

ROLE OF FURFURALDEHYDE ON THE ELECTRODEPOSITION OF ZINC

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The kinetics of zinc electrodeposition on steel from alkaline tartrate bath was studied as a function of tartrate, sodium hydroxide and zinc ion concentrations. The rate of build up of the zinc deposition was found to obey the equation $v = \text{rate of build up} = k (\text{Zn}^{2+})^{1.6} (\text{OH}^-)^{1.5} (\text{tartrate})^{1.5}$. Additions of furfuraldehyde to the bath inhibited the rate of build up and the inhibition was due to adsorption of furfuraldehyde molecules on the growth sites of the zinc nucleus and controlled its growth. This inhibition decreased with current density. The hydrogen evolution reaction was favoured by furfuraldehyde.

Keywords: Electrodeposition, zinc, kinetics.

INTRODUCTION

Organic compounds are added to plating baths to increase polarisation even at relatively low current densities. They improve the quality of the deposit in terms of adherence, size and grain homogenisation. They may also inhibit the formation of dendrites and whiskers [1]. These compounds adsorb on the electrode surface, then block the high energy sites for the crystallisation of the metal [2]. The formation of critical micelle concentration is also viewed as a mechanism of the action of organic compounds on the electrodeposition of metals [3].

Furfuraldehyde addition to the alkaline tartrate plating bath helped to obtain slate grey deposits [4]. The present work is aimed to understand the role of furfuraldehyde in influencing the zinc electrodeposition.

EXPERIMENTAL

Mild steel substrates of size 7.5 x 2.5 x 0.1 cm were used. They were polished mechanically, degreased with trichloroethylene, cleaned cathodically for 3 minutes and then anodically for one minute at a current density of 1 A/sq.dm in Na_2CO_3 - NaOH solutions [5]. The specimens were washed, treated in a 5% H_2SO_4 solution, again washed, rinsed and taken to the plating bath. The plating bath consisted of ZnO:12 gpl; NaOH:120 gpl; and Rochelle salt:

75 gpl. The current efficiency of zinc electrodeposition was calculated as,

TABLE I: Influence of current density, temperature on the current efficiency and rate of build up

Temperature K	Current density (A/dm ²)	Current efficiency (%)	Rate of build up ($\mu\text{m/h}$)
303	0.5	98.5	16.8
	1.0	80.2	20.6
	1.5	75.1	37.4
	2.0	71.3	57.8
	2.5	80.6	68.9
	3.0	78.9	80.7
313	0.5	92.7	15.8
	1.0	86.8	29.2
	1.5	77.9	42.7
	2.0	92.5	63.4
	2.5	84.7	71.8
	3.0	79.0	80.8
323	0.5	92.0	15.7
	1.0	87.1	29.7
	1.5	87.6	46.1
	2.0	95.0	64.8
	2.5	85.0	72.3
	3.0	81.2	83.1

RESULTS AND DISCUSSIONS

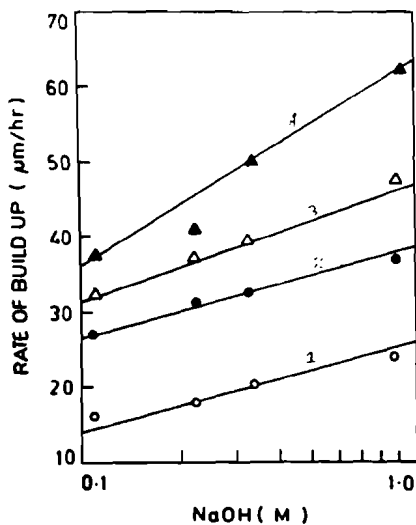


Fig. 1: Variation of the rate of build up with NaOH concentration at constant zinc and tartrate ion concentrations (1) 0.5 (2) 1 (3) 1.5 (4) 2 A.dm⁻²

$$\% \text{ current efficiency} = \frac{X}{Y} \times 100$$

where X = Amount of zinc deposited and Y = Theoretical amount of zinc deposited for given quantity of electricity

The thickness of the electrodeposits was determined by means of weight gain and coulometric methods [6]. The thickness of the deposit at various points were determined and the scatter was within 10%.

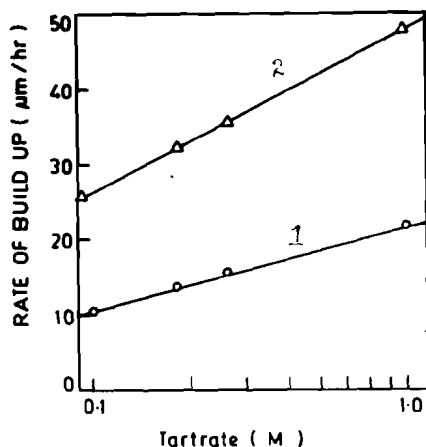


Fig. 2: Variation of the rate of build up with tartrate concentration at constant zinc and OH⁻ ion concentrations (1) 0.5 (2) 1.5 A.dm⁻²

Rochelle salt, potassium sodium tartrate, is a wellknown bath component in the electroplating of many metals and alloys. It produces fine grained deposits. It is chosen as an alternate complexing agent to replace cyanide in alkaline solutions. An increase of temperature and current density decreased the current efficiency, while the rate of build up increased with current density (Table I). The change in cathode efficiency and rate of build up was found to depend on the temperature and on the concentration of zinc, hydroxyl and tartrate ions (Figs. 1- 3).

If v is taken as the rate of deposition, then $dw/dt = v$, is proportional to concentration of zinc, hydroxyl and tartrate ions as $(dw/dt = K (Zn)^x(OH^-)^y(tartrate)^z$ where K is proportionally constant. It was found that the rate of zinc deposition varied linearly with $\log(Zn^{2+})$ concentration with a slope of 1.6 ± 0.2 per decade, with $\log(OH^-)$ concentration and $\log(tartrate)$ concentration with each having slopes of 1.5 ± 0.1 decade⁻¹. Hence the rate of build up of zinc deposit is

$$v = K (Zn)^{1.6} (OH^-)^{1.5} (tartrate)^{1.5}$$

Furfuraldehyde was reported as a brightener for the electrodeposition of zinc from nitrilotriacetate bath [7]. The furfuraldehyde was chosen as additive to obtain slate grey deposits in this bath. Table II presents results on the influence of furfuraldehyde (28 g/l) on the rate of build up, current efficiency of zinc and hydrogen evolution reaction. The rate of hydrogen evolution was found to increase while

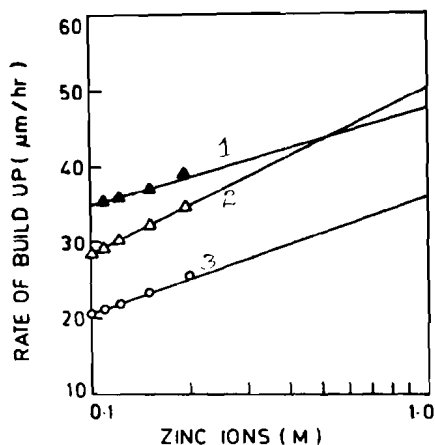


Fig. 3: Variation of the rate of build up with zinc concentration at constant tartrate and OH⁻ ions concentrations (1) 2 (2) 1.5 (3) 1 A.dm⁻²

TABLE II: Influence of furfuraldehyde (28 gpl) on the rate of build up, current efficiencies of zinc and hydrogen evolution

Current density (A/dm ²)	Without furfuraldehyde			With furfuraldehyde		
	Rate of build up (μm/h)	Current efficiency % of zinc deposition	Current efficiency % of hydrogen evolution	Rate of build up (μm/h)	Current efficiency % of zinc deposition	Current efficiency % of hydrogen evolution
0.5	16.8	90.3	9.7	6.6	77.3	22.7
1.0	20.2	99.0	1.0	11.0	64.4	35.6
1.5	28.2	90.3	9.7	16.7	65.4	34.6
2.0	27.4	81.9	10.1	16.5	48.2	51.8
2.5	23.0	78.2	21.8	17.8	41.2	58.8
3.0	20.2	70.4	29.6	18.0	35.1	64.9

that of zinc deposition decreased. Inhibition of zinc deposition was found to be more at lower current densities.

Activation energy

The rate of build up (μm/h) of zinc electrodeposit was studied in the presence and absence of furfuraldehyde at different temperatures. The activation energy was calculated to be -4.72 Kcal/mole for zinc deposition. The presence of furfuraldehyde increased the activation energy to -7.10 Kcal/mole (Fig. 4). The decrease in zinc deposition might be due to the adsorption of the organic compound on the growth sites of zinc nuclei.

Percentage inhibition of zinc deposition was calculated from following equation

$$\% \text{ inhibition of zinc deposition} = \frac{V' - V}{V} \times 100$$

where V' is the rate of build up of zinc in the absence of furfuraldehyde in the bath and V is the rate of build up of zinc in the presence of furfuraldehyde in the bath. The organic molecules accelerated the hydrogen evolution reaction (h.e.r.). This acceleration of h.e.r. may be expressed as

$$\% \text{ acceleration for h.e.r.} = \frac{C.E.' - C.E.}{C.E.} \times 100$$

where C.E. is the current efficiency for h.e.r. in the absence of furfuraldehyde and C.E.' is the current efficiency for h.e.r. in the presence of furfuraldehyde.

Fig. 5 presents the percentage inhibition of zinc electrodeposition and percentage acceleration of hydrogen

evolution. It may be seen that furfuraldehyde accelerates hydrogen evolution reaction with current density.

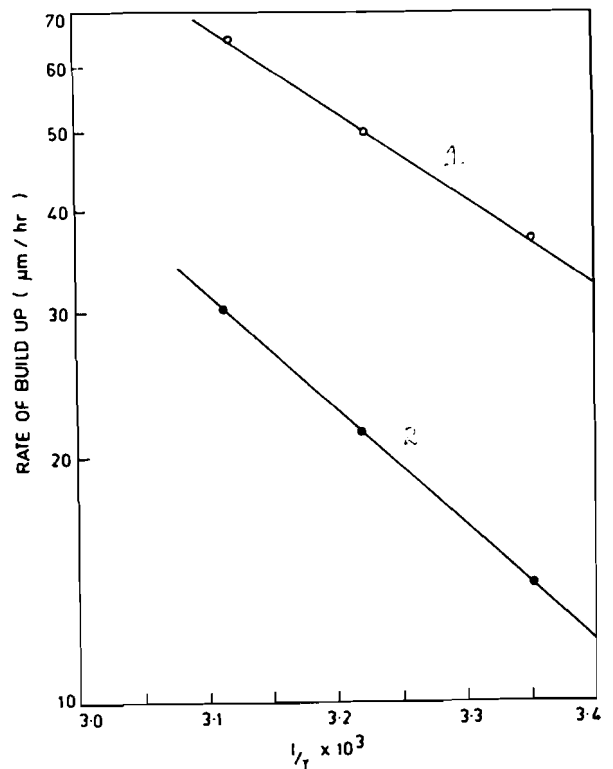


Fig. 4: Arrhenius plot - Rate of build up at 1.5 A.dm⁻² vs 1/T plot for zinc deposition (1) No furfuraldehyde (2) 10⁻³ furfuraldehyde

CONCLUSIONS

Furfuraldehyde molecules adsorbed on the growing zinc nuclei and prevented the growth of zinc deposition. They enhanced the hydrogen evolution reaction.

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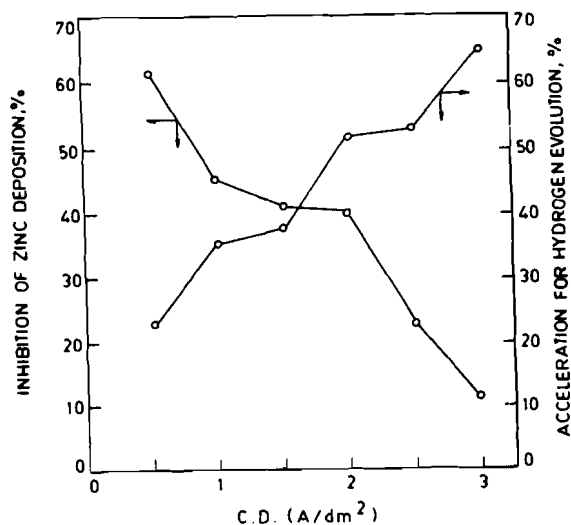


Fig. 5: Effect of current density on the % inhibition of zinc deposition and % acceleration of h.e.r. in the presence of 10^{-3} furfuraldehyde