

Kinetics of growth of zinc dendrite precursors in zincate solutions

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By means of microscopic measurements on a rotating disc electrode under potentiostatic conditions it is established that the propagation rate of the precursors is constant within the limits of the diffusion layer boundary. The propagation kinetics follow the expression of Diggle, Despić and Bockris [3] if it is assumed that the radii of curvature at the tip of the growing precursors r increase proportionally with the height of the precursors y . The overpotential dependence of the ratio y/r is linear and probably reflects the Kelvin relation. At constant diffusion layer thickness the moment of the visual appearance of the dendrites coincides with the transition time on the potentiostatic $I-t$ curves. The average height y at this moment is equal to the diffusion layer thickness δ . The average rate of growth of precursors is inversely proportional to δ . An equation for the time of appearance of dendrites which accounts for the effect of diffusion is derived and experimentally tested. The effect of lead ions on the time of appearance is discussed in terms of the kinetic equation.

1. Introduction

The deposition of zinc from alkaline zincate solutions has been intensively studied in recent years not only because of the significance of the alkaline zinc/zinc oxide electrode in high energy density batteries but also because of the great variety of morphologies of the zinc deposits. Being undesirable in the battery, the dendritic form of growth presents a difficult problem for the battery engineer. For the electrochemist on the other hand the dendritic form of growth opens a wide field of research. On the basis of the theory of dendritic electrocrystallization developed by Barton and Bockris [1] in the case of silver deposition, Despić Diggle and Bockris [2] advanced a model for the growth of zinc dendrites in alkaline solutions. In a subsequent paper the same authors [3] derived expressions for the propagation kinetics of the dendrites and experimentally confirmed most of the relations obtained from these expressions. According to the basic model [3] dendrites are initiated as a result of pyramidal growth at screw dislocations under bulk diffusion control until conditions for spherical diffusion are attained. The importance of diffusion in general and of

convection in particular has led Naybour [4] to study the effect of electrolyte flow on the morphology of zinc deposits from alkaline solutions.

The present paper is an effort to study the kinetics of growth of the dendrite precursors, i.e. the crystallites that first appear and grow on the smooth electrode surface and, upon reaching the diffusion layer boundary, develop into the typical sword-like or fern-like dendrites. The morphology of the zinc dendrite precursors was studied in detail by Bockris, Nagy and Drazić [5] but the propagation kinetics of this initial form of growth were not considered. Inasmuch as both dendrites and their precursors appear and grow under conditions of prevailing diffusion control it was considered most appropriate to make use of the rotating disk electrode (RDE).

2. Experimental

All experiments were carried out in a three compartment glass cell with a water jacket at 25°C with two tubes for bubbling nitrogen (in and above the test solution). The RDE was the bottom of the cylinder (ϕ 3 mm) machined from high purity zinc (99.995%) laterally isolated by a Perspex sleeve

(ϕ 10 mm) and mounted on a rigid stainless steel shaft. Prior to each experiment the electrode surface was mechanically polished by a series of finely ground glass plates and etched in 1:4 HNO_3 solutions for 5–6 s. A cathodic treatment followed consisting of a 5 min polarization at 10 mA cm^{-2} in a 2 N KOH solution. The reference electrode was made from the same zinc metal as the test electrode and was connected to the Luggin capillary via a salt bridge of the test solution. The test solutions were prepared from AR grade reagents and triply distilled water. Concentrated zincate stock solutions were made by dissolving calcined ZnO in concentrated CO_2 -free KOH solution at 80 – 90°C in a flask under reflux in a nitrogen atmosphere. Traces of heavy metal ions were eliminated by bubbling for 24 h with pure nitrogen at ambient temperature with a small amount of high purity zinc powder. After dilution all test solutions were analyzed for zinc by EDTA titration and for KOH by acidimetric titration.

The measurements were carried out at a constant potential maintained by a Wenking potentiostat. The resulting I - t curves were recorded by a potentiometer recorder. A Solartron pulse generator and an oscilloscope were employed to determine the Ohmic drop correction. All potentials are referred to the Zn reference electrode and are corrected for IR drop. The electrochemical measurements were accompanied in most cases by microscopic measurement of the precursors' height normal to the electrode plane. After a definite time of deposition the electrode was taken out of the cell, then washed and dried, and finally fixed on the microscope. The precursors' height measurement was performed by consecutively focussing the Perspex base level and then the majority of the tips of the precursors. Ten readings at various sites of the electrode surface were carried out to obtain the average precursor height.

It should be pointed out here that the present method of height measurement is statistical in nature and in this way differs from that of Diggle, Despić and Bockris [3] where the propagation of single dendrites only was followed. Having in mind the statistical nature of the phenomenon and the parameters which govern it (overpotential, concentration, mass transfer) the statistical approach of measuring the height appears more appropriate.

3. Results and discussion

3.1. Potentiostatic current-time curves

A typical potentiostatic I - t curve recorded during the electrodeposition of zinc on the RDE at -100 mV and 1000 rpm in a 0.34 M zincate solution with 8 N KOH is shown in Fig. 1. Three characteristic regions can be distinguished in each I - t curve. Region 'a' is comparatively short. It was established that by increasing the duration of the cathodic pre-treatment the minimum in this region gradually disappears until finally the current attains its steady state value almost immediately after the applying of the cathodic overpotential. It may be supposed that the minimum in region 'a' is associated either with the removal of an oxide film or with the desorption of some species.

Within the horizontal region 'b' the current is constant despite the increase of the surface roughness due to the growth of the precursors (see below). It was established that the current in this region corresponds to the diffusion limiting current I_1 . Fig. 2 presents the dependence of I_1 on the square root of the rotation speed ω at an overvoltage -150 mV for two zincate solutions (0.13 and 0.34 M). As required by the equation of Levich [6] the plots are linear and their slopes yield the value of the diffusion coefficient according to

$$I_1 = 0.62nFDA \nu^{-1/6} \omega^{1/2} C_0 \quad (\text{A}) \quad (1)$$

where A is the electrode surface area (cm^2), ω the angular velocity of the RDE (rad s^{-1}), D the diffusion coefficient of the zincate ions, ν the kinematic viscosity of the solution ($\text{cm}^2 \text{ s}^{-1}$),

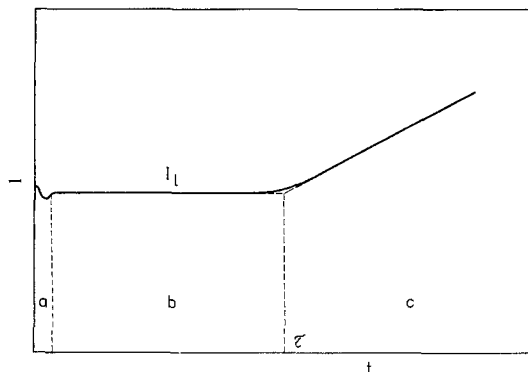


Fig. 1. Typical potentiostatic I - t curve on the RDE.

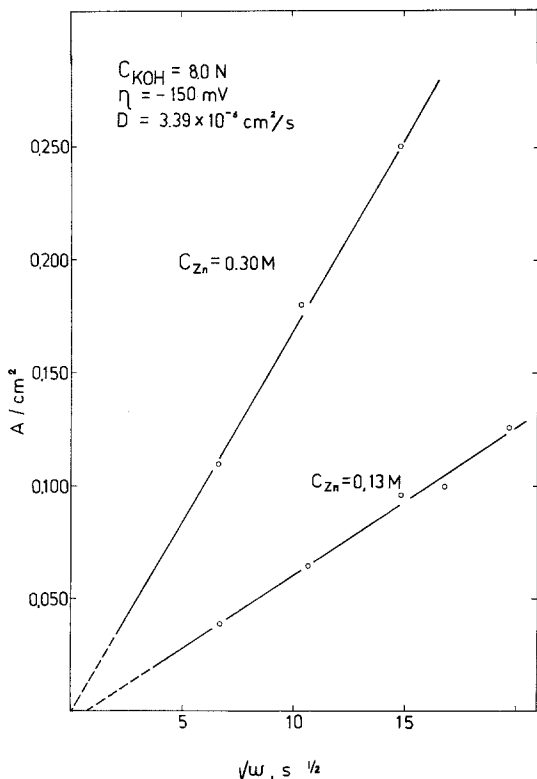


Fig. 2. Rotation speed dependence of the diffusion limiting current density at a constant overpotential and at two different zincate concentrations.

and C_0 the zincate concentration (mol cm^{-2}). Using the experimental values for the kinematic viscosity of the two solutions (2.50×10^{-2} and $2.62 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$) the respective values of D are 3.65×10^{-6} and $3.50 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in agreement with literature data [3].

3.2. Transition time τ_i and the appearance of dendrites

The horizontal region 'b' in the $I-t$ curves (Fig. 1) is followed by a linear rise in the current (region 'c'). The intercept of the two linear regions defines the transition time τ_i . Previous investigations using spherical [3] or vertical plane [7] electrodes in quiescent solutions have reported a quadratic time dependence of I . The present result, i.e. a linear $I-t$ dependence can be attributed to the constancy of the diffusion layer thickness maintained on the surface of the RDE.

Fig. 3 illustrates the effect on τ_i of the rotation speed of the RDE at a constant overpotential (η) in a 0.34 M zincate solution. Fig. 4 presents the overvoltage dependence of τ_i at a constant rotation speed in the same test solution. It can be seen that the increase of either η or ω results in a decrease of τ_i .

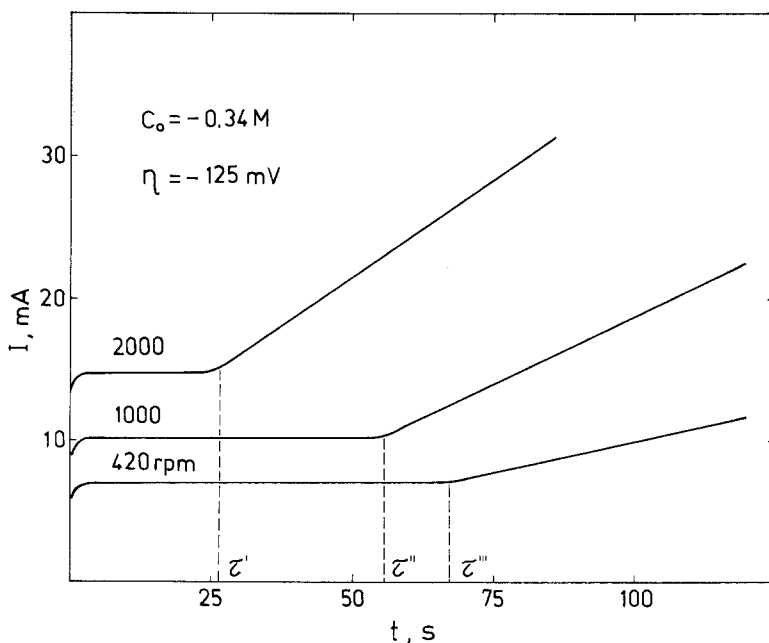


Fig. 3. Effect of rotation speed of the RDE on the $I-t$ curves at a constant overpotential; $\eta = -125 \text{ mV}$, $C_0 = 0.34 \text{ M}$.

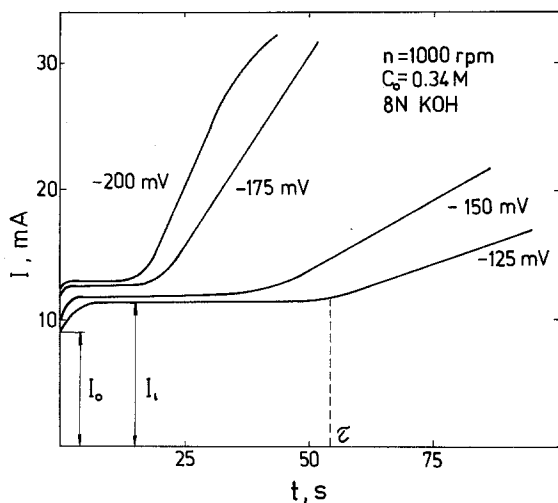


Fig. 4. Effect of the overpotential on the $I-t$ curves at a constant rotation speed; $n = 100$ rpm, $C_0 = 0.34$ M.

The increase of the average height of the precursors y with time during the deposition of zinc at constant overvoltage and constant rotation speed of the RDE is shown in Fig. 5. The average height is determined microscopically. The corresponding $I-t$ curve is shown in the same graph.

Fig. 6 presents a series of micrographs which reveal the changes in the morphology of the zinc precursors during their growth under the same conditions as in Fig. 5. The micrographs are taken at the moments denoted a-f in the $y-t$ plot in Fig. 5. Pictures e and f pertain to the same moment, but picture f is focussed slightly higher

than picture e so as to see more clearly the tips of the dendrites which have outgrown from the precursors seen in picture e.

By a series of similar simultaneous microscopic and $I-t$ experiments under different conditions (overvoltage, rotation speed, and zincate concentration) it was established that:

(i) The moment of the visual observation of the typical sword-like or fern-like dendrites corresponds invariably to the transition time τ_1 determined on the $I-t$ curve.

(ii) The mean height of the precursors y at the moment $t = \tau_1$ measured microscopically is equal to the diffusion layer thickness δ as calculated by the expression of Levich [6] for the RDE.

$$\delta = 1.16(D/\nu)^{2/3}(\nu/\omega)^{1/2} \text{ (cm)}. \quad (2)$$

The comparison of micrographs e and f shows that the number of dendrites per unit area is considerably lower than that of the precursors. The possibility that single dendrites may appear earlier than the moment f is not ruled out, but their number is not sufficient to cause an increase in the current. A minimum number of protrusions is seemingly necessary to disturb the laminar flow over the RDE and cause a respective increase in the rate of mass transfer. The emerging of the precursors' tips above the boundary of the diffusion layer is, according to [2], a prerequisite for the establishing of spherical diffusion conditions necessary for the formation of the dendrites. This seems to explain the

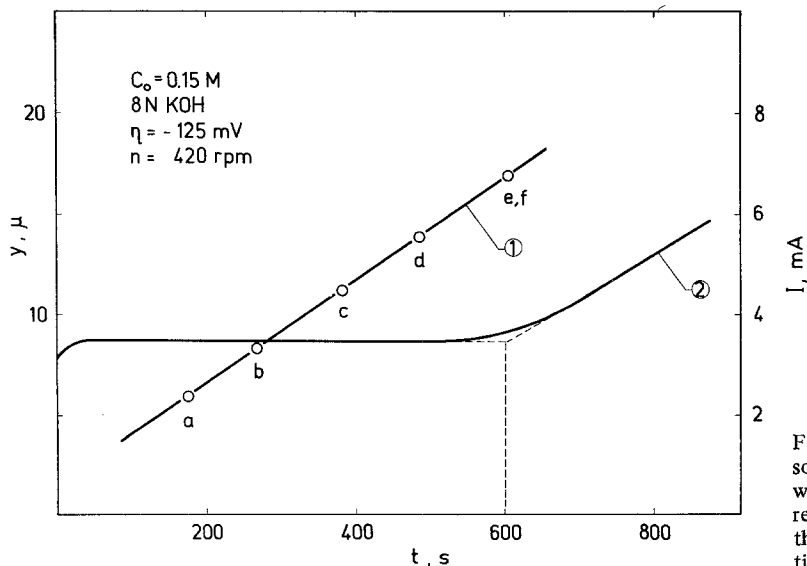


Fig. 5. Increase of height of precursors (measured microscopically) with time at 420 rpm (1) and the respective $I-t$ curve recorded under the same conditions (2). (The notations a to f refer to Fig. 6)

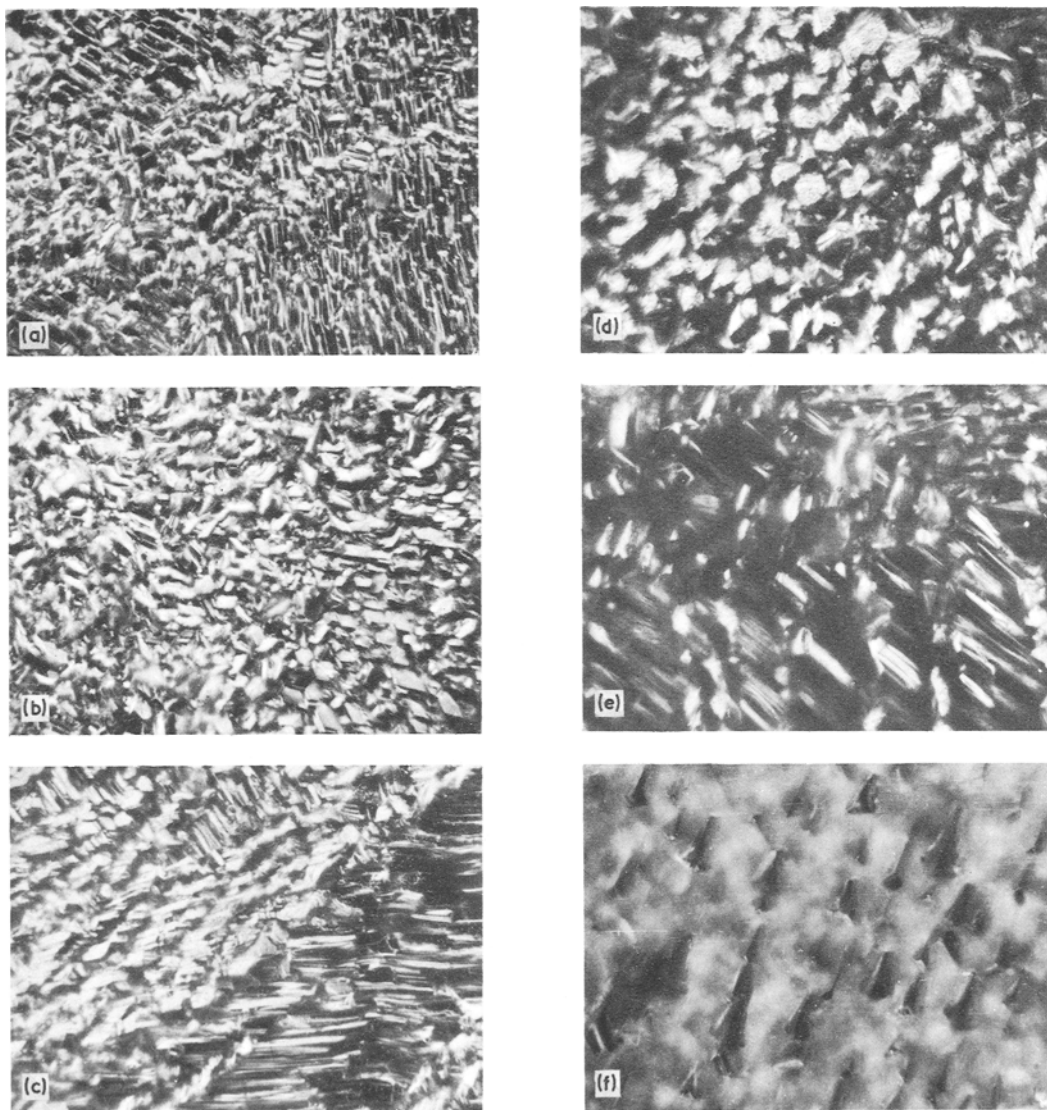


Fig. 6. Micrographs of the electrode surface with precursors grown under conditions and times of deposition indicated in Fig. 5 (1 cm = 30 μm).

coincidence of τ_1 with the moment of the visual observation of the dendrites. This fact and the finding that the average rate of the precursors growth v_p is constant (Fig. 5) makes it possible to write.

$$v_p = y/t = \delta/\tau_1. \quad (3)$$

3.3. Kinetics of the precursors growth

The general differential equation for the instantaneous rate of growth of Zn protrusions at constant overpotential η under conditions of mixed

control is given by Diggle, Despić and Bockris (Equation 13 in [3]). In the case of higher cathodic polarizations where the anodic reaction is fully suppressed this equation can be presented as

$$(\partial y/\partial t)_\eta = v'_p = [V'_c/(nF)] [1 + (i_r/i_1 y)]^{-1} \text{ cm s}^{-1}. \quad (4)$$

Here v'_p is the instantaneous propagation rate of the precursors,

$$\begin{aligned} i_c &= i_o \exp[-\alpha\eta F/(RT)] \\ &= i_o \exp(-\eta/b_c) \text{ A cm}^{-2} \end{aligned} \quad (5)$$

is the cathodic current density, i_o the exchange current density, b_c the Tafel slope of the cathodic deposition reaction

$$i_1 = nFDC_o/\delta \quad (\text{A cm}^{-2}) \quad (6)$$

is the linear diffusion limiting current density. In Equation 4 V is the molar volume of zinc, r is the curvature radius at the tip of the precursor, and y the average height of the precursors.

According to Diggle, Despić and Bockris [3] r is diminishing with the increase of y , and hence the ratio y/r in Equation 4 is a decaying function of time. This implies according to Equation 4 that the rate of growth v_p' should increase with time. Assuming the validity of Equation 4, the present finding that \bar{v}_p is constant strongly suggests that the ratio r/y also remains constant during the growth of the precursors. This conclusion is supported by the microscopic observations of the Zn deposits (Fig. 6) which reveal that the curvature radii of the precursors' tips are actually increasing with their height. It appears reasonable to assume therefore that the ratio r/y remains constant during the propagation of the zinc precursors within the limits of the diffusion layer. Hence at any moment of the precursors growth $v_p' = \bar{v}_p = y/t$.

Having in mind the expression for the rate of dendritic growth beyond the limits of the diffusion layer given in [3]

$$v_d = [Vi_c/(nF)] \text{ cm s}^{-1} \quad (7)$$

and introducing i_1 from Equation 6, Equation 4 can be rewritten as

$$1/\bar{v}_p = 1/v_d + [\delta r/(yVDC_o)] \text{ s cm}^{-1}. \quad (8)$$

Equation 8 reveals that the reciprocal rate of the precursors growth is proportional to the diffusion layer thickness. Fig. 7 presents the experimental plots of $1/\bar{v}_p$ v. δ at several overpotentials. The values of $\bar{v}_p = \delta/\tau_i$ are obtained from $I-t$ curves at different rotation speeds with values of δ calculated by Equation 2. The linearity of the plots in Fig. 7 supports the validity of Equation 8 and the assumption that y/r is constant. The intercepts of the plots in Fig. 7 yield the values of v_d which are plotted v. the overpotential in Fig. 8. As required by Equations 4 and 5 the overpotential dependence of v_d is linear with slope 115 mV. This result is in good agreement with earlier reported data [9] for the Tafel slope of the cathodic deposition reaction

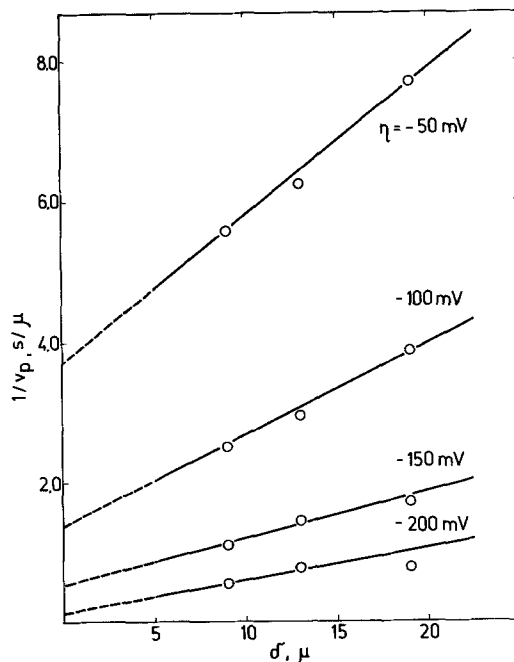


Fig. 7. Reciprocal propagation rate of precursors ($1/v_p$) as a function of the diffusion layer thickness at different overpotentials, $C_o = 0.34 \text{ M}$.

of Zn. The exchange current density of the same reaction can be estimated by Equations 5 and 7 with the intercept of the plot in Fig. 8. The present

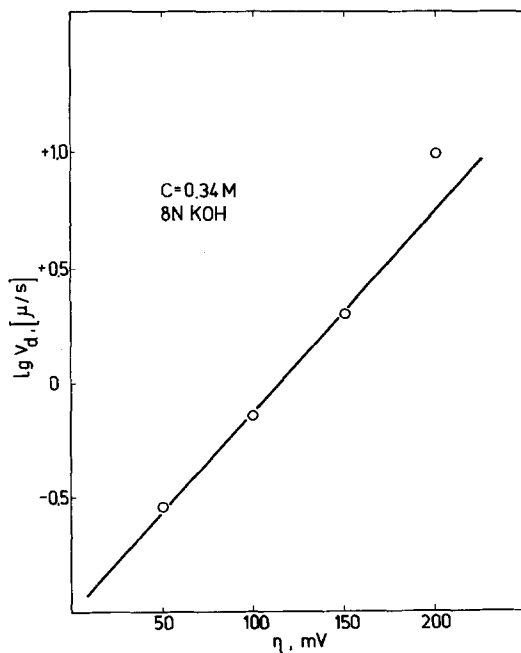


Fig. 8. Overpotential dependence of the rate of dendritic growth v_d .

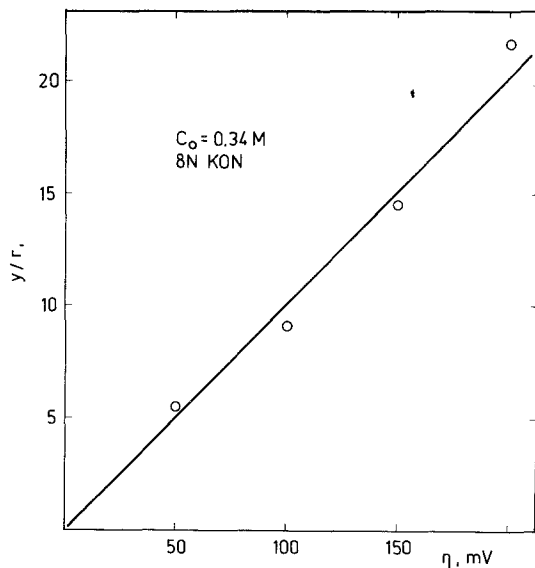


Fig. 9. Overpotential dependence of the ratio of the curvature radius to the height of the precursors.

experimental value $i_o = 0.22 \text{ A cm}^{-2}$ is close to literature data [8, 9], $i_o = 0.15 \text{ A cm}^{-2}$, for the same zincate concentration.

From the slopes of the relations in Fig. 7 it is possible to evaluate the ratio y/r for different overpotentials. The linear overpotential dependence of y/r presented in Fig. 9 probably reflects the well-known Kelvin relation

$$\eta_c = [2V\gamma/(nFr)] \quad \text{V} \quad (9)$$

where η_c is the curvature overpotential and γ the surface energy of the zinc-electrolyte interface. The linear relation between y/r and η presented in Fig. 9 is to be expected only in the case where the curvature overpotential is proportional to the overall potential accessible for measurement.

With a mean value of $y = 1 \times 10^{-3} \text{ cm}$ the ratios of y/r in the overpotential range studied yield from 5×10^{-5} – $1.8 \times 10^{-4} \text{ cm}$ for the values of r . This is in fair agreement with the experimental value of $4 \times 10^{-4} \text{ cm}$ obtained at -100 mV in a 0.1 M zincate solution and reported in [3].

3.4. Time of dendrite appearance

According to Diggle, Despić and Bockris [3] the time of appearance of the dendrites as calculated from the expression for the rate of growth of dendrites is equal to

Table 1. Calculated values of τ' and τ'' as functions of η and δ

η (mV)	$\delta = 9 \mu$		$\delta = 13 \mu$		$\delta = 20 \mu$	
	τ'	τ''	τ'	τ''	τ'	τ''
-50	32	16	46	34	71	78
-100	13	11	19	20	29	44
-150	4.5	6	6.5	13.5	10	30
-200	0.9	4.4	1.3	9.3	2	20

$$\tau_d = -y_o nF/i_c V = -y_o/v_d \quad \text{s} \quad (10)$$

where the constant y_o is the negative intercept of the $y-t$ plot at $t = 0$. The experimental data in [3] showed that y_o is not a constant and that the agreement between experimental and calculated values of τ_d is not very good. It appeared therefore more correct to derive an expression from the equation for the rate of growth of the precursors for the time of appearance. Thus multiplying Equation 8 by δ and having in mind that $y = \delta$ at $t = \tau_i$ we obtain

$$\tau = \delta/v_d + [\delta r/(VDC_o)] \quad \text{s} \quad (11a)$$

or

$$\tau = \tau' + \tau'' \quad \text{s.} \quad (11b)$$

The first right-hand term in Equation 11 τ' corresponds formally to Equation 10, but the constant y_o has a definite physical meaning, $y_o = \delta$. The second right-hand term reflects the effect of diffusion on the rate of growth of the precursors. Table 1 presents values of τ' and τ'' calculated by Equation 11 with the experimental data from the plots in Figs. 7, 8, and 9. The data in Table 1 reveal that the contribution of τ'' to the time of appearance τ at higher overpotentials can be as large as 90%, implying that Equation 10 has but a limited application even if y_o is assumed to be equivalent to δ . On the other hand, the present experimental values of τ and those calculated by Equation 11 are in agreement within 5–10%.

3.5. The transition period

As transition period of the $I-t$ curves we take here the relatively short curved line linking the two rectilinear regions 'b' and 'c' (Fig. 1). The microscopic observation of the zinc deposits within this period revealed that the transition period begins with the appearance of the first single dendrites

and terminates when the number of dendrites per unit area acquires a relatively constant value. It is within this period also that the average rate of growth of the zinc protrusions (including precursors and dendrites) increases from v_p to v_d . From the ratio

$$(v_d/v_p) = 1 + (i_c r/i_1 y) \quad (12)$$

obtained from Equations 4 and 7 it can be concluded that the transition period is characterized by a gradual decrease of the second right-hand term in Equation 12 until at the end of the period the condition

$$(i_c r/i_1 y) \ll 1 \quad (13)$$

will prevail.

As shown above, the transition period is marked also by a change in the morphology of the zinc crystallites from the plate-like precursors to the sword-like sharp-tipped dendrites. The former grow under linear diffusion control, but as soon as they emerge above the diffusion layer boundary, conditions for spherical diffusion are established [2], implying that δ in Equation 6 should be substituted by the much smaller quantity r . According to Equation 12 this will result in an increase in the average rate of growth until the value of v_d is also finally attained.

Parallel to this under the prevailing spherical diffusion conditions the concentration overpotential is lowered, whereby the curvature overpotential will be raised. According to Equation 9 this will result in a reduction of the curvature radius of the crystallites growing above the diffusion layer boundary, and this is actually what occurs (Fig. 6, f).

The rise of the diffusion limiting current on the RDE at a constant rotation speed cannot be attributed only to the increase of the surface area. Most probably this is due mainly to a transition from laminar to turbulent conditions of flow, which enhance the mass transfer across the solution-electrode interface.

It should be pointed out that although fewer in number with respect to the precursors ($\sim 0.1\%$ according to [5]) the dendrites draw away the major part of the current thus totally suppressing the growth of the underlying precursors. As the number of dendrites reaches a saturation value, determined by the overall current and the shape of the dendrites, the slope of the $I-t$ curve be-

comes constant (region 'c' in Fig. 1). The investigation of this part of the $I-t$ curves is the object of a subsequent paper.

3.6. Effect of zincate concentration on the time of appearance

It can be derived from Equations 11, 5, and 7 that

$$\tau = (nF/V)[\delta/i_0^0 C_0^p \exp(-\eta/b_c)] + (\delta r/nFDC_0) \text{ s} \quad (14)$$

where i_0^0 is the standard exchange current density and p is the slope of the $\log i_c - \log C_0$ dependence at a constant overpotential. As a first approximation p may be assumed to be equal to the reaction order with respect to the zincate ion, i.e. the slope of the $\log i_c - \log C_0$ relation at a constant potential, which as reported in [9] is equal to unity. Hence Equation 14 can be rewritten as

$$\tau C_0 = (nF/V)[\delta/i_0^0 \exp(-\eta/b_c)] + (\delta r/nFD) \text{ mol s cm}^{-2}. \quad (15)$$

Equation 13 implies that at a constant overpotential and rotation speed the product τC_0 should also be constant. Table 2 presents experimental values of τC_0 at four different zincate concentrations in 8 N KOH as a function of the overpotential at constant rotation speed, 1000 rpm. As seen from Table 2 the product τC_0 varies insignificantly with C_0 and diminishes with the increase of the overpotential as required by Equation 15.

3.7. Effect of lead ions

The effect of lead ions on the morphology of zinc dendritic growth has been reported in a number of papers [10-15]. Little is known however of the

Table 2. Values of τC_0 in 8 N KOH at 1000 rpm as a function of the overpotential

C_0 (M)	τC_0 (mol s l ⁻¹)		
	-100 mV	-150 mV	-200 mV
0.10	42.6	14.5	10.0
0.27	41.4	13.5	9.5
0.54	49.1	18.9	9.4
0.73	36.5	19.7	8.8

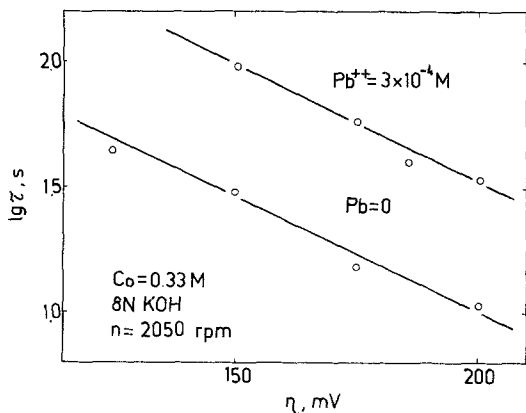


Fig. 10. Effect of lead ions on the overpotential dependence of the time of appearance $C_0 = 0.33$ M, 8 N KOH, and 2050 rpm.

influence of these ions on the rate of the precursors growth and on the time of dendrite appearance respectively. Fig. 10 presents the overpotential dependence of the time of appearance as measured in a 0.34 M zincate solution with 8 N KOH at a constant rotation speed, 1000 rpm. The first plot pertains to a solution free of lead ions and the second one to a solution into which lead ions have been added to a 3×10^{-4} M concentration. Thus the molar ratio of zinc to lead in this solution is c. 10^3 . It can be seen that the ratio of the times of the appearance in the two solutions $\tau_{Pb} : \tau_0$ in the potential range studied is equal to 3.3 implying that the ratio of the rate of precursors growth $(v_p)_0 : (v_p)_{Pb}$ has approximately the same value. The inhibiting effect of Pb on the precursors' rate of growth can be attributed to the effect of lead ions either on the exchange current density or on the radius of the precursors' curvature at their tip (cf. Equation 4). Independent polarization measurements of the exchange current density on a smooth Zn electrode in the same solution have revealed that the ratio $(i_0)_0 : (i_0)_{Pb}$ is close to 3.3 suggesting that the effect of the lead ions on the exchange current density is predominant. Microscopic observations on the other hand have shown that upon the introduction of Pb ions the morphology of the precursors from plates and ridges changes into boulders. The larger effective radius of curvature of the boulders suggests that the influence of Pb on r should not be neglected. It should be pointed out here that in the present investigation performed under conditions of forced convection no boulders were observed in the Pb-free solutions even at high

overpotentials up to 200 mV. This is in disagreement with the findings of Bockris, Nagy and Drazic [5] who have observed boulders in Pb-free solutions at overpotentials higher than -100 mV but under natural convection conditions.

4. Conclusions

- The rate of growth of zinc dendrite precursors in zincate solutions under definite diffusion conditions is constant within the diffusion layer boundaries.
- The average radius of curvature r at the tips of the growing precursors increases proportionally with their height y .
- The effect of the overpotential on the ratio y/r reflects the Kelvin relation between the curvature radius r and the curvature overpotential.
- Under conditions of a constant thickness of the diffusion layer the moment of the visual appearance of the dendrites coincides with the transition time on the potentiostatic $I-t$ curves. The average height of the precursors y at this moment is equal to the diffusion layer thickness calculated by the equation of Levich.
- The effect of the diffusion layer thickness on the rate of the growth of the precursors expected from the kinetic equation is confirmed experimentally.
- An equation is derived for the time of appearance of dendrites, which accounts for the effect of diffusion control.
- The effect of zincate concentration on the time of appearance supports the equation for the growth of precursors.

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