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Mass transfer during metal electrodeposition into the pores of anodic aluminum oxide from a binary electrolyte under the potentiostatic and galvanostatic conditions

Daniil A. Bograchev[a], Vladimir M. Volgin[b,1], Alexey D. Davydov[c,*,1]

[a] National Research University Higher School of Economics (HSE), ul. Tallinskaya 34, Moscow, 123458 Russia
[b] Tula State University, pr. Lenina 92, Tula, 300012 Russia
[c] Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119071 Russia

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ABSTRACT

The mass transfer during the nanowire formation by the metal electrodeposition into the pores with a high aspect ratio from a binary electrolyte is studied theoretically. The application of quasi-steady-state approximation is justified. The equations for the ion concentration and electric potential at the bottom and in the mouth of the pores, the reaction overpotential, and the variation of the current density with time are obtained. The problem of time dependence of unfilled pore part length is solved numerically. The distinctions between the results obtained under the potentiostatic and galvanostatic conditions are demonstrated.

1. Introduction

In recent years, a large number of works have been devoted to the formation of new nanomaterials by using the method of metal or alloy electrodeposition into the pores of the films of anodic aluminum oxide or another dielectric material, which is used as a template, for example, [1–18]. In the anodic aluminum oxide, the pore length (commonly, several tens μm) is by two-three orders of magnitude larger than their diameter.

Great interest in these systems is associated with their potential application in the fields of high-density magnetic memories, optoelectronic devices, catalytically active electrodes for the analysis of solution composition, etc.

Fig. 1 gives a scheme of a fragment of porous anodic oxide film with partially filled pores.

The majority of published works are experimental; they showed a possibility of commercial production of these systems. In these works, the process was performed by using various electric modes: potentiostatic, alternating current, pulsed, galvanostatic modes and a combined mode involving a transition from the galvanostatic to the potentiostatic conditions. For example, the potentiostatic mode was used in [7,12,13,14,16], and the galvanostatic mode was used in [19–21].

Several works [7,15,16,22–24] were devoted to the analysis of mass transfer as applied to the metal electrodeposition in the cylindrical pores with a high aspect ratio (a ratio between the pore length and diameter), predominantly, in porous aluminum oxide and in the track-etched polycarbonate membrane. The problem is rather complex; therefore, some authors of theoretical works used not always justified simplifications.

Valizadeh et al. [7] considered the cobalt deposition into the pores of track-etched polycarbonate membrane. A current flowing through a pore was determined by the equation for the steady-state limiting current to the recessed disk [25]. From the condition of equal flows of electroactive ions through a pore and through a corresponding region of outer non-steady-state diffusion layer, which is described by the Cottrell equation, the fractional surface pore area was determined. In other words, the current in the pore was considered to be steady-state and, in the outer diffusion layer, non-steady-state. As a result, an analytical equation for the variation of the current density with the time was obtained. This approach leads to the time dependence of the fractional surface pore area and, consequently, the membrane porosity.

Schuchert et al. [12] proposed a quantitative model for the potentiostatic copper electrodeposition into the pores of track-etched polycarbonate membranes. Based on the analysis of experimental data, the authors recognized six periods of time,

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[*] Corresponding author. Tel.: +7 495 9547216.
E-mail address: davydov@elchem.ac.ru (A.D. Davydov).
[1] ISE member.

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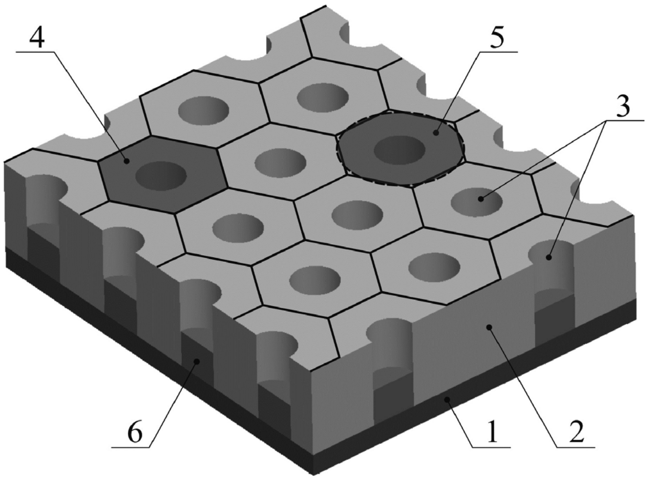

Fig. 1. The template with partially filled pores. (1) Conducting layer serves as the cathode, (2) template, (3) pores, (4) template surface area corresponding to a single pore, (5) axisymmetric approximation of the template surface area corresponding to a single pore, (6) a nanowire that partly fills a pore.

which correspond to various stages of the process. A short period of time, when the copper deposition is controlled by the charge transfer. Then a transition period, when the contributions of the charge transfer and diffusion are comparable. In the following three periods, to diffusion control takes place. For each period of time, the metal deposition process was theoretically analyzed. For the stages of diffusion control, the Cottrell equation was used; its parameters were adjusted using the experimental data. However, no equations for determining the boundaries of each period were presented.

A similar approach was used by Philippe et al. [26]. The main difference is the substitution of equation of non-steady-state diffusion to a hemicylindrical electrode lying on an infinite, insulating plane [27] for the Cottrell equation for a plane electrode. In [26], it was not explained how the equations for a hemicylindrical electrode can be used for a plane electrode located at the bottom of cylindrical pore. As well as in [12], in [26], the kinetics of electrode reaction was taken into consideration by using a model involving the equation of one-dimensional non-steady-state diffusion in the semispace and the Butler-Volmer equation. This means that the kinetics of electrode reaction was considered ignoring the geometric characteristics of a pore.

Hariri et al. [28] used a model proposed in [26] to study the electrodeposition of gold nanowires and nanotubes.

Lopes et al. [15] developed a model for the metal electrodeposition inside the porous anodic alumina template, which deals with only one potentiostatic pulse applied to one pore. The authors used a two-dimensional mathematical model involving the Laplace's equation for the distribution of potential over the template and the equation of non-steady-state diffusion inside a pore and in the electrolyte solution layer adjacent to the pore. Based on the numerical solution of transfer equations throughout the computational region (in general case, the model is three-dimensional and is characterized by a high ratio between the template thickness and pore diameter), the time dependences of the current density were obtained for two limiting cases: electrically inactive and electrically active pore walls.

Lopes et al. [15] obtained a solution for a plane problem, i.e. actually, the results correspond not to a cylindrical pore, but to a groove with rectangular cross-section and relatively small ratio between its length and width. No time dependences of the current, concentration of metal cations in the pore mouth and on the surface of growing deposit in the explicit form were presented in the work. This gives no way of determining the pore filling time. In addition, the model ignored real value of membrane porosity.

Ghahremaninezhad and Dolati [29] proposed a mathematical model of the growth of cobalt nanowires in the pores of aluminum oxide membrane. It was assumed that the distribution of concentration of metal cations in a pore was linear, and the concentration of cations in the pore mouth was determined by the condition of equal fluxes of electroactive ions in the pore and in the outer diffusion layer. The analytical equations for the current density (a modified Cottrell equation) was obtained in the absence of overlapping of outer diffusion layers of neighboring pores, in the case of their partial overlapping, and their complete overlapping. However, some assumptions made by the authors, for example, a constant rate of nanowire growth (this assumption corresponds to a constant current) are inconsistent with the modified Cottrell equation obtained in the work.

Blanco et al. [16] performed the experiments on the copper deposition in track-etched polycarbonate membranes in the diffusion mode in excess of supporting electrolyte. The experimental results were analyzed theoretically within the models of one-dimensional diffusion in a pore and spherical or plane non-steady-state diffusion in the outer diffusion layer taking into account that the fluxes are conjugated in the pore's mouth.

The process was divided into three stages. The first stage: one-dimensional non-steady-state diffusion inside a pore; the second stage: linear diffusion inside a pore and diffusion in the outer hemispherical diffusion layer outside a pore; and the third stage: linear diffusion both inside a pore and in the outer diffusion layer. It is shown that, in this case, the duration of the first stage is less than 0.1 s and the duration of the second stage is about 0.001 s. Thus, two first stages do not have a noticeable effect on the pore filling, which proceeds at the third stage. As well as in [7], the transfer processes at the third stage were analyzed by using the Cottrell equation for the diffusion in a semispace to a plane electrode. The calculated and experimental data agreed well only at the first stage corresponding to the growth of diffusion layer inside a pore. The second short stage cannot be adequately determined by the experimental data. In the analysis of the third stage, the authors of [16] explained a deviation of the calculated results from the experimental data by the development of natural-convective instability in the solution above the template surface [30].

In [31], the equation of non-steady-state diffusion inside a pore under the conditions of limiting current was used as the mathematical model. The outer diffusion layer was ignored; the concentration of metal cations in the pore mouth was taken to be equal to the concentration in the bulk electrolyte solution. It was shown that, under these simplifications, the distribution of the concentration of electroactive ions inside a pore depends on a single dimensionless parameter β. The value of this parameter is determined by the electrochemical equivalent of the metal, the current efficiency, and the bulk concentration of electroactive ions. As it follows from the results obtained in [31], the non-steady ionic transport in the pore should be taken into account only at $\beta > 0.25$ (Fig. 2a in [31]), whereas in the majority of practically important cases, $\beta < 0.01$. In these cases, the quasi-steady-state approximation may be used.

Bograchev et al. [22] used a model of electrochemical growth of metal deposit in the pores of anodic aluminum oxide under the potentiostatic conditions. The model took into consideration the transfer of metal cations inside the pores and in the outer diffusion layer of a constant thickness, which was determined by the outer hydrodynamic conditions. The kinetics of charge transfer through the interface was described by the equation of mixed kinetics. The time dependences of the current and unfilled pore length, the equation for calculating the pore filling time, and other