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Modeling of Single Phase Electrocrystallization Processes

Growth of Paraboloids with Concurrent Evolution of Hydrogen

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A generalized form of the current time transient (CTT) has been derived for the charge transfer controlled model of growth of paraboloids. The transient current is shown to pass through a single maximum before approaching a steady-state value. The maximum is estimated to be coincidental with 77% of the substrate coverage in the case of ''instantaneous'' nucleation and with 90% coverage for the ''progressive'' nucleation and growth of paraboloids. The dependence of the surface area of the paraboloidal growth forms on time is formulated and, consequently, the kinetics of the concurrent evolution of hydrogen has been incorporated in the formulation of the CTTs. A particular CTT equation is thereby derived for the growth of paraboloids that are ''instantaneously'' formed on a monolayer of deposit. It is shown that the exact shape of some of the CTTs recorded during the electrocrystallization of cobalt can be reproduced by the derived CTT.

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The rate of electrocrystallization is principally governed by the rate of nucleation as well as the rates of crystals growth. In modelling single-phase electrocrystallization processes the rate of nucleation is generally assumed to follow[1-4] a first order rate law. However, the growth rates are generally considered to be controlled either by the rate of charge transfer at,[1-3,6-11] or by the rate of diffusion of the depositing species to,[4,5,12-15] the growing interface. In this paper, we are interested in the modelling of electrocrystallization processes the kinetics of which is controlled by the rate of charge transfer at the growing interface.

A particular model of growth, which is capable of approximately representing a wide range of growth geometries (from a very elongated to a very flattened outlook), is the growth of hemispheroids. A key disadvantage of this form of growth, as a general growth model for electrocrystallization processes, is its inability to represent nucleation contact angles other than $\pi/2$. A growth geometry the CTTs for which have, as yet, not been formulated is that of paraboloids. The advantage of this growth model over that of hemispheroids is its ability to represent growth forms of contact angles varying from 0 to just below $\pi/2$ (a realistic range for all metal deposition processes, except for Hg).

Apart from right-circular cone, all other growth forms that have been considered so far[7-11] are capable of accounting for the existence of a single maximum in the experimentally recorded CTTs.[16-18] However, none of these growth forms are capable of accounting for the observed difference between the recorded maximum current, $i_{\max}$, and its steady-state value, i_{st}. (The differences between $i_{\max}$ and i_{st} recorded during the electrocrystallization of cobalt are, invariably, larger than those theoretically predicted.)

The purpose of this paper is threefold: The first is to derive the behavior of the CTTs for a model which, in addition to being capable of representing a wide range of growth forms, is also capable of relating the shape of the CTTs to the contact angles for nucleation. The second is to extend the modeling to account for the evolving topography of the surfaces of the growth forms over which hydrogen is evolving. And, finally, the third is to show the important role of the evolution of hydrogen in the definition of the forms of the recorded transients.

CTTs Due to the Model of Growth of Paraboloids

In a Cartesian coordinate system, a parabola with its vertex lying on the y-axis is defined by an equation

$$x^2 = -4py \qquad [1]$$

where p is the distance from the vertex to the focus (or directrix). A paraboloid is evolved when the parabola is rotated through π about its y-axis. The equation in a cylindrical coordinate system for a paraboloid that has been formed right at the beginning of the process, that is at $t = 0$, and is growing at speeds of v (cm s^{-1}) and v$'$ (cm s^{-1}) in the directions parallel and perpendicular to the electrode surface is, respectively, given by, Fig. 1

$$r^2 = -4p(y - v't) \qquad [2]$$

Imposing the following restriction $\{y = 0, r = vt\}$ on Eq. 2 results in

$$p = v^2 t/4v' \qquad [3]$$

The current density, j, for any form of growth is related to V (cm^3/cm^2), the volume of the deposit per unit area of the electrode, through

$$j(V) = \frac{zF\rho}{M}\frac{dV}{dt} \qquad [4]$$

where, zF (C mol^{-1}) is the charge transfer per deposition of one mole and M (g mol^{-1}) and ρ (g cm^{-3}) are the molar mass and the density of the deposit, respectively. The volume, V, is defined by, Fig. 2

$$V(t) = \int_0^{\text{v}'t} S_{\text{u}} dy \qquad [5]$$

where, S_{u}, the fractional area of the deposit cut through by a slice of height $dy(=\text{v}'du)$, is given by[7]

$$S_{\text{u}} = 1 - \exp(-E) \qquad [6]$$

E is the number of growth centres expected to cross, within the time period t, a random point P, situated at a distance y, Fig. 2. (Detailed formulation of E is given in the Appendix.)

The general CTT equation is obtained by combining Eq. 4, 5, and 6 with Eq. A-8 of the appendix. The nondimensional form of the CTT equation is, therefore, given by

$$\left.\begin{aligned} I &= j/zFk' = \int_0^{\text{t}} \frac{dE}{dt}\exp(-E)du \\ E &= (\tau^2 - \tau s) - \frac{2\tau - s}{\lambda} + \frac{2}{\lambda^2} - \frac{2 - \lambda s}{\lambda^2}\exp[-\lambda(\tau - s)] \end{aligned}\right\} \qquad [7]$$

where

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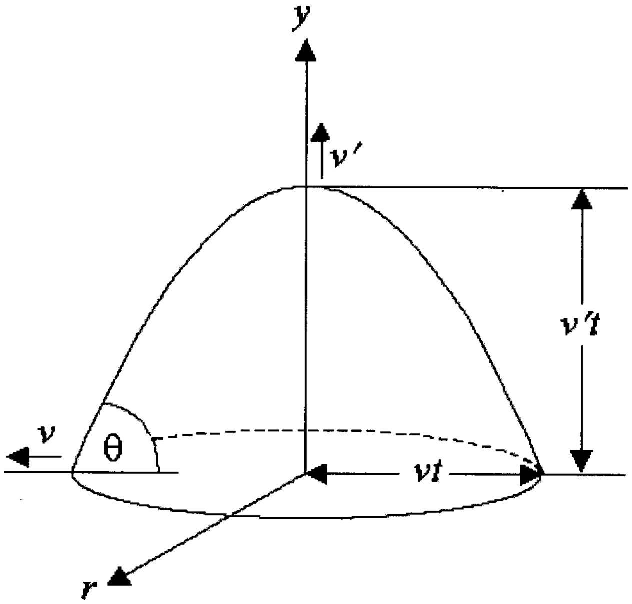

Figure 1. Schematic representation of the growth of a lone paraboloidal center.

$$\left.\begin{aligned} \tau &= t\sqrt{P} \\ s &= u\sqrt{P} \\ \lambda &= A'/\sqrt{P} \\ P &= \pi v^2 N_0 \end{aligned}\right\} \qquad [8]$$

A ($\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$) and A' (s^{-1}) are the steady-state nucleation rate and the number of times that a given random position within the domain of a substrate is expected to have transformed into a nucleus in one second, respectively. Figure 3 and 4 represent the CTT patterns displayed by Eq. 7 at low, intermediate, and high rates of nucleation.

The Effects of Concurrent Hydrogen Evolution

The current density due to the evolution of hydrogen on the surfaces of the paraboloidal growth centres can be written as

$$j_{\mathrm{H}} = z_{\mathrm{H}} F k_{\mathrm{H}} S \qquad [9]$$

where S is the surface area of the paraboloids. To derive the dependence of S on the deposition time, t, we consider a particular center of age t_g, Fig. 5, which was formed after a nucleation period t_u, where $t_u = t - t_g$. The r-coordinate of a point such as P at any given time t can be obtained by substituting in Eq. 2 the y-coordinate of point P ($y = v'u$) as well as the definition of p given by Eq. 3. Therefore

$$r = v(t - t_u)^{1/2}[t - t_u - u]^{1/2} \qquad [10]$$

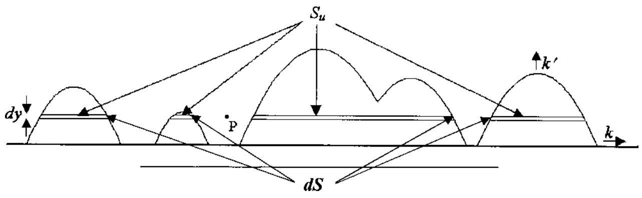

Figure 2. Schematic representation of the growth and overlap of a number of paraboloidal centers formed progressively in time.

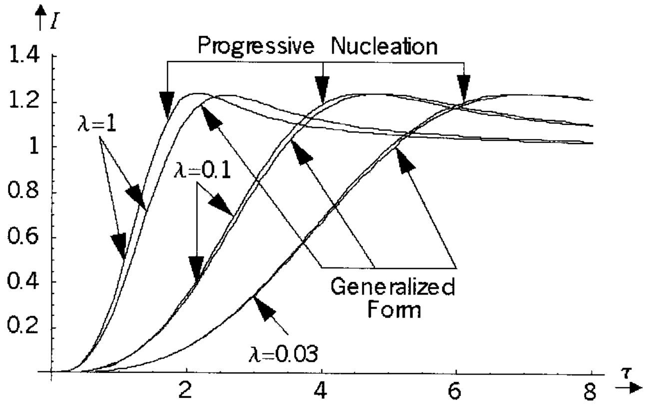

Figure 3. Comparison between the forms of the transients that are due to the progressive mode of nucleation and those that are due to the general formulation.

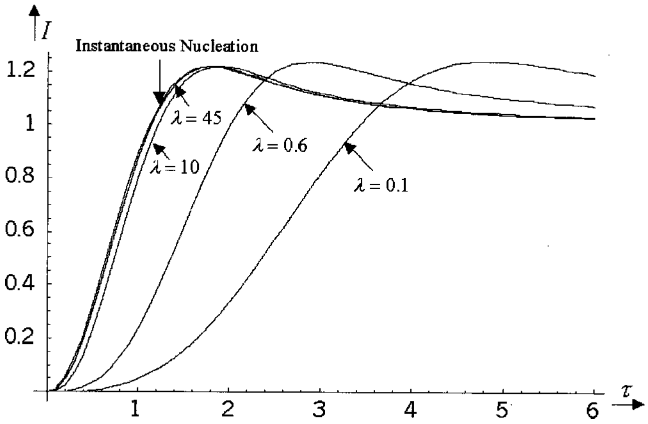

Figure 4. Comparison between the forms of the transients that are due to the instantaneous mode of nucleation and those that are due to the general formulation.

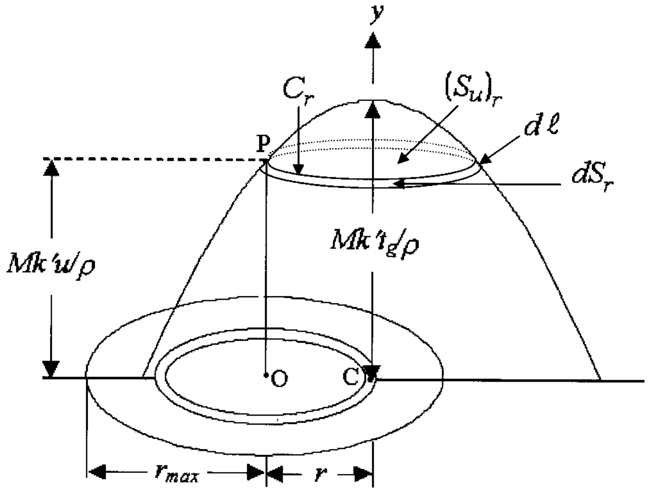

Figure 5. Graphical representation of a single paraboloidal center, formed within the annulus dr, with just enough chance of reaching point P in time t.

However, that portion of the surface area of the lone center that has been cut through by a horizontal slice at point P is given by[10]

$$dS_{\mathrm{r}} = C_{\mathrm{r}} d\ell = \frac{d(S_{\mathrm{u}})_{\mathrm{r}}}{dr} d\ell = \frac{d(S_{\mathrm{u}})_{\mathrm{r}}}{dt}\frac{dt}{dr} d\ell \qquad [11]$$

where C_{r} is the length of the circumference of the center cut through by a slice and $(S_{\mathrm{u}})_{\mathrm{r}}$ is the top surface area of the slice. But Fig. 5 shows that

$$d\ell = (dr^2 + dy^2)^{1/2} \qquad [12]$$

Combining Eq. 11, 12, and $y = \mathrm{v}'u$ with the inverse of the differential of r, Eq. 10, with respect to t leads to

$$dS_{\mathrm{r}} = \frac{d(S_{\mathrm{u}})_{\mathrm{r}}}{dt} \times \left\{\frac{(t - t_{\mathrm{u}})^{1/2}[\mathrm{v}^2(t - t_{\mathrm{u}}) + 4\mathrm{v}'^2(t - t_{\mathrm{u}} - u)]^{1/2}}{\mathrm{v}[2(t - t_{\mathrm{u}}) - u]}\right\} du \qquad [13]$$

Evidently, the portion of the surface area of the whole deposit (dS in Fig. 2) cut through by the same slice is the summation of dS_{r} for all centers. It is not immediately obvious how to find a closed form solution for such a summation as t_{u} has a unique value for each and every center. But in the case of 'instantaneous' nucleation $t_{\mathrm{u}} = 0$ for all centers. It then follows that

$$(dS)_{\mathrm{inst}} = \frac{d(S_{\mathrm{u}})_{\mathrm{inst}}}{dt}\left\{\frac{t^{1/2}[\mathrm{v}^2 t + 4\mathrm{v}'^2(t - u)]^{1/2}}{\mathrm{v}(2t - u)}\right\} du \qquad [14]$$

However, combining Eq. A-2 and A-1 of the appendix with Eq. 6 leads to

$$(S_{\mathrm{u}})_{\mathrm{inst}} = 1 - \exp[-\pi \mathrm{v}^2(t^2 - tu)N_0] \qquad [15]$$

Therefore, substituting the differential of Eq. 15 with respect to t into Eq. 14 and integrating the resulting equation would lead to the definition of S_{inst}, which is also the nondimensional representation of the transient current, $I_{\mathrm{H,inst}}$ (see Eq. 9). Thus

$$I_{\mathrm{H,inst}} = \mathrm{e}^{-\tau^2}\int_0^{\tau}[(1 + \tan^2\theta)\tau^2 - \tau s \tan^2\theta]^{1/2}\mathrm{e}^{\tau s} ds \qquad [16]$$

where τ and s are defined in Eq. 8 and

$$\tan\theta = 2\mathrm{v}'/\mathrm{v} \qquad [17]$$

Electrocrystallization of Cobalt

The CTTs recorded at the lowest possible applied nucleating potentials during the electrocrystallization of cobalt on a vitreous carbon electrode was first studied in 1990.[18] This study was carried out by developing some appropriate models for the electrocrystallization processes and by assessing the extent of the fit of the recorded CTTs to the derived equations using the nonlinear regression software.[19] The general pattern of the recorded CTTs is illustrated in Fig. 6. The flow of current, having reached its peak, i_{max}, at $t = t_2$, is progressively reduced until steady-state (a constant flow of current, i_{st}) is reached. There principally exists a mismatch between the experimentally recorded values of $i_{\mathrm{max}}/i_{\mathrm{st}}$[18] and those which were theoretically derived.[7-11] Here we show that provided the concurrent evolution of hydrogen is correctly taken into consideration the theoretically derived CTTs are capable of reproducing the exact forms of the experimentally observed transients.

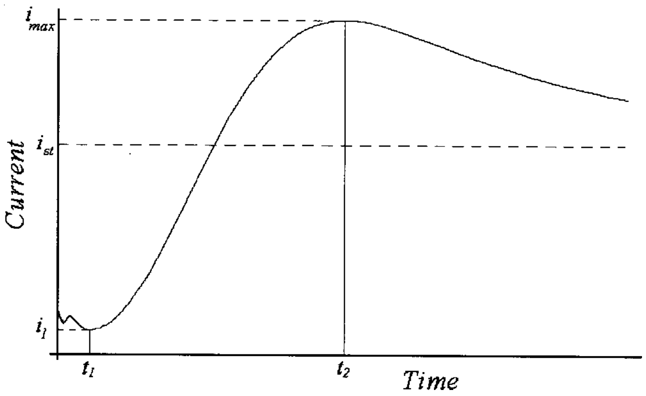

Figure 6. A general CTT pattern representative of the transients recorded during the electrocrystallization of cobalt.

The magnitude of the current i_1 at $t = t_1$, Fig. 6, that is the magnitude just prior to the formation and growth of three-dimensional centers, is representative of the rate of evolution of hydrogen on the surface of the monolayer. However, after t_1 the surface of the monolayer is progressively covered with the 3D growth forms. Hence, the current density due to the evolution of hydrogen at $t > t_1$ is, on one hand, being reduced because of the coverage of the monolayer by the 3D growth forms and, on the other hand, is being simultaneously increased by the evolution of hydrogen on the top surfaces of 3D growth forms. Thus, for paraboloids instantaneously formed on top of a monolayer of deposit, the component of current density due to the evolution of hydrogen can be written as

$$j_{\mathrm{H,inst}} = z_{\mathrm{H}} F k_{\mathrm{H}}[\mathrm{e}^{-\tau^2} + I_{\mathrm{H,inst}}] \qquad [18]$$

where the first term in the square bracket represents progressive coverage of the monolayer and $I_{\mathrm{H,inst}}$ represents the surface area of the 3D growth forms (see Eq. 16). In Eq. 18, the parameter τ (defined in Eq. 8) possess a time element, which must be modified so as to include the period t_1 during which the monolayer has been formed. The final CTT equation is then obtained by adding $j_{\mathrm{H,inst}}$ (after modification of τ) to j in Eq. 7 with the expectation E in its simplified 'instantaneous' form (that is, in the form provided by Eq. A-2 of the appendix). The final form of the CTT is therefore given by

$$j_{\mathrm{inst}} = z_{\mathrm{H}} F k_{\mathrm{H}} \mathrm{e}^{-\mathrm{P}(\mathrm{t}-\mathrm{t}_1)^2}\left\{1 + \int_0^{(\mathrm{t}-\mathrm{t}_1)}[P(1 + \tan^2\theta)(t - t_1)^2 - P\tan^2\theta(t - t_1)\mathrm{u}]^{1/2}\mathrm{e}^{\mathrm{P}(\mathrm{t}-\mathrm{t}_1)\mathrm{u}} du\right\} + zFk'\left\{\frac{1 + P(t - t_1)^2 - [1 + 2P(t - t_1)^2]\exp[-P(t - t_1)^2]}{P(t - t_1)^2}\right\} \qquad [19]$$

The nondimensional form of Eq. 19 is obtained by dividing j_{inst} by $z_{\mathrm{H}} F k_{\mathrm{H}}$. Hence

$$\left.\begin{aligned}I_{\text{inst}} &= e^{-\tau'^2}\left\{1 + \int_0^{\tau'}[(1+\tan^2\theta)\tau'^2 - \tau' s\tan^2\theta]^{1/2}e^{\tau' s}ds\right\} + k_r\left[\frac{1+\tau'^2-(1+2\tau'^2)\exp(-\tau'^2)}{\tau'^2}\right]\\ \text{where } \tau' &= \sqrt{P}(t-t_1)\\ \text{and } k_r &= k'/k_H\end{aligned}\right\}\quad[20]$$

Figure 7 represents the pattern of behavior defined by Eq. 20 for $k_r = 14$ and for the angle of contact changing from 45 to 89°. The transients are shown to be virtually independent of the magnitudes of the angles of contact for $\theta \leqslant 60°$. The ratio of $i_{\max}$ to i_{st} appears to be accentuated only at contact angles close to 90°.

Discussion

Equation 7 predicts the pattern of behavior of the CTTs that are expected from nucleation and growth of crystals of paraboloidal appearance. Apart from the dependence of the form of the CTT on λ, Eq. 7 is independent of any other parameters; in particular, the form of the CTT is independent of the contact angle, θ, which each nucleus makes with the substrate electrode. The contact angle is related to the rates of growth by the definition provided in Eq. 17.

Figure 3 and 4 demonstrates that this equation reduces to the limiting forms, that is to the instantaneous and to the progressive modes of nucleation, at high and low rates of nucleation, respectively. Figure 3 shows that the behavior of Eq. 7 approaches the pattern expected from the 'progressive' nucleation at values of $\lambda \leqslant 0.03$. Figure 4, on the other hand, demonstrates that nucleation can be considered 'instantaneous' at $\lambda \geqslant 45$. As expected, the early stages of the CTT profiles are characterized by a $j \propto t^2$ correlation at $\lambda \geqslant 45$ and by a $j \propto t^3$ relation at $\lambda \leqslant 0.03$. It follows that the early parts of the rising transient in the prevailing intervals, $45 > \lambda > 0.03$, would be characterized by $j \propto t^n$, where $3 > n > 2$.[3]

Therefore in conformity with a previous findings,[11] vis-à-vis the model of growth of hemispheroids, the required conditions for the application of the instantaneous and progressive limiting forms of the CTT are, respectively, specified by

$$A' \leqslant v\sqrt{A/A'}/20 \quad [21]$$

and

$$A' \geqslant 60v\sqrt{A/A'} \quad [22]$$

The above equations indicate that the kinetics of electrocrystallisation can be assumed to be governed by the 'instantaneous' and 'progressive' modes of nucleation whenever the expected rate of turning a given site into a nucleus is either 60 times higher or 20 times lower than the rate of covering the site by the act of growth. The ratio, $i_{\max}/i_{\text{st}}$, is found to be only slightly dependent on the rate of nucleation and its value is about 1.244.

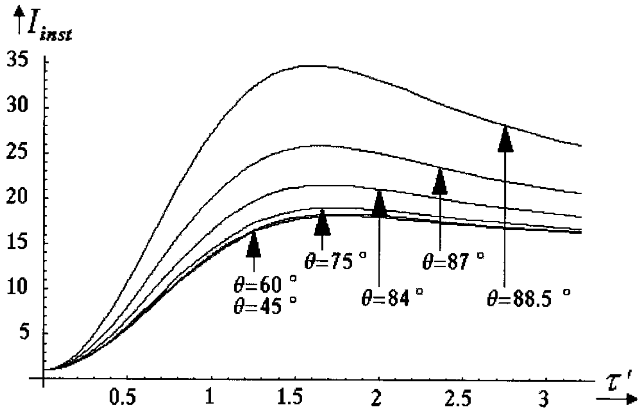

Figure 7. The CTT pattern predicted by Eq. 20 for $k_r = 14$.

Figure 8 shows the observed behavior of the transient, dotted curve, recorded during the electrocrystallization of cobalt on a vitreous carbon electrode at an applied potential of −0.875 V(SCE). To account for $i_{\max}/i_{\text{st}} > 1.244$ Eq. 19 has been derived. The full line in Fig. 7 portrays the form of the CTT as defined by Eq. 19, for the specific values of $z_H F k_H = 150\ \mu\text{A cm}^{-2}$, $\theta = 88.5°$, $zFk' = 2100\ \mu\text{A cm}^{-2}$, $t_1 = 1.8$ s and $P = 0.0033\ \text{s}^{-2}$. The values of $z_H F k_H$ and t_1 are, respectively, estimated from the magnitudes of the current density, i_1, and from the time at which the monolayer is considered to have been formed, Fig. 8. The contact angle of 88.5° and the value chosen to represent zFk' are the result of comparing Fig. 7 with Fig. 8. (From the definition of k_r provided in (20) $zFk' = 150 \times k_r = 150 \times 14\ \mu\text{A cm}^{-2}$.) A very close fit between the experimental data, dotted curve, and the theoretically derived equation, full curve, is observed indicating the crucial role which the evolution of hydrogen plays in the definition of the recorded CTTs.

Note that despite a very close fit of the experimentally observed transient to the theoretically derived CTT, we do not propose the paraboloidal growth geometry to be the only form of growth capable of reproducing the form of the recorded transients. By analyzing the paraboloidal growth geometry we have shown that the variation in the experimentally observed values of $i_{\max}/i_{\text{st}}$ can be explained by the concurrent evolution of hydrogen, and the recorded CTTs due to the electrocrystallization of cobalt can adequately be described by an appropriate model of growth of paraboloids if and only if the contact angles for growth forms are assumed to be approaching $\pi/2$.

Conclusions

A generalized form of the CTT equation, which is operative over all rates of nucleation, has been derived for the model of growth of paraboloids. The limiting forms of this equation, the so-called in-

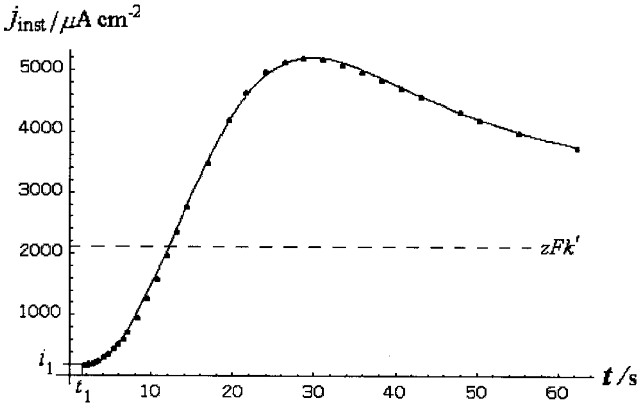

Figure 8. ····· The observed CTT pattern recorded during the electrocrystallization of cobalt onto a vitreous carbon electrode at an applied potential of −0.8 V (SCE). Solution composition: 240 g dm^{-3} $CoSo_4 \cdot 7H_2O$, 36 g dm^{-3} $CoCl_2 \cdot 6H_2O$, and 36 g dm^{-3} H_3BO_3. —— The pattern expected from Eq. 19 for: $z_H F k_H = 150\ \mu\text{A cm}^{-2}$, $\theta = 88.5°$, $zFk' = 2100\ \mu\text{A cm}^{-2}$, $t_1 = 1.8$ s, and $P = 0.0033\ \text{s}^{-2}$.

stantaneous and the progressive limits, are shown to be, respectively, operative whenever the expected rate of turning a given site into a nucleus is either 60 times higher or 20 times lower than the rate of covering the site by the act of growth.

The form of the equation, Eq. 7, is independent of the nucleation contact angle. The transient current is shown to pass through a single maximum before approaching its steady-state value and the ratio of the maximum current to the steady-state value is observed to be about 1.244. The maximum flow of current is estimated to be coincidental with 77% of the coverage of the electrode by the deposit in instantaneous nucleation and with 90% coverage in progressive nucleation.

The dependence of the surface area of the deposit on time has been derived for the specific case of instantaneous nucleation and growth of paraboloids and, as a result, the component of the transient current due to the hydrogen evolution reaction has been formulated.

The CTT due to the instantaneous nucleation and growth of paraboloids has been modified to correctly incorporate the concurrent hydrogen evolution reactions. This is achieved by accounting, on one hand, for the reduction in the hydrogen evolution (due to the progressive coverage of the monolayer by the 3D growth centers) and by considering the evolution of hydrogen on the top surfaces of the 3D growth forms.

The modified CTT is shown to simulate the transient pattern recorded during the electrocrystallization of cobalt.

Appendix

Formulation of the expectation, E.—The expectation value is formulated here in accordance with the method of formulation, first identified in 1982[7] for the transformations due to surface nucleation and 3D growth. Figure 9 represents two growth centers, which are imagined to have formed right at the beginning of the electrocrystallization process on the rim of a circular region of the electrode surface of radius $r_{\max}$. It is noted that $r_{\max}$, the r-coordinate of any of the two centers, can be obtained by substituting in Eq. 2 the y-coordinate of point P, the definition of p given by Eq. 3 as well as the equality $v = Mk/\rho$. Thus

$$r_{\max} = Mk(t^2 - tu)^{1/2}/\rho \qquad \text{[A-1]}$$

Figure 9 implies that those crystals that are formed at sites outside the circular region have no possibility whatsoever to reach point P in time t. It is only in the case of the instantaneous formation of crystals that each and every one of the centers formed within the circular region are also expected to cross point P in time t. Therefore

$$E_{\text{inst}} = \pi r_{\max}^2 N_0 \qquad \text{[A-2]}$$

where N_0 (cm^{-2}) is the maximum number of nuclei, per unit area of the electrode surface, that can possibly form at the potential concerned.

For any other case, we first consider an annulus dr within the circular region, Fig. 9, and determine the maximum period, t_u, during which all growth centers formed within the annulus reach P in time t. Figure 5 is a representation of a particular growth center of age t_g, centred at a point C within the annulus dr shown in Fig. 9. This is a very special center in that it is the last of the centers formed within the annulus that arrives at point P. Thus, only those growth centers within the annulus that are formed during a period t_u, defined by $t_u = t - t_g$, have any chance whatsoever to cross point P in time t. If the number of these growth units, per unit area of the electrode surface, is denoted by $N(t_u)$, then

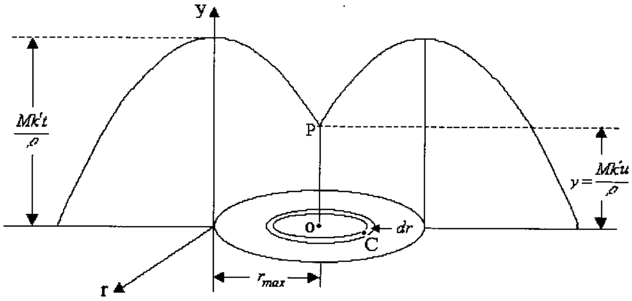

Figure 9. Graphical representation of two paraboloidal growth forms with just enough chance of reaching point P in time t.

$$E = \int_0^{r_{\max}} 2\pi r N(t_u) dr \qquad \text{[A-3]}$$

If the number of these growth units, per unit area of the electrode surface, is denoted by $N(t_u)$, then

$$N(t_u) = \frac{A}{A'}[1 - \exp(-A't_u)] \qquad \text{[A-4]}$$

The dependence of r, Fig. 5, as a function of u can be obtained by substituting t_g in place of t in Eq. A-1. Thus

$$r = \frac{Mk}{\rho}(t_g^2 - t_g u)^{1/2} \qquad \text{[A-5]}$$

On the other hand r, in terms of its own time step υ, can be written as

$$r = \frac{Mk}{\rho}\upsilon \qquad \text{[A-6]}$$

Combination of Eq. A-5 and A-6 with $t_u = t - t_g$ leads to the definition of the maximum permitted period, t_u, during which time all centers formed within the annulus are expected to cross point P. Thus

$$t_u = t - \frac{u + \sqrt{u^2 + 4\upsilon^2}}{2} \qquad \text{[A-7]}$$

The general form of the expectation, E, can, therefore, be derived by combining Eq. A-1, A-3, and A-4 with A-7. Hence

$$E = 2P \int_0^{\sqrt{t(t-u)}} \upsilon \left\{1 - \exp\left[-A'\left(t - \frac{u + \sqrt{u^2 + 4\upsilon^2}}{2}\right)\right]\right\} d\upsilon \qquad \text{[A-8]}$$

List of Symbols

A	nucleation rate constant, cm^{-2} s^{-1}
A'	expected frequency of the formation of a nucleus at a given site, s^{-1}
E	number of growth centres expected to cross a given point P in time t
F	Faraday constant, C mol^{-1}
i	current (A)
j	current density, A cm^{-2}
k	rate of crystal growth in the direction parallel to the electrode surface, mol cm^{-2} s^{-1}
k'	rate of the outward growth of crystals, mol cm^{-2} s^{-1}
M	molar mass of the deposit, g mol^{-1}
N_0	density of nucleation sites, cm^{-2}
P	$=\pi M^2 k^2 A/A'\rho^2$, s^{-2}
$r_{\max}$	the radius of a circular region of an electrode the growth forms within which may reach point P in time t
s	$=u\sqrt{P}$
S	the surface area of the deposit per unit area of the electrode surface
S_u	the fractional area of the deposit cut through by a slice of width dy
t	time (s)
υ	$=Mk/\rho$, growth rate in the direction parallel to the electrode surface, cm s^{-1}
υ'	$=Mk'/\rho$, growth rate in the direction perpendicular to the electrode surface, cm s^{-1}
V	the volume of the deposit per unit area of the electrode surface, cm^3/cm^2
z	the number of electron transfer per ion
ϵ	the ellipticity value
λ	$=A'/\sqrt{P}$
θ	nuclei contact angle
ρ	the density of the deposit, g cm^{-3}
τ	$=t\sqrt{P}$

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