including anodic reactions proposed to reduce the high energy requirement. The addition of sulphurous acid to a copper sulphate electrolyte has been studied to avoid oxygen evolution at the anode which requires a potential in excess of 2 V. In particular, the effect of different anode materials, concentration of sulphurous acid, current density, copper and sulphuric acid concentrations in the electrolyte have been investigated. Measurements of anode potential, cell voltage, current efficiency and energy consumption during the electrowinning of copper have been made using a diaphragm cell. It was found that graphite and lead coated with Ir–O_2 are better electrode materials than lead and DSA anodes and sulphurous acid can be used as anodic depolarizer.

1. Introduction

Conventional electrowinning of copper is highly energy intensive mainly because 70% of the total voltage is due to the anode potential [1]. If the anode reaction is changed to the oxidation of sulphur dioxide, the cell voltage can be cut almost in half reducing the overall energy consumption of hydrometallurgical processes which conventionally involves oxygen evolution as the anodic reaction [2–10].

Ammonium sulphite has been used by Spring and Evans [2, 3] for sulphate ion oxidation as an alternative anodic reaction in the fluidized bed electrolysis of copper sulphate–sulphuric acid system. The authors reported that the oxidation of ammonium sulphite was attractive provided the cells are operating at a current density of more than 5500 A m^{-2}. Wiesner [4] found that carbon anodes are not suitable for the anodic oxidation of sulphite. He carried out his studies in sulphuric acid solution using porous carbon electrodes and these electrodes coated with catalysts. Seo and Sawyer [5] studied the polarographic behaviour of sulphur dioxide at platinum electrodes.

The literature indicates [6–10] that the cell voltage and anode potential can be reduced considerably in electrowinning using sulphur dioxide or soluble sulphites by modifying the anodic reaction. Sulphur dioxide has also been used in conjunction with Fe(II) to subsequently reduce Fe(III) [6]. Sandoval and Lei [11] found that the variables such as Fe(II) concentration, electrolyte temperature and the degree of agitation play a major role in reducing the cell voltage. Fe(II) is a stronger anodic depolarizer in the presence of sulphur dioxide and with sufficient agitation. However, literature on the utilization of sulphurous acid as an anodic depolarizer and its effect on different anode materials is scarce. Hence, an attempt has been made in this investigation to obtain information along these lines using a diaphragm cell.

In the present study an attempt has been made to reduce the cell voltage during copper electrowinning by adding a fixed concentration of sulphur dioxide in the form of sodium sulphite to a typical acidic copper sulphate electrolyte. The effect of different catalysts on the anode potential was also studied. In the presence of excess sulphuric acid, sulphite ion is protonated and the addition of sulphite ion produces sulphurous acid or dissolved sulphur dioxide under controlled conditions. It is assumed that the amount of sulphurous acid produced is in accordance with the following equation.

$$H_2SO_4 + Na_2SO_3 \longrightarrow H_2SO_3 + Na_2SO_4 \qquad (1)$$

Detailed studies of the effects of different anode materials, sulphurous acid and ferrous sulphate concentration in the anolyte, and variation of sulphuric acid and copper concentration in the electrolyte on the anode potential, cell voltage, current efficiency were carried out.

2. Experimental details

Copper sulphate, sodium sulphite and sulphuric acid used in the present study were of analytical reagent grade. The electrolyte was prepared by dissolving the required amounts of chemicals in deionized water. Unless stated otherwise the electrolyte contained 40 g dm^{-3} Cu(II) and 150 g dm^{-3} H_2SO_4.

A laboratory cell was constructed in which the electrodes (10 cm × 5 cm) were separated by microporous polyethylene diaphragm material. The cell was covered with a Perspex lid with a provision to keep the distance between the anode and the cathode constant and also the distance between the anode and the reference electrode. Lead, activated lead (Pb coated with Ir–O_2), and dimensionally stable anodes i.e., titanium coated with Ir–O_2 and Ir–Co were used as anodes. Stainless steel 316 was used as the cathode material. A saturated calomel electrode was used as the reference electrode. A constant current meter with a maximum capacity of 4 A was used as the d.c. current source. The anode potential and the cell voltage were measured by a Hewlett Packard multimeter (model E2373). A Rikadenki (model BC82010) chart recorder was connected to record the anode potential continuously.

The electrolysis was carried out at a room temperature of approximately 20 °C. Copper was deposited from a copper sulphate–sulphuric acid bath. A precision ammeter was connected in series to measure the current. After the electrolysis was over, the cathode was removed, thoroughly washed, dried in the oven and then weighed.

3. Results and discussion

3.1. *Different anode materials*

Lu and Amman [12] investigated different electrode materials for the anodic oxidation of sulphur dioxide and concluded that palladium and palladium oxide materials are better catalysts than platinum. In the present study pure lead, D.S.A. (Ir–Co), D.S.A. (Ir–O_2), graphite and activated lead (Pb coated with Ir–O_2) materials were used to see the effect of sulphurous acid concentration (Table 1). In the absence of sulphur dioxide, the lowest values of the anode potentials were obtained with activated lead and then with D.S.A. Ir–O_2, D.S.A. Ir–Co, graphite but was highest with pure lead. The anode potential decreased substantially with graphite and the activated lead electrode in the presence of 32.8 g dm^{-3} sulphurous acid and the data is shown in Table 1. About a 50% and an 18.5% decrease in the anode potential were observed with the graphite electrode and with the activated lead electrodes, respectively, due to the presence of sulphurous acid in the electrolyte. About a 9.7% and a 5.9% decrease were observed with D.S.A. Ir–O_2 and pure lead electrodes respectively with the addition of sulphurous acid.

Table 1. Effect of anode substrate on anode potential
Cu 40 g dm^{-3}, current density 200 A m^{-2}

Test	Electrode material	Anode potential/V vs SCE	
		Absence of H_2SO_3	32.8 g dm^{-3} H_2SO_3
1	Pure lead	1.80	1.52
2	Activated lead	1.35	1.10
3	DSA (Ir–Co)	1.52	–
4	DSA (Ir–O_2)	1.48	1.30
5	Graphite	1.68	0.80

3.2. *Effect of sulphurous acid concentration*

A comparison of the cell voltage, current efficiency and energy consumption using activated lead and titanium coated with Ir–O_2 materials with increase of sulphurous acid concentration is shown in Table 2.

The concentration of sulphurous acid was varied from 0 to 113.24 g dm^{-3} in the anolyte. With an increase of sulphurous acid concentration, the anode potential decreased from 1.48 to 1.00 V in the case of the D.S.A. Ir–O_2 electrode whereas with the activated lead electrode, the decrease in the anode potential was from 1.35 to 0.94 V. However, better results were obtained with the graphite electrode under similar conditions. The anode potential was reduced from 1.68 to 0.70 V and the cell voltage reduced from 1.80 to 0.77 V with an energy saving of nearly 60% even with a sulphurous acid

Table 2. Effect of sulphurous acid concentration in the anolyte on current efficiency and energy consumption
Cu 40 g dm^{-3}, current density 200 A m^{-2}

Test	H_2SO_3 /g dm^{-3}	H_2SO_4 /g dm^{-3}	Activated lead			DSA Ir–O_2		
			Cell voltage /V	C.E. /%	Energy /kWh (kg Cu)$^{-1}$	Cell voltage /V	C.E. /%	Energy /kWh (kg Cu)$^{-1}$
1	0	150	1.51	100	1.28	1.65	99.8	1.39
2	28.31	116.17	1.43	99.8	1.21	1.59	99.8	1.34
3	42.76	98.9	1.32	99.8	1.12	1.51	99.8	1.27
4	56.62	82.33	1.24	98.4	1.07	1.41	99.8	1.19
5	84.86	48.58	1.18	100	0.99	1.30	100	1.10
6	113.24	14.67	1.16	100	0.99	1.31	100	1.10

concentration of 41 g dm^{-3}. Similarly, the cell voltage was reduced from 1.88 to 1.55 V, 1.65 to 1.50 V and 1.51 to 1.40 V with pure lead, D.S.A. Ir–O$_2$, and activated lead electrode respectively. The effects of sulphurous acid on the anode potential for different electrode materials are compared in Figure 1. Due to the reaction of H_2SO_4 with the sulphite ion to produce H_2SO_3, the concentration of free H^+decreased. Hence the overall cell voltage did not decrease as much as the anodic cell voltage.

3.3. *Effect of ferrous sulphate addition*

Addition of ferrous sulphate up to 69.5 g dm^{-3} in the electrolyte produced little reduction in the anode potential with a pure lead electrode, DSA Ir–O$_2$ electrode and the activated lead electrode. But a graphite anode was found to reduce the anode potential by 0.18 V. Cooke et al. [9] reported that the oxidation of sulphur dioxide in the presence of ferrous sulphate requires vigorous stirring of the electrolyte.

The effect of ferrous sulphate on the anode potential with the graphite anode in the presence and absence of sulphurous acid is shown in Figure 2. Clearly in a still electrolyte, SO_2 oxidation is favoured over Fe(II) oxidation at comparable concentrations.

3.4. *Impurity effect*

To test the effect of other metal ions which can undergo oxidation at the anode, and possibly catalyse SO_2 oxidation, 100 ppm of Fe, Co and Mn were added to 150 g dm^{-3} H_2SO_4 as iron(II) sulphate, cobalt(II) sulphate, manganese(II) sulphate and the solutions saturated with SO_2. Solid V_2O_5 was also added since it is used as a catalyst in the oxidation of sulphur dioxide for sulphuric acid manufacture. However, the anode potentials and the cell voltages with the different potentially catalytic materials against time showed hardly any change. The results are shown in Table 3.

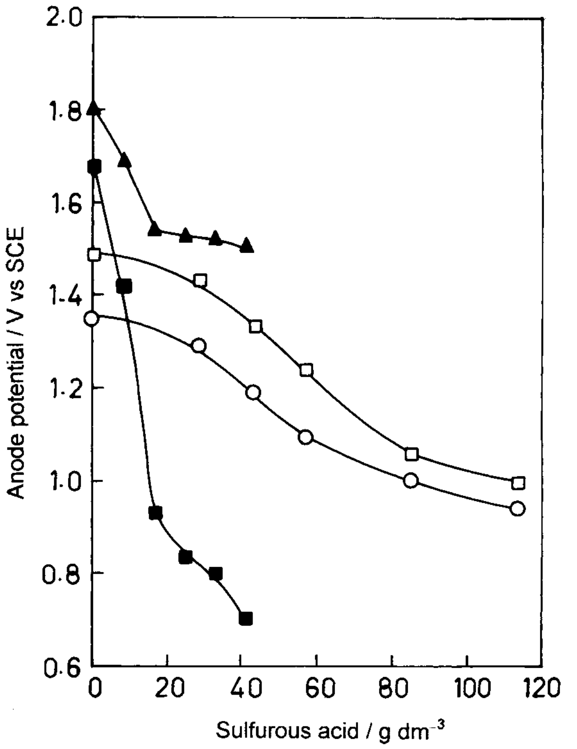

Fig. 1. Effects of sulfurous acid on anode potential. Key: (■) graphite; (▲) pure lead; (□) D.S.A. (Ir–O$_2$); (○) activated lead.

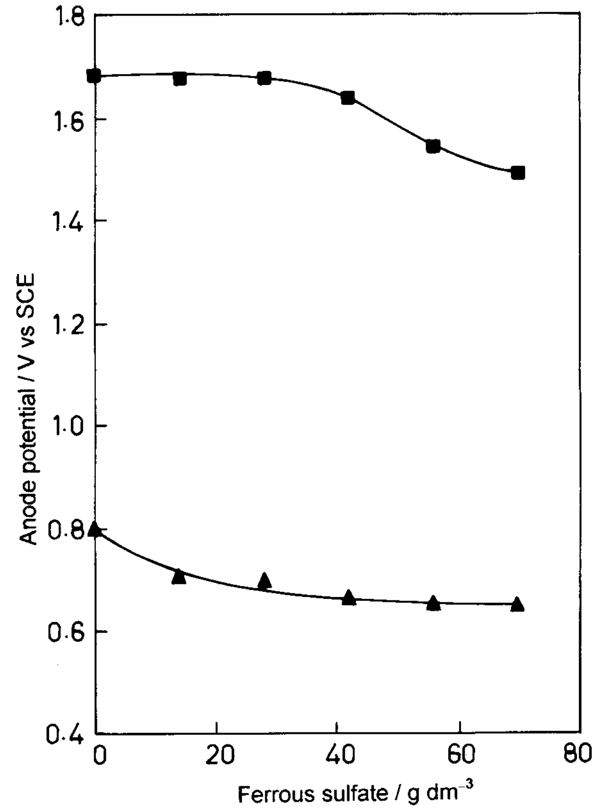

Fig. 2. Effect of ferrous sulfate on anode potential with graphite anode. Sulfurous acid: (■) 0 and (▲) 32.8 g dm^{-3}.

3.5. *Sulphuric acid concentration*

The activated lead electrode was chosen for further studies as it gave the best result other than that for graphite and little was known about the behaviour of this electrode material. The concentration of sulphuric acid was varied from 33 to 233 g dm^{-3} while the concentration of sulphurous acid in the anolyte was kept at 56.62 g dm^{-3}. With an increase of sulphuric acid concentration, the anode potential increased from 1.1 to

Table 3. Effect of other impurities on anode potential

Test	Element 100 ppm in 150 g dm^{-3} sulphuric acid	Anode potential/V vs SCE Time/min		
		5	10	15
1	–	0.64	0.65	0.65
2	Fe(II)	0.61	0.61	0.62
3	Co(II)	0.62	0.62	0.63
4	V(V)	0.62	0.63	0.63
5	Mn(II)	0.62	0.63	0.63

1.32 V (Figure 3) due to the decrease in the solubility of SO_2. However, there was no appreciable change in the cell voltage up to 133 g dm^{-3} due to greater conductivity of the electrolyte. At higher concentrations of acid, the cell voltage increased from 1.35 to 1.52 V. The net effect of adding sulphuric acid is to reduce the saturated concentration of sulphur dioxide in the solution which, in turn, increases the anode potential (Figure 3) when an activated lead electrode is used. This observation is typical of the other electrodes.

3.6. *Current density*

Current density was varied from 100 to 400 A m^{-2} with the activated lead electrode in the presence of 56.62 g dm^{-3} sulphurous acid in the anolyte. With an increase of current density from 100 to 400 A m^{-2} the anode potential increased from 0.92 to 1.39 V and the cell voltage from 1.00 to 1.65 V. A nearly 65% increase in the cell voltage was observed due to the increase of current density (Figure 4). The effect of current density on current efficiency and energy consumption is shown in Table 4. Similar trends were obtained by Mishra and Cooper [13] using Fe(II) as a depolarizer in a gas sparged electrolyte.

3.7. *Copper concentration*

The copper concentration is expected to affect the cathode potential only and the potential of the activated lead anode used in this study remains unchanged as the copper concentration is increased. Using the activated lead electrode, the copper concentration was varied from 10 to 50 g dm^{-3} in the electrolyte while the sulphuric acid concentration was maintained at 82.33 and the anolyte contained 56.62 g dm^{-3} sulphurous acid. With an increase in copper concentration there was little change in the anode potential as expected. However, at copper concentrations below 20 g dm^{-3} the cell voltage increased due to the increase in cathodic concentration overpotential and current density. Clearly the lower limit of Cu concentration depends on temperature, stirring and the cell design. The cell potential rises rapidly as the cathodic reaction becomes mass transport limited when copper concentration is lowered in the solution. Mishra and Cooper [13] studied the electrochemical aspects of the direct electrowinning of copper from sulphuric acid leach solution in the presence of iron(II) using gas sparging. These data indicated that

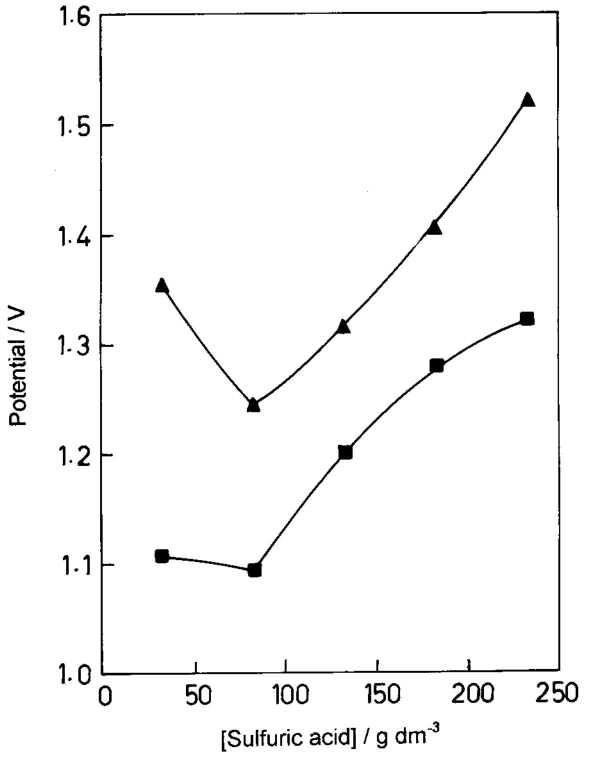

Fig. 3. Effect of sulfuric acid on anode potential and cell voltage. (Activated lead, sulfurous acid 56.62 g dm^{-3}.) Key: (■) anode potential vs SCE; (▲) cell voltage.

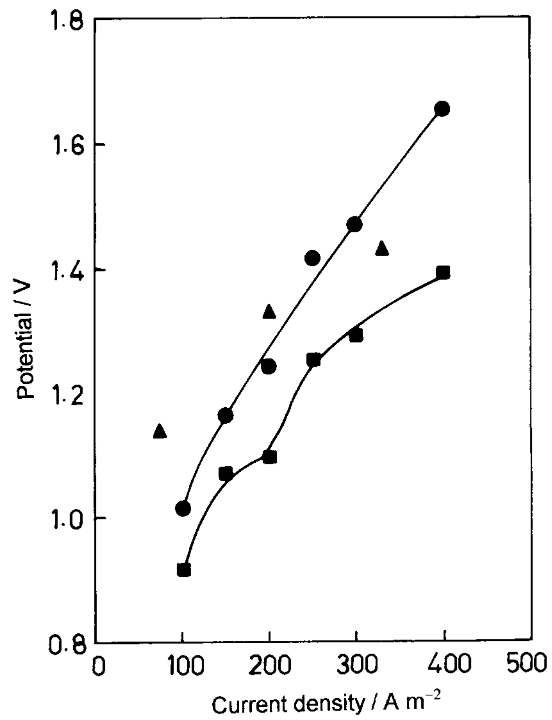

Fig. 4. Effect of current density on anode potential and cell voltage. (Activated lead, sulfurous acid 56.62 g dm^{-3}.) Key: (■) anode potential vs SCE; (●) cell voltage; (▲) literature [13].

Table 4. Effect of current density on energy consumption
Cu 40 g dm^{-3}, H_2SO_4 82.33 g dm^{-3}, H_2SO_3 56.62 g dm^{-3}, activated lead electrode

Test	Current density /A m^{-2}	Energy consumption /kWh (kg Cu)$^{-1}$
1	100	0.87
2	150	0.98
3	200	1.07
4	250	1.20
5	300	1.24
6	400	1.40

increasing the operating current density beyond a certain critical value resulted in poor quality black and impure deposits. This critical current density decreases with a decrease in the copper concentration. In the present study also it was observed at copper concentration of 20 g dm^{-3} the quality of the deposit is poor and at 10 g dm^{-3}, black and powdery deposit is obtained. Robinson also [1] mentioned that the concentration affects the operating current density and the optimum current density will be 161.5 A m^{-2} for a concentration of 30 g dm^{-3} copper in the electrolyte. Mass transfer theory suggests that the kinetics will be improved if the iron(II) concentration in the electrolyte is increased.

3.8. *Effect of SO_2 on copper morphology*

The surface morphology of copper electrodeposits is affected by various parameters such as cathode over voltage, temperature, orientation of the substrate and the presence of organic inhibitors. The concentration of sulphurous acid was varied from 28.31 g dm^{-3} to 113.24 in the anolyte. The copper deposits were stripped and a crystal size increase from 2 to 20 μm was observed with an increase in sodium sulphite concentration. The micrographs of the copper deposits are shown in Figures 5 and 6 with a magnification of 1200 times. Cooper and Mishra [14] also observed a crystal size of about 20 μm and found that numerous fine crystals were generated in the early stages and as the thickness of the deposit increased, the crystal size also increased to a relatively constant size. Gopala Krishna and Das [15] studied the morphology of copper deposits in the presence of iron(II) from the copper sulphate–sulphuric acid system. With increase in iron(II) concentration, the cathode deposit morphology changed from well developed crystalline to nodular growth.

3.9. *XRD analysis*

The crystallograph orientations of each cathode deposit was determined by X-ray diffraction. The XRD of copper deposits in the presence of sulphurous acid showed no evidence of formation of sulphur compounds in the deposits. Cooper and Mishra [14] studied the nature of copper electrowon in the presence of 8 g dm^{-3} iron(II) by sparging 15% sulphur dioxide/air mixture into an electrolyte containing 10 g dm^{-3} copper and 50 g dm^{-3} sulphuric acid. It was observed that sulphur pick up from the electrolyte in the presence of sulphur dioxide can be kept to a minimum by operating the cell at a current density well below the limiting value. In the present case, the high concentration of copper in the

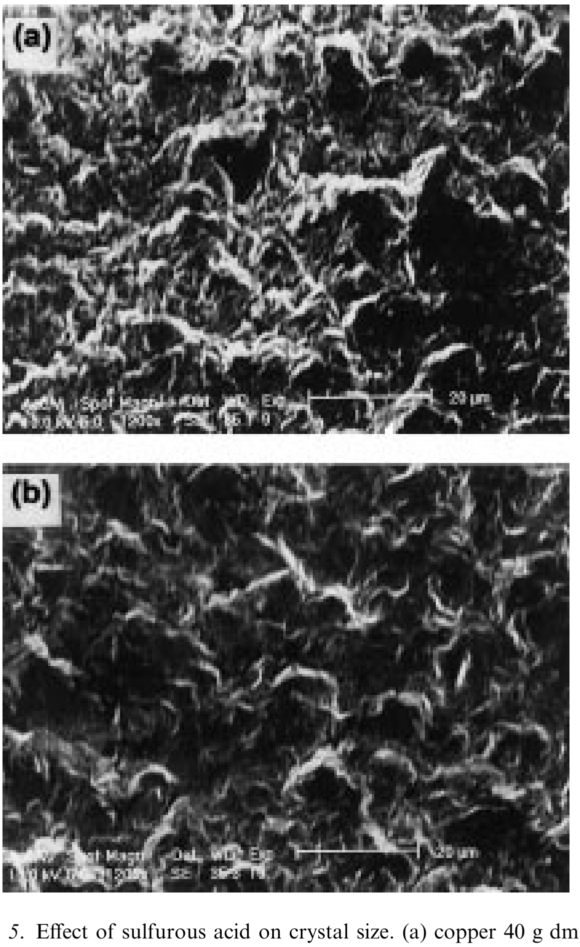

Fig. 5. Effect of sulfurous acid on crystal size. (a) copper 40 g dm^{-3}, H_2SO_4 116.2 g dm^{-3} and H_2SO_3 28.3 g dm^{-3}; (b) copper 40 g dm^{-3}, H_2SO_4 98.9 g dm^{-3} and H_2SO_3 42.7 g dm^{-3}.

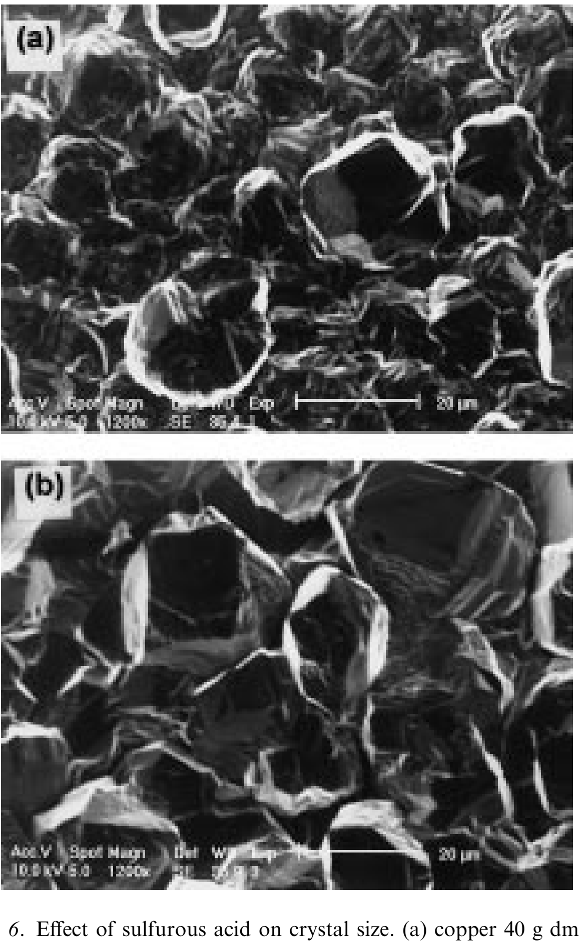

Fig. 6. Effect of sulfurous acid on crystal size. (a) copper 40 g dm^{-3}, H_2SO_4 82.33 g dm^{-3} and H_2SO_3 56.63 g dm^{-3}; (b) copper 40 g dm^{-3}, H_2SO_4 14.67 g dm^{-3} and H_2SO_3 113.2 g dm^{-3}.

electrolyte and the low current density prevented the occurrence of sulphur compounds in the deposit.

3.10. *Industrial application*

In industrial copper electrowinning the cell potential is approximately 2 V. In the present study by using sulphurous acid, the cell voltage has been reduced from 1.8 V to 0.77 V and hence considerable saving in energy can be obtained. During copper electrowinning one mole of sulphuric acid is produced for each mole of copper produced, but in this case two moles of sulphuric acid are produced as per the reaction [1] for each mole of copper deposited. The extra mole of sulphuric acid produced in this process has to be eliminated or consumed for integration of the circuit. In general hydrometallurgical processes involve unit operations such as leaching, solid liquid separation, solvent extration and electrowinning. The tertiary amine such as Alamine 336 (Henkel Corporation, trade name) can be used to remove acid produced and this acid can be utilized during leaching.

4. Conclusions

(i) Activated lead (Pb coated with Ir–O_2) is a better anode material at higher SO_2 concentrations in the anolyte when compared to D.S.A. Ir–O_2, D.S.A. Ir–Co and pure lead but graphite gave the lowest anodic potential. With an increase of sulphurous acid concentration, the anode potential and the cell voltage decreased considerably.

(ii) With an increase in SO_2 concentration using a graphite anode, the anode potential and the cell voltage could be lowered by more than 1.0 V with a saving of 60% in the energy required. This value can be further enhanced up to 62% in the presence of sulphurous acid and ferrous sulphate.

(iii) With sulphurous acid in the anolyte, the crystal size of the copper deposits increased from 2 to 20 μm. There was no evidence of the formation of sulphur compounds in the deposits.

(iv) With an increase in current density, the energy consumption increased in the presence of sulphurous acid.

(v) The reduction in the anode potential and the cell voltage depend on the anode material.

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