Electrochemical nucleation and three-dimensional growth under mixed kinetic-diffusion control: analytical approximation of the current transient

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ABSTRACT

An analytical expression is derived for the current transient generated by electrochemical nucleation and three-dimensional growth of metal nanoparticles under mixed kinetic-diffusion control. The expression is the approximate solution of a novel mathematical model and describes the dependence of the current transient on nucleation rate, number density of active sites and charge transfer kinetic constant. Relative difference between the current predicted by the analytical expression and numerical solution of the original model is invariably lower than 0.1.

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1. Introduction

Electrodeposition is an effective technique to produce metal nanoparticles immobilized onto conductive substrates [1]. With this technique, deposits varying from compact nanocrystals to dendritic and fractal structures can be produced by varying the electrode potential and/or the concentration of precursor metal ion. Nanoparticles with purposefully tailored physicochemical properties can thus be produced provided that the influence of potential and metal ion concentration on morphology is characterized [2,3].

Electrodeposition includes the formation of nuclei at active sites and growth of nuclei by incorporation of precursor metal ions [4,5]. Active sites can be assumed to be randomly distributed over the electrode surface with number density N_0, while the evolution of the number density $N(t)$ of nucleated particles can be described as follows:

$$N(t) = N_0[1 - Exp(-At)] \qquad (1)$$

where A and t denote nucleation rate and time, respectively. Growth proceeds through diffusion of metal ions to nuclei, followed by charge transfer reaction at metal/solution interface. Diffusion, mixed kinetic-diffusion and kinetic control regimes can

be distinguished if the ratio between the diffusion and charge transfer characteristic times is much greater, around or much lower than unity, respectively. In any of these growth regimes, morphology and size of electrodeposited nanoparticles are influenced by N_0 and A [6]. Therefore, it is fundamental to evaluate how electrodeposition parameters (potential and metal ion concentration) influence A and N_0. For this purpose, mathematical models that predict the current transient as A and N_0 vary can be employed. These models can be fitted to experimental current transient data to estimate A and N_0.

Several models were proposed to compute the current transient generated by electrochemical nucleation and diffusion controlled growth [7–11]. However, little attention has been paid to analysing the case of mixed kinetic-diffusion control. If growth proceeds under mixed kinetic-diffusion control and models valid under diffusion control are implemented to fit current transient data, large errors in the estimated A and N_0 can be found [12]. The need for models predicting the current transient generated by nucleation and growth under mixed-kinetic-diffusion control was raised by several authors including, for example, Reazei et al. (2012) [13] and Milchev and Zapryanova, (2006a,b) [14,15]. A model was proposed in ref. [14] to compute the current transient generated during the early stage of electrodeposition in case of mixed kinetic-diffusion control. However, this model cannot reproduce the transition to planar diffusion induced by the overlapping of the diffusion boundary layers.

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In the present article, an approximate analytical expression is derived to compute the current transient generated by electrochemical nucleation and growth under mixed kinetic diffusion control. For this purpose, a mathematical model that extends the formulation presented in ref. [7] to the case of mixed kinetic-diffusion control is employed. The model cannot be solved in closed form. Nevertheless, an approximate analytical solution is derived. This approximate solution can predict the dependence of the current transient on nucleation rate, number density of active sites and charge transfer kinetic constant.

The article is structured as follows. In Section 1, the implemented mathematical model is described. In Section 2, the approximate model solution is derived. Final remarks end the article.

2. Mathematical model

The current generated by electrochemical nucleation and growth can be computed by multiplying the planar diffusion flux by the electrode area covered by diffusion zones [7]. These are the areas of the electrode towards which diffuses by planar diffusion the same flux that would be transferred, through three-dimensional spherical diffusion, to the isolated (that is, in absence of overlapping diffusion layers) hemispherical particles. Accordingly, the radius R_P of diffusion zones can be computed by solving the following equation:

$$J_P \pi R_P^2 = J_D 2\pi R_D^2 \tag{2}$$

where R_D is the radius of an isolated hemispherical particle, and J_P and J_D denote, respectively, the planar and the spherical diffusion fluxes under mixed kinetic-diffusion control. In the assumption of irreversible first-order charge transfer reaction, the following expressions are found for J_P and J_D [16]:

$$J_P = k_G C_0 \exp\left(\frac{k_G^2 t}{D}\right) \mathrm{erfc}\left(\frac{k_G t^{1/2}}{D^{1/2}}\right) \tag{3}$$

$$J_D = \frac{DC_0 k_G / D}{1 + R_D k_G / D} \tag{4}$$

where k_G, D and C_0 denote charge transfer kinetic constant, diffusion coefficient of metal ions and metal ion concentration, respectively. The following expression for R_D is derived by solving the mass balance of an isolated particle:

$$R_D = \frac{\sqrt{1 + 2Ht} - 1}{\gamma} \tag{5}$$

where $\gamma = k_G / D$ and $H = C_0 k_G^2 V_M / D$, V_M being the metal molar volume. By substituting Eqs. (3)–(5) in Eq. (2) and solving, the following expression can be derived for R_P:

$$R_P = \sqrt{\frac{4C_0 D(1 + Ht - \sqrt{1 + 2Ht})}{J_P \gamma \sqrt{1 + 2Ht}}} \tag{6}$$

The fractional area θ covered by diffusion zones can then be computed as follows:

$$\theta(t) = 1 - \exp(-E(t)) \tag{7}$$

where $E(t)$ is the expectation factor that diffusion zones cover a representative point at time t. $E(t)$ can be computed as follows:

$$E(t) = N_0 \pi R_P^2(t) - 2\pi N_0 \exp(-At) \int_0^t \exp(Au) R_P(u) \frac{dR_P(u)}{du} du \tag{8}$$

As aforementioned, the current transient can be computed by multiplying θ and J_P:

$$I_v(t) = z\,FJ_P[1 - \exp(-E(t))] \tag{9}$$

Improved predictions of the current transient are found in case of progressive nucleation $(A << DN_0)$ by replacing zFJ_P with $I_{ex}(t)/E(t)$ in Eq. (9), $I_{ex}(t)$ denoting the extended current density [9]:

$$I_{ex}(t) = zF \int_0^t 2\pi R_D^2(t - u) J_D(t - u) \frac{dN}{du} du \tag{10}$$

To identify the minimal set of parameters governing electrodeposition dynamics, the formulated model is rewritten in dimensionless form. The interparticle distance $N_0^{-1/2}$ and the characteristic diffusion time $(DN_0)^{-1}$ are employed to scale length and time, respectively. This allows rewriting the derived model as follows:

$$\bar{I}_v(\tau) = \bar{J}_P[1 - \exp(-E(\tau))] \tag{11}$$

$$E(\tau) = \pi \bar{R}_P^2(\tau) - 2\pi \exp(-K_N \tau) \int_0^\tau \exp(K_N u) \bar{R}_P(u) \frac{d\bar{R}_P(u)}{du} du =$$
$$= \pi \bar{R}_P^2(\tau) - 2\pi \exp(-K_N \tau) \bar{P}(0, \tau) \tag{12}$$

$$\bar{J}_P = K_{GD} \exp\left(K_{GD}^2 \tau\right) \mathrm{Erfc}\left(K_{GD} \tau^{1/2}\right) \tag{13}$$

$$\bar{J}_D = \frac{K_{GD}}{1 + K_{GD} \bar{R}_D} \tag{14}$$

$$\bar{I}_{ex}(\tau) = \int_0^\tau 2\pi \bar{R}_D^2(\tau - u) \bar{J}_D(\tau - u) d\frac{\bar{N}}{du} du \tag{15}$$

$$\bar{R}_D = \frac{\sqrt{1 + 2\bar{V}_M K_{GD}^2 \tau} - 1}{K_{GD}} \tag{16}$$

$$\bar{R}_P = \sqrt{\frac{4\left(1 + \bar{V}_M K_{GD}^2 \tau - \sqrt{1 + 2\bar{V}_M K_{GD}^2 \tau}\right)}{\bar{J}_P K_{GD} \sqrt{1 + 2\bar{V}_M K_{GD}^2 \tau}}} \tag{17}$$

The symbols adopted for dimensionless variables are defined by adding an over-line to the symbols adopted for corresponding dimensional variables. Main dimensionless parameters are defined as follows:

$$K_{GD} = \frac{k_G}{D\sqrt{N_0}}; \quad K_N = \frac{A}{DN_0}; \quad \bar{V}_M = V_M C_0;$$

$$\bar{J}_i = \frac{J_i}{D\sqrt{N_0} C_0} \ (i = P, D); \quad \bar{I}_k = \frac{I_k}{zFD\sqrt{N_0} C_0} \ (k = v, ex); \tag{18}$$

The proposed model can describe the current transient only if coalescence of particles can be excluded. This requires that the average particle diameter is lower than the interparticle distance, that is $2\bar{R}_D < 1$ (equivalently, in dimensional form, $2R < N_0^{-0.5}$). In applications of practical relevance, N_0 varies between 10^8 and