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Studies concerning the growth of cadmium dendrites. III. Theoretical treatment

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The growth of dendritic cadmium during electrodeposition in alkaline and acid media has been investigated. By combining electrochemical data with measurements taken from scanning electron micrographs, a selection of which have been presented in parts I and II, it is shown that the theoretical approach of Diggle, Despic and Bockris [5] is in good agreement with the experimental results. The total current versus time behaviour for the alkaline system can be predicted using the exponential limiting form of the equations with the assumption that the dendrites approximate to rectangular rods and follow a first order progressive initiation law. The very different behaviour in the acidic media is predicted from the linear limiting form of the equations with the assumption that the dendrites approximate to cylindrical rods and follow an instantaneous initiation law.

1. Introduction

In the third part of this investigation the electrochemical data are combined with the measurements taken from the scanning electron micrographs (SEM) given in parts I and II [1, 2] to gain a further understanding of the parameters controlling the growth of cadmium dendrites in aqueous media.

The main quantitative theoretical treatments stem from the investigations of Barton and Bockris [3] into the growth of silver dendrites from a fused salt system. Later treatments by Diggle *et al.* [4, 5], Despic and Purenovic [6], and Popov and co-workers [7–10], have retained many of the fundamental concepts proposed by Barton and Bockris [3] whilst extending their area of applicability.

The theory must be able to adequately explain and predict the well established conditions that appear to be required before dendrite growth takes place which may be summarized as follows:

(a) a minimum overpotential η_{crit} (critical overpotential) is required before dendrites appear

(b) there is an induction period, t_i, prior to dendrite growth

(c) there is an optimum tip radius for maximum rate of growth

(d) the total current increases with time at constant overpotential once dendrites have been initiated

(e) the yield of dendrites increases with overpotential above η_{crit}

(f) the length of dendrites increases exponentially with time whilst the dendrites are growing well within the Nernst diffusion layer appropriate to a planar substrate.

(g) dendrite growth appears to be nearly linear with time for dendrite lengths well in excess of the Nernst diffusion layer thickness δ (in cm).

The theoretical treatment which adequately explains our data is based on the equations derived by Barton and Bockris [3] and Diggle *et al.* [5]. We find no agreement with the treatment of Popov *et al.* [10].

The total overpotential, η, at the propagating dendrite tip is the sum of three contributions [3]: an activation overpotential, η_a, a concentration overpotential, η_c, and a Kelvin type overpotential, η_K, which are required because of the small radii of the growing tips.

$$\eta = \eta_a + \eta_c + \eta_K \tag{1}$$

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For the Tafel region of overpotential, Diggle *et al.* [5] shows that η is given by

$$\eta = \frac{RT}{-\alpha_c nF}\ln\left(\frac{i_{\mathrm{tip}}}{i_0}\right) + \frac{RT}{nF}\ln\left(1-\frac{i_{\mathrm{tip}}}{i_{\mathrm{L}}}\right) + \frac{2\gamma V}{nFr} \qquad (2)$$

where η is expressed in negative volts for the cadmium deposition reaction, $-\alpha_c = -0.5$, T is temperature in Kelvin, $n = 1$ for the rate determining step and $n = 2$ for the overall reaction, γ is the surface tension of cadmium, V is the molar volume of cadmium (= 12.994), r is the radius of curvature of the dendrite tip (in cm), i_0 is the exchange current density, i_{L} is the planar limiting current density and the dendrite tip current density (in A cm^{-2}), i_{tip} is the only unknown quantity. From Equation 2, the tip density is given [5] by:

$$i_{\mathrm{tip}} = i_0\left[\left(1-\frac{i_{\mathrm{t}}}{i_{\mathrm{L\,tip}}}\right)\exp\left(\frac{-\alpha_c nF\eta}{RT}\right) - \exp\left(\frac{2\gamma V}{RTr}\right)\exp\left(\frac{\alpha_a nF\eta}{RT}\right)\right] \qquad (3)$$

(where $i_{\mathrm{L\,tip}}$ is the planar limiting diffusion current density at the dendrite tip, i_{t} is the total current at the electrode and $\alpha_a = 0.5$) assuming that during the early stages the contribution to the total current by the dendrites is negligible such that

$$i_{\mathrm{t}} = i_0 \exp(-\alpha_c nF\eta/RT) \qquad (4)$$

The propagation rate of the dendrite tip, $\bar{V}$, and the tip current density are related [3] by:

$$\bar{V} = \frac{\mathrm{d}h}{\mathrm{d}t} = \frac{V}{nF} i_{\mathrm{tip}} \qquad (5)$$

where h is the dendrite height in cm at time t s.

By substituting Equation 3 for i_{tip} into Equation 5 and then integrating between h and h_0, where h_0 is the height of dendrite precursors when $t = 0$, Diggle *et al.* [5] derive the general equation for growth of a dendrite with time:

$$\frac{h}{i_0 u} + \frac{r\ln(h)\exp(C)}{i_{\mathrm{L}} u} = \frac{Vt}{nF} + \frac{h_0}{i_0 u} + \frac{r\ln(h_0)\exp(C)}{i_{\mathrm{L}}\eta} \qquad (6)$$

where $C = -\alpha_c nF\eta/RT$ and

$$u = \left[\exp\left(\frac{-\alpha_c nF\eta}{RT}\right) - \exp\left(\frac{2\gamma V}{RTr}\right)\exp\left(\frac{\alpha_a nF\eta}{RT}\right)\right] \qquad (7)$$

or for brevity

$$u = [\exp(C) - \exp(B)\exp(A)] \qquad (8)$$

$A = \alpha_a nF\eta/RT$ and $B = 2\gamma V/RTr$. The general Equation 6 for the length versus time relation during dendrite growth leads to two limiting cases given in Equations 9 and 12.

$$\frac{h}{i_0 u} \gg \frac{r\ln(h)\exp(C)}{i_{\mathrm{L}} u} \qquad (9)$$

Equation 9 leads to a linear relationship between h and t

$$h = \frac{i_0 u V t}{nF} + h_0 \qquad (10)$$

and

$$i_{\mathrm{tip}} = i_0 u \qquad (11)$$

$$\frac{h}{i_0 u} \ll \frac{r\ln(h)\exp(C)}{i_{\mathrm{L}} u} \qquad (12)$$

Equation 12 leads to an exponential relationship between h and t

$$\frac{r\exp(C)}{i_{\mathrm{L}} u}\cdot(\ln h - \ln h_0) = \frac{Vt}{nF} \qquad (13)$$

therefore

$$\ln\left(\frac{h}{h_0}\right) = \frac{Vti_{\mathrm{L}}u}{nFr\exp(C)} = K_1 t \qquad (14)$$

where $K_1 = i_{\mathrm{L}} u V/nFr \exp(C)$. Expressed in the exponential form Equation 14 becomes

$$h = h_0 \exp(K_1 t) \qquad (15)$$

and from Equation 5

$$i_{\mathrm{tip}} = h_0 \frac{V}{nF} K_1 \exp(K_1 t) \qquad (16)$$

Given the two sets of equations for the limiting cases which predict the length versus time and tip current versus time relations it is now possible to derive expressions for the total current versus time.

The total current increases with time beyond the current minimum at t_i because of the increase in electrode area due to the growing dendrites. The total current is therefore the sum of the current due to the planar substrate and the sum of the currents of the individual dendrites

$$i_{\mathrm{t}} = i_{\mathrm{substrate}} + i_{\mathrm{dendrites}} \qquad (17)$$

$$i_{\mathrm{t}} = i_{\mathrm{L}} + \sum_{1}^{N_{\mathrm{t}}} N_i A_i i_{\mathrm{d}} \qquad (18)$$

where N_i is the ith dendrite of area A_i and current density i_d, and the total number of dendrites is N_t.

Various approximations can now be made concerning the area of a dendrite and expressions for the current obtained.

For example a rectangular dendrite length h, width w and thickness d cm at time t has an area of

$$2wh + 2dh + wd \tag{19}$$

If the current density at the sides of the dendrite is assumed to be the planar limiting diffusion current [5] i_L and at the tip to be i_{tip} then the total current due to the dendrite is

$$i_{dendrite} = 2h(w + d)i_L + wdi_{tip} \tag{20}$$

Similarly, for a cylindrical dendrite length h and diameter $2r_c$

$$i_{dendrite} = 2\pi r_c h i_L + \pi r_c^2 i_{tip} \tag{21}$$

To evaluate the sum of the contributions to the current due to the dendrites a type of dendrite initiation law is required. For example, if the initiation is instantaneous, N_t will be a constant (time independent) for given conditions, all the dendrites will have the same dimensions, and the value of $\Sigma N_i A_i i_d$ will be dependent only on the length versus time relation. However, for progressive initiation N_t will be time dependent and $\Sigma N_i A_i i_d$ will be more complex as there will be a range of dendrite dimensions. For a first order initiation law

$$N_t = N_0 K_0 t \tag{22}$$

where N_0 is the number of possible dendrite initiation sites and K_0 is the dendrite initiation rate constant in s^{-1}.

2. Results and discussion

From the introduction it is clear that the starting point in applying the theoretical treatment is to determine

(a) whether the dendrite growth occurs wholly within one of the limiting regions where the exponential or linear limiting equations apply, or changes from exponential to linear in which case the full equations must be used and

(b) the type of dendrite initiation law operating.

Thus the experimental quantities of interest are the dendrite length, the tip radius, and the total number of dendrites, as a function of time and overpotential at a particular concentration. In this work these quantities were determined from a large number of scanning electron micrographs a selection of which were presented in parts I and II [1, 2].

2.1. *Alkaline system: cadmium deposition onto a rotating nickel disc electrode in 1.05×10^{-4} mol dm^{-3} $Cd(OH)_4^{2-}$/30% KOH*

The length of the longest dendrite at a given time is plotted against time in Fig. 1 for a range of overpotentials. The length versus time relation clearly has an exponential character indicating that the exponential limiting equations might apply. This is confirmed by the good agreement between the experimental values and the predicted length versus time relation calculated using Equation 15 which is also shown in Fig. 1. The tip radii used to evaluate Equation 15 are shown as a function of overpotential in Fig. 2, r being given by $r = 10^{(2.684\eta - 3.63)}$.

The i_{tip} versus time relation can be calculated using Equation 16, and as expected is of the same form as the height versus time plot as shown in Fig. 3. Both i_{tip} and h are very sensitive to the value of the tip radius. For example, after 1200 min deposition at -160 mV a change in r from 0.9 to 0.1 μm produces a change in the calculated i_{tip} from 1.23×10^{-3} to $6.69 \times 10^{+15}$ A cm^{-2}.

To determine whether all the dendrite growth occurred under the limiting exponential conditions the two sides of Equation 9 were evaluated by an iterative technique and the critical height for dendrite growth, h_{crit}, where the two sides became equal was noted for all the overpotentials used. The value of the height when the two sides became equal is where the changeover from the exponential to the linear limiting condition occurs, although for heights of the order of h_{crit} the full length versus time equations should be used. The height h_{crit} is plotted versus potential in Fig. 4 along with the longest experimentally observed dendrite length for each potential. It is clear that for all experiments in alkaline media the longest lengths are well below the calculated critical

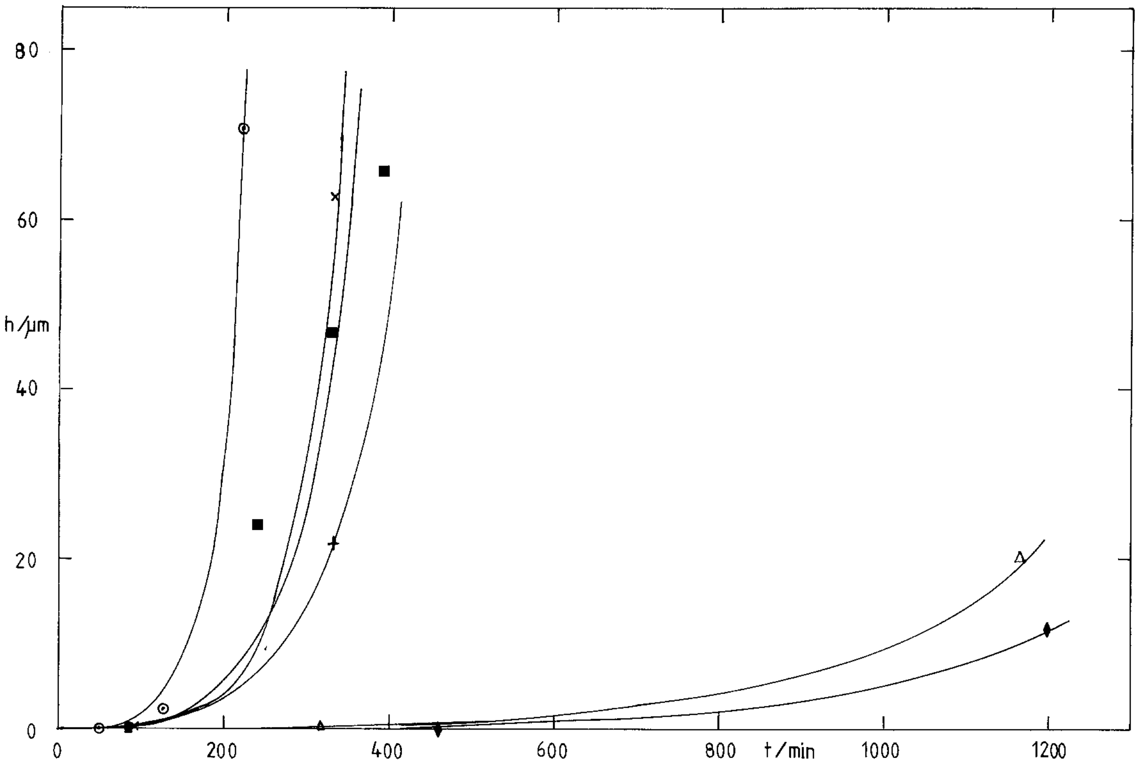

Fig. 1. Cadmium deposition onto a rotating nickel disc electrode in 1.05×10^{-4} mol dm^{-3} $Cd(OH)_4^{2-}$/30% KOH. Dendrite length versus time for a range of overpotentials: ⊙ —500 mV; x —375 mV; + —350 mV; ■ —325 mV; △ —180 mV; ♦ —160 mV; —— calculated using Equation 15.

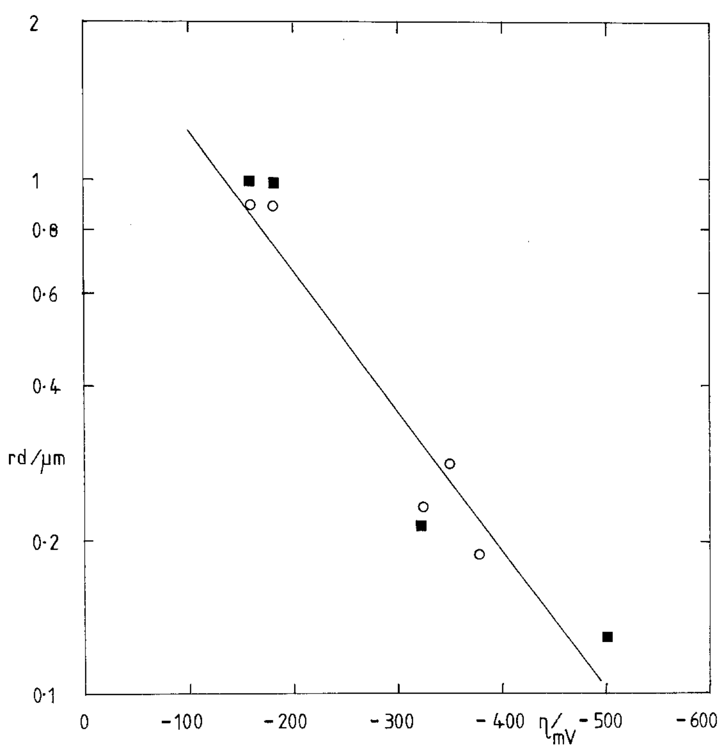

Fig. 2. Cadmium deposition onto a rotating nickel disc electrode in 1.05×10^{-4} mol dm^{-3} $Cd(OH)_4^{2-}$/30% KOH. Tip radius versus overpotential. ■ Tip radius measured from SEM micrographs ○ Tip radius calculated from length versus time data using Equation 15 (to show good agreement between theory and experimental results).

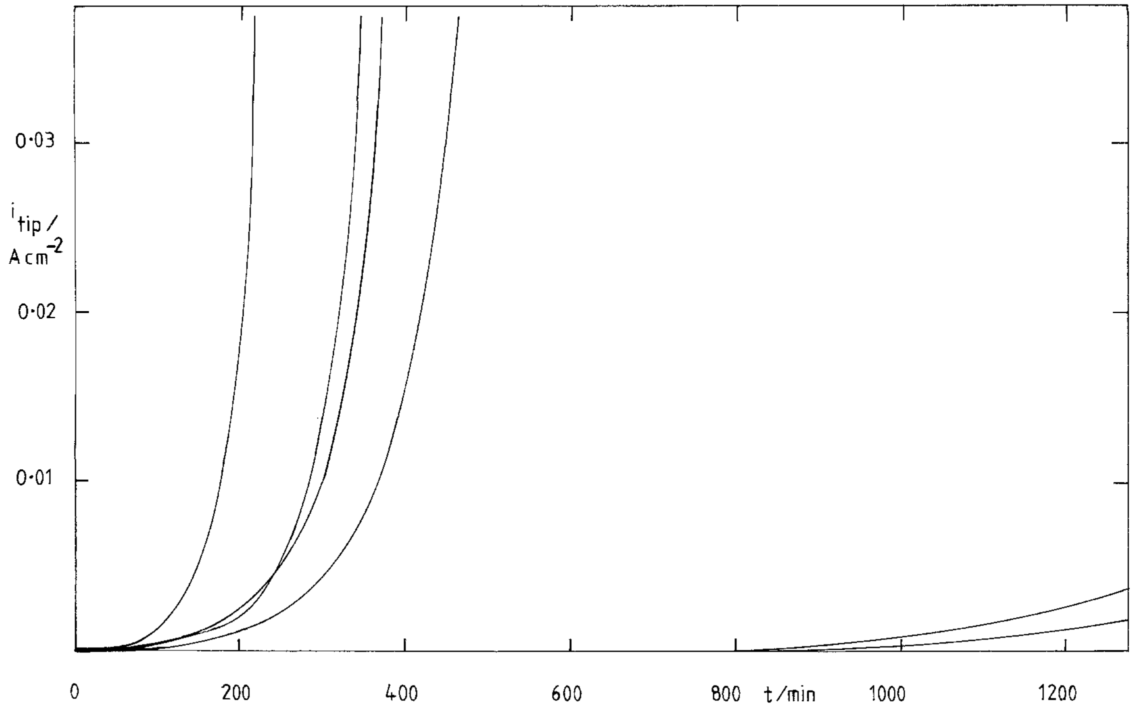

Fig. 3. Cadmium deposition onto a rotating nickel disc electrode in 1.05×10^{-4} mol dm^{-3} $Cd(OH)_4^{2-}$/30% KOH. Tip current density versus time, calculated using Equation 16.

height, and the approximation of exponential limiting conditions is valid.

It is interesting to note that h_{crit} is not simply limiting to the value of the Nernst diffusion layer thickness δ. For the range of overpotentials used, to a good approximation, $u \approx \exp(C)$ so Equation 12 reduces to

$$\frac{h_{crit}}{i_0 \exp(C)} = \frac{r \ln(h_{crit})}{i_L} \tag{23}$$

where i_L is the planar limiting diffusion current

$$i_L = nFDC_b/\delta \tag{24}$$

(D is the diffusion coefficient and C_b is the bulk concentration of depositing species.) Hence, h_{crit} can be greater than δ or considerably less than δ depending on the values of the other parameters.

The exponential height–time curves also give an indication of how induction times may appear. We have previously pointed out that the observed total current is dependent on the increasing area of the growing dendrites and there will be an experimental detection limit to the change in current. Thus the length of dendrites to cause a sufficient increase in area and hence a change in current greater than the detection limit may lead to an apparent induction time greater than any real induction time. In Fig. 5 the experimental induction times determined from the minimum in the current–time curves are shown as a function of overpotential. As indicated in an earlier paper [1] there are no dendrites visible by SEM at times corresponding to these current minima, but dendrites are clearly visible a short time after the current has started to rise. The induction time t_i can be introduced into Equation 15 to give h_i, the height of a surface protrusion or dendrite precursor at t_i:

$$h_i = h_0 \exp(K_1 t_i) \tag{25}$$

which can be rearranged as

$$t_i = [\ln(h_i/h_0)]/K_1 \tag{26}$$

A good agreement between experimental induction times and those calculated from Equation 26 is achieved when $h_i = 0.5$ μm as shown on Fig. 5. This implies that the height of a surface protrusion must be of the order of 0.5 μm for this system before the required conditions for

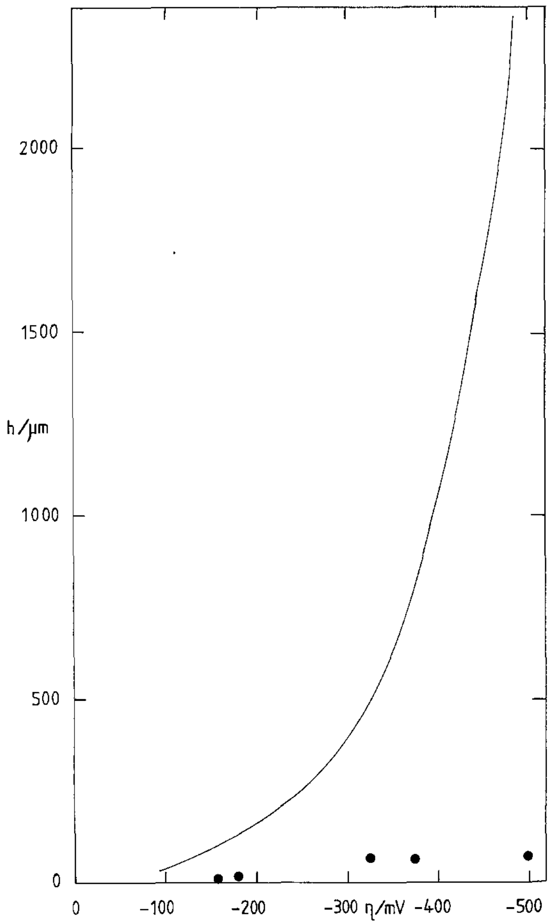

Fig. 4. Cadmium deposition onto a rotating nickel disc electrode in 1.05×10^{-4} mol dm^{-3} $Cd(OH)_4^{2-}$/30% KOH. Critical height where changeover from exponential to linear limiting growth occurs, versus overpotential. • Maximum observed dendrite lengths.

dendrite growth are reached. The induction time is that taken to reach the conditions for dendrite growth, possibly the point at which the diffusion conditions change from being approximated by linear diffusion conditions to being approximated by spherical conditions. The induction time may also be changed by factors such as hydrogen evolution and thin films on the substrate. Having firmly established that growth is under exponential limiting conditions, the dendrite initiation law must be determined before the total current–time curves can be calculated. From the SEM photographs [1] the dendrites have a wide range of lengths for a particular time of deposition and therefore progressive initiation is indicated. N_0, the number of initiation sites counted from the areas between dendrites is plotted versus potential in Fig. 6. N_0 was also calculated assuming

$$N_0 = \frac{1}{\pi r^2} \tag{27}$$

and a good agreement with the experimental values is found as shown on Fig. 6. From the total number of dendrites, N_t, at time t and the number of initiation sites N_0, the rate constant, K_0 for dendrite initiation under a first order law can be calculated by rearranging Equation 22 to give

$$K_0 = N_t/N_0 t \tag{28}$$

K_0 appears to be independent of overpotential, having a value of $\sim 3.5 \times 10^{-6}$.

Assuming that the dendrites may be approximated to rectangular rods such that $i_{\text{dendrites}}$ are given by Equation 20, then the total current will be given by

$$i_t = i_L + \int_{t_{\min}}^{t} [2h(w+d)i_L + wdi_{\text{tip}}] N_0 K_0 \, dt \tag{29}$$

where $t_{\min}$ is the time at current minimum, with h given by Equation 15 and i_{tip} given by Equation 16, thus Equation 29 becomes

$$i_t = \int_{t_{\min}}^{t} \left[2(w+d)i_L + \frac{wdnFK_1}{V}\right] \times h_0 \exp(K_1 t) N_0 K_0 \, dt \tag{30}$$

or in abbreviated form

$$i_t = \int_{t_{\min}}^{t} Q \exp(K_1 t) \tag{31}$$

where $Q = N_0 K_0 [2(w+d)i_L + (wdnFK_1/V)]h_0$, which on integrating gives

$$i_t = {}_{t_{\min}}^{\;t}\left[\frac{Q}{K_1}\exp(K_1 t)\right] + Z \tag{32}$$

where Z is a constant of integration and is $i_{\min} - [(Q/K_1)\exp(K_1 t_{\min})]$ where $i_{\min}$ is the current density at minimum.

The constant of integration can be evaluated as follows: at $t_{\min}$ the total current is $i_{\min}$

$$i_{\min} = \left[\frac{Q}{K_1}\exp(K_1 t_{\min})\right] + Z \tag{33}$$

so that

$$Z = i_{\min} - \left[\frac{Q}{K_1}\exp(K_1 t_{\min})\right] \tag{34}$$

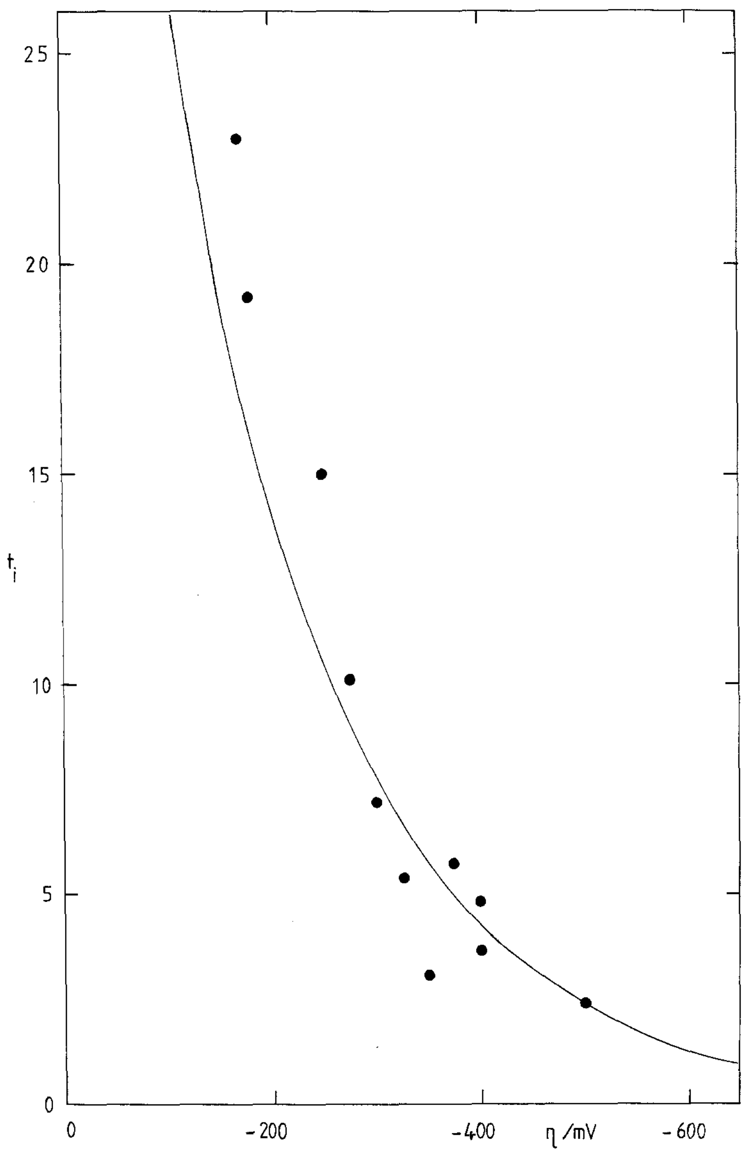

Fig. 5. Cadmium deposition onto a rotating nickel disc electrode in 1.05×10^{-4} mol dm^{-3} Cd$(OH)_4^{2-}$/30% KOH. Induction time versus overpotential. • experimental; —— calculated using Equation 26.

and Equation 32 becomes

$$i_t = {}_{t_{\min}}^{t}\left[\frac{Q}{K_1}\exp(K_1 t)\right] + i_{\min} - \left[\frac{Q}{K_1}\exp(K_1 t_{\min})\right] \quad (35)$$

Fig. 7 shows the experimental log current–time behaviour and the calculated behaviour using Equation 35 which shows a very reasonable fit to the experimental data. Thus, for the alkaline system and a rotating nickel disc electrode over the time scales used the experimental behaviour of dendrite growth can be satisfactorily explained using the exponential limiting equations of Diggle *et al.* [5] for the period of deposition after the current minima assuming a first order progressive initiation law and that dendrites may be approximated to rectangular rods.

2.2. *Acid system: cadmium deposition onto a stationary cadmium electrode in 10^{-1} mol dm^{-3} $CdSO_4$/0.5 mol dm^{-3} H_2SO_4*

The five striking differences between the experimental results at this concentration and those in alkali described above are:

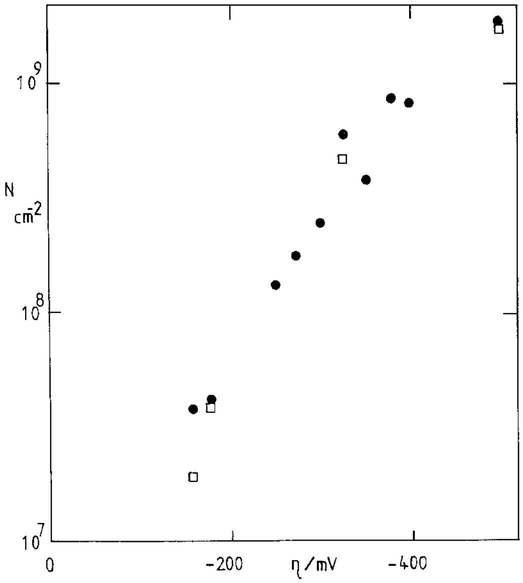

Fig. 6. Cadmium deposition onto a rotating nickel disc electrode in 1.05×10^{-4} mol dm^{-3} $Cd(OH)_4^{2-}$/30% KOH. Number of initiation sites versus overpotential. □ experimental; △ calculated using Equation 27.

(a) there is a very small induction period (less than 30 s) before the total current begins to rise

(b) the total current-versus-time plots are approximately linear, particularly for the larger deposition times (>50 min) as shown in Fig. 8

(c) the height-versus-time relation appears to be linear

(d) the distribution of dendrite lengths at the end of the deposition period is Gaussian

(e) the morphology has changed to hexagonal boulders.

This behaviour indicates that the dendrite growth conditions may be approximating to the linear limiting conditions given by Equation 10 and possibly by an instantaneous initiation process.

Fig. 9 shows a histogram of a number of dendrites within each length range for 110 minutes deposition at −20 mV. The histogram shows an approximately Gaussian distribution indicative of an instantaneous law. If we assume these hexagonal boulders approximate to cylinders of height h and radius r_c then the current due to one dendrite is given by Equation 21. For instantaneous nucleation, N_t is a constant and the total current due to dendrites becomes

$$i_{\text{dendrites}} = N_t[(2\pi r_c h)i_L + (\pi r_c^2 i_{\text{tip}})] \tag{36}$$

If the linear limiting equation for height as a function of time (Equation 10) is substituted into Equation 36 with the assumption that h_0 is negligible, along with the corresponding Equation 11 for i_{tip} then

$$i_{\text{dendrites}} = N_t\left(2\pi r_c i_L \frac{i_0 u V t}{nF} + \pi r_c^2 i_0 u\right) \tag{37}$$

$$i_{\text{dendrites}} = N_t i_0 u \pi r_c \left[\frac{2 i_L V t}{nF} + r_c\right] \tag{38}$$

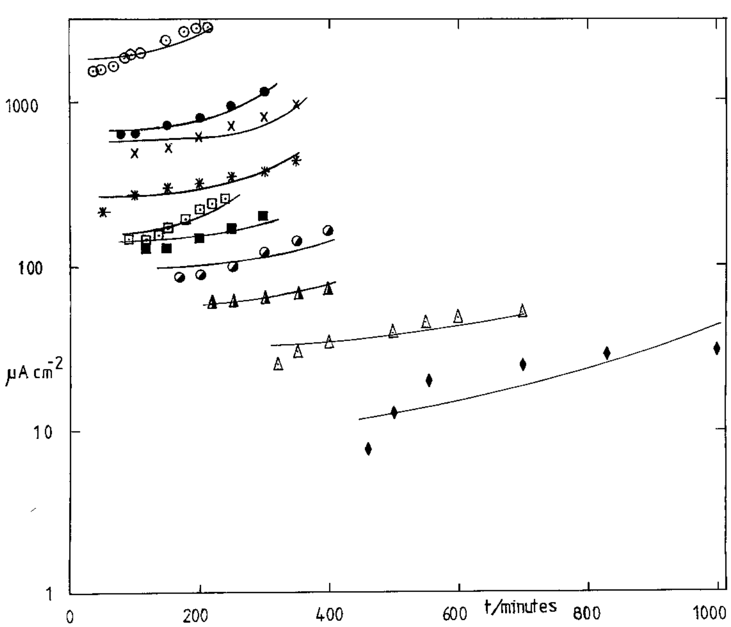

Fig. 7. Cadmium deposition onto a rotating nickel disc electrode in 1.05×10^{-4} mol dm^{-3} $Cd(OH)_4^{2-}$/30% KOH. log (total current) versus time. ⊙ −500 mV; ● −400 mV: × −375 mV; ∗ −350 mV; □ −325 mV; ■ −300 mV; ◑ −275 mV; ▲ −250 mV; △ −180 mV; ♦ −160 mV; —— calculated using Equation 35 for each overpotential.

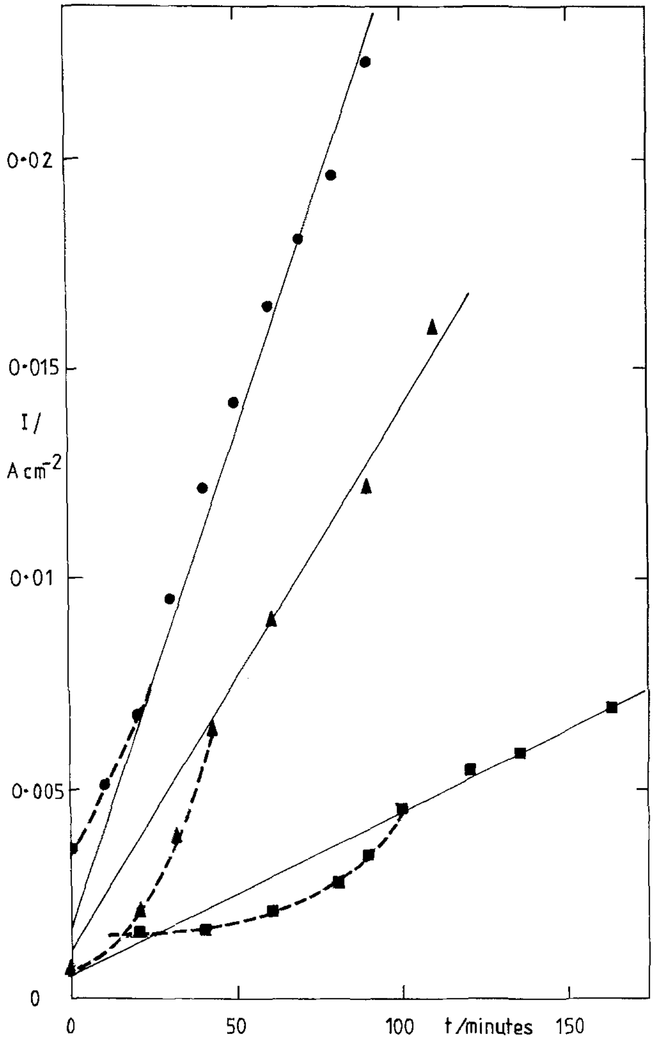

Fig. 8. Cadmium deposition onto stationary cadmium electrodes in 10^{-1} mol dm^{-3} $CdSO_4$/0.5 mol dm^{-3} H_2SO_4. Total current versus time. ● — 35 mV; ▲ — 20 mV; ■ — 10 mV; —— calculated using Equation 38.

The lines drawn through the experimental points in Fig. 8 were calculated using Equation 38 and show a good agreement with the experimental data. The dashed line shows the exponential region of growth and h_{crit} calculated for this range of potential appears approximately constant at 12 ± 2 μm.

Thus the growth of cadmium dendrites in acidic media can also be explained using the theoretical approach of Diggle *et al.* [1] using the linear limiting equations with an instantaneous initiation law.

3. Conclusions

For cadmium dendrite growth in 1.05 × 10^{-4} mol dm^{-3} $Cd(OH)_4^{2-}$/30% KOH over the range of overpotentials examined the dendrite length versus time curve has an exponential form and the wide range of dendrite lengths observed after a given deposition time are indicative of progressive dendrite initiation.

The total current–time behaviour can be predicted using the Diggle *et al.* approach [5] assuming the dendrites approximate to rectangular rods and follow a first order progressive initiation law.

The induction period prior to dendrite growth is given by $t_i = [\ln(h_i/h_0)] K_1$ and corresponds to a height of 0.5 μm required before the conditions necessary for dendrite growth are realized.

The tip current and dendrite length are very sensitive to the value of the dendrite tip radius of curvature.

The critical height where the limiting

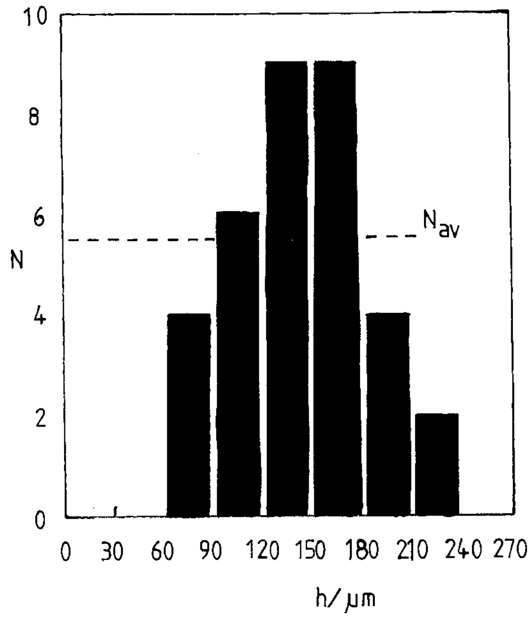

Fig. 9. Cadmium deposition onto stationary cadmium electrodes in 10^{-1} mol dm^{-3} $CdSO_4$/0.5 mol dm^{-3} H_2SO_4. Histogram of number of dendrites in each dendrite length range after 110 min deposition at −20 mV.

conditions change from approximating to exponential to approximating to linear growth does not necessarily limit to the Nernst diffusion layer thickness.

For cadmium dendrite growth in 10^{-1} mol dm^{-3} $CdSO_4$/0.5 mol dm^{-3} H_2SO_4 the dendrite length-versus-time relation is linear and the Gaussian distribution of dendrite lengths observed after a given deposition time are indicative of instantaneous dendrite initiation. The induction period prior to dendrite growth is less than 30 s.

The total current–time behaviour can be predicted using the Diggle *et al.* approach [5] assuming the dendrites approximate to cylindrical rods and an instantaneous initiation law applies.

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