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Theory of progressive nucleation and growth accounting for the ohmic drop in the electrolyte. I

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The theory of progressive nucleation under combined phase boundary and ohmic limitations of growth of the stable clusters is developed. The theoretical model is used for the interpretation of experimental current transients obtained in the case of mercury electrodeposition on platinum.

1. Introduction

Experimental studies of electrochemical nucleation often consist in the recording of potentiostatic current transients. The interpretation of the experimental results is usually based on a general theoretical expression for the overall current of growth of stable clusters given by the integral

$$i(t) = \int_0^t J(u)[1 - \theta(u)]i_1(t - u)\,du \qquad (1)$$

In Equation 1, J is the nucleation rate related to the free electrode surface, θ is the fractional surface area covered by nucleation exclusion zones and i_1 is the growth current of a single cluster.

Obviously, in order to derive a theoretical $i(t)$ relationship suitable for the interpretation of experimental current transients it is necessary to know the $J(t)$, $\theta(t)$ and $i_1(t)$ dependencies corresponding to the given experimental conditions.

Let us first consider the time dependence of the nucleation rate $J(t)$. The electrochemical phase formation on a foreign substrate takes place on a finite number, N_0, of active sites present on the electrode surface. The formula for $J(t)$, accounting for the progressive occupation of the active sites by the nuclei of the new phase, is

$$J(t) = N_0 A(t) \exp\left[-\int_0^t A(u)\,du\right] \qquad (2)$$

where the nucleation frequency A (s^{-1}) relates to one active site and can, in principle, be a time-dependent quantity.

Since at the very beginning of the nucleation process the decrease in the number of free active sites on the substrate can be neglected, the $J(t)$ dependence can be presented in a simpler form

$$J(t) = N_0 A(t) \qquad (2')$$

Many experimental studies [1–7] of the initial stage of nucleus formation have shown that $J(t)$ is a monotonic rising function of time, attaining a steady-state value $J_{st} = N_0 A_{st}$ after a time lag t_0. However, it is not a trivial problem to find the actual $J(t)$ dependence corresponding to the non-steady-state nucleation kinetics in a given experimental system.

For instance, if the nucleation kinetics are described in terms of the macroscopic Zeldovich–Frenkel theory the $J(t)$ dependence is given by [8]

$$J(t) = J_{st}\left[1 - 2\sum_1^{\infty}(-1)^n \exp(-n^2 t/\tau)\right] \qquad (3)$$

where τ is the time needed to reach a steady state size distribution of subcritical clusters on the electrode surface. At the same time, detailed nucleation experiments performed in some electrochemical systems [7, 9] have shown that the experimental time lag is not always related to the nucleation induction time, τ. Thus it was found that in the case of silver and mercury nucleation on platinum, the non-steady-state effects are most probably attributable to a preceding redox reaction leading to the appearance of active sites for nucleation on the initially oxidized platinum substrate. In this case the $J(t)$ relationship is given by [10]

$$J(t) = J_{st}[1 - \exp(-t/\tau_a)] \qquad (4)$$

where τ_a is the mean time of appearance of an active site on the electrode surface and, therefore, reflects the changes in the surface state of the substrate.

All this means that, in general, the non-steady-state nucleation kinetics may be determined by both pure nucleation effects and parallel electrochemical reactions modifying the electrode surface. Therefore, additional detailed experimentation is needed in most cases in order to find out the actual $J(t)$ relationship corresponding to a particular experimental system. That is why many authors prefer to work in the framework of the well known steady-state approximation ($J(t) = J_{st}$) completely ignoring the non-steady-state effects in the nucleation kinetics. We should however emphasize that this simple approach is justified only if it is previously proved that the experimental situation corresponds to a steady-state nucleus formation process.

As is seen from Equation 1 the calculation of a progressive current transient requires knowledge of the time functions $i_1(t)$ and $\theta(t)$. The electrochemical growth of a single cluster has been considered

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by many authors [11–19] and different expressions were obtained for i_1 depending on the rate determining step. In this study we shall calculate the current of progressive nucleation (Equation 1) using the $i_1(t)$ relationship derived for the case of combined phase-boundary and ohmic limitations of the growth process [19].

Finally, let us briefly comment upon the physical nature of the nucleation exclusion zones which play a significant role in the advanced stage of nucleus formation. Three different cases can, in principle, be considered:

(i) In dilute solutions zones of reduced concentration of electrodepositing species arise around the growing stable clusters. The $\theta(t)$ dependence accounting for the spread and overlap of such zones is derived in several papers [12, 20–23].

(ii) In concentrated electrolytes the nucleation exclusion zones are, in fact, zones of reduced overpotential appearing around the growing clusters as a result of the local ohmic drop in the electrolyte [14, 19, 24]. The $\theta(t)$ relationship for the case of combined phase-boundary and ohmic limitations will be considered elsewhere [25].

(ii) In the very initial stage of the growth process, when the ohmic and diffusion resistances can be neglected, the $\theta(t)$ dependence accounts only for the spreading and coalescence of the stable clusters themselves. Such phenomena have been studied in [12, 26–32] for different cluster geometries.

It is the aim of this study to consider the current of progressive nucleation in concentrated solutions of electrodepositing ions under the following assumptions:

(i) The nucleus formation is a steady-state process ($J(t) = J_{st}$).

(ii) Combined phase boundary and ohmic limitations determine the growth current of the single cluster.

(iii) The spread of nucleation exclusion zones can be neglected in the initial stage of the deposition process ($\theta(t) = 0$).

2. Theory

Detailed study [19] of the mixed phase boundary and ohmic controlled growth of the single cluster shows that in this case the exact $i_1(t)$ relationship can be presented only in the form of a numerical solution. Correspondingly, the current i of progressive nucleation should be obtained by numerical integration of Equation 1. The circles in Fig. 1 illustrate the results from the calculation of the current of steady-state nucleation and growth of hemispherical silver clusters ($z = 1$, $v_m = 1.71 \times 10^{-23}\,\text{cm}^3$) at the overpotential $\Delta E = 0.1\,\text{V}$. The values of the specific conductivity (k_e), the exchange current density (i_0) and the transition coefficient (α) used in these calculations are $k_e = 0.2\,\Omega^{-1}\,\text{cm}^{-1}$, $i_0 = 10\,\text{A}\,\text{cm}^{-2}$ and $\alpha = 0.8$, respectively. The steady-state nucleation rate is assumed to be $J_{st} = 1\,\text{s}^{-1}\,\text{cm}^{-2}$.

The influence of the non-steady-state nucleation kinetics on the progressive nucleation current is demonstrated by points in Fig. 1. These data are obtained using Equation 4 for $J(t)$ with $\tau_a = 0.1\,\text{s}$. As is seen, the non-steady-state effects cause a decrease in the current i in the very initial stage of the nucleation process. For sufficiently long time, $t > 1.5\,\text{s}$, both current transients almost coincide.

As shown in [19] the growth current of the single cluster can be approximately presented by the analytical relationship

$$i_1(t) = a\left[\frac{1 + bt}{(1 + 2bt)^{1/2}} - 1\right] \qquad (5)$$

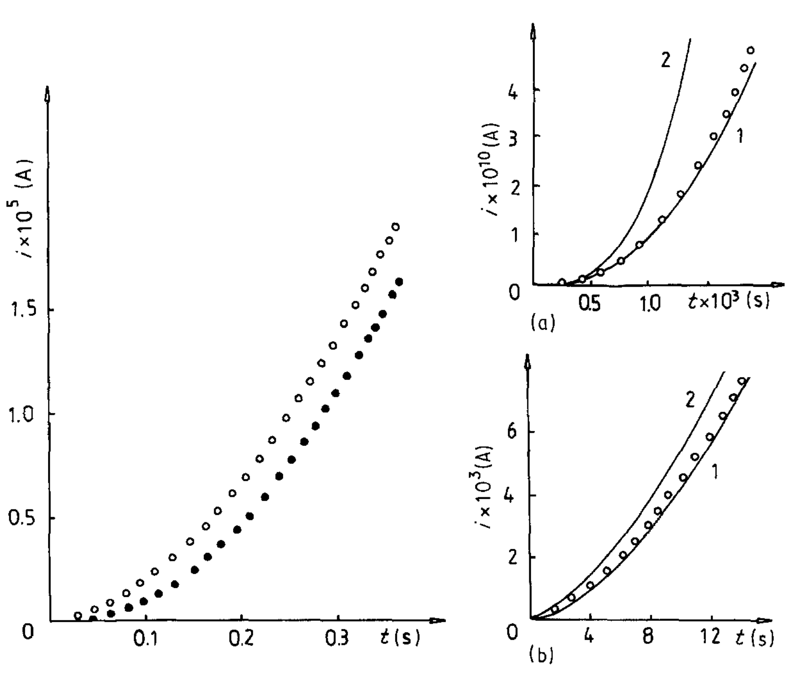

Fig. 1. Time dependence of the current of progressive nucleation and growth for a steady-state (○) and a non-steady-state (●) nucleation process.

Equation 5 holds good for short times if

$$a = a_s = \frac{2\pi C}{\psi i_0}\left(\frac{kTfk_e}{zeB}\right)^2 \tag{6}$$

$$b = b_s = \frac{2\psi^2}{\phi}\frac{CB}{kTfk_e}i_0^2 v_m \tag{7}$$

and for long times if

$$a = a_l = \frac{1}{\psi}\frac{2\pi\Delta EkTf^2k_e^2}{i_0 ze} \tag{8}$$

$$b = b_l = \frac{2\psi^2}{\phi}\frac{ze\Delta E}{fk_e(kT)^2}i_0^2 v_m \tag{9}$$

The parameters C and B in Equations 6 and 7 are given by

$$C = \exp(\alpha ze\Delta E/kT) - \exp[-(1-\alpha)ze\Delta E/kT]$$

$$B = \alpha\exp(\alpha ze\Delta E/kT) + (1-\alpha)\exp[-(1-\alpha)ze\Delta E/kT]$$

and ψ and ϕ are functions of the wetting angle γ. f is a dimensionless coefficient [19].

Combining Equations 5 and 1 with $J(t) = J_{st}$ and $\theta(t) = 0$ one obtains an approximate analytical expression for the progressive nucleation current

$$i(t) = J_{st}\frac{a}{3b}[(1+2bt)^{3/2} + 3(1+2bt)^{1/2} - 6bt - 4] \tag{10}$$

Lines 1 in Fig. 1a and b demonstrate Equation 10 for short and long times, respectively. As can be seen the analytical current transients are good approximations to the exact solution for times shorter than 2 ms and longer than 2 s, respectively.

For comparison line 2 in Fig. 1a presents the steady-state current transient in the case when the ion transition across the electrical double layer is the only rate determining step of the growth process. As is known in this case the current, i, of progressive nucleation is given by [12]

$$i(t) = J_{st}\frac{\psi^3}{\phi^2}\frac{4\pi}{3(ze)^2}v_m^2 i_0^3 C^3 t^3 \tag{11}$$

Correspondingly, line 2 in Fig. 1b shows the progressive current transient when the growth kinetics are determined only by ohmic limitations from the very beginning of the deposition process. Under these conditions the current of the single cluster is given by [11]

$$i_1(t) = 2\pi\left(\frac{v_m}{ze\phi}\right)^{1/2}(fk_e\Delta E)^{3/2}t^{1/2} \tag{12}$$

and after integration for the steady-state current transient one obtains

$$i(t) = J_{st}\frac{4\pi}{3}\left(\frac{v_m}{ze\phi}\right)^{1/2}(fk_e\Delta E)^{3/2}t^{3/2} \tag{13}$$

It is seen from Fig. 1a and b that the two limiting cases – pure phase boundary transition control and pure ohmic control of growth (lines 2) – differ significantly from the exact numerical solution.

Another approximate expression for the progressive nucleation current which is of particular interest for the interpretation of some experimental results is now considered. It was shown in [19] that within the time interval

$$\Delta t = \frac{190(kT)^2fk_e}{v_m ze\Delta E}\frac{1}{i_0^2}\frac{\phi}{\psi^2} \tag{14}$$

the current, i_1, of growth of the single cluster can be represented by

$$i_1(t) = 2\pi(fk_e\Delta E)^{3/2}(v_m/ze\phi)^{1/2}t^{1/2} - \frac{2\pi\Delta EkTf^2k_e^2}{\psi i_0 ze} \tag{15}$$

In this case substituting Equation 15 into Equation 1 gives the following progressive current transient

$$i(t) = J_{st}\frac{4\pi}{3}(fk_e\Delta E)^{3/2}(v_m/ze\phi)^{1/2}t^{3/2} - J_{st}\frac{2\pi\Delta EkTf^2k_e^2}{\psi i_0 ze}t \tag{16}$$

Thus the experimental data for the current i should be linearized in coordinates i/t against $t^{1/2}$ (Fig. 2). The slope and the intercept allow calculation of the exchange current density, i_0, and the steady-state nucleation rate J_{st}.

3. Experimental

3.1. *Electrolyte, electrodes, experimental method*

The electrolyte was 1 M aqueous solution of $Hg_2(NO_3)_2$ containing 3×10^{-6} M of the safronic dye used previously in another study [33]. The working electrode was a platinum polyfaced single crystal sealed in a glass tube. Bulk mercury was used as a reference electrode and all overpotentials were referred to its equilibrium potential E_0 ($\eta = E_0 - E$). The design of the electrochemical cell allowed permanent temperature control of the electrochemical

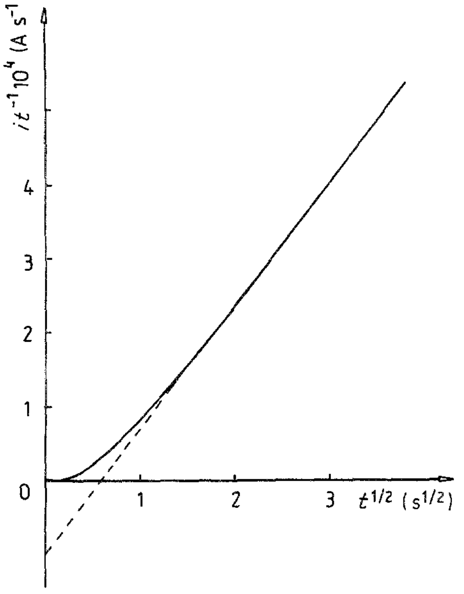

Fig. 2. Plot of it^{-1} against $t^{1/2}$ according to Equation 16.

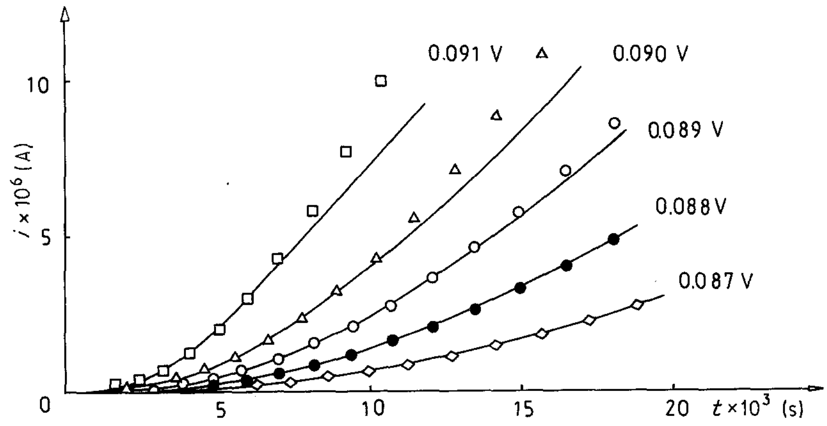

Fig. 3. Experimental current transients (lines) obtained at different overpotentials and calculated values of i (□, △, ○, ●, ◇) resulting from the best fit procedure.

system ($T = 308$ K) and direct microscopic observation of the working electrode.

The experimental study was performed by two independent methods.

1. Microscopic registration of the 'number of nuclei (N)–time (t)' relationships using the well known double pulse technique [1–7];
2. Simultaneous recording of potentiostatic current transients by means of a Tektronix 5441 storage oscilloscope.

The first method provides direct information on the nucleation rate ($J(t) = dN/dt$); the second one allows data for the nucleation and growth parameters to be obtained using a suitable theoretical model for the interpretation of the current transients.

4. Results and discussion

Figures 3 and 4 show sets of current transients and 'number of nuclei–time' relationships recorded in the same time interval. As can be seen from Fig. 4, after a short induction time the nucleation rate (the slope of the $N(t)$ curves) at each overpotential becomes constant. This justifies the steady-state approximation ($J(t) = J_{st}$) for the interpretation of the experimental current transients. Note, however, that the steady-state approximation is not justified when the nucleation occurs in pure mercury nitrate. Indeed, in this case the intercept, t_0, from the time axis of the $N(t)$ relationship (line 1 in the insert of Fig. 4) is commensurate with the length L of its linear portion corresponding to the steady-state nucleation process, $t_0/L = 0.5$. The same ratio calculated in the presence of the safronic dye (line 2 in the insert) is much lower, $t_0/L \sim 0.05$. As for the marked non-linear behaviour of the $N(t)$ curve (line 1) at long times, this is due to the spread and overlap of the nucleation exclusion zones which cannot be neglected in pure 1 M $Hg_2(NO_3)_2$ solution.

In the following we attempt to describe the experimental current transients (lines in Fig. 3) by numerical integration of Equation 1 with $\theta(t) = 0$, $z = 2$, $v_m = 4.90 \times 10^{-23}$ cm^3, $\alpha = 0.7$, $T = 308$ K. The steady-state nucleation rate, J_{st}, needed for this calculation is determined for each overpotential, η (except for $\eta = 0.088$ V), from the slope of the corresponding $N(t)$ relationship (Fig. 4). The value of the effective specific conductivity $fk_e = 0.057\,\Omega^{-1}\,\text{cm}^{-1}$ is found by an independent experiment measuring the growth current of macroscopic mercury droplets in the same experimental system and interpreting the current transients according to Equation 12. (the specific conductivity found by conductometric measurements in the same electrolyte is $k_e = 0.051\,\Omega^{-1}\,\text{cm}^{-1}$. This means that in the case under consideration f is close to unity ($f = 1.12$)). The value of the wetting angle, $\gamma = 140°$, is taken from [34]. Thus, only one experimental parameter is needed to calculate the progressive current

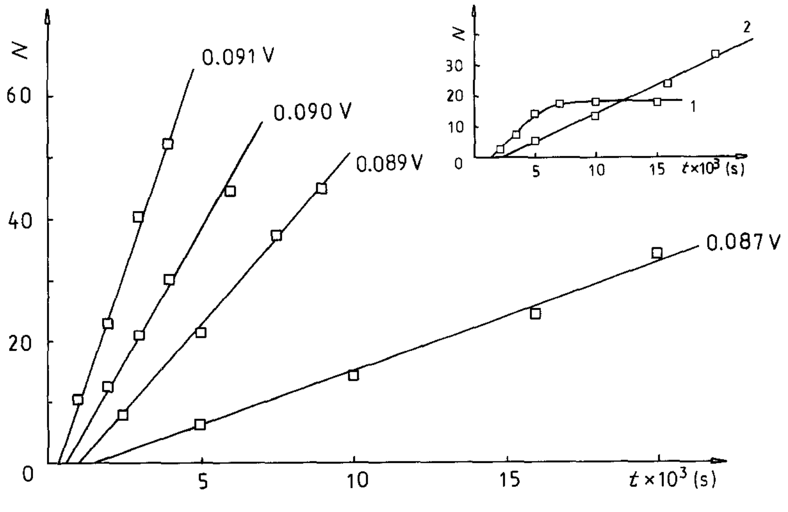

Fig. 4. 'Number of nuclei–time' relationships obtained for different overpotentials. Insert: $N(t)$ relationships obtained at $\eta = 0.087$ V in pure 1 M $Hg_2(NO_3)_2$ (line 1) and in presence of safronic dye (line 2).

transients, namely, the exchange current density, i_0, which must not depend on the overpotential, η.

The results of a best fit procedure based on Equation 1, with i_0 as a free parameter, are shown in Fig. 3 where the circles represent the fitted values of i obtained with $i_0 = 0.37\,\mathrm{A\,cm^{-2}}$ for $\eta = 0.087$ and $\eta = 0.090\,\mathrm{V}$, $i_0 = 0.36\,\mathrm{A\,cm^{-2}}$ for $\eta = 0.089\,\mathrm{V}$ and $i_0 = 0.41\,\mathrm{A\,cm^{-2}}$ for $\eta = 0.091\,\mathrm{V}$. Note that for each overpotential the fitting is restricted to a time interval corresponding to the linear parts of the $N(t)$ relationships. Thus we avoid the possible effects of spread and overlap of the nucleation exclusion zones which would decrease the overall progressive nucleation current. Such effects explain the disagreement between the experimental and the fitted transients observed at long times.

Since at $\eta = 0.088\,\mathrm{V}$ an experimental $N(t)$ relationship was not measured the fitting procedure at this overpotential was carried out in a different manner. A mean value of $0.38\,\mathrm{A\,cm^{-2}}$ was used for i_0 and J_{st} was determined as a free parameter. As is seen from the $\ln J_{\mathrm{st}}$ against η plot (Fig. 5), the value of the nucleation rate found in this way ($J_{\mathrm{st}} = 3.2 \times 10^3\,\mathrm{s^{-1}}$) agrees well with the data from the direct $N(t)$ experiment. From the slope of the linear plot of $\ln J_{\mathrm{st}}$ against η

$$\frac{\mathrm{d}\ln J_{\mathrm{st}}}{\mathrm{d}\eta} = (n_{\mathrm{k}} + \alpha)ze/kT \qquad (17)$$

the size n_{k} of the critical nucleus corresponding to this experiment was found to be $n_{\mathrm{k}} = 6$ atoms.

5. Conclusions

The present study proposes theoretical expressions for the progressive nucleation and growth current in concentrated solutions of the electrodepositing species. The theoretical model does not account for the spread and overlap of nucleation exclusion zones and should only be used for the interpretation of experimental current transients registered in the initial stage of the deposition process. The attempt to describe experimental 'current–time ' relationships obtained in the case of mercury electrodeposition demonstrated a good qualitative agreement with the theoretical considerations. It is worth noting here that the well known theoretical models for the progressive nucleation and growth current (Equations 11 and 13) failed to give a satisfactory description of these experimental transients: the data for the current could not be linearized in an i against t^3 plot as predicted by Equation 11. As for their analysis in an i against $t^{3/2}$ plot (see Equation 13), it led to unrealistic values for the specific conductivity ($k_{\mathrm{e}} \sim 8 \times 10^{-3}\,\Omega^{-1}\,\mathrm{cm^{-1}}$).

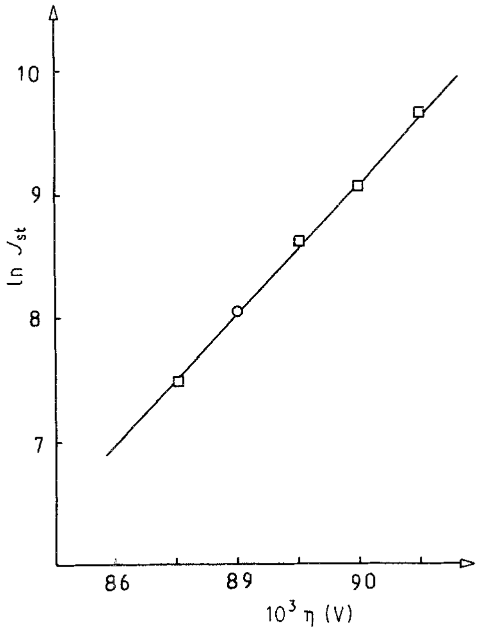

Fig. 5. Plot of $\ln J_{\mathrm{st}}$ against η for the data obtained from the $N(t)$ experiment (□) and by fitting of current transient (○).

Our experimental study consisted in simultaneous recording of $N(t)$ and $i(t)$ relationships and this allowed use of only one free parameter (i_0) for the theoretical analysis of the potentiostatic current transients. Thus, the fitting procedure, although performed for a relatively short part of the current transient, was rather sensitive to small changes (in the order of 10%) in the value of the exchange current density. It is known, however, that much experimental work on electrochemical phase formation is carried out by measuring only the 'current–time' dependence. In such cases the experimental results should be interpreted by using more free parameters, i_0, J_{st} and also the wetting angle, γ, and the effective specific conductivity, fk_{e}, if the last two quantities are not determined by independent measurements. Bearing in mind that the exact $i(t)$ dependence cannot be presented as an analytical function of time, it is clear that such an interpretation will involve complicated numerical calculations. The mathematical treatment can be simplified by the approximate analytical expression for the progressive nucleation current given by Equation 5. Of course, only approximate estimates of the nucleation and growth parameters will be obtained in this case.

Another crucial point in the analysis of experimental current transients is how to restrict the fitting procedure on the time scale where the fractional surface area, θ, is negligibly small. To find θ under given experimental conditions is in fact a rather complicated problem which will be considered in detail elsewhere [25]. An approximate estimate of this quantity can be made assuming that all nuclei appear simultaneously at the very beginning of the deposition process. In this case

$$\theta = N\pi\varrho^2/S \qquad (18)$$

where the zone radius, ϱ, is [19]

$$\varrho = i_1(t)/[2\pi f k_{\mathrm{e}}\Delta E(1 - \eta_\varrho/\Delta E)] \qquad (19)$$

In Equations 18 and 19, N is the number of nuclei formed instantaneously at the very beginning of a potentiostatic pulse of duration t. S is the electrode surface area and η_ϱ is the actual overpotential at the zone periphery. Obviously, such an estimate of θ would be strongly exaggerated when the nucleation is a ‘progressive’ ($N = J_{st}t$) and not an ‘instantaneous’ process.

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