

The effects of 4-ethylpyridine and 2-cyanopyridine on zinc electrowinning from acidic sulfate solutions

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Received 27 February 1996; revised 18 October 1996

The effects of 4-ethylpyridine and 2-cyanopyridine on the electrowinning of zinc in the presence and absence of antimony have been studied. The results are compared with those of a common industrial additive, gum arabic. Addition of either compound reduced current efficiency, increased power consumption and lowered the surface quality of electrodeposited zinc. Both the additives showed similar polarization behaviour to gum arabic. Addition of 0.04 mg dm^{-3} antimony increased current efficiency, reduced power consumption and altered the surface morphology and crystallographic orientations. Combinations of antimony with 4-ethylpyridine resulted in very good current efficiencies, and zinc morphology and quality.

1. Introduction

A number of organic additives appear to perform better than traditional glues [1–11] in the electro-winning of zinc. For example, Piron *et al.* [11] have reported increased current efficiencies in the presence of 2-butyne-1, 4-diol. MacKinnon and co-workers [12–14] have studied a number of organic compounds and have shown that tetrabutylammonium chloride (TBACl) improves surface morphology and current efficiency during zinc electrowinning from acidic chloride solutions, Fray and Thomas [15] claimed TBACl enabled current densities of up to 2000 A m^{-2} to be achieved. Recently, Hosny [16] and Karavastev *et al.* [17, 18] used surfactants to improve the deposit morphology and current efficiency.

Pyridine and its derivatives act as corrosion inhibitors [19–21] and as levelling agents [22, 23]. These compounds are protonated (cationic) in acid solution [24] and are adsorbed on active sites on the metal surfaces [20]. The introduction of hydrocarbon substituents onto the pyridine ring increases their inhibition efficiency. The present study was undertaken to obtain information on the effect of 4-ethylpyridine and 2-cyanopyridine on the current efficiency, power consumption, surface deposit quality and morphology and polarization behaviour for zinc deposition from a sulfate electrolyte. The results are compared with data for gum arabic which is widely used in industrial zinc electrowinning as a levelling agent.

2. Experimental details

2.1. Apparatus and materials

The 200 cm^3 electrolysis cell used for the galvanostatic experiments was of conventional design with a polypropylene lid provided with openings to accommodate the electrodes. Pure aluminium and platinum (99.9%) sheets were used as the cathode and anode respectively. The working cathode area was 10 cm^2 .

The zinc electrolyte was prepared from $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (AR, Ajax, Australia) and H_2SO_4 (AR, Sigma, USA). The 4-ethylpyridine, 2-cyanopyridine and potassium antimony tartrate were also of reagent grade purity. Gum arabic was from Hindustan Zinc Ltd., Udaipur, India. All solutions were prepared with Millipore Milli-Q water.

2.2. Electrolysis

In all the electrowinning experiments the metal was deposited for 2 h at a current density of 400 A m^{-2} and 25°C . The electrolytic solution contained 55 g dm^{-3} zinc and 150 g dm^{-3} sulfuric acid. The additives and antimony additions were made as aliquots from their respective stock solutions. After electrolysis, the cathode was removed from the cell, thoroughly washed with water, then acetone, and finally dried in an oven at 60°C under a nitrogen atmosphere. The cathodic current efficiency was calculated from the cathode weight and was reproducible within 0.5%.

2.3. Deposit examination

Photographs of the deposit surface were taken using a stereomicroscope. A Philips PW 1050 X-ray diffractometer was used to examine sections of the deposits by X-ray diffraction (XRD) to determine their orientation relative to ASTM standard for zinc powder. The surface morphologies of deposits were examined by scanning electron microscopy (SEM) using a Philips SE101B microscope.

2.4. Cyclic voltammetry

Cyclic voltammetry experiments were conducted at 25 °C to determine the polarization characteristics of zinc deposition in the presence of additives and Sb. A rotating disc apparatus and cell of standard design were used for these experiments. The polarization experiments were carried out using a 3 mm diameter aluminium disc as cathode, a platinum counter electrode and saturated calomel electrode (SCE) as reference. The aluminium electrode was prepared by wet polishing (at 150 rpm) using 4000 carbide paper. The electrode was then washed thoroughly with deionized water, acetone, distilled water and finally dried with filter paper. The freshly prepared electrode was transferred to the cell containing zinc electrolyte whilst sparging with pure nitrogen. The electrode was kept in the solution for 10 minutes before the cycle started.

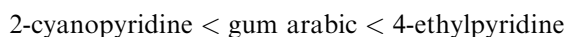
A PAR 175 Universal Programmer was used to drive a PAR 173 potentiostat. The cathodic potential was cycled between -0.7 and -1.3 V vs SCE at a potential sweep rate of 50 mV s^{-1} using a rotating electrode (2000 rpm). The cyclic voltammograms were recorded as i against E plots on a Bryans 26000 X - Y recorder. All the cyclic voltammetry tests were conducted with 200 cm^3 of the zinc electrolyte.

3. Results and discussion

3.1. Current efficiency

The effects of 4-ethylpyridine and 2-cyanopyridine on current efficiency and power consumption during zinc deposition were studied in the concentration range 0 – 40 mg dm^{-3} and the results were compared with

those of gum arabic (Table 1). The current efficiency decreased with increasing additive concentrations in the order:



The power consumption followed the opposite order (Table 1).

Drops in current efficiency during zinc deposition due to the addition of surface active agents are well documented [16, 25–27] and have been attributed [19] to surface coverage by a strongly adsorbed additive layer. Such adsorption increases the interfacial viscosity [16] causing a decrease in the diffusivity of zinc ions and hence the mass transfer and zinc deposition rates. Pyridine and its derivatives are protonated in acid solutions [24] and are adsorbed on the active sites of the metal surface [20]. Because of the adsorptive nature of these compounds, it is expected that their effect on current efficiency will be similar to that of glues [16, 25–27]. Such behaviour has been observed on addition of 2-picoline (a hydrocarbon substituted pyridine compound) to zinc electrolytes [28].

Antimony is one of the most deleterious impurities affecting coulombic efficiency during zinc electro-winning [29, 30]. However, in combination with glue, it gives rise to optimum coulombic efficiency and the preferred deposit morphology [26, 31, 32]. The results obtained in the present paper are compared with those in the presence of gum arabic in Table 1. The combination of Sb and 4-ethylpyridine improved the current efficiency by about 12% which resulted in reduction of the power consumption by about 400 kWh t^{-1} of zinc. Combination of 2-cyanopyridine and Sb acted less effectively with the current efficiency improving by about 2%. On the other hand, for gum arabic the current efficiency dropped from 74 to 67% causing an increase in power consumption from 3537 to 3870 kWh t^{-1} of zinc. The unexpected decrease in current efficiency in the presence of gum arabic is probably due to the gum arabic/Sb concentrations not being optimized.

The increase in current efficiency in the presence of the pyridine derivatives is almost certainly related to their adsorption at the cathode surface. During zinc deposition from acidic sulfate electrolytes, there exists a strong interaction between H^+ and Zn^{2+} .

Table 1. Effect of additives on current efficiency (CE) and power consumption

| Concentration / mg dm^{-3} | Additives | | | | | |
|----------------------------------------|-----------------|--------------------------------|-------------|--------------------------------|-----------------|--------------------------------|
| | 4-Ethylpyridine | | Gum arabic | | 2-Cyanopyridine | |
| | C.E. / % | Power / kWh t^{-1} | C.E. / % | Power / kWh t^{-1} | C.E. / % | Power / kWh t^{-1} |
| 0 | 89.6 | 2891 | 89.6 | 2891 | 89.6 | 2891 |
| 5 | 86.5 | 3076 | 86.1 | 3043 | 78.0 | 3397 |
| 10 | 84.2 | 3225 | 86.2 | 3104 | 76.3 | 3446 |
| 20 | 83.0 | 3217 | 72.7 | 3615 | 72.0 | 3767 |
| 40 | 82.6 | 3238 | 74.5 | 3537 | 69.0 | 3934 |
| 40 + 0.04 Sb | 93.5 | 2812 | 67.8 | 3870 | 71.0 | 3725 |

Cachet and Wiart [33] explained this in terms of a model based on a competition between the autocatalytic production of an adsorbed intermediate, Zn_{ads}^+ ($Zn^{2+} + Zn_{ads}^+ + e^- = 2Zn_{ads}^+$) and the adsorption of H_{ads} which acts primarily as an inhibitor. Antimony interferes with the hydrogen adsorption by forming a volatile hydride in the double layer [34] thus preventing H_{ads} from acting as an inhibitor for the deposition of zinc.

The two pyridines differ markedly in their basicities. As no experimental data are available for pK_a of 2-cyanopyridine it was calculated using a commercial package (Pallas 1.3, Compu Drug Chemistry Ltd H-1395, Budapest 62, POB.405 Hungary). The pK_a value so obtained is 1.12. This is similar to the experimental values for 3 and 4 cyanopyridines [35]. As a further check, the pK_a of 4-ethylpyridine was calculated by the same programme giving a value of 6.14, in excellent agreement with the experimental value of 6.17 [36]. Remembering that even moderately concentrated solutions of sulfuric acid behave like a 1:1 rather than a 1:2 electrolyte, a 150 g dm^{-3} ($\sim 1.5\text{ mol dm}^{-3}$) solution of H_2SO_4 will have $pH \sim 0$ (allowing for activity coefficient effects). This means that 4-ethylpyridine will be completely protonated whereas a significant fraction (about 10%) of 2-cyanopyridine will still be present in solution as neutral molecules. Prediction of the adsorption of a pyridine derivative at a solid aluminium cathode in concentrated acidic zinc sulfate solutions is not simple. In addition to the effects of charge (on both the adsorbant and the electrode), the hydrophobicity and complexation ability of the additive must also be considered.

The hydrophobicity of organic molecules has a major effect on their adsorption characteristics at electrode surfaces. Hydrophobicity is often estimated in terms of the distribution coefficient ($\log P$) of the molecule between 1-octanol and water [37]. The values of $\log P$ calculated using a commercial package (Biobyte Corporation, 201, West 4th St. Suite 204, CA 91711, USA) were 0.273 and 1.673 for 2-cyanopyridine and 4-ethylpyridine respectively. That is, the ethyl derivative is more hydrophobic. However, this situation changes markedly when the protonated species are considered. The absorption of the pyridine derivatives will also be affected by their ability to complex any species present at the electrode surface. Under the present circumstances this would include $Sb(III)$, $Zn(II)$, Zn_{ads} , H_{ads} and possibly other species. Such data are generally not available but it may be noted that the very much higher basicity (see above) of 4-ethylpyridine and its consequent complete protonation in concentrated H_2SO_4 solutions suggest that complexation factors are unlikely to be significant. On the other hand the adsorption of 2-cyanopyridine, a very weak base and complexing agent (cation solvator) [38], is unlikely to be significantly affected by complexation phenomena.

Taking protonation, hydrophobicity and complexation into account it seems that 2-cyanopyridine

(as the neutral molecules) is more likely to be strongly adsorbed at the cathode than 4-ethylpyridine (which will be fully protonated). This is consistent with the deleterious effect of 2-cyanopyridine on the zinc deposition process (Table 1).

3.2. Surface quality

Surface active agents not only affect current efficiency but also cause significant changes in the surface quality of the zinc deposits. The deposits obtained in the presence of pyridine derivatives and gum arabic showed marked changes in the surface quality depending on the additive concentrations. The surface quality improved with 4-ethylpyridine concentration in the range of $10\text{--}20\text{ mg dm}^{-3}$ but at 40 mg dm^{-3} bundles of outgrowth appeared on a comparatively smooth surface. However, the surface became smooth again on the addition of 0.04 mg dm^{-3} $Sb(III)$ as potassium antimony tartrate. On the other hand, addition of 5 mg dm^{-3} of gum arabic produced relatively smooth deposits but at higher concentrations comparatively coarser deposits were obtained. Addition of Sb further increased the surface roughness.

The surface quality of deposits in the presence of 2-cyanopyridine declined at the lowest additive concentrations (5 mg dm^{-3}), however, at higher concentration (40 mg dm^{-3}) it improved to some extent. Addition of Sb , further improved the deposit quality but the surfaces were never as smooth as those produced in the presence of 4-ethylpyridine.

3.3. Polarization curves

Figure 1 shows the effect of 4-ethylpyridine, with and without Sb , on the polarization characteristics of the zinc deposition process. Scans were initially swept cathodically from -0.7 V vs SCE (point A in Fig. 1). Negligible current flowed until B (-1.2 V vs SCE) where the current increased sharply due to zinc deposition on the aluminium substrate. The scan direction was reversed at C (-1.3 V vs SCE). The current decreased and became zero at the cross-over potential, D beyond which the deposited zinc started dissolving. Addition of up to 40 mg dm^{-3} of 4-ethylpyridine did not change the activation overpotential (B–D), the cross-over potential D or the (anodic/cathodic) peak currents (curves 1 and 2). This is consistent with the observations of Mackinnon *et al.* [12] and Das *et al.* [28] or the zinc deposition process in the presence of other additives.

It can also be seen from Fig. 1 (curve 3) that addition of 0.04 mg dm^{-3} of Sb strongly influenced the cyclic voltammogram. There was a significant increase in the cathodic, as well as anodic, peak currents and also a decrease in the activation overpotential. Such changes in the polarization curve are reflected in the surface quality and current efficiency (Table 1). Almost identical effects were observed for gum arabic in the absence and presence of Sb .

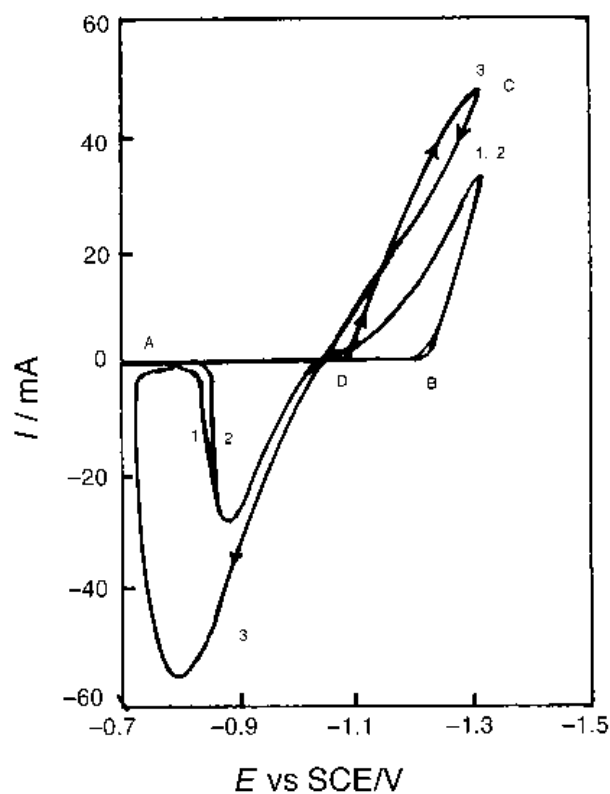


Fig. 1. Voltammograms on Al electrode for zinc electrolyte. (1) No addition, (2) 4-ethylpyridine (40 mg dm^{-3}), (3) 4-ethylpyridine (40 mg dm^{-3}) + Sb (0.04 mg dm^{-3}).

The effects of 2-cyanopyridine are shown in Fig. 2. Addition of 10 mg dm^{-3} of 2-cyanopyridine causes an increase in the zinc deposition overpotential (B becomes more negative curve 2, Fig 2(a)) and a decrease in the zinc deposition current, until at 20 mg dm^{-3} no zinc deposition occurs, at least down to -1.3 V (Fig. 2(a), curve 3). This indicates that 2-cyanopyridine completely covers the surface and thus inhibits the zinc deposition process. Fig. 2(b) shows the combined effect of 2-cyanopyridine (40 mg dm^{-3}) and Sb (0.04 mg dm^{-3}). The addition of Sb increased the cathodic current and decreased the activation overpotential (Fig. 2(b), curves 3). However, the shape of the cathodic portion of the cyclic voltammogram was completely different from that in the presence of 4-ethylpyridine. Thus, the cathodic current densities (compare curve 3 in Fig. 1 and Fig. 2(b)) were higher at all potentials and the overpotential much smaller in the presence of 4-ethylpyridine.

3.4. Deposit morphology and orientation

The zinc deposits were examined using scanning electron microscopy and X-ray diffraction to determine the surface morphology and crystallographic orientations. The results are reported in Figs 3 and 4 and Table 2.

Figure 3(a) shows the typical morphology of a zinc deposit obtained from addition-free electrolyte. The hexagonal platelets had moderate size and were randomly oriented with preferred crystal planes in the

order (103) (102) (114) (101) (112). The order of preferred crystal planes reported by MacKinnon *et al.* [31] for addition-free electrolyte was (102) (112) (114) (101) (103). They obtained a similar morphology to that of O'Keefe *et al.* [26] who reported the preferred planes as (101) (102) (103) for addition-free and balanced electrolytes.

The addition of a low concentration of 4-ethylpyridine changed the preferred deposit orientations to (103) (101) (102) (112) (114) (Table 2). This corresponded to a surface morphology where crystallite size increased. Increase in the additive concentration

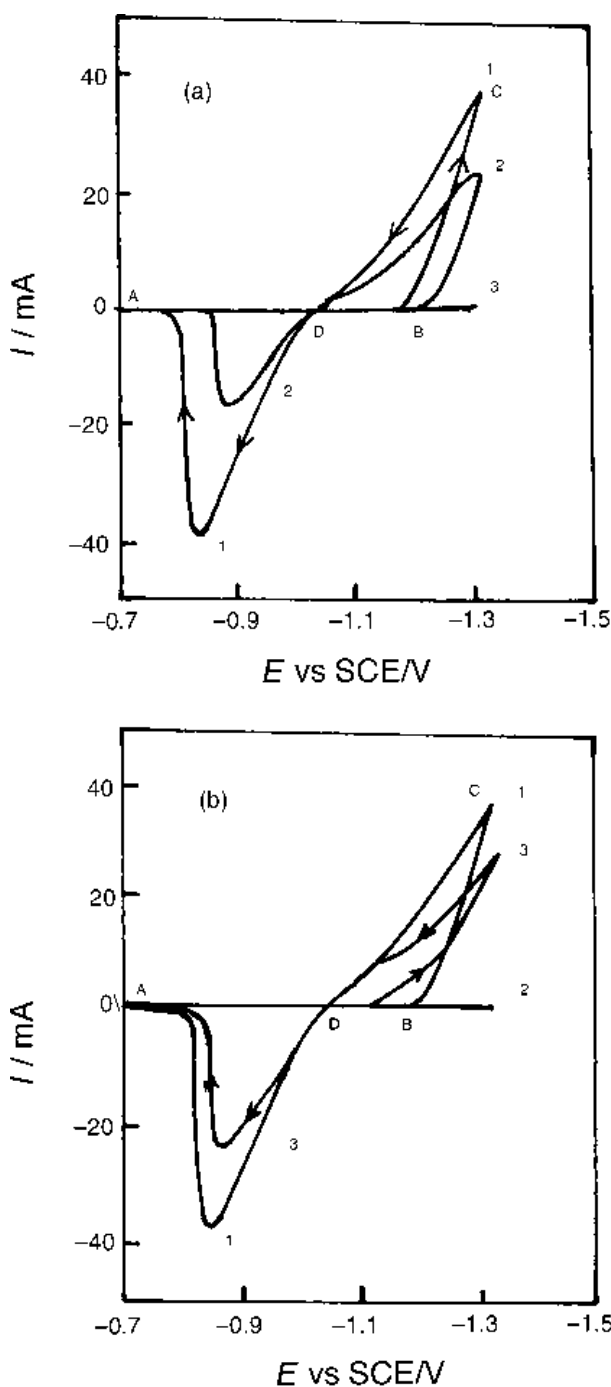


Fig. 2. (a) (1) No addition; (2) cyanopyridine (10 mg dm^{-3}); (3) cyanopyridine (20 mg dm^{-3}). (b) (1) No addition; (2) cyanopyridine (40 mg dm^{-3}); (3) cyanopyridine (40 mg dm^{-3}) + Sb (0.04 mg dm^{-3}).

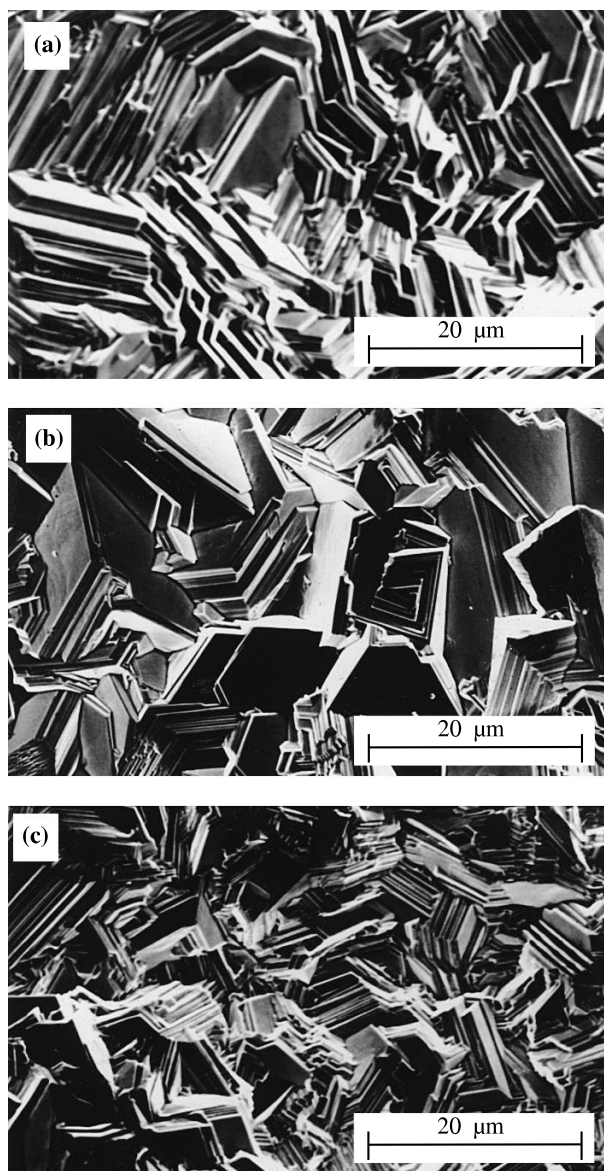


Fig. 3. SEM photomicrographs of zinc deposits. (a) No addition; (b) 4-ethylpyridine (40 mg dm^{-3}); (c) 4-ethylpyridine (40 mg dm^{-3}) + Sb (0.04 mg dm^{-3}).

to 40 mg dm^{-3} promoted the growth of (110) plane and resulted in a decrease in crystallite size (Fig. 3(b)). Addition of 0.04 mg dm^{-3} Sb with 4-ethylpyridine suppressed the growth of the (110) plane and the order of preferred planes changed to (101) (112) (102) (103) (114). This produced a compact morphology (Fig. 3(c)) where the crystallites were randomly oriented with substantial reduction in size. Such changes were reflected in the deposit quality, current efficiency and also in power consumption.

Low concentration (10 mg dm^{-3}) of gum arabic produced crystal orientations (101) (102) (103) (112) (114) and resulted in a reduction in crystallite size similar to that reported by Fosnacht and O'Keefe [39]. The hexagonal zinc platelets were closely packed and produced a cluster type morphology. Gum arabic concentrations above 10 mg dm^{-3} promoted growth of the (002) plane which is parallel to aluminium substrate. The crystallite size further decreased with for-

mation of more clusters. Addition of 0.04 mg dm^{-3} of Sb to 40 mg dm^{-3} of gum arabic produced an entirely different morphology. The platelet size was reduced to produce a fine needle-like structure. The morphology was characterized by clusters of non-uniform large nodules growing on the surface (Fig. 4(a)). These changes were reflected in a significant fall in current efficiency and further deterioration of deposit quality.

The results on crystallographic orientations and surface morphology for zinc deposits in the presence of 2-cyanopyridine are shown in Table 2 and SEM photographs in Fig. 4. It may be seen from these results that 2-cyanopyridine behaved differently from 4-ethylpyridine and gum arabic. Addition of 10 mg dm^{-3} of the additive changed the crystal orientations from (103) (102) (114) (101) (112) to (101) (100) (103) (110) (201) where growth of (100) and (110) crystal

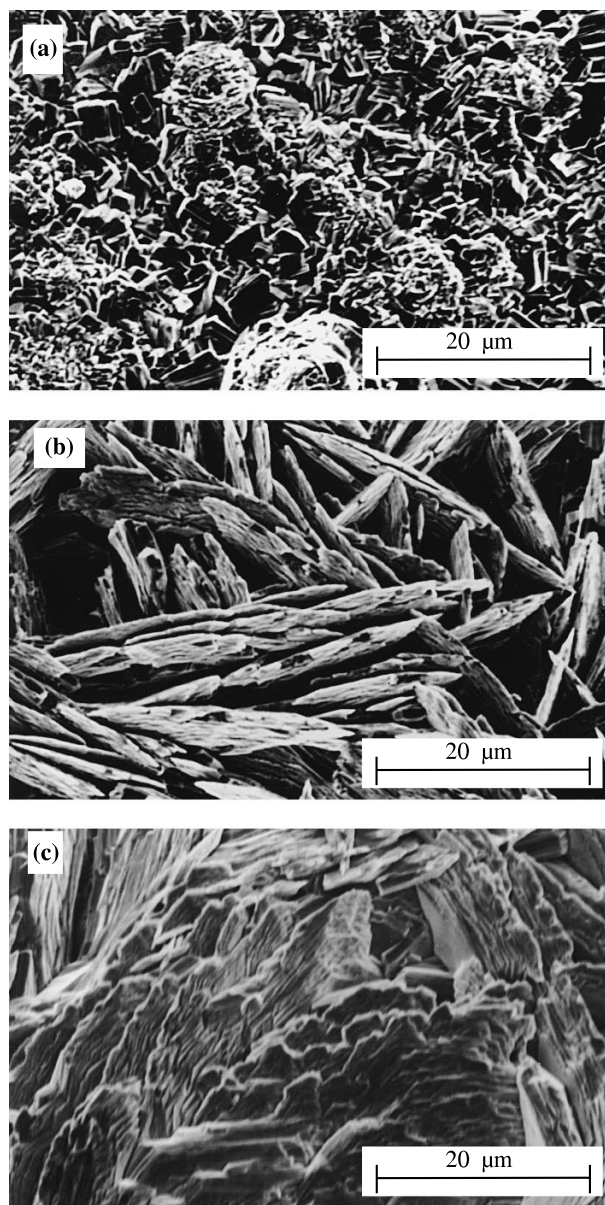


Fig. 4. SEM photomicrographs of zinc deposits. (a) Gum arabic (40 mg dm^{-3}) + Sb (0.04 mg dm^{-3}); (b) cyanopyridine (40 mg dm^{-3}); (c) cyanopyridine (40 mg dm^{-3}) + Sb (0.04 mg dm^{-3}).

Table 2. Crystallographic orientations of cathode zinc with 4-ethylpyridine and gum arabic

| [Additive] / mg dm ⁻³ | Crystallographic orientations (h k l) | | | | | | | |
|-------------------------------------|---------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| | Peak heights / cm | | | | | | | |
| | (100) | (101) | (102) | (103) | (114) | (112) | (110) | (201) |
| 4-Ethylpyridine | | | | | | | | |
| 0 | | 3.6 | 6.0 | 10.7 | 4.6 | 2.8 | – | – |
| 10 | | 12.8 | 10.2 | 13.2 | 4.8 | 4.9 | – | – |
| 20 | | 18.0 | 13.0 | 13.0 | 5.3 | 6.7 | 11.2 | – |
| 40 | | 20.0 | 15.0 | 13.0 | 5.8 | 8.6 | 13.5 | – |
| 40 + 0.04 Sb | | 22.0 | 8.6 | 6.0 | 3.7 | 11.2 | 3.5 | – |
| Gum arabic | | | | | | | | |
| 10 | | 14.3 | 8.4 | 8.4 | 4.7 | 7.1 | – | – |
| 20 | | 35.0 | 13.2 | 10.1 | 3.5 | 5.9 | – | – |
| 40 | | 15.2 | 6.4 | 6.1 | 2.6 | 4.2 | – | – |
| 2-Cyanopyridine | | | | | | | | |
| 10 | 23.2 | 31.5 | – | 13.1 | – | 3.3 | 11.0 | 7.8 |
| 20 | 30.5 | 22.2 | – | 13.2 | – | 2.7 | 11.4 | 9.0 |
| 40 | 23.2 | 22.2 | – | 13.0 | – | 3.6 | 11.3 | 7.2 |
| 40 + 0.04 Sb | 18.5 | 29.7 | – | 10.1 | – | 4.5 | nil | 5.4 |

planes were favoured (Table 2). This corresponded to a morphology where crystallites in bands were grown perpendicular to the substrate. Increase in the additive concentration above 20 mg dm⁻³ promoted growth of the (1 0 0) plane with a significant modification in the surface morphology (Fig. 4(b)). Addition of 0.04 mg dm⁻³ of Sb together with 40 mg dm⁻³ of 2-cyanopyridine suppressed the growth (1 1 0) plane whilst simultaneously favouring the (1 1 2) crystal plane. This resulted in an entirely different morphology (Fig. 4(c)) than with cyanopyridine alone.

4. Conclusions

- (i) Addition of 4-ethylpyridine or 2-cyanopyridine to acidic zinc sulfate solutions causes a reduction in current efficiency, an increase in power consumption and modification of the surface quality of electrodeposited zinc similar to gum arabic, the conventional industrial additive.
- (ii) On combination with antimony, 4-ethylpyridine produced a smooth surface with increased current efficiency and reduced power consumption but there was marginal change with 2-cyanopyridine.
- (iii) The polarization behaviour of 4-ethylpyridine alone or in combination with antimony was similar to that with gum arabic. However, the zinc deposition/dissolution peaks disappeared with 2-cyanopyridine concentrations above 10 mg dm⁻³.
- (iv) 4-ethylpyridine plus antimony produced a desirable zinc morphology with the preferred crystal orientations (1 0 1) (1 1 2) (1 0 2) (1 0 3) (1 1 4). On the other hand, 2-cyanopyridine with antimony produced an unusual morphology with crystallographic orientations (1 0 1) (1 0 0) (1 0 3) (2 0 1) (1 1 2) predominating.

- (v) 4-ethylpyridine in combination with antimony may act as an effective levelling agent for the electrowinning of zinc from acidic sulfate electrolyte.

Acknowledgements

The authors thanks Dr B. Clare for the hydrophobicity and pK_a calculations and J. Biddle for help in characterizing the zinc deposits. This work was funded by the Targeted Institutional Links Program of the Australian Government. S. C. Das thanks R. P. Das and H. S. Ray (RRL-Bhubaneswar) for their constant encouragement.

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