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# Effect of zinc on the electrocrystallization of cobalt

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The effects of zinc on the current efficiency, power consumption, deposit quality and contamination of cathode deposit during electrocrystallization of cobalt were studied. The presence of zinc affected current efficiency at all temperatures and the effect was intensified at lower temperature. Increase in power consumption was significant at lower temperature. The quantity of zinc in the electrodeposited cobalt invariably increased with increase in zinc concentration in the electrolyte, however, the zinc content of the deposit was significantly low at higher temperature. The tolerance limit of zinc in the electrolyte with respect to deposit quality was also greater at higher temperature. Increase in current density decreased the current efficiency, increased the power consumption and lowered the cathode contamination.

## 1. Introduction

Cobalt is mainly recovered as a coproduct of copper in Central Africa, and as a byproduct of hydrometallurgical nickel refining elsewhere. Because of its high cost and scarcity it is at present recovered from secondaries/wastes. Most virgin cobalt is produced by electrowinning from a solution of its sulfate salt [1–4]. The cobalt electrolyte is usually contaminated with a number of inorganic impurities either at ppm or even higher levels, leading to some cathode contamination. Since high purity cobalt is required for high technology materials, the cathodes produced from such industries are subjected to fire refining [5] if their level of contamination is too high.

The probable impurities which are associated with cobalt electrolyte are $Cu^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, PO_4^{3-}, AsO_4^{3-}$ etc. These impurities, in general, have the tendency to affect the cathode quality, the current efficiency and the crystal structure of the electrodeposited cobalt. The anions not only affect the transport of the metal ions to be deposited, but also their motion and discharge in the double layer and build-up of the crystal lattice [6]. They also retard the discharge of ions by blocking the active sites by specific adsorption [7]. Cationic impurities, on the other hand, have a tendency to reduce the current efficiency either by a process of coreduction or by simultaneous codeposition brought about by precipitation followed by adsorption [8]. Among these cationic impurities zinc behaves differently. Although its redox potential is much lower than that of cobalt, it always associates with cathode cobalt. Thus, cobalt electrolyte is subjected to rigorous purification from zinc, either by precipitation [9] or ion exchange [10]. In spite of such treatment, zinc always appears in the cobalt electrolyte at ppm levels. When cobalt is produced through a solvent extraction–electrowinning circuit, zinc always builds up in the circuit. There is very limited information [11–14] on the effect of zinc in cobalt electrowinning.

In the present work a detailed investigation on the electrowinning of cobalt from sulfate electrolyte containing different amounts of zinc was carried out. The effects of major variables, such as cobalt concentration, bath temperature and current density, were considered while studying the zinc effect.

## 2. Experimental details

### 2.1. *Apparatus and materials*

A 500 ml Corning beaker with a lid having provisions to accommodate the electrodes was used as the cell. Stainless steel and Pb–Sb (Sb 7%) sheets were used as cathodes and anodes, respectively. The effective cathode area was 100 $mm^2$.

The electrolytic solution was prepared from reagent grade cobalt sulfate crystals ($CoSO_4.7H_2O$) and distilled water. Its pH ($4.0 \pm 0.1$) was adjusted by adding sodium hydroxide or sulfuric acid. To study the effect of zinc the corresponding sulfate was used. All these chemicals were also of reagent grade.

### 2.2. *Electrolysis*

All the electrowinning experiments were carried out for 2 h at a current density of 230 A $m^{-2}$ (except for current density experiment) and at 60 g $dm^{-3}$ cobalt unless otherwise specified. The electrolysis temperature was maintained within ± 1 °C variation by using a thermostat. The bath pH was initially adjusted to 4.0 ± 0.1 for each experiment. The change in pH during the electrolysis period was observed to be almost the same in each case. Thus, all the experiments were carried out in the same pH range. Impurity addition was made as aliquots from the corresponding stock solution. After electrolysis the cathode was removed and thoroughly washed with water and acetone followed by drying. The cathode current efficiency was calculated from the increased weight of the cathode.

## 3. Results and discussion

### 3.1. *Zinc concentration*

The effect of zinc concentration in the cobalt bath at different temperatures are reported in Figs 1–3. The presence of zinc affected the cathode current efficiency at all temperatures (Fig. 1), though the extent varied with temperature. The current efficiency dropped up to about 1000 mg dm$^{-3}$ of zinc at low temperature, whereas at high temperature, it dropped to a level of about 500 mg dm$^{-3}$ of zinc. Thereafter, the current efficiency values remained nearly constant in both cases. This may be due to suppression of hydrogen evolution increase at higher zinc concentrations [15]. From the present results, it appears that the amount of zinc present in the bath probably controls the hydrogen evolution reaction rate so that the bath pH is maintained constant. In addition to current efficiency, zinc also affected the power consumption (Fig. 2). Though at higher temperature the influence was insignificant, a marked rise in power consumption was observed at low temperature (25 °C). The extent of zinc contamination of the cathode cobalt with increase in its concentration in the bath at different temperatures is shown in Fig. 3. As observed, the zinc content in the deposit increased with increase in zinc in the bath at all temperatures. However, the zinc contamination was significantly low at higher temperature.

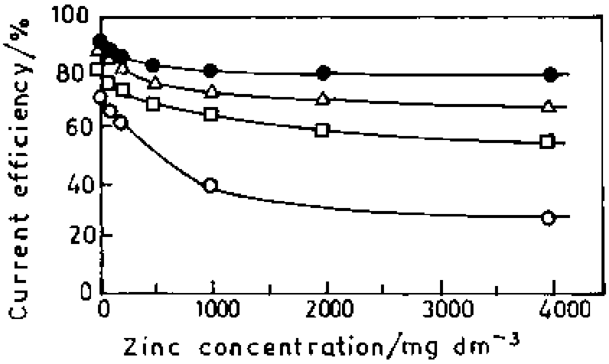

Fig. 1. Effect of zinc concentration on current efficiency at different temperatures: (○) 25 (□) 50, (△) 60 and (●) 70 °C. Current density 230 A m$^{-2}$.

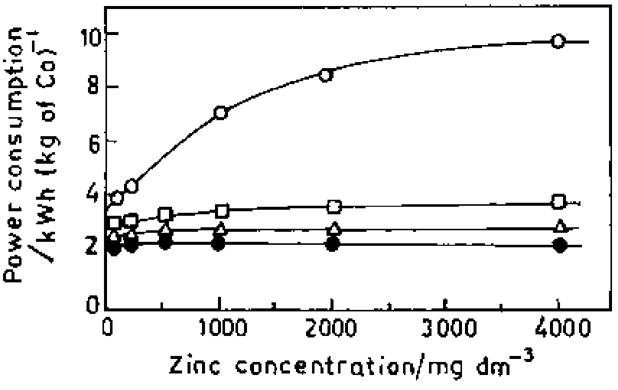

Fig. 2. Effect of zinc concentration on power consumption at different temperatures: (○) 25, (□) 50, (△) 60 and (●) 70 °C. Current density 230 A m$^{-2}$.

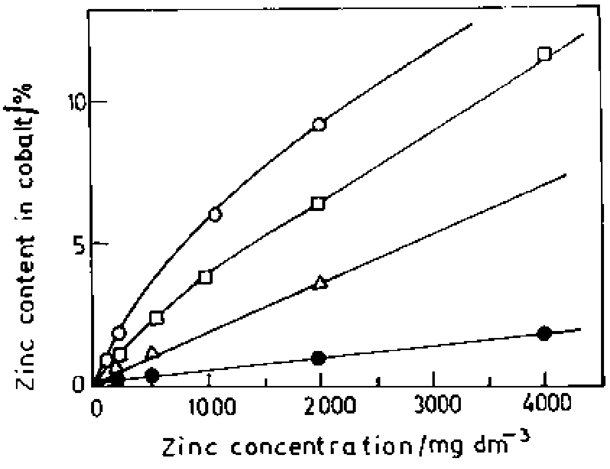

Fig. 3. Effect of zinc concentration on cobalt contamination at different temperatures: (○) 25, (□) 50, (△) 60 and (●) 70 °C. Current density 230 A m$^{-2}$.

The contamination of cathode cobalt with zinc may be due to precipitation of zinc as hydroxide at the surface and subsequent adsorption [15–19] or by codeposition either by anomalous codeposition [20–22] or by underpotential deposition [23]. It has been reported [24] that the electrodeposition of zinc and iron group metals from sulfate bath proceed through anomalous codeposition where zinc deposits preferentially under most plating conditions. Many hypotheses have been proposed [24–26] so far as anomalous codeposition is concerned. One of the most plausible mechanisms [27–29] includes the assumption that the pH in the vicinity of cathode increases and causes precipitation of metal hydroxide on the cathode. The pH change is due to hydrogen evolution:

$$2\,H_3O^+ + 2e^- = H_2 + 2H_2O \qquad (1)$$

and

$$2\,H_2O + 2e^- = H_2 + 2OH^- \qquad (2)$$

Increase in pH at the cathode in sulfate solution and precipitation of zinc hydroxide during anomalous codeposition have also been established [30–32]. Codeposition of Zn–Co alloy has also been studied in detail [29, 30, 33, 34]. It has been reported by Raub

[29] that zinc deposition takes place more readily with preceding $Zn(OH)^+$ or $Zn(OH)_2$ formation than in direct discharge of $Zn^{2+}$ ions. Fukushima *et al.* [30, 31] have also demonstrated that pH in the cathode layer increases to the critical pH of $Zn(OH)_2$ precipitation.

During electrodeposition of cobalt from aqueous solutions, the hydrogen evolution reaction takes place more readily because of its position in the e.m.f. series (Table 1). This may lead to the formation of $OH^-$ ions causing a local pH increase in the diffusion layer which may ultimately change the metal deposition kinetics [35]. Since cobalt and nickel belong to the same group and their standard electrode potentials do not differ much, it is expected that they will have similar deposition mechanism [36]. It has been reported [37, 38] that electrodeposition of Ni proceeds through discharge of $NiOH^+$ ion. Heusler [36] and Winand *et al.* [39] have proposed a similar mechanism for cobalt deposition where the deposition proceeds through formation of $CoOH^+$ [36] or $CoOH^+$ and $Co(OH)_2$ [39]. According to Winand *et al.* [39], at more acidic pH, the surface is covered by adsorbed hydrogen and the reaction proceeds through

$$Co^{2+} + OH^- = CoOH^+ \tag{3}$$

$$H^+ + e^- = H_{ads} \tag{4}$$

$$CoOH^+ + H_{ads} + 2\,e^- = Co + OH^- + H_{ads} \tag{5}$$

$Co^{2+}$ ions are hydrolysed as per Equation 3. At pH 4 and 4.5, the reaction proceeds through

$$Co^{2+} + 2OH^- = Co(OH)_2 \tag{6}$$

$$Co(OH)_2 + e^- = Co(OH)_{ads} + OH^- \tag{7}$$

$$Co(OH)_{ads} + e^- = Co + OH^- \tag{8}$$

Since, $OH^-$ is formed by Equations 7 and 8, this mechanism does not involve any hydrogen evolution. This mechanism also indicates pH rise at the cathode surface during cobalt electrowinning. The pH rise is not due to Reaction 2 alone, as reported by several workers [25–34], but probably due to the combined effects of Equations 2, 5, 7 and 8. Zinc hydroxide precipitates [29–31] when the pH at the diffusion layer approaches its critical value of 5.1 [30].

At lower zinc concentrations contamination of cathode cobalt with zinc is most likely due to inclusion of zinc hydroxide in the cobalt and not by anomalous codeposition, as suggested [25–34] for Zn–Ni and Zn–Co alloy depositions. In these cases, the Co or Ni to Zn weight ratio in the bath varies between approximately 1:2 to 1:10, but in the present study, the cobalt to zinc ratio was found to be very large. The presence of even 10 mg $dm^{-3}$ of zinc along with 60 g $dm^{-3}$ cobalt in the bath caused contamination of the cathode deposit with zinc. However, at higher zinc levels, when the cobalt to zinc ratio is closer, the inclusion of zinc in the cathode cobalt may take place through the mechanism suggested by Fukushima *et al.* [15, 24]. The tolerance limit of the deposit with respect to its quality was greater at higher temperature (Table 2). The cathode purity remained nearly the same between 50 °C and 70 °C, in spite of the wide difference in the tolerance limit and current efficiency.

*Table 1. Standard electrode potentials at 25 °C*

| *Element* | *Anode reaction* | *Reversible electrode potential*/ V |
|---|---|---|
| Zn | $Zn = Zn^{2+} + 2e^-$ | −0.76 |
| Co | $Co = Co^{2+} + 2e^-$ | −0.28 |
| Ni | $Ni = Ni^{2+} + 2e^-$ | −0.25 |
| $H_2$ | $H_2 = 2H^+ + 2e^-$ | 0.00 |
| Cu | $Cu = Cu^{2+} + 2e^-$ | +0.34 |
| $O_2$ | $2H_2O = O_2 + 4H^+ + 4e^-$ | +1.23 |

### 3.2. *Cobalt concentration*

The results on the effect of zinc at different cobalt concentrations are reported in Figs 4–7. Figure 4 shows the plot of current efficiency (CE) against $Co^{2+}$ at different zinc concentrations and temperatures. The increase in current efficiency with cobalt concentration was found to be dependent on zinc concentration and temperature. Increase in CE with

*Table 2. Tolerance limit* of cathode cobalt at different temperatures*

| *Temperature* /°C | [*Zn in bath*] /mg $dm^{-3}$ | *Current efficiency* /% | *Cathode purity* /% |
|---|---|---|---|
| 25 | 100 | 66.9 | 99.3 |
| 50 | 500 | 69.7 | 97.1 |
| 60 | 1000 | 76.0 | 98.5 |
| 70 | 4000 | 79.2 | 98.0 |

* with respect to deterioration

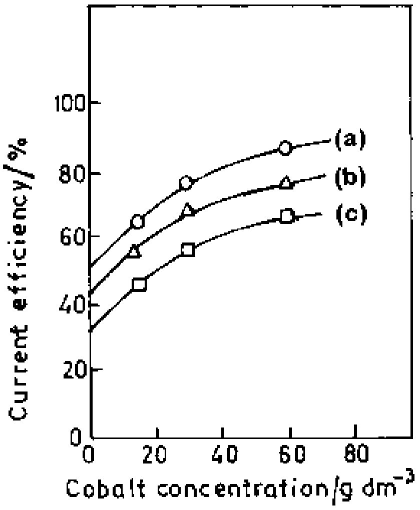

Fig. 4. Effect of cobalt concentration on current efficiency at different temperatures and zinc concentrations. [A] Zn 50 mg $dm^{-3}$ (a) 60 °C, (c) 25 °C and [B] Zn 500 mg $dm^{-3}$ (b) 60 °C. Current density 230 A $m^{-2}$.

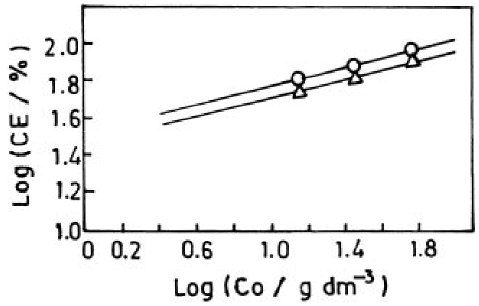

Fig. 5. Plot of log[CE] against log[Co] at 60 °C. (○) Zn 50 mg dm$^{-3}$ and (△) Zn 500 mg dm$^{-3}$. Current density 230 A m$^{-2}$.

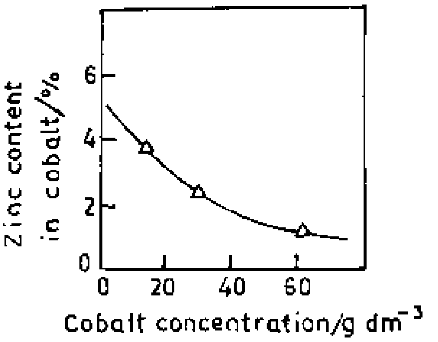

Fig. 7. Effect of cobalt concentration on cobalt contamination in the presence of 500mg dm$^{-3}$ zinc at 60 °C. Current density 230 A m$^{-2}$.

cobalt concentration was also observed by Das *et al.* [40, 41] during electrodeposition of cobalt from pure bath. When zinc concentration was raised from 50 to 500 mg dm$^{-3}$, the current efficiency dropped at all cobalt concentrations (Fig. 4). The plot of log CE against log [Co] at 50 and 500 mg dm$^{-3}$ of zinc is shown in Fig. 5. From the data obtained, an empirical equation for calculation of current efficiency is proposed:

$$\mathrm{CE}(\%) = \mathrm{K}\,[\mathrm{Co}]^{0.26} \tag{9}$$

where the $K$ values at 50 and 500 mg dm$^{-3}$ of zinc are 31.62 and 27.54, respectively, and the slope is 0.26. The variation in the cell voltage and power consumption at different cobalt concentrations are shown in Fig. 6. At both the temperatures (25 °C and 60 °C) the cell voltage, as well as the power consumption, decreased with increase in cobalt concentration. However, there was a steep fall in the cell voltage at higher temperature with increase in cobalt concentration. This may be due to a decrease in the electrolyte resistance because of higher temperature and cobalt concentration. The zinc content in the deposit was high at lower cobalt concentrations which decreased with increase in cobalt concentration. But there was a substantial fall in the impurity level at higher zinc concentration and temperature (Fig. 7). Higher contamination of the deposit at lower cobalt concentration may be attributed to the higher hydrogen evolution reaction rate resulting in increase in the pH and $Zn(OH)_2$ formation. Variation in cobalt concentration not only affected the current efficiency, energy consumption and contamination of the deposit, but also affected the cathode quality. Smooth, bright and adherent cobalt deposits were obtained from electrolytes containing upto 50 mg dm$^{-3}$ of zinc in the range of temperature and cobalt concentration studied. When the zinc concentration was raised to 500 mg dm$^{-3}$ cobalt was deposited in the form of scales at low cobalt concentration (upto 30 g dm$^{-3}$) and low temperature (25 °C). At higher bath temperature (i.e, 60 °C), cracking of the deposit was observed at low cobalt concentration (15 g dm$^{-3}$) whereas blackish deposits were obtained at cobalt concentration greater than 15 g dm$^{-3}$. The deterioration of the cathode deposits may be due to inclusion of $Zn(OH)_2$ and zinc into the cobalt resulting in changes to its mechanical properties.

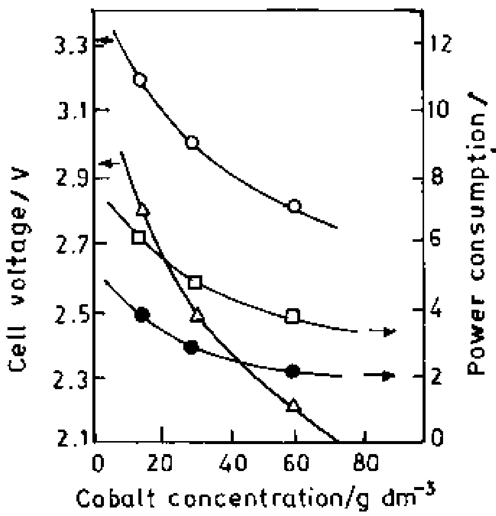

Fig. 6. Effect of cobalt concentration on cell voltage and power consumption at different temperatures in the presence of 50 mg dm$^{-3}$ zinc: (○) 25, (△) 60, (□) 25 and (●) 60 °C. Current density 230 A m$^{-2}$.

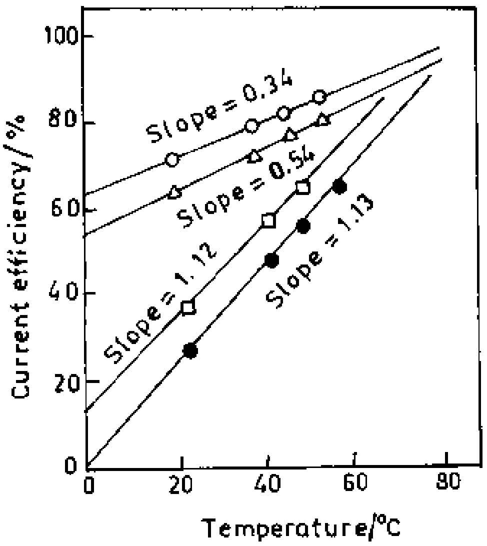

Fig. 8. Effect of temperature on current efficiency at different zinc concentrations: (○) 0, (△) 100, (□) 1000 and (●) 4000 mg dm$^{-3}$. Current density 230 A m$^{-2}$.

### 3.3. *Electrolysis temperature*

Temperature always plays an important role during electrowinning of cobalt as it increases current yield and decreases the energy requirement [42]. It has been suggested [40, 43] that a bath temperature of 60 °C or above is the best operating condition. Thus, the temperature effect was investigated in the range 25–70 °C at different zinc concentrations. The variation in current efficiency with temperature at different zinc concentrations is shown in Fig. 8. The increase in current efficiency showed linearity with temperature, irrespective of the zinc concentration. However, the rate of increase in current efficiency appears to be dependent of zinc concentration since the slope at higher zinc levels ($>500\,\mathrm{mg\,dm^{-3}}$) is nearly double than that at lower levels ($<500\,\mathrm{mg\,dm^{-3}}$) (Fig. 8).

Although the power consumption decreased with increase in temperature, the consumption was relatively greater at higher zinc concentrations at temperatures below 60 °C. However, the gap in the consumption became narrow with increase in bath temperature. The zinc content in the deposit also decreased linearly (Fig. 9) with increase in temperature and was least at 70 °C. Similar observations were also reported by Charles *et al.* [12] and Nzengu [13].

### 3.4. *Current density*

The effect of current density was investigated in the range 200 to 1000 A $\mathrm{m^{-2}}$ at 50 mg $\mathrm{dm^{-3}}$ of zinc at two different cobalt concentrations and temperatures (Figs 10–12). At both cobalt concentrations and temperatures (Fig. 10) the current efficiency decreased linearly with current density and higher efficiency was only achieved at higher cobalt concentrations and temperatures. Decrease in the current efficiency with current density was also observed by Das *et al.* [40, 41] and Gogia *et al.* [44] during electrowinning of cobalt and nickel, respectively. Such a fall in current efficiency with increase in current density may be explained as follows. Cobalt deposits under interfacial electron transfer or mass transfer control [45]. As the current density increases, concentration polarization becomes increasingly important as the surface cobalt concentration continues to decrease due to an inadequate supply of $\mathrm{Co^{2+}}$ from the bulk. The situation favours an increase in the hydrogen evolution reaction rate and, thus, leads to a pH increase in the cathode diffusion layer which may change the cobalt deposition kinetics [35]. Further, a rise in pH in the diffusion layer also causes precipitation of $\mathrm{Zn(OH)_2}$ and its adsorption which, finally, tends to inhibit cobalt deposition [24, 46, 47].

The effect of current density on power consumption is shown in Fig. 11. The power consumption increased linearly with increase in current density. The slope at lower temperature was relatively greater than at higher temperature. This implies that the rate of power consumption is higher at lower temperature.

Figure 12 shows the effect of current density on cathode contamination. At both the temperatures and cobalt concentrations, the zinc content in the deposit decreased with increase in current density.

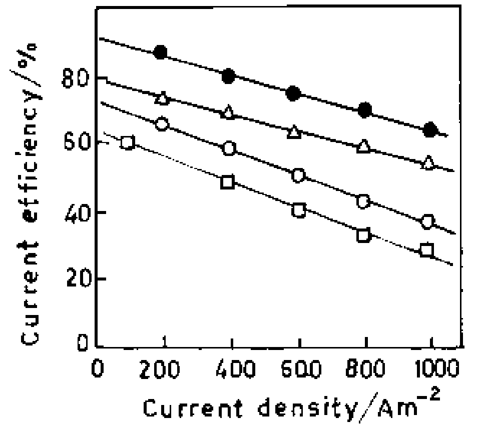

Fig. 10. Effect of current density on current efficiency in the presence of $50\,\mathrm{mg\,dm^{-3}}$ zinc at different cobalt concentrations and temperatures: [A] Co $15\,\mathrm{g\,dm^{-3}}$ (□) 40 °C and (○) 60 °C; [B] Co $60\,\mathrm{g\,dm^{-3}}$ (△) 40 °C and (●) 60 °C.

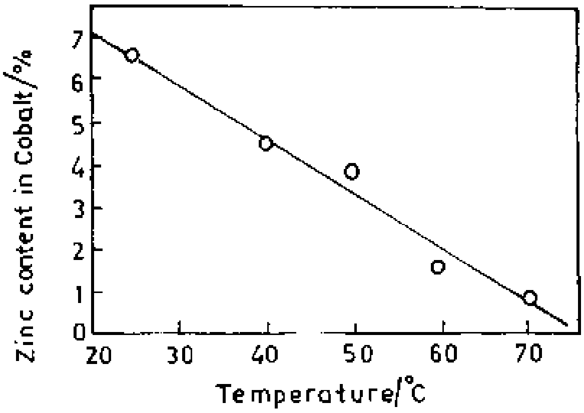

Fig. 9. Effect of temperature on cobalt contamination in the presence of $1000\,\mathrm{mg\,dm^{-3}}$ zinc. Current density $230\,\mathrm{A\,m^{-2}}$.

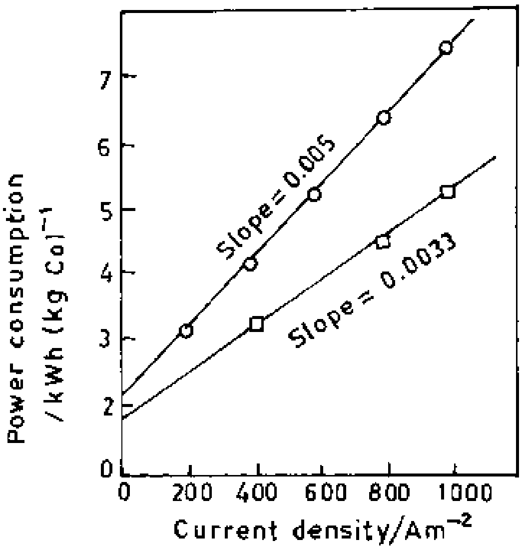

Fig. 11. Effect of current density on power consumption in the presence of $50\,\mathrm{mg\,dm^{-3}}$ zinc in a bath containing $60\,\mathrm{g\,dm^{-3}}$ cobalt at different temperatures: (○) 40 °C and (□) 60 °C.

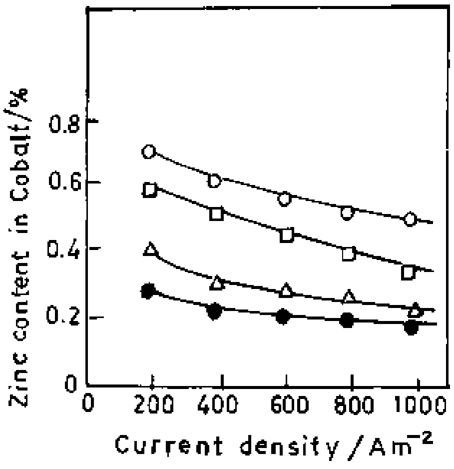

Fig. 12. Effect of current density on cobalt contamination in the presence of 50 mg dm$^{-3}$ zinc at different cobalt concentrations and temperatures: [A] Co 15 g dm$^{-3}$ (○) 40 °C and (□) 60 °C; [B] Co 60 g dm$^{-3}$ (△) 40 °C and (●) 60 °C.

However, the contamination remained at higher levels at lower temperature throughout. The reason for lower cathode contamination at higher current densities may be the fact that an increase in current density favours an increase in the rate of hydrogen evolution [48] and this leads to a pH increase, resulting in $Zn(OH)_2$ precipitation and subsequent adsorption. When the current density exceeds the critical value (in the present case this appears to be 200 A m$^{-2}$) $Zn(OH)_2$ precipitation is probably inhibited due to nonavailability of $Zn^{2+}$ ions in the diffusion layer. This situation favours a further rise in pH exceeding critical pH (pH 5.7, Fukushima *et al.* [30]) for cobalt hydroxide precipitation [48]. In fact, the precipitation of cobalt hydroxide and its occlusion into the cobalt cathode has been reported by Nakahara and Mahajan [49]. Similar observations have also been reported by Fukushima *et al.* [50] during Zn–Co alloy and by Roventi *et al.* [51] during Zn–Ni alloy deposition.

The cathode quality was not affected at lower cobalt concentration and temperature with increase in current density, but at higher temperature the deposit became rough at current density $> 800$ A m$^{-2}$. However, change in current density did not affect the deposit at higher cobalt concentrations under the present experimental conditions.

## 4. Conclusions

The following conclusions are drawn:

(i) The presence of zinc in the cobalt electrolyte causes a fall in current efficiency in the temperature range studied. The drop in current efficiency is higher at lower temperature.

(ii) The power consumption is comparatively low at higher temperature than that at lower temperature.

(iii) The cathode cobalt is contaminated with zinc even in the presence of 10 mg dm$^{-3}$ of zinc in the electrolyte. The zinc content increases with increase in zinc concentration and decreases with increase in cobalt concentration.

(iv) At higher zinc ($>$50 mg dm$^{-3}$) and lower cobalt concentration ($<$30 g dm$^{-3}$), cathode deposits begin to deteriorate. The deterioration is intensified with increase in electrolyte temperature.

(v) Increase in current density decreases current efficiency, increases power consumption and lowers cathode contamination.

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