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The critical overpotential for zinc dendrite formation

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The critical overpotential for zinc dendrite growth is determined as 173 mV by the method described by Popov *et al.* [1]. It was shown that this procedure can be applied successfully to metal deposition processes when there is a large codeposition of hydrogen.

1. Introduction

It was shown recently [1] that the critical overpotential for dendritic growth can be determined on the basis of differences in the mechanisms of surface roughening in the regions of overpotential where surface irregularities are amplified and where dendrites grow. It was assumed that codeposition of hydrogen could be neglected and it is the purpose of this work to extend this procedure to metal deposition processes occurring with extensive evolution of hydrogen.

2. Experimental

Zinc was deposited on a vertical platinum wire electrode (radius 0·5 mm length 0·75 cm) from solutions containing 55 g dm^{-3} Zn and 120 g dm^{-3} H_2SO_4. The potentiostatic technique was used throughout the work. The counter electrode was made of lead. All experiments were carried out at 25 ± 0·1° C. Deposition was performed at overpotentials of 213, 203, 193, 183, 173, 163 and 153 mV and a stationary polarization curve and current–time relationships were plotted.

3. Results and discussion

A stationary polarization curve for zinc deposition is presented in Fig. 1. It is seen that a limiting current plateau cannot be observed. Current–time responses are shown in Fig. 2. Log $(I_t - I_0)$ values extracted from the data presented in Fig. 2 are plotted as functions of time in Fig. 3 (I_0 is the initial current and I_t the current at time t). These currents consist of both zinc ion reduction and the hydrogen codeposition current. In Fig. 4 the slopes of the straight lines of Fig. 3 are plotted as a function of the square of the overpotential, and the critical overpotential of zinc dendrite growth was determined as 173 mV. This result is valid if the procedure used, described for copper deposition [1], can be applied when there is codeposition of hydrogen. It was shown by Popov *et al.* [1] that in the overpotential range where surface irregularities are amplified

$$I_{M,t} - I_{M,0} = A\,[\exp(t/\tau) - 1] \qquad (1)$$

where A is a constant, t time and τ the time constant for surface roughness amplification and in the overpotential range where dendrites grow

$$I_{M,t} - I_{M,0} = B\,[\exp(K\eta^2 t) - 1] \qquad (2)$$

where B and K are constants and η is the overpotential for deposition. $I_{M,t}$ and $I_{M,0}$ in Equations 1 and 2 are the currents for metal deposition in the beginning and at time t of deposition. In the case of zinc deposition the total currents I_t and I_0 are given by

$$I_0 = I_{M,0} + I_{H_2,0} \qquad (3)$$

and

$$I_t = I_{M,t} + I_{H_2,t} \qquad (4)$$

where $I_{H_2,0}$ and $I_{H_2,t}$ are the initial current and current at time t for hydrogen evolution. Hydrogen evolution is activation controlled, and so the current depends only on overpotential and electrode area. If the surface of any protrusion can be taken to be proportional to the height (i.e.

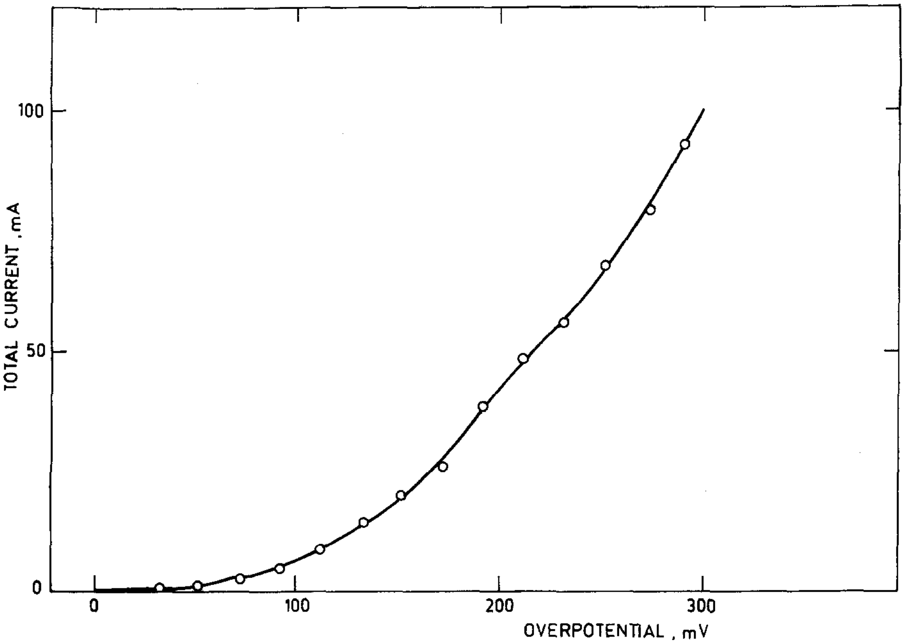

Fig. 1. Stationary polarization curve for zinc deposition.

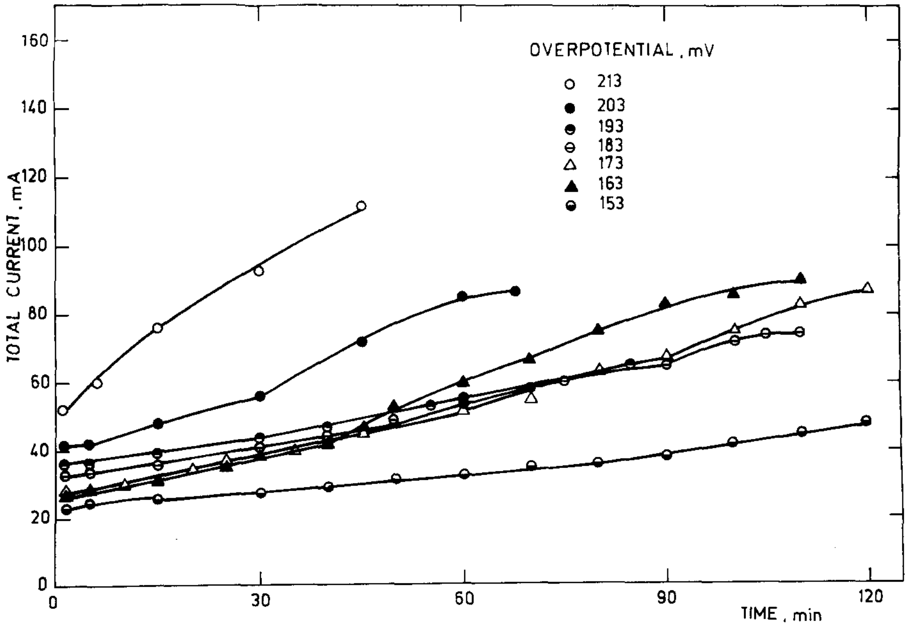

Fig. 2. Current–time relationships for zinc deposition at different overpotentials.

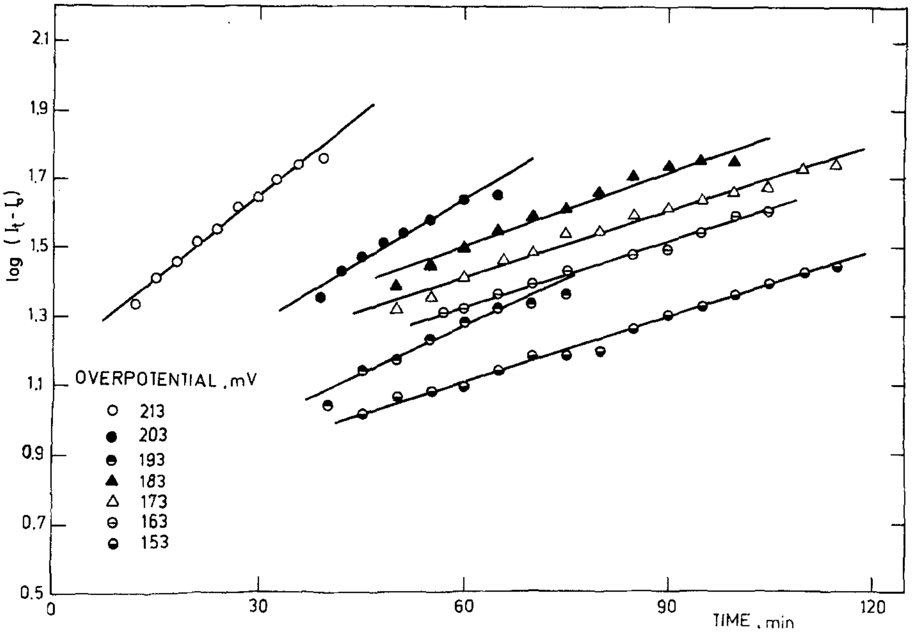

Fig. 3. log $(I_t - I_0)$ versus time relations for zinc deposition at different overpotentials.

neglecting the surface area of the tip) one can write

$$I_{\mathrm{H}_2,0} = S\theta i_{\mathrm{H}_2} + S\frac{1-\theta}{N} i_{\mathrm{H}_2} \sum_{i=1}^{N} k_i h_{i,0} \quad (5)$$

and

$$I_{\mathrm{H}_2,t} = S\theta i_{\mathrm{H}_2} + S\frac{1-\theta}{N} i_{\mathrm{H}_2} \sum_{i=1}^{N} k_i h_{i,t} \quad (6)$$

or

$$I_{\mathrm{H}_2,t} - I_{\mathrm{H}_2,0} = S\frac{1-\theta}{N} i_{\mathrm{H}_2} \sum_{i=1}^{N} k_i (h_{i,t} - h_{i,0}) \quad (7)$$

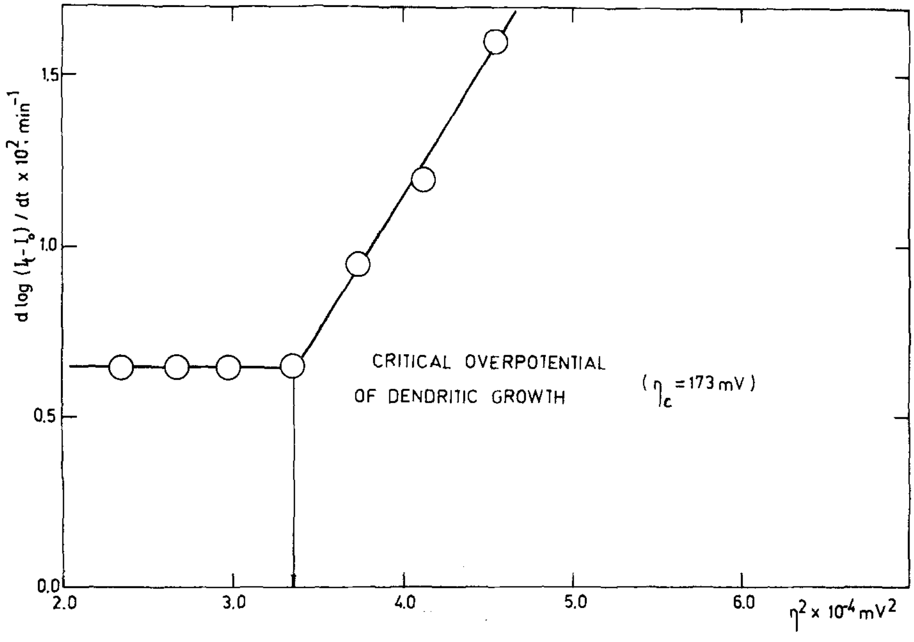

Fig. 4. Plot of the slopes of the lines presented in Fig. 3 as a function of square of overpotential.

where S is the electrode surface area, θ the fraction of flat surface, N the number of protrusions, i_{H_2} the current density for hydrogen evolution at any overpotential, k_i the constant relating height of protrusion to the protrusion surface area, $h_{i,0}$ the initial height of the protrusion, and $h_{i,t}$ the height of the protrusion at time t. Because, as shown in the previous paper [1]

$$h_{i,t} = h_{i,0} \exp(t/\tau) \tag{8}$$

and

$$h_{i,t} = h_{i,0} \exp(K\eta^2 t) \tag{9}$$

for surface roughening and dendritic growth respectively, one can write

$$I_{H_2,t} - I_{H_2,0} = S\frac{1-\theta}{N} i_{H_2} [\exp(t/\tau) - 1] \sum_{i=1}^{N} k_i h_{i,0} \tag{10}$$

for the increase in the hydrogen evolution current because of the increase of surface area caused by the initial surface roughness and

$$I_{H_2,t} - I_{H_2,0} = S\frac{1-\theta}{N} i_{H_2} [\exp(K\eta^2 t) - 1] \sum_{i=1}^{N} k_i h_{i,0} \tag{11}$$

for the case of dendritic growth, or

$$I_{H_2,t} - I_{H_2,0} = C[\exp(t/\tau) - 1] \tag{12}$$

and

$$I_{H_2,t} - I_{H_2,0} = C[\exp(K\eta^2 t) - 1] \tag{13}$$

where

$$C = S\frac{1-\theta}{N} i_{H_2} \sum_{i=1}^{N} k_i h_{i,0}. \tag{14}$$

Hence, by substitution of Equations 1, 2, 12 and 13 into Equations 3 and 4, subtraction and rearrangement one obtains

$$I_t - I_0 = (A + C)[\exp(t/\tau) - 1] \tag{15}$$

and

$$I_t - I_0 = (B + C)[\exp(K\eta^2 t - 1)] \tag{16}$$

Hence, for $\exp(t/\tau) \gg 1$ and $\exp(K\eta^2 t) \gg 1$ we can write

$$\log(I_t - I_0) = \log(A + C) + \frac{1}{2{\cdot}3}\frac{t}{\tau} \tag{17}$$

and

$$\log(I_t - I_0) = \log(B + C) + \frac{1}{2{\cdot}3}K\eta^2 t \tag{18}$$

and the determination of the critical overpotential for dendritic growth from the plot of $d\log(I_t - I_0)/dt$ versus η^2 is shown to be possible even with co-evolution of hydrogen.

Reference

[1] K. I. Popov, Lj. M. Djukić, M. G. Pavlović, M. D. Maksimović, *J. Appl. Electrochem.* 9 (1979) 527.