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Two-dimensional progressive and instantaneous nucleation with overlap: The case of multi-step electrochemical reactions

Alexander Milchev*, Ivan Krastev

Rostislaw Kaischew Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. G.Bonchev Str. Bl. 11, 1113 Sofia, Bulgaria

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Dedicated to the memory of our teachers, Professor Rostislaw Kaischew and Professor Evgeni Budevski, who contributed significantly to the theoretical and experimental studies of the two- and three-dimensional electrochemical nucleation and growth phenomena.

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ABSTRACT

Two-dimensional nucleation and growth phenomena are examined in case of multi-step electrochemical reactions accounting for the cluster overlap. Theoretical expressions are derived for the current of progressive and instantaneous nucleation at a multinuclear-monolayer, direct attachment mechanism of growth at a constant overpotential.

1. Introduction

The process of two-dimensional nucleation was first considered by Gibbs [1] and Volmer and Weber [2] and Volmer [3]. Later, significant results on this subject were reported also by Brandes [4], Erdey-Gruz and Volmer [5], Kaischew and Stranski [6], Kaischew [7,8], Kaischew et al. [9] and Budevski et al. [10–14] (see also the books of Volmer [15], Thirsk and Harrison [16], Budevski et al. [17], Milchev [18] and the references cited therein). The authors of the above mentioned articles, who have examined the two-dimensional *electrochemical* nucleation and growth phenomena considered one-step ions' discharge. It is our purpose to comment upon the more general case of multi-step reactions, thus supplementing the existing theory of electrochemical two-dimensional progressive and instantaneous nucleation.

Parsons [19] was among the first who made significant contribution to the theory of multi-step electrochemical reactions. Later his results were commented and included in the books of Bockris and Reddy [20], Damaskin and Petrii [21] and Damaskin et al. [22] (see also the recent review article of Fletcher [23] and the references cited therein).

Recently we examined the nucleation and crystal growth phenomena in case of multi-step electrochemical reactions [24–30], deriving theoretical expressions both for the linear size and the growth current of single two- and three-dimensional (2D and 3D) clusters and for the currents of progressive and instantaneous nucleation. The more general case of growth under combined charge transfer and diffusion limitations was considered for single 3D clusters and experimental data were obtained for the exchange current density. For, neither the cluster overlap nor the overlap of nucleation exclusion zones was taken into account in [24–30] the present article extends the theoretical considerations of two dimensional nucleation accounting for the 2D clusters overlap at a multinuclear-monolayer, direct attachment mechanism of growth.

2. Theory

If a single circular or polygonized 2D cluster grows on a flat surface at a constant overpotential η and ions' transfer control, the theoretical formulae for the time dependence of the cluster's edge length $l_{2D}(t)$, the growth rate $\upsilon_{2D} = dl_{2D}(t)/dt$, the growth cur-

* Corresponding author. Tel.: +359 2 979 2557/2558/8727550; fax: +359 2 971 26 88.
E-mail address: amilchev@ipc.bas.bg (A. Milchev).

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Nomenclature

l_{2D}	2D cluster edge length (cm)
h	2D cluster's height equal to the atomic diameter (cm)
b, b'	non-dimensional numerical constants depending on the 2D cluster geometry
$I_{1,2D}$	growth current of a single 2D cluster (A)
j_{2D}	current density of stationary 2D progressive nucleation without overlap (A cm^{-2})
$I_{st,2D}$	stationary nucleation rate (cm^{-2} s^{-1})
Q_{2D}	non-dimensional quantity accounting for the overpotential dependence of the growth current in case of single- and multi-step electrochemical reactions
$j_{2D,p}$	current density of progressive 2D nucleation with overlap (A cm^{-2})
$j_{2D,ins}$	current density of instantaneous 2D nucleation with overlap (A cm^{-2})
N_0	number of instantaneously formed 2D nuclei (cm^{-2})

rent $I_{1,2D}(t)$ and the current density $j_{2D}(t)$ of stationary progressive nucleation without cluster overlap read [27,29]:

$$l_{2D}(t) = \frac{j_{0,2D}b'V_M}{2bzF}Q_{2D}t \tag{1}$$

$$\upsilon_{2D} = \frac{j_{0,2D}b'V_M}{2bzF}Q_{2D} \tag{2}$$

$$I_{1,2D}(t) = \frac{j_{0,2D}^2 b'^2 hV_M}{2bzF}Q_{2D}^2 t \tag{3}$$

$$j_{2D}(t) = \frac{j_{0,2D}^2 b'^2 hV_M}{4bzF}I_{st,2D}Q_{2D}^2 t^2 \tag{4}$$

In Eqs. (1)–(4) $j_{0,2D}$ is the exchange current density referred to unit edge area, V_M is the molar volume of the depositing metal, $I_{st,2D}$ is the stationary nucleation rate, h is the cluster's height, which equals the atomic diameter and b and b' are constants depending on the cluster geometry. Thus $b=1$, $b'=4$ for a quadratic cluster, $b=(3/2)\sqrt{3}$, $b'=6$ for a hexagon, $b=\pi$, $b'=2\pi$ for a disk with a radius $l(t)$, etc. The quantity Q_{2D} in Eqs. (1)–(4) determines the overpotential dependence of the growth process and for a z-step, one-electron reaction is given by [27]:

$$Q_{2D,1} = \exp\left[\frac{\alpha_1 zF\eta}{R'T}\right] - \exp\left[-\frac{(1-\alpha_1)zF\eta}{R'T}\right] \tag{5}$$

In the more complex case when z electrons are exchanged in z one-electron successive steps, z_f of which are fast and precede the rate determining one, that is repeated ν times and is followed by $z-z_f-\nu$ fast steps the quantity Q_{2D} in Eqs. (1)–(4) reads [27]:

$$Q_{2D,2} = \exp\left[\left(\frac{z_f}{\nu}+\alpha_2\right)\frac{F\eta}{R'T}\right] - \exp\left[-\left(\frac{z-z_f}{\nu}-\alpha_2\right)\frac{F\eta}{R'T}\right] \tag{6}$$

2.1. Progressive nucleation

Suppose now that 2D circular, disk-shaped clusters ($b=\pi$, $b'=2\pi$) appear progressively on a plain surface and may overlap during the growth. In this case, the current $j_{2D,p}(t)$ of progressive two-dimensional nucleation is given by the general formula (see e.g. [27] and the references cited therein):

$$j_{2D,p}(t) = I_{st,2D}\int_0^t [1-\theta(u)]I_{1,2D}(t-u)\,du \tag{7}$$

where $I_{1,2D}(t-u)$ is the growth current, at the time moment t, of a single 2D cluster formed at the time moment $u<t$ and $\theta(u)$ is the actual surface fraction covered by growing two-dimensional crystals at $t=u$. According to the Kolmogorov–Avrami theory [31–34], the latter quantity is given by:

$$\theta = 1-\exp(-\theta_{ext}) \tag{8}$$

where

$$\theta_{ext} = \pi I_{st,2D}\int_0^t\left[\int_0^t \upsilon_{2D}(u')\,du'\right]^2 du \tag{8'}$$

is the fraction of the total surface area, which would be covered by the 2D clusters if none overlap.

Substituting Eqs. (3), (8) and (8′) into Eq. (7) and solving the integrals, for the current $j_{2D,p}(t)$ of progressive two-dimensional nucleation accounting for the cluster overlap one obtains:

$$j_{2D,p}(t) = \frac{\pi}{zF}hV_M j_{0,2D}^2 I_{st,2D}Q_{2D}^2 t^2 \exp\left[-\frac{\pi}{3(zF)^2}V_M^2 j_{0,2D}^2 I_{st,2D}Q_{2D}^2 t^3\right] \tag{9}$$

The *current–time* relationship given by Eq. (9) displays a maximum at time $t=t_{p,m}$,

$$t_{p,m} = \left(\frac{2^{1/2}zF}{\pi^{1/2}V_M j_{0,2D}I_{st,2D}^{1/2}Q_{2D}}\right)^{2/3} \tag{10}$$

and the value of the maximal current $j_{2D,p}(t_{max})$ is given by

$$j_{2D,p,m} = \left(\frac{4\pi zFh^3 j_{0,2D}^2 I_{st,2D}Q_{2D}^2}{V_M}\right)^{1/3}\exp\left(-\frac{2}{3}\right) \tag{11}$$

Note that the product $j_{2D,p,m}t_{p,m}$,

$$j_{2D,p,m}t_{p,m} = \frac{2zFh}{V_M}\exp\left(-\frac{2}{3}\right) \tag{12}$$

contains only material constants characterizing the deposited species and does not depend on the nucleation and growth kinetics.

It is readily seen that Eq. (9) can also be presented as a linear relationship, $\ln[j_{2D,p}(t)/t^2]$ vs. t^3,

$$\ln\left[\frac{j_{2D,p}(t)}{t^2}\right] = \ln\left(\frac{\pi}{zF}hV_M j_{0,2D}^2 I_{st,2D}Q_{2D}^2\right) - \frac{\pi}{3(zF)^2}V_M^2 j_{0,2D}^2 I_{st,2D}Q_{2D}^2 t^3 \tag{9'}$$

with a slope $[\pi/3(zF)^2]V_M^2 j_{0,2D}^2 I_{st,2D}Q_{2D}^2$ and an intercept $\ln[(\pi/(zF)hV_M j_{0,2D}^2 I_{st,2D}Q_{2D}]$, which allows a straightforward interpretation of experimental results.

Fig. 1 (circles) shows a theoretical current transient calculated by means of Eq. (9) using the following values of the constants involved[1]: $z=2$, $z_f=0$, $\nu=1$, $V_M=7.1$ cm^3/mol, $h=2.4\times10^{-8}$ cm, $\alpha_2=0.5$, $\eta=0.030$ V, $j_{0,2D}=0.2$ A cm^{-2}, $I_{st,2D}=1\times10^5$ cm^{-2} s^{-1}, $T=298$ K and $Q_{2D}=Q'_{2D,2}=1.62$, which correspond to a two-step electrochemical reaction of type (a) (Table 1).

In order to evaluate the significance of the multi-step electrochemical reactions' effect let us now assume that the circles in Fig. 1 represent an experimental current transient and fit it making use of a theoretical equation containing two free parameters, P_1 and P_2:

$$j_{2D,p}(t) = P_1 t^2\exp(-P_2 t^3) \tag{13}$$

[1] The values of z, z_f, ν, V_M and h correspond to copper electrodeposition. The values of α_2, η, $j_{0,2D}$ and $I_{st,2D}$ are arbitrarily chosen.