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Zinc-nickel alloy deposition in the presence of citrate ions

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A new bath for zinc–nickel alloy electrodeposition has been studied using citrate as a complexant. Citrate ion was found to increase the zinc content of the alloy. Cyclic voltammetric studies were carried out to elucidate the effect of citrate ion in codeposition. The cathodic and anodic peaks indicate that due to efficient control of surface pH citrate ions cause depolarization during deposition. The absence of two cathodic peaks with decreasing nickel/zinc ratio reappeared in the presence of citrate ion. This led, not only to increased zinc content in the alloy, but also to reduced impurity content which affected the mechanical properties. This effect has been studied at varying zinc/nickel ratios and scanning potential ranges.

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1. Introduction

Zinc alloy electrodeposition is of interest since the alloy provides better corrosion protection than unalloyed zinc coatings on steel [1–3]. Improved resistance to corrosion in salt spray tests has been claimed as a result of codeposition of 5–15 wt % of nickel [3–5]. In such tests zinc deposition containing 15–18 wt % nickel had four times the corrosion resistance of cadmium-titanium deposits [6]. Our earlier publications in this subject dealt with properties of the alloy deposits [7, 8]. Experiments showed that each of the constituents of the bath had a specific role in deciding the alloy composition. In a recent paper [9] the influence of boric acid on the composition of the alloy was addressed. Dini *et al.* [10] indicate that the presence of nonmetallic inclusions in the alloy deposit affect colour and quality. Addition of ammonium salts leads to specific waste treatment problems [11]. Hence, it was felt that the use of certain complexants may be helpful in overcoming the problem of inclusions in the alloy deposit. Since citrate ion is a well known complexant in electroplating its effect on alloy composition was studied using cyclic voltammetry.

2. Experimental details

Voltammetric studies were carried out in a conventional three-compartment cell using a copper working electrode of 0.2826 cm^2 area embedded in a Teflon sleeve. Platinum foil was used as a counter electrode. Potential scanning was effected using a potentiogalvanoscan (Wenking model PSG 81) connected to a scan generator (Wenking SG 79) and an X–Y–t recorder. Potentials were measured with respect to the saturated calomel electrode (SCE).

Electrolytes were prepared using analytical grade salts in triple distilled water and deaerated with purified nitrogen before each experiment. The effect of addition of trisodium citrate on nickel and zinc deposition was studied in individual systems and then in combination. A sulfate electrolyte containing 0.66 M boric acid was chosen as the medium. Cyclic voltammograms were obtained by varying the nickel/zinc concentration ratio and the switching potentials. The experiments were conducted at pH 3.0 and at 30 ± 2 °C and at the scan rate of 10 mV s^{-1}. The stripping charge was calculated from the area of the voltammogram.

3. Results and discussion

Boric acid is a weak acid with pK value of 9.0. At high concentrations and at high temperature it forms polymeric species with a pK of 6.8 [12]. In this study, since the bath operates at room temperature, such a possibility does not arise. Though surface buffering is not related to the pK value of the acid, boric acid is generally considered to be an ineffective buffer in nickel plating electrolyte and its function is mainly attributed to the specific adsorption at the electrode surface suppressing hydrogen discharge and catalysing metal reduction [13]. Also, it reduces the overvoltage for water electrolysis. On the other hand citrate ion easily dissociates to give H$^+$ ions. The kinetics of the dissociation, which appear to be the crucial factor for surface buffering, are much faster for citrate ion than for boric acid.

Results in solutions of 0.5 M sodium sulfate containing 0.1 M citrate ion at a pH of 3.0 (Fig. 1), show a much larger I_l for H$^+$ discharge, than that observed in the presence of boric acid, which is utilized to control the surface pH at the electrode surface. Estimation of the buffer capacity by pH-metry, in solutions containing 0.6 M nickel sulfate and 0.66 M boric acid (Fig. 2) indicates the role played by citrate ion against surface pH changes.

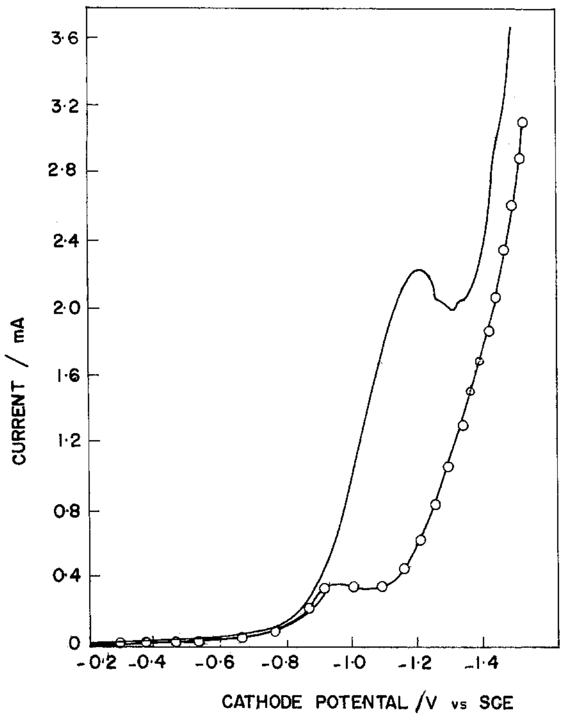

Fig. 1. Voltammogram showing the effect of boric acid and citrate ion in 0.5 M sodium sulfate, pH 3, 10 mV s^{-1}. Key: (O) with boric acid, (—) with citrate.

It was observed that boric acid suppressed zinc deposition and also influenced H^+ discharge. When the Ni/Zn concentration ratio was maintained between 5 and 6, two cathodic peaks were obtained, and below this ratio only a single cathodic peak was observed. The reason for the second peak was attributed to the increased polarization associated with nickel deposition and the decrease in overpotential for hydrogen evolution in the presence of boric acid. The latter reaction should have masked the second peak. If this assumption is correct then with the addition of an efficient buffering agent, viz., citrate ion, the above peak should reappear because of the considerable decrease in the surface pH at the electrode.

3.1. *Effect of citrate addition on nickel deposition*

Figure 3 presents the effect of citrate addition during nickel deposition. Considerable depolarization is observed along with a distinct hump at the foot of the voltammogram with progressive increase in citrate concentration. It can be inferred that the depolarization caused must be due to the decrease in the surface pH at the cathode. However, the peak current showed a gradual decrease which may be attributed to the complexation of nickel by citrate ion. In the anodic cycle no significant change was observed except a slight shift in the peak potential in the positive direction, indicating the existence of only alpha-nickel and increase in the peak current with increasing citrate concentration indicating easy dissolution of nickel with the ionization of hydrogen. Considering the above facts, it was felt that the deposit quality may be improved by the addition of citrate ion if its concentration is maintained at about 0.1 M.

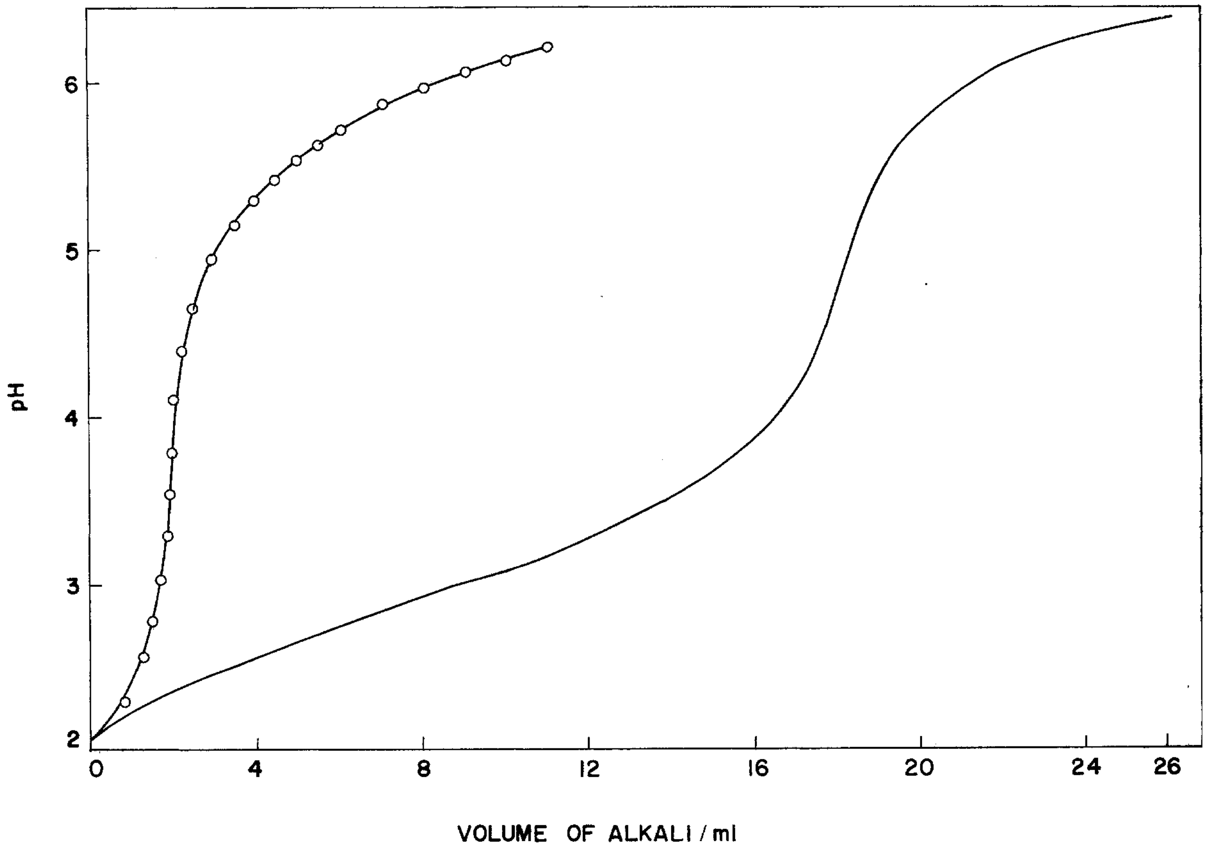

Fig. 2. pH metry curves showing the effect of boric acid and sodium citrate in Watt's bath at pH 3. Key: (O) 0.66 M boric acid, (—) 0.66 M boric acid + 0.1 M sodium citrate.

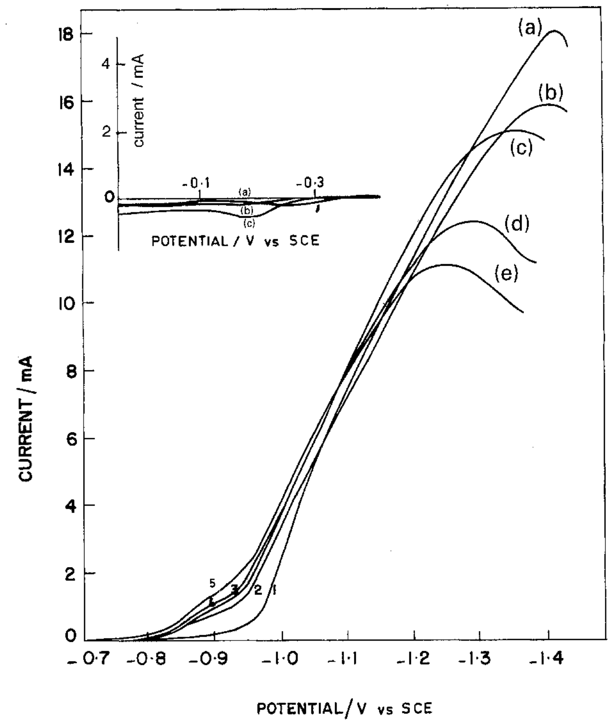

Fig. 3. CV showing the effect of sodium citrate concentration in nickel deposition at pH3, $10\,\mathrm{mV\,s^{-1}}$. Electrolyte: 0.6 M $NiSO_4$, 0.66 M H_3BO_3, sodium citrate: (a) 0, (b) 0.05, (c) 0.10, (d) 0.15 and (e) 0.20 M. Insert: anodic peaks obtained under the above conditions.

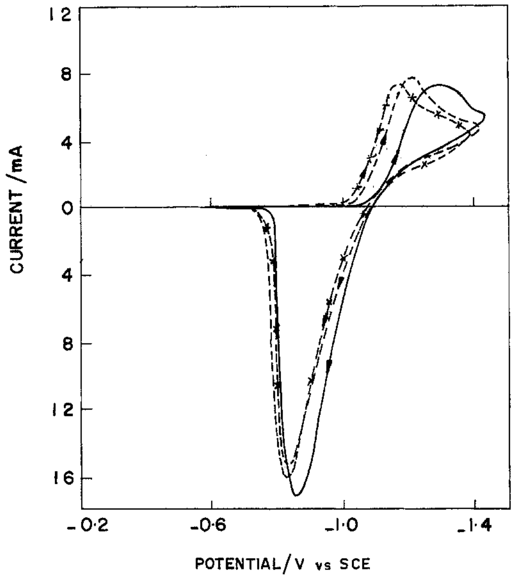

Fig. 4. CV showing the effect of sodium citrate in zinc deposition: electrolyte: 0.20 M $ZnSO_4$ + 0.66 M H_3BO_3 in 0.50 M sodium sulfate. Sodium citrate: (—) 0, (---) 0.05 and (x) 0.10 M. pH3, $10\,\mathrm{mV\,s^{-1}}$.

3.2. *Effect of citrate addition on zinc deposition*

Figure 4 presents the voltammogram obtained in the presence of increasing amounts of citrate concentration in a zinc bath. Though depolarization similar to that observed during nickel deposition occurred, the peak current remained almost unaltered, indicating the absence of complexation with zinc ions. However, some inhibition to anodic dissolution was observed.

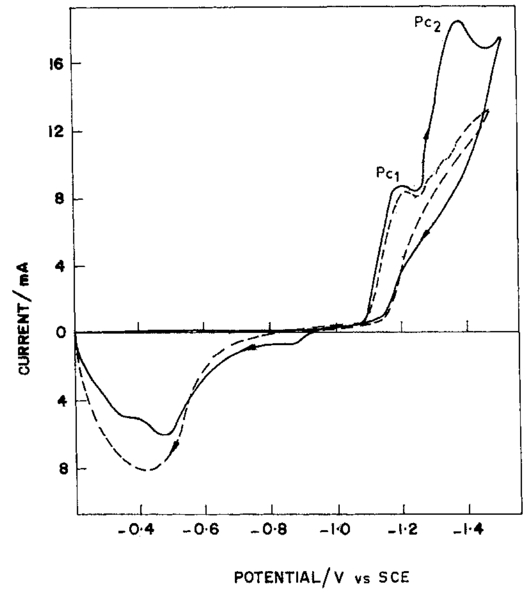

Fig. 5. CV showing the effect of sodium citrate during alloy deposition. Ni/Zn: 2, H_3BO_3 0.6 M, pH3, $10\,\mathrm{mV\,s^{-1}}$. Key: (---) without citrate, (—) with 0.1 M citrate.

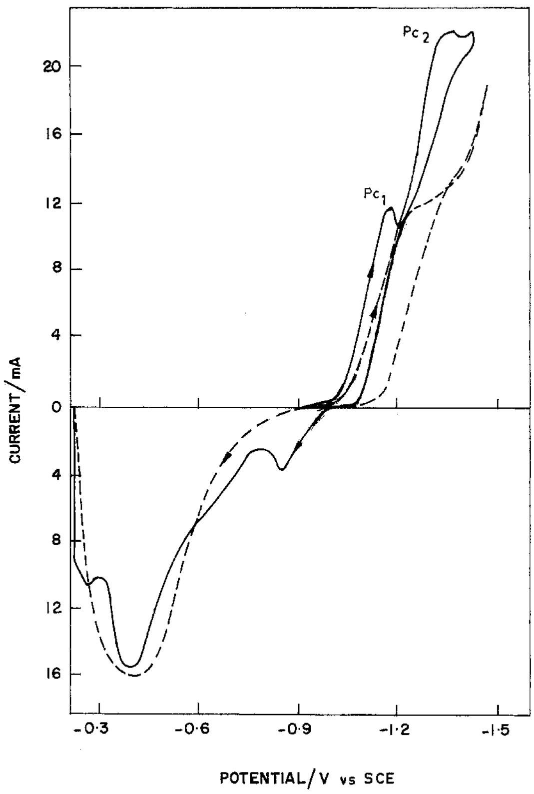

Fig. 6. CV showing the effect of sodium citrate during alloy deposition. Ni/Zn: 1; remaining conditions and key as in Fig. 5.

3.3. *Effect of citrate ion on alloy deposition*

Figures 5 and 6 present the effect of citrate addition on alloy deposition. As expected the second cathodic peak Pc_2 appeared in the presence of citrate ion indicating the decisive role played by citrate ion in maintaining the surface pH at a low level. A small hump observed at the foot of the voltammogram confirmed that the dissociation of citrate ion caused high H^+ discharge which helped in maintaining the surface pH, especially at high overpotentials.

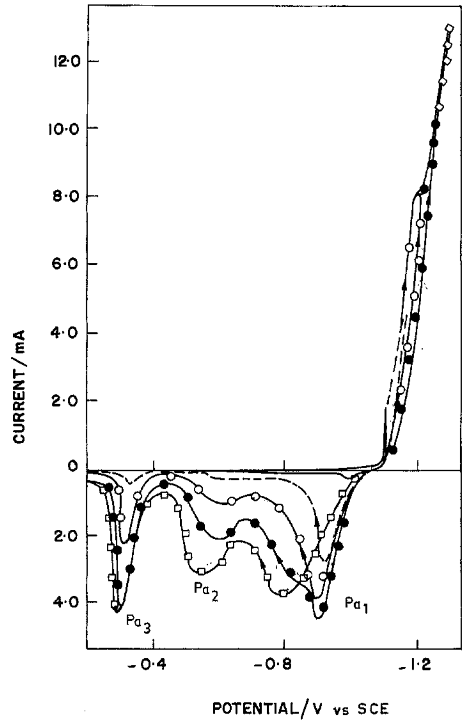

Fig. 7. CV showing the effect of scanning the potential from −100 mV to (—) −1.1 V, (---) −1.15 V, (○) −1.2 V, (●) −1.25 V, (□) −1.3 V. Sodium citrate 0.1 M. Other conditions as in Fig. 5.

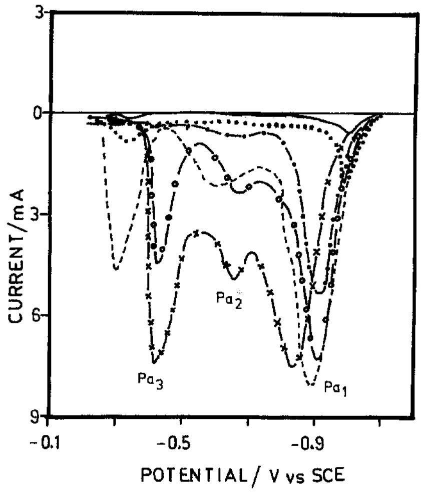

Fig. 8. Anodic dissolution peaks showing the effect of boric acid and sodium citrate. Ni/Zn: 2, H_3BO_3 0.6 M, sodium citrate 0.1 M, pH 3, 10 mV s^{-1}. With citrate: (—) 1.16 V, (–·–·–) −1.15 V, (---) −1.2 V. Without citrate: (···) −1.1 V, (●) −1.15 V, (×) −1.2 V.

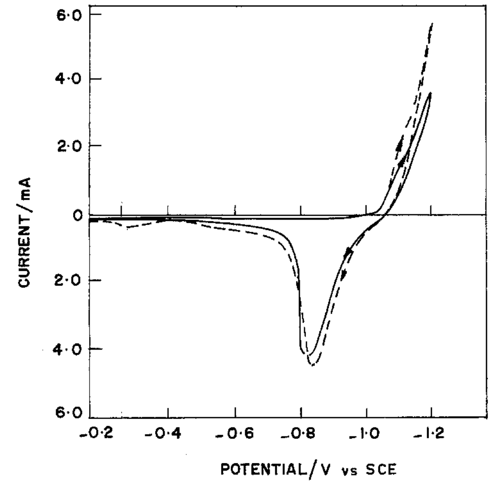

Fig. 9. Dissolution peaks showing the effect of boric acid and sodium citrate. Ni/Zn: 2, pH 3, 10 mV s^{-1}. Key: (—) without citrate, (---) with citrate.

From the above results, it follows that in the absence of good buffering, the deposits obtained at or above Pc$_1$ should contain nonmetallic inclusions, besides codeposited hydrogen, as also indicated by Dini *et al.* [10]. Absence of nonmetallic impurities in the alloy deposits in the presence of citrate ion has been confirmed by X-ray diffraction analyses [9].

In the anodic cycle, when the potential was scanned up to −1400 mV (I_1 region for peak Pc$_2$), three peaks corresponding to (i) gamma-phase zinc rich alloy, (ii) alpha-phase (which could be due to phase transformation during dissolution of the gamma-phase) and (iii) porous nickel [15] were identified, in contrast to a broad single peak observed in the absence of citrate. However, further conformation on the anodic peaks was done by progressively varying the switching potentials from −1100 to −1300 mV.

Figure 7 presents the stripping peaks obtained in the presence of citrate ion with varying switching potentials. Comparing this behaviour with that on boric acid addition (Fig. 8), it was clear that the deposition started in the presence of citrate ion only at −1100 mV, whereas it started at −1080 mV itself in the absence of citrate. The anodic peak currents for both zinc and nickel were lower in the presence of citrate ion due to factors already mentioned, while dealing with the parent metals. Likewise, the anodic peak for the porous nickel also showed a slight shift towards more positive potentials as observed in nickel dissolution. The alpha-phase (Pa$_2$), which is due to phase transformation during the dissolution of the gamma-phase, appeared when scanned up to −1.15 V in the absence of citrate, while its presence could be realized only at −1.2 V in the presence of citrate (Fig. 8). The peak currents for Pa$_3$ are much higher, above −1.15 V, in the absence of citrate. This is due to the higher amounts of nickel in the alloy and due to the ionization of hydrogen and other nonmetallic impurities present in the porous nickel layer, since at this potential deposition occurs at or near the I_1 range for Pc$_1$. In the presence of citrate ion I_1 for Pc$_1$ was a little higher, which may be the reason for the enhanced zinc content of the alloy. In the presence of citrate the dissolution peak current for Pa$_3$ was nearly half that obtained in its absence and the potential shifted to more positive values, indicating that the porous nickel corresponds to the alpha-phase.

The effects of Ni/Zn concentration ratio on the anodic peaks are presented in Figs 8, 9 and 10. In all the figures, though the peak currents show a marked decrease, the peak was more pronounced for the porous nickel layer. Inhibition of dissolution by citrate ion (Fig. 4) was observed only for zinc and not for nickel. However, when the switching potential

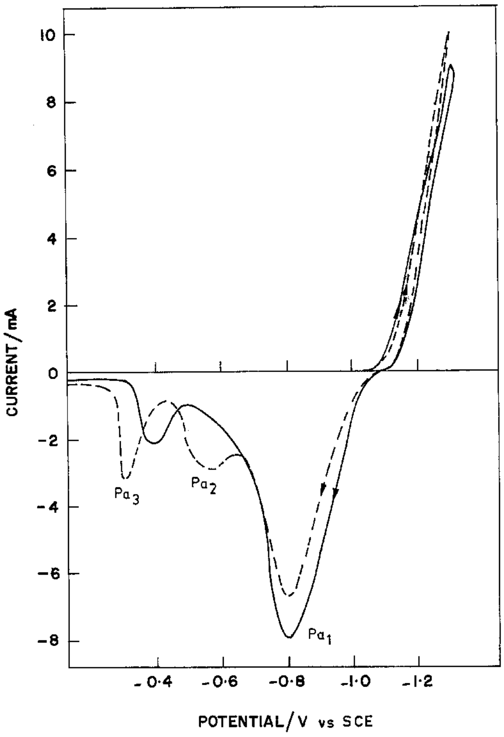

Fig. 10. As in Fig. 9 when Ni/Zn: 1 and potential scanned up to −1.3 V.

Table 1. Dependence of anodic charge on Zn^{++} mole fraction for solutions with 0.66 M *boric acid and 0.66* M *boric acid +0.1* M *sodium citrate*

Zinc mole fraction in the electrolyte	*Anodic charge*	
	H_3BO_3/mC	H_3BO_3 + *Sod.citrate*/mC
0.16	5.11	3.65
0.33	9.28	9.03
0.50	7.50	5.95
0.80	6.60	6.62

was increased to −1300 mV (Fig. 10) an increase in nickel content was observed, since at this potential zinc deposition was in the diffusion limiting range. Because of the depolarizing effect of citrate ion, the nickel content increases at this potential.

Table 1 shows the anodic charge obtained by varying the zinc mole per cent in the electrolyte. A gradual increase in the charge was observed, except at a mole fraction of 0.33 which has been attributed to the formation of an intermediate phase Ni_5Zn_{22} [13]. From Tables 2 and 3, it may be inferred that the reduction in the peak current in the presence of citrate ion is less significant for the gamma-phase zinc alloy than for the porous nickel layer.

Table 2. Dependence of peak current Pa$_1$ on the Zn^{++} mole fractions

Zinc mole fraction in the electrolyte	*Peak current*/mA		*Reduction* /%
	H_3BO_3	H_3BO_3 + *Sod.Citrate*	
0.16	3.20	1.40	4.6
0.33	2.80	2.50	11.0
0.50	4.30	3.95	10.4
0.80	4.20	3.80	9.5

Table 3. Dependence of peak current Pa$_3$ on the Zn^{++} mole fractions

Zinc mole fraction in the electrolyte	*Peak current*/mA		*Reduction* /%
	H_3BO_3	H_3BO_3 + *Sod.Citrate*	
0.16	0.70	0.30	57
0.33	1.90	0.60	68
0.50	0.40	0.25	38
0.80	0.45	0.30	25

4. Conclusion

The presence of citrate ion in a zinc–nickel alloy plating bath controls the nickel content of the alloy. Citrate ion minimized the inclusion of hydrogen and other inorganic compounds in the deposit, by decreasing the overpotential for deposition of the alloy at concentrations lower than 0.1 M.

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