

"Some Studies on the Cathodic polarization Curves on the Electrodepositing process of Zinc on Steel"¹

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Summary

In past part from this search, it was showed that zinc was electrodeposited onto steel substrates from citrate baths. Attempts had been done in order to obtain a sound and satisfactory deposits from an optimum bath. The effect of operating variables such as: bath constituent, concentrations of zinc ions, current density, pH, temperature and duration time on the electrodeposition of zinc was studied. Moreover, the effect of some addition agents on the process of zinc electrodeposition from these baths was studied. Surface morphology and micro hardness of deposits studied.

Now; in this part from study, the effect on operating variables such as: bath constituent, concentrations of zinc ions, pH, and temperature on the cathodic polarization curves on the electrodepositing processes of zinc on steel.

Moreover, the effect of superimposing a sinusoidal a. c. on a d. c. on the cathodic polarization curves of zinc from the citrate baths was investigated.

In addition, the effect of some addition agents on the process of zinc electrodeposition and the cathodic polarization curves from these baths was studied.

Key: Cathodic polarization curves, Alternating Current, Steel, Electrodeposition, Zinc, Corrosion.

¹ For the paper in Arabic see pages (147-148).

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1. Introduction:

In past part from this search, it achieved zinc was electrodeposited onto steel substrates from citrate baths. Attempts had been done in order to obtain a sound and satisfactory deposits from an optimum bath. The effect of operating variables such as: bath constituent, concentrations of zinc ions, current density, pH, temperature and duration time on the electrodeposition of zinc was studied. Moreover, the effect of some addition agents on the process of zinc electrodeposition from these baths was studied. Surface morphology and micro hardness of deposits studied. Now; in this part from study, the effect on operating variables such as: bath constituent, concentrations of zinc ions, pH, and temperature on the cathodic polarization curves on the electrodepositing processes of zinc on steel.

Moreover, the effect of superimposing a sinusoidal **a. c.** on a **d. c.** on the electrodeposition of zinc from the citrate baths was investigated. In addition, the effect of some addition agents on the process of zinc electrodeposition from these baths was studied.

Baths used for the electrodeposition of zinc are presented in **Table 1**.

1.1- Cathodic Polarization:

When no external potential is applied to the electrolytic cell of similar cathode and anode, the potentials of the anode and cathode are equal, at least within a fraction of a millivolt. If the electrodes are connected externally, no current flows. To produce a current, an external potential must be furnished, this potential is called polarization.

At each electrode of the unpolarized cell, anodic and cathodic reactions proceed at equal rates, so that there is no net change from these exchange currents. Application of the polarizing potential lowers the potential at the cathode, thus accelerating the deposition reaction and retarding the dissolution reaction (anodic reaction), so that there is net cathodic current and corresponding deposition of metal.

At the anode the potential is raised with the opposite consequences. The shift in potential at either electrode is its polarization, overpotential, or overvoltage.

The overpotential is produced by inhibiting factors of various kinds which affect the electrode reaction. Depending on the kind and site of the inhibitions, different kinds of overpotential or polarization may be distinguished [1].

Activation polarization:

Cathodic polarization shifts the energy level of ions in the double layer towards the potential barrier, so that more of them can cross per unit time to form a deposit on the cathode. (Activation energy may be regarded as a potential barrier over which the reactants must pass). Simultaneously the energy of lattice ions is shifted away from the barrier level, so that the rate at which they cross over and enter the solution is diminished. The portion of the total electrode polarization which produces these effects is termed activation polarization.

Concentration polarization:

As soon as deposition has proceeded for a finite time, the concentration of metal ions at the double layer is decreased, because replenishment by mass transport is not sufficient to maintain the original concentrations.

Resistance polarization:

Besides these contributions to polarization, to produce a flow of current through the ohmic resistance of the bath requires still further overvoltage. This quantity is called resistance or ohmic polarization.

Several Kinds of polarization are usually superimposed during the electrodeposition of metals. In bath in which hydrated metal ion are present, the concentration polarization is therefore, normally correspondingly small. In electrolytes of a solution containing complex metal ions, considerable concentration polarization may be met even at small current densities.

The polarization exists during the metal electrodeposition depends on the kind of metals, the nature and composition of the bath, the presence of addition agent, the temperature and the current density .

1.2- Superimposed Alternating Current:

Direct current (**d. c.**) is most commonly employed in ordinary electrodeposition. However, several investigations have been carried out with superimposed alternating current (**a. c.**), in the form of sinusoidal, triangle or square waves, on the direct current during electrodeposition.

When sinusoidal alternating current passes through an electrode, the latter acts similarly to a combination of capacitances and resistances [2]. From the value of the electrode impedance, the nature and characteristics of the electrode processes can be deduced. In practice this can be visualizes in the following way: if a sinusoidal **a. c.** of sufficiently small amplitude is applied to an electrode, and if we neglect the non-linearity of the

polarization curve, that assumes a linear dependence of current on potential, the resulting current will also be sinusoidal and will have the same frequency as the applied **a. c.** In reality, due to the non linearity of the polarization curve or, in other words, due to the non linear characteristics of the electrode, the sinusoidal wave of **a. c.** suffers a distortion at the electrode. As a result, the **a. c.** changes the polarization curves of the anodic and cathodic processes to a degree which depends on its density and frequency [3]. The validity of this hypothesis was checked by a substitution circuit containing suitable arranged condensers and resistances [4].

Therefore, the **a. c.** has a significant influences on many electrode processes and is widely used in such electrochemical investigations as the study of the electrical double layers [5], fast electrode reactions [6], the kinetics of the formation and dissolution of the oxide films [7] and in the electrodeposition and dissolution of metals [8,9 and 10] .

2. Experimental work

All the plating baths and reagents used were made from annular chemicals and doubly distilled water. The compositions of the examined baths for zinc electrodeposition are given in **Table 1**. For electrodeposition, a steel cathode and platinum sheet anode each of dimensions (**2.5 cm × 3.0 cm**) was used.

The plating cell used was a rectangular Perspex trough (**10 cm × 3.0 cm**) provided with vertical grooves, on each of the side walls, to fix the electrodes. Before each run, steel cathode was mechanically polished with different grade emery papers, **600, 800, 1000** and **1500** and then washed with distilled water, rinsed with ethanol and weighed. Direct current (**d. c.**) was supplied by **d. c.** power supply model (**GPS-3030D**).

The Cathodic current efficiencies **f** were determined with the help of **Cu-coulometer**, ($f = \mathbf{Wt}_{\text{exp.}} / \mathbf{Wt}_{\text{theo.}}$) where \mathbf{Wt}_{exp} is the weight of the deposit obtained experimentally and $\mathbf{Wt}_{\text{theo}}$ is the weight of the deposit calculated theoretically according to **Faraday's law**.

Most of the experiments were carried out at **25 ± 2 °C**. The plating duration was **20** minutes. In some experiments, a sinusoidal **a. c.** superimposed on the **d. c.** was supplied by **a. c.** generator of the type (**GF 20 Rc-Generator Claman & Grahnert Dresden**) connected directly to the cathode and the anode. To achieve separation of the external **d. c.** and **a. c.** circuits, an induction coil (**2.5 H- 0.25 A**) was introduced in the

direct current circuit and a condenser of (**100 μ F-12 V**) was joined to the **a. c.** circuit.

Potentiodynamic Cathodic polarization measurements were performed in the rectangular cell. A potentiostat / Galvanostat (**EG&G model 273**) controlled by PC was used for Cathodic polarization measurements.

All potentials were measured relative to a saturated calomel electrode (**SCE**). To avoid contamination, the reference electrode was connected to the working steel cathode via a bridge provided with **Luggin-Haber** tip and filled with the solution under test. The tip was placed very close to the electrode surface. All potentials were measured and recorded vs. the saturated calomel electrode.

3. Results and discussion

The study of the cathodic polarization (**i-E**) curves is very important because polarization affects the electrodeposition processes and helps us in understanding the nature of electrodeposition. For this reasons, the cathodic polarization curves of zinc deposition on steel cathodes were recorded potentiodynamically (**in presence of d. c. alone**) and galvanostatically (**in presence of a. c. superimposed on d. c.**) under different operating conditions.

The potentiodynamic measurements were swept from the rest potentials in the negative potential direction with scan rate **10 mVs⁻¹**.

Generally, the deposition of zinc from citrate baths is characterized by high polarization, and appearance of cathodic **peak C** before the deposition potential of zinc.

The cathodic **peak C** is assigned to the discharge of the H⁺ ions. The drop in the cathodic current beyond the peak potential of the **peak C** indicates suppression of hydrogen evolution [11]. Such behaviour could be attributed to the formation of an inhibitory Zn hydroxide formed and adsorbed on a cathode surface. It is probable that some of the evolution sites for hydrogen are occupied by adsorbed Zn hydroxide. In hydrogen evolution in the presence of Zn ions, Zn hydroxide formed by hydrolysis due to the predominant hydrogen evolution within the region of **peak C** [12]. It seems that the hydrolysis of Zn ions begins at the peak potential of **peak C** Similar results have been reported for the cathodic polarization of Zn in acetate bath [13].

The effect of increasing **Zn²⁺** ion concentrations on the cathodic polarization curves is shown in **Fig. 1 (curves a-c)**. The data depict that

with increasing Zn^{2+} ions concentrations, a slight decrease of cathodic polarization is observed. These results could be attributed to an increase in relative concentration of Zn^{2+} in the cathodic diffusion layer and this is reflected in a decrease in concentration polarization associated with zinc deposition.

Addition of **tri-sod. citrate (Fig.1 curves d, e)** resulted in a remarkable shift in the cathodic polarization curves towards the more negative values. This could be attributed to the adsorption of citrate ions on the cathode surface and blocking the active site available for electroreduction of zinc ions.

Nevertheless, the reverse was observed, which is the decrease of cathodic polarization, with increasing concentration of citric acid in the bath (**Fig. 2**). The height of the cathodic peak is increased with increasing citric acid concentrations. This is a clear cut that this **peak C** is due to H^+ discharge.

To throw more light on the cathodic peak and in order to prove that this **peak C** is due to hydrogen evolution, a potentiodynamic polarization curve was traced for a solution contains only citric and tri-sod. citrate ions.

Fig. 3 curve a, represents the discharge of H^+ ions and this proves that the peak formed in **Fig. 2** is due to the discharge of H^+ ions.

In presence of Zn^{2+} ions in the bath, H^+ ions (**the nobler species**) discharge firstly and then as a result of H_2 evolution, pH at the cathode surface increased and consequently, Zn hydroxide starts to form and precipitate on the electrode surface. The deposition of Zn hydroxide inhibits the discharge of H^+ ions and this is reflected in the appearance of cathodic **peak C** prior to the electroreduction of Zn^{2+} (**the less noble species**) on the cathode surface.

Fig. 4 illustrates the influence of pH on the cathodic polarization curves. The data show that the cathodic peak height is strongly depended on pH of the solution. Decreasing pH increases the cathodic peak height as a further proves that this peak is due to H^+ discharge.

Fig. 5 shows the influence of bath temperature on the cathodic polarization curves. The data depict that the deposition potentials of hydrogen and zinc become more noble with increase in temperature. The higher the elevation in temperature, the greater is the decrease in cathodic polarization. An increase in temperature increases the concentration of

the two ions (zinc and hydrogen) in the cathode diffusion layer, because rate of diffusion increases with temperature. In addition, increasing temperature decreases the activation type of polarization of the two ions; such effect is reflected in a decrease in cathodic polarization.

Figs. 6, 7 show the effect of a sinusoidal **a. c.** of variable density and frequency superimposed on a **d. c.** on the cathodic polarization curves of zinc deposition. The data reveal that, superimposing **a. c.** on **d. c.** slightly increases the cathodic polarization for Zn deposition. However, superimposed **a. c.** of variable frequency has no remarkable effect on cathodic polarization.

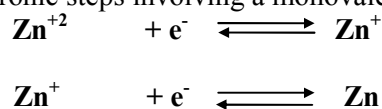
The influence of superimposing **a. c.** on **d. c.** on the cathodic current efficiency **f %** was investigated and the results are given in **Table 2**. Inspection of the data shows that superimposing **a. c.** on **d. c.** decreases the **f%**.

However changing the **a. c.** frequency at constant **a. c.** density has no significant influence on the value of **f %**. These results agree well with the effect of superimposed **a. c.** on the cathodic polarization curves **Figs. 6, 7**.

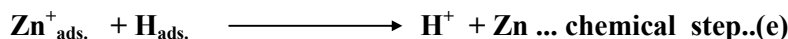
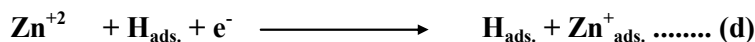
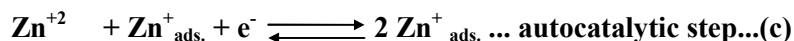
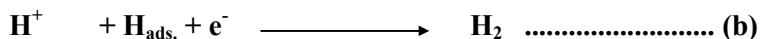
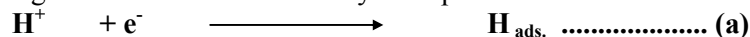
In order to improve the smoothness and brightness of zinc plated, some organic additives were added. Among these organic additives, **SGN1** was found to be the best one of them giving not only a semi-bright deposit but also deposits of good quality.

Moreover, sod. lauryl sulphate (**SLS**) was added to remove the black spots formed on surface of the deposits. The polarization curves for zinc deposition in the presence of **SLS** and/or **SGN1** were traced as shown in **Fig. 8**. Addition of **SLS** or **SGN1** into the bath (**Zn -10**), decreases the cathodic polarization. Mixture addition of **SLS** and **SGN1** shows greater effect on decreasing polarization than the individual addition of **SLS** or **SGN1** under the same conditions.

Several mechanisms have been proposed for the overall cathodic discharge of Zn^{2+} ions at acidic pH's. Some authors [14, 15 and 16] suggested that charge transfer occurs from the bivalent metal ions Zn^{2+} , which can either be solvated or complexes in the electrolyte, in two successive one electronic steps involving a monovalent intermediate Zn^+ :



A model proposed for discharge of Zn^{2+} based on a coupling between heterogeneous reactions is given by **Epelbon et. al. [17]**. The proposed discharge model includes autocatalytic steps as shown below:



Reaction (a) corresponding to the hydrogen adsorption on the cathode surface, and **reaction (b)** to the hydrogen evolution. The divalent Zn^{2+} is adsorbed on the surface via the autocatalytic **reaction (c)** and also via **reaction (d)** which is catalyzed by $H_{ads.}$ and this adsorption produces the intermediate $Zn^+_{ads.}$

From the above it could be conclude that, there is a competition between zinc and hydrogen for deposition. Increasing Zn^{2+} ions in the bath favours Zn deposition to compete hydrogen evolution while increasing H^+ (**by increasing citric acid concentration**) enhances evolution of hydrogen on the expense of Zn deposition.

4. Conclusion:

Adherent and smooth deposits of zinc were successfully electroplated onto steel substrates from aqueous citrate baths studied. The bath was characterized by high cathodic current efficiency. The deposits were sound and satisfactory under most conditions. An explanation has been offered for the various trends observed during the investigation in the light of cathodic polarization phenomena. The effect of sinusoidal a. c. of variable density and frequency superimposed on a d. c. is slightly on cathodic polarization and no remarkable effect for variable frequency, but the influence was on the cathodic current efficiency.

The optimum plating variables are: $ZnSO_4 \cdot 7H_2O$ 100 g/l, Tri-Sod. Citrate 50 g/l, Citric Acid 20 g/l, C. D. 2 A/dm², pH 5, Temperature 25°C, Time 20 min. .

Table 1: Composition of the zinc electroplating solutions.

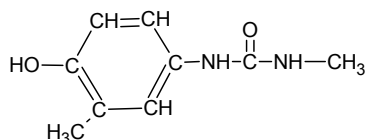
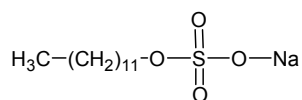
Bath No.	Concentrations (g ^l ⁻¹)							C (conductivity) (Ω ⁻¹ .cm ⁻¹)	pH
	ZnSO ₄ 7H ₂ O	citric acid	tri-sod. citrate	SLS	SGN.1	SGN.2	SGN.3		
Zn- 1	60	-	-	-	-	-	-	14.73	5.35
Zn- 2	80	-	-	-	-	-	-	17.44	5.25
Zn- 3	100	-	-	-	-	-	-	19.99	5.20
Zn- 4	100	-	20	-	-	-	-	22.44	5.15
Zn- 5	100	-	50	-	-	-	-	29.17	5.15
Zn- 6	100	10	-	-	-	-	-	21.42	2.40
Zn- 7	100	20	-	-	-	-	-	23.05	2.25
Zn- 8	100	20	50	-	-	-	-	28.25	3.70
Zn- 9	100	20	50	-	-	-	-	30.90	4.50
Zn-10	100	20	50	-	-	-	-	33.04	5.00
Zn-11	100	20	50	-	-	-	-	36.11	6.00
Zn-12	100	20	50	0.5	-	-	-	-	5.00
Zn-13	100	20	50	-	0.05	-	-	-	5.00
Zn-14	100	20	50	-	-	0.05	-	-	5.00
Zn-15	100	20	50	-	-	-	0.05	-	5.00
Zn-16	100	20	50	0.5	0.05	-	-	-	5.00
Zn-17	100	20	50	0.5	-	0.05	-	-	5.00
Zn-18	100	20	50	0.5	-	-	0.05	-	5.00

Table 2 : Effect of a.c. frequency (ia.c = 2 Adm-2) and effect of a.c. density ($\omega = 50\text{Hz}$) on the cathodic current efficiency from the bath Zn-10.

(id.c = 2 Adm-2, t = 20 min., pH = 5.0) from Zn-10 bath.

frequency (Hz)	f %	ia.c. density (Adm-2)	f %
50	89.23	0.00	96.94
100	91.85	0.33	89.88
500	92.56	1.33	89.88
1000	95.13	2.00	89.23

The structures of some organic compounds are used in the search:

**SGN 1****SLS**

References

- [1] - E. Raub and K. Muller "Fundamentals of Metal Deposition" Elsevier Publishing Co., London- New York, (1967).
- [2] - T. Erdey-Gruz, J. Devay, Gy. Horanyi, I. Vajasdi and L. Meszaros; *Acta. Chim. Acad. Sci. Hung.*, 30(1962)413.
- [3] - J. Devay; *Veszpremi Vegyipari Egyetem Kozlemenyei*, 9(1965)35.
- [4]- J. Devay and L. Meszaros, *Acta. Chim. Acad. Sci. Hung.*, 43(1965)17.
- [5] - D. C. Graham, *J. Am. Chem. Soc.*, 63(1941)1207.
- [6] - J. E. R. Randles; *Discussion Faraday Soc.*, 1(1947)11.
- [7] - B. V. Ershlder, *Trans. 2nd Meeting on Metal Corrosion, Acad. Sci. USSR*, 2 (1943) 52.
- [8] - A. T. Vagraman and Z. A. Soleveva, *Technology of Electrodeposition*, Robert Draper Ltd. Teddington, (1961).
- [9] - J. Devay, S. S. Abd El Rehim and V. Takes; *Acta. Chim. Acad. Sci. Hung.*, 52(1967)63.
- [10] - S. S. Abd El Rehim and A. M. Abd El Halim, *Acta. Chim. Acad. Sci. Hung.*, 80(1974)65.
- [11] - S. S. Abd El Rehim et. al., *J. METALL*, 52(5)(1998)304-308.
- [12] - S. S. Abd El Rehim et. al., *J. Trans. Inst. Metal. Finish (IMF)*, 77(1)(1999)31.
- [13] - S. S. Abd El Rehim, S. M. Abd El Wahaab, E. E. Fouad, and H. H. Hassan, *J. Appl. Electrochem.*, 24(1994)350 - 354.
- [14] - K. E. Heusler and R. Kondler, *Electrochim. Acta*.18(1973)855.
- [15] - L. Gaiser and K. E. Heusler, *Electrochim. Acta*, 15(1970)161.
- [16] - T. Hurlen and E. Eriksurd, *J. Elctranal. Chem.*, 45(1973)405.
- [17] - I. Epelboin, M. Ksouri, and R. Wiart, *J. Elctrochem. Soc.*, 122(9) (1975)206.

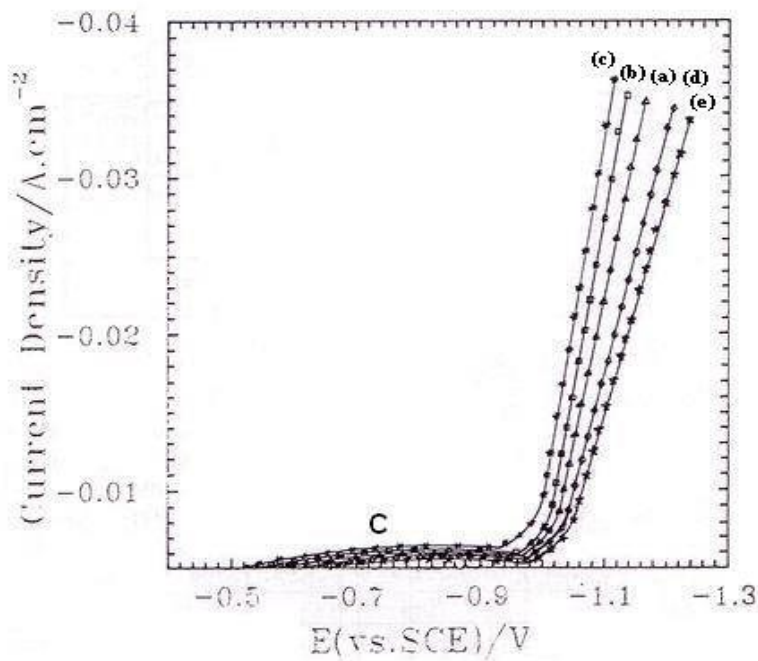


Fig. 1 : Polarization curves during Zn-electrodeposition from solution baths (Zn-1 curve a, Zn-2 curve b, Zn-3 curve c, Zn-4 curve d, Zn-5 curve e).

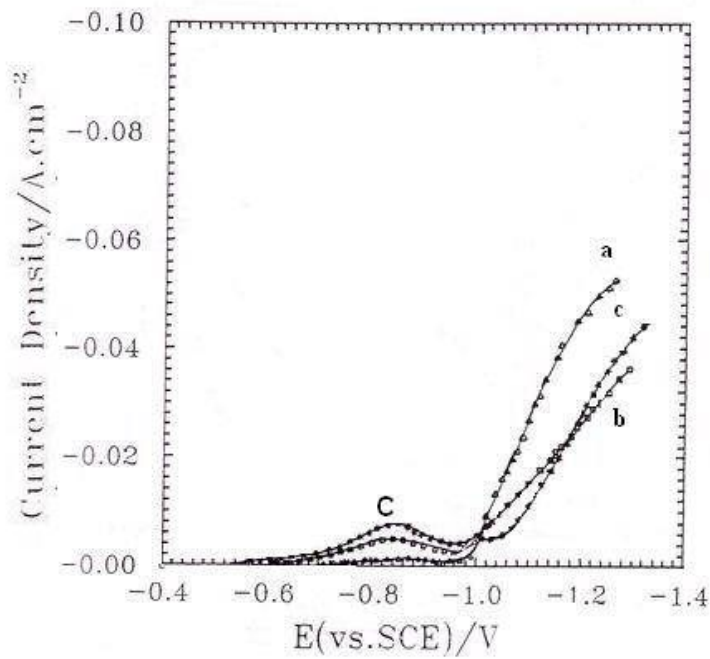


Fig. 2 : Polarization curves during Zn-electrodeposition from solution baths (Zn-3curve a, Zn-6 curve b, Zn-7 curve c)

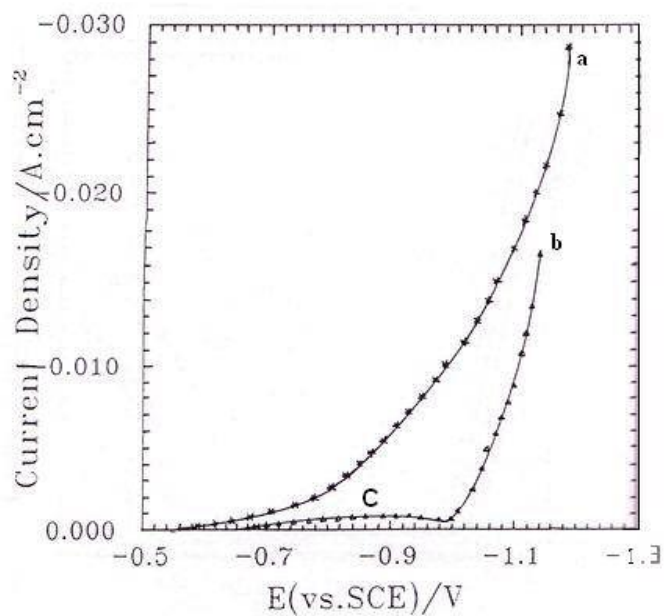


Fig. 3 : Polarization curves during Zn-electrodeposition from solution baths (tri-sod.citrate + citric acid only curve a Zn -10 curve b).

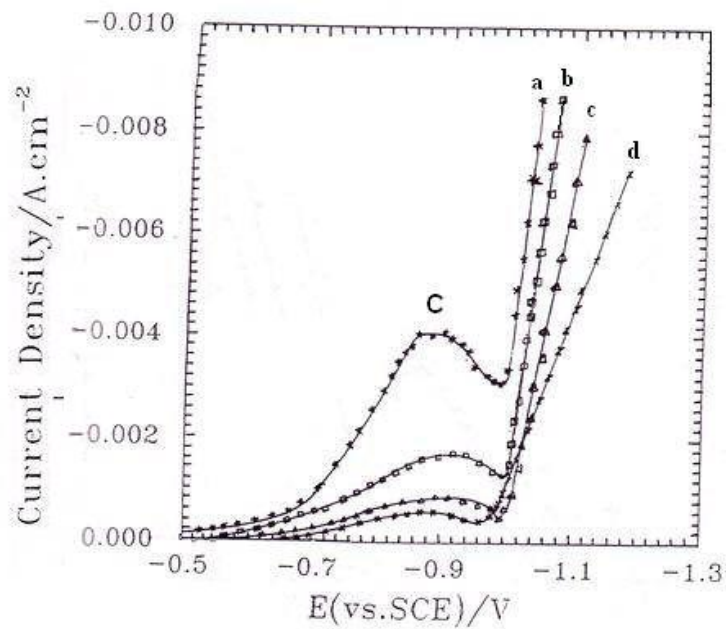


Fig. 4 : Polarization curves during Zn-electrodeposition from solution bath Zn-8 at (pH =3.7 curve a, 4.5 curve b, 5.0 curve c, and pH = 6.0 curve d) .

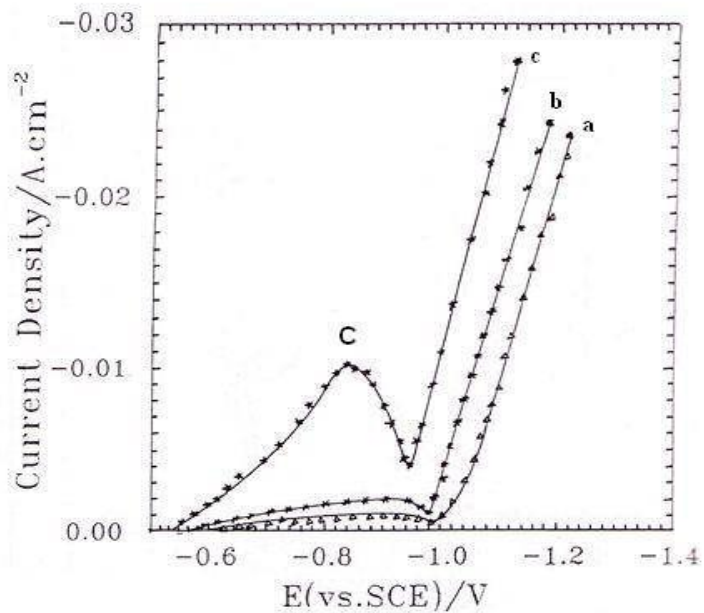


Fig. 5 : Polarization curves during Zn-electrodeposition from solution bath Zn-10 at (T = 25°C curve a, 35°C curve b and T= 50°C curve c).

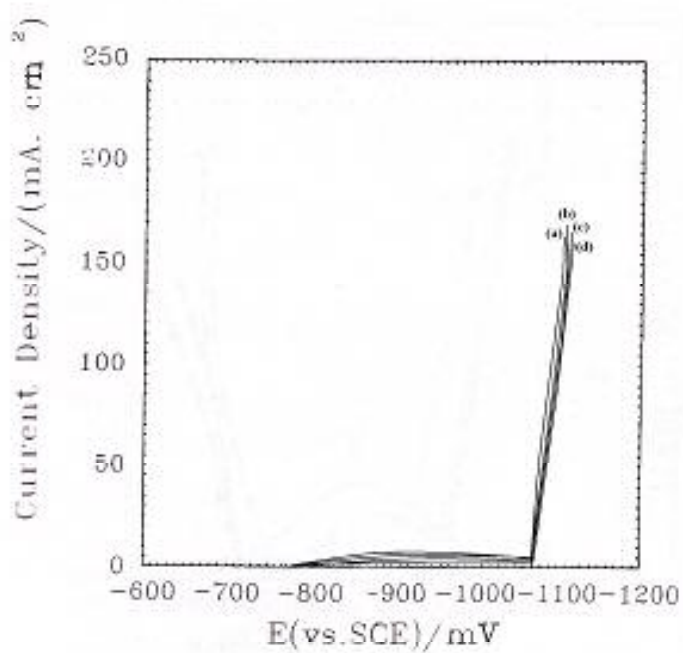


Fig. 6 : Polarization curves during Zn-electrodeposition from solution bath Zn-10 with superimposed a.c. (i.e. -2Am^{-2}) of varying frequency ($\omega=50\text{Hz}$ curve a, 100 curve b, 500 curve c and $\omega=1000\text{ Hz}$ curve d).

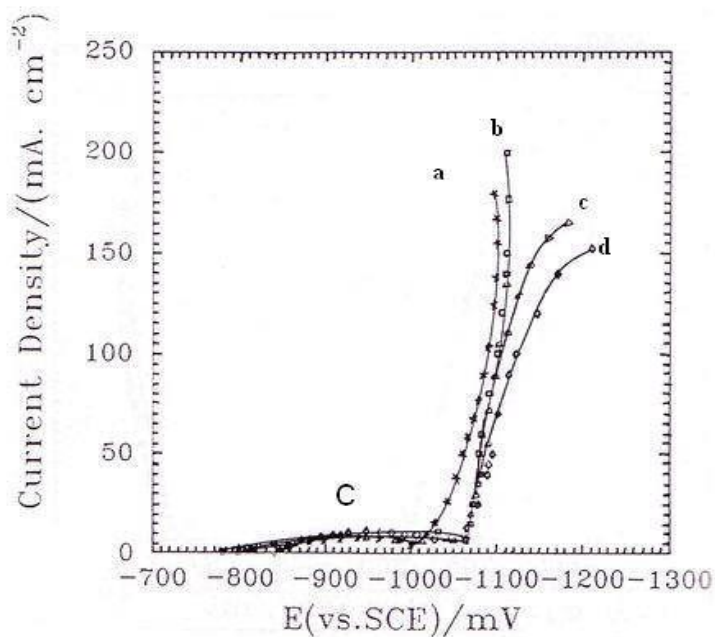


Fig. 7 : Polarization curves during Zn-electrodeposition from solution bath Zn-10 with superimposed a.c. (50Hz) of varying density ($i_{a.c}=0$ Adm⁻² curve a, 1.33 curve b, 2.00 curve c and 2.66 Adm⁻² curve d)

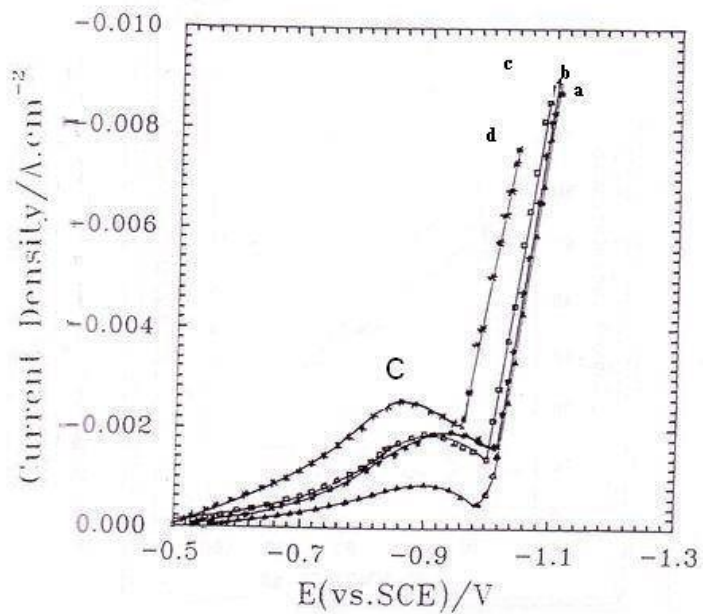


Fig. 8 : Polarization curves during Zn-electrodeposition from solution bath Zn-10 with addition agents (Zn-10 curve a, SLS curve b, SGN 1 curve c, SLS+SGN 1 curve d).

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