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A new model for the nucleation and growth of thick polycrystal films. II. Investigation of i–η–t responses

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The general behaviour of *i–η–t* responses is calculated for the nucleation and growth of thick polycrystal films. The model on which the calculations are based is that described in our previous paper [1] on the geometry-conserving model.

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1. Introduction

In Part 1 of this series we calculated the volume transformation for the case of '2½ D' nucleation and growth of polycrystal films [1]. Here we extend that result by calculating various *i–η–t* responses expected in various electrochemical experiments. Both 'instantaneous' and 'progressive' nucleation are considered.

2. *i–t* transient for instantaneous nucleation at constant potential

Previously we showed that the volume transformation for instantaneous nucleation was

$$V_T \propto \rho^{-1/2}\,[1-\exp(-\theta_X)]^{3/2} \qquad (1)$$

where V_T was the (real) transformed volume per unit area of substrate. This equation can be written identically as

$$q \propto \rho^{-1/2}\,[1-\exp(-\theta_X)]^{3/2} \qquad (2)$$

where q is the charge passed in creating the layer and θ_X is given by

$$\theta_X = \alpha\left(\int_0^t x\,\mathrm{d}t\right)^2, \qquad \alpha = \text{constant}. \qquad (3)$$

Here x is the growth rate of a crystal in some specified linear direction X. At constant potential, $x = k$ (a constant) and so $\theta_X = \alpha k^2 t^2$. Thus

$$q \propto \rho^{-1/2}\,[1-\exp(-\alpha k^2 t^2)]^{3/2}. \qquad (4)$$

Normalizing the time-scales by setting $\alpha k^2 t^2 = \tau^2$ we obtain directly

$$i \propto \frac{\mathrm{d}q}{\mathrm{d}t}$$

$$\propto \tau \exp(-\tau^2)\,[1-\exp(-\tau^2)]^{1/2}. \qquad (5)$$

This equation therefore gives the form of the *i–t* response; this is illustrated in Fig. 1. Differentiating Equation 5 to get the transient maximum parameters i_m and t_m we have

$$i_m \propto (\alpha/\rho)^{1/2}\,k \qquad (6)$$

$$t_m \propto (1/\alpha)^{1/2}\,(1/k) \qquad (7)$$

and the total charge passed in creating a complete polycrystal layer is given by

$$q_{\text{Total}} \propto \rho^{-1/2}. \qquad (8)$$

3. η–*t* transient for instantaneous nucleation at constant current

As in the above derivation, we again need Equation 2 coupled to Equation 3. But in this case x is not constant; we shall assume that x is of the form[†]

$$x = (e^{\eta} - e^{-\eta})^{\theta} \qquad (9)$$

where η is a reduced potential scale and θ is a

[†] The term in parentheses corresponds to the assumption that the crystal growth process occurs via ion transfer. The kinetic coefficient θ is introduced to accommodate the fact that the number of microscopic sites in the crystal at which growth occurs may itself be a function of potential.

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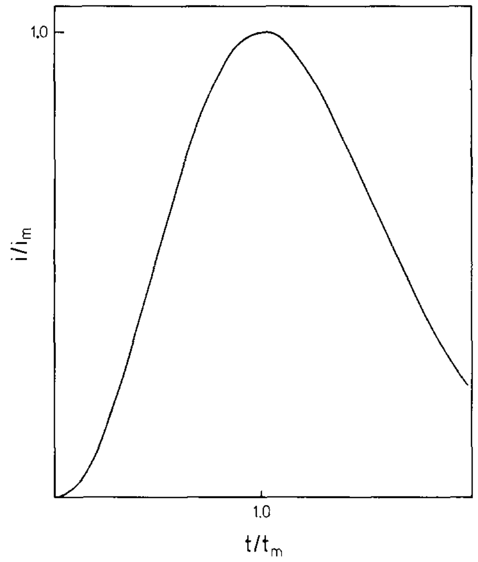

Fig. 1. Current–time transient for 'instantaneous' nucleation and growth.

kinetic coefficient. Since we are considering constant-current conditions, it also follows that

$$q = \int_0^t i\mathrm{d}t = it. \qquad (10)$$

Calling the total charge expended in producing the layer q_{Total}, Equation 10 predicts an 'extinction time' t_{ext} given by

$$q_{\mathrm{Total}} = i\, t_{\mathrm{ext}}. \qquad (11)$$

This expression allows us to introduce a normalized time-scale T where

$$T = (t/t_{\mathrm{ext}})^{2/3}. \qquad (12)$$

Substitution of Equations 3, 9 and 12 into Equation 2 yields, after a little rearrangement,

$$(2\sinh\eta)^\theta \propto \frac{1}{3\alpha^{1/2}}\left[\ln\left(\frac{1}{1-T}\right)\right]^{-1/2}\frac{T}{1-T}\,\frac{1}{t} \qquad (13)$$

which is the desired result. At short times, this expression simplifies to

$$(2\sinh\eta)^\theta \propto \frac{1}{3\alpha^{1/2}}\,\frac{1}{T}\,\frac{1}{t} \qquad (14)$$

which is a falling transient. The limit of Equation 13 at long times is obtained using l'Hôpitals rule to give

$$(2\sinh\eta)^\theta \propto \frac{\sqrt{2}}{3\alpha^{1/2}}\,\frac{1}{(1-T)}\,\frac{1}{t_{\mathrm{ext}}} \qquad (15)$$

which is a rising transient. Equation 13 is a U-shaped function, and the properties of the minimum of the η–t response can be obtained straightforwardly by differentiation of Equation 13. This leads to the result that $(2\sinh\eta)^\theta$ has a minimum at $T = 0.56$, i.e. at $\tau = 0.42$. It also follows that $(2\sinh\eta_{\mathrm{min}})^\theta$ varies as i/q_{Total}.

4. *i*–η–*t* response for instantaneous nucleation in linear potential scan

For a fixed number of nuclei, we can cast Equations 2 and 3 in the form

$$q = [1 - \exp(-\alpha y^2)]^{3/2} \qquad (16)$$

where $\mathrm{d}y/\mathrm{d}t = x$ and $\mathrm{d}x/\mathrm{d}t = z$. It turns out that the LPS response in this case is not soluble in terms of simple functions for the full range of η in Equation 9, so we consider the two limiting forms of Equation 9 separately. First we deal with $\eta \to 0$, in which case, setting $\eta = \nu t$ gives

$$x = (2\nu t)^\theta \qquad (17)$$

$$y = (2\nu)^\theta\,\frac{t^{\theta+1}}{\theta+1} \qquad (18)$$

$$z = \theta(2\nu)^\theta\, t^{\theta-1}. \qquad (19)$$

Differentiation of Equation 16 gives the i–t response

$$i = \frac{\mathrm{d}q}{\mathrm{d}t}$$

$$= \frac{3}{2}[1 - \exp(-\alpha y^2)]^{1/2}\, 2\alpha xy \exp(-\alpha y^2). \qquad (20)$$

Usually the maximum parameters, i_{p} and η_{p}, are of interest. These can be obtained by differentiating Equation 20 and setting $\mathrm{d}i/\mathrm{d}t = 0$. Now, letting $\psi = 1 - \exp(-\alpha y_{\mathrm{p}}^2)$, this procedure produces the simple result

$$\left(\frac{3\psi - 1}{\psi}\right)\alpha y_{\mathrm{p}}^2 = 1 + \frac{z_{\mathrm{p}}y_{\mathrm{p}}}{x_{\mathrm{p}}^2} \qquad (21)$$

and substitution of $x_{\mathrm{p}}, y_{\mathrm{p}}$ and z_{p} from Equations 17–19 leads immediately to

$$\left(\frac{3\psi - 1}{\psi}\right)\alpha y_{\mathrm{p}}^2 = \frac{2\theta + 1}{\theta + 1} \qquad (22)$$

which proves that αy_{p}^2 is a constant, independent of ν. Further substitution, this time of Equation

22 back into Equation 20, yields

$$i_p \propto x_p y_p. \tag{23}$$

Hence

$$i_p \propto \nu^{[\theta/(1+\theta)]} \tag{24}$$

and

$$\eta_p \propto \nu^{[1/(1+\theta)]}. \tag{25}$$

The other limiting form of Equation 9, in which $\eta \to \infty$, can be tackled in a similar way. In this case

$$x = e^{\theta\nu t} \tag{26}$$

$$y = \frac{1}{\theta\nu}(e^{\theta\nu t} - 1) \tag{27}$$

$$z = \theta\nu e^{\theta\nu t} \tag{28}$$

and substitution of x_p, y_p and z_p back into Equation 21 shows that

$$\left(\frac{3\psi - 1}{\psi}\right)\alpha y_p^2 = 1 + \frac{\theta\nu y_p}{\theta\nu y_p + 1.} \tag{29}$$

The left-hand side of this equation obviously goes to 2 as $\nu \to \infty$, showing that $\alpha y_p^2 \to$ constant. This leads directly to

$$i_p \propto 2\theta\nu \tag{30}$$

$$\eta_p \propto \ln(\theta\nu). \tag{31}$$

5. *i–t* transient for progressive nucleation at constant potential

From [1] we know that the volume transformation for progressive nucleation is of the form

$$V_T \propto \left[\int_0^t A_X(t)(1 - S_T(t))\,dt\right]^{-1/2}$$
$$\times \left[1 - \exp\left(-\int_0^t A_X(t)\,{}_1S_X(\tau - t)\,dt\right)\right]^{3/2} \tag{32}$$

and at constant potential, this takes the form

$$q \propto A^{-1/2}\left[\int_0^t \exp(-Ak^2t^3)\,dt\right]^{-1/2}$$
$$\times [1 - \exp(-Ak^2t^3)]^{3/2} \tag{33}$$

where A is the appearance rate of crystals and k is the spreading rate of crystals. Unfortunately we cannot get an explicit solution to this equation in terms of familiar functions, although it can be solved numerically. In the limit of $Ak^2t^3 \to \infty$ we note that

$$q \propto \left[A(Ak^2)^{-1/3}\int_0^\infty \exp(-\tau^3)\,d\tau\right]^{-1/2}$$
$$\times [1 - \exp(-Ak^2t^3)]^{3/2} \tag{34}$$

and since

$$\int_0^\infty \exp(-\tau^3)\,d\tau = \left(\frac{1}{3}\right)\Gamma\left(\frac{1}{3}\right) = 0.894 \tag{35}$$

it follows that as $t \to \infty$

$$q_T \propto [A(Ak^2)^{-1/3}]^{-1/2}$$
$$\propto \left(\frac{k}{A}\right)^{1/3}. \tag{36}$$

It is also of interest to calculate the *i–t* transient maximum parameters, i_m and t_m. To do this we first expand $\exp(-Ak^2t^3)$ as a power series, thus

$$\exp(-Ak^2t^3) = 1 - (Ak^2)t^3 + \frac{(Ak^2)^2t^6}{2!}\ldots \tag{37}$$

and

$$\int_0^t \exp(-Ak^2t^3)\,dt$$
$$= t\left[1 - \frac{(Ak^2)t^3}{4} + \frac{(Ak^2)^2t^6}{7 \times 2!}\ldots\right]. \tag{38}$$

Above $Ak^2t^3 = 1$ a large number of terms are required to make this series converge. But a useful result is that $\int_0^t \exp(-Ak^2t^3)\,dt \to t$ faster than $\exp(-Ak^2t^3) \to 1$ as $t \to 0$, which suggests that a reasonable approximation to Equation 33 is

$$q \propto [At]^{-1/2}[1 - \exp(-Ak^2\mathrm{t}^3)]^{3/2} \tag{39}$$

provided $t \to 0$. Thus we can now use this approximate formula to investigate the transient maximum parameters. Differentiating Equation 39 twice, and setting $d^2q/dt^2 = di/dt = 0$ leads to the result that

$$3Ak^2t_m^3 = \frac{1 \pm \gamma^{-1/2}}{1 - \gamma} \tag{40}$$

where

$$\gamma = \frac{1}{2}\left[\frac{\exp(-Ak^2t_m^3)}{1 - \exp(-Ak^2t_m^3)}\right]. \tag{41}$$

Solving the transcendental Equation 41 gives the

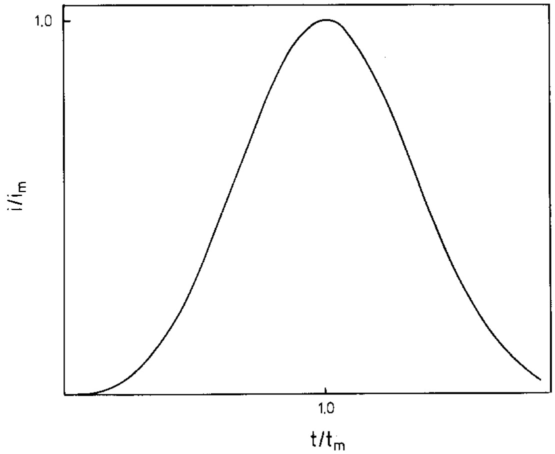

Fig. 2. Current–time transient for 'progressive' nucleation and growth.

result that

$$3Ak^2t_m^3 \simeq 3.0 \quad (42)$$

and hence

$$t_m \propto (Ak^2)^{-1/3}. \quad (43)$$

Differentiation of Equation 39 gives an expression for $\mathrm{d}q/\mathrm{d}t = i$, and substitution of Equation 43 yields

$$i_m \propto k. \quad (44)$$

Combination of Equations 44 and 43 gives

$$i_m^2 t_m^3 \propto \frac{1}{A} \quad (45)$$

i.e. it is possible to 'deconvolve' A and k using the transient maximum parameters.

As we stated earlier the current–time plot corresponding to the derivative of Equation 33 can be evaluated numerically. This was achieved and the result is shown in Fig. 2. The result is in close agreement with experimental data as the model requires [2].

6. Other i–η–t responses for progressive nucleation

Since the potentiostatic i–t response cannot be solved explicitly it follows that other perturbations such as linear potential scans and galvanostatic steps are also intractable. They could, however, be tackled by approximation methods similar to the above, or else they could be solved numerically.

7. Incorporating diffusion into the model

In the case of the formation of anodic films it is interesting to speculate on the effects of diffusion from bare electrode surface to the growing nuclei. (Normally this will be a fast process and hence will not influence the interfacial kinetics.) To properly incorporate slow diffusion into the model would be a difficult procedure because of the complex interactions of the randomly distributed diffusion zones. However we can visualize the overall effect (in the case of instantaneous nucleation) by considering Equation 5. The effect of a slow diffusion process would be to reduce the value of k, and hence of q, and this in turn would result in a 'flattening' of the observed i–t transient as compared with those calculated in the present theory.

8. Conclusion

In [1] we calculated the approximate volume transformation for the 'geometry-conserving' limit of '$2\frac{1}{2}$D' nucleation and growth. In this latter part of the paper we have used this result to calculate some general i–η–t responses of experimental interest. As it turned out the instantaneous nucleation cases proved to be more tractable, but an approximate treatment of the progressive nucleation cases suggested the possibility of deconvolving A and k.

The present model is restricted by the form of the volume transformation assumed at the outset; this is a good approximation at short times but when applied to a real system will become increasingly inaccurate as the intercrystal collisions become highly developed. It follows that, although the results obtained at the transient maxima are almost certainly correct in their general form, any absolute values of constants calculated using the theory must be treated with caution. It also follows that, at long times in the transient responses, large errors are to be expected because the volume transformation is wholly inadequate in describing the highly developed, and idiosyncratic, behaviour of intercrystal collisions in individual systems. The only proper resolution of this last point appears to be by computer simulation.

References

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