Modeling of Metal Electrodeposition Through Colloidal Crystal Mask

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The metal electrodeposition through a colloidal crystal mask is simulated by using the multi-level approach. The space near the cathode surface is divided into several zones with different characteristics of transport processes. In each zone, 1D or 3D approximations may be used. In the zones of 1D type, the distributions of electroactive ion concentration and potential are calculated by the analytical equations; in the zones of 3D type, the numerical finite element method is used. The transport processes in the neighboring zones are conjugated by using the condition of equal currents through the boundary between these zones.

In this work, we develop the method of simulation of metal electrodeposition in the solution with an excess of supporting electrolyte: the migration transfer of all ions is taken into account and the electrode reaction governed by the equation of Butler-Volmer is considered. The developed mathematical model involves the Laplace equation for the concentration of electroactive ion, effective concentration of supporting electrolyte, and potential. It is shown that the model can be reduced to a single Laplace equation for the concentration of electroactive ion with the corresponding boundary conditions.

As a result of modeling, the distributions of electroactive ion concentration and cathodic current density are obtained for various instants of time (deposit of various thicknesses). The calculated dependences of current on the deposit thickness agree with the literature data. The relative amplitude of current oscillations, which is determined by the variation of relative pore area along the height of colloidal crystal, depends on the ratio of an average current density to the limiting current density: when an average current approaches the limiting one, the relative amplitude of current oscillations decreases.

1. Introduction

Colloidal crystals, which are formed by orderly arranged monodispersed spherical particles, are used as the templates for production of nano-ordered structures of metals, semiconductors, inorganic oxides, polymers, diamond, glassy carbon, etc. (Velev et al., 1999; 2000; Stein, 2001; Braun and Wiltzius, 2002; Texter, 2003; Meseguer, 2005; Asoh et al., 2007; Paquet and Kumacheva, 2008; Nair and Vijaya, 2010).

In general case, the production of nano-ordered structures by using the colloidal crystal mask involves three stages:

(1) the self-assembling of mask on the substrate surface;
(2) filling the pores between the template spherical particles;
(3) removal of template by chemical or thermal etching. (In some cases, for example, in the production of photonic crystals, the template is not removed.)

The electrochemical deposition through a colloidal crystal mask enables one to produce high-density metal deposits, which exhibit no considerable shrinkage when the template is removed (Bartlett et al., 2002; Spada et al., 2008; Xia et al., 2010). In addition, the deposits of various metals with prescribed structure can be produced, and the thickness and properties of deposited layer can be controlled accurately.

During the potentiostatic electrodeposition through multilayer colloidal crystal, the current oscillations are observed. They are explained by the variation in the electroactive area, when the pores between the
particles are filled in the course of deposit growth (Sumida et al., 2002; Spada et al., 2008; Sapoletova et al., 2010). This is caused by (1) the presence of defects in the colloidal crystal; (2) nonuniform rate of deposit growth over the electrode surface; and (3) nonplanar deposit front in a pore. Depending on the electrodeposition conditions, an average current over an oscillation period can decrease (Sumida et al., 2002) or increase with time (Sapoletova et al., 2010).

In spite of a large number of the works devoted to the experimental study of electrodeposition through a colloidal crystal mask, only some papers are concerned with the theoretical study of the process (Newton et al., 2004; Volgin et al., 2012) in these papers the Laplace’s equation in a unit cell with triangular cross-section for the face-centered cubic (fcc) colloidal crystal was solved numerically. The process of pore filling and the variation of the mass-transfer conditions with increasing deposit thickness were not considered. Recently, Bograchev et al. (2013a; 2013b) have proposed approximate models and the methods of calculation of mass-transfer processes and pore filling for the metal electrodeposition through a mask with regularly arranged cylindrical pores.

This work is devoted to the numerical simulation of mass-transfer processes in the metal electrodeposition through a colloidal crystal mask with regard for the variation of deposited layer thickness with the time.

2. Statement of problem and basic equations

In the electrodeposition through a colloidal crystal mask, several zones near the electrode can be recognized (Figure 1):
(I) a zone adjacent to the substrate, where the distributions of concentration and potential are 3D (zone of colloidal crystal mask);
(II) the outer part of diffusion layer, where the distributions of concentration and potential can be considered as 1D (zone of diffusion layer in electrolyte solution);
(III) – bulk electrolyte solution, where the concentrations are constant and potential varies linearly as we move away from the substrate with colloidal crystal mask.

We will restrict our consideration to the case of metal electrodeposition from the solution containing three types of ions, for example, a solution of metal salt and supporting electrolyte containing a common anion. Within the theory of dilute electrolytes, under the assumption of solution electroneutrality, the equations of ionic transport in the diffusion layer adjacent to the substrate can be written as follows:

$$\frac{\partial c_1}{\partial t} = D_1 \nabla^2 c_1,$$

$$\frac{\partial c_2}{\partial t} = D_2 \nabla^2 c_2 + \nabla \left[ \frac{Fz_2 D_1 c_1}{RT} \nabla \phi \right],$$

$$\frac{\partial c_3}{\partial t} = D_3 \nabla^2 c_3 + \nabla \left[ \frac{Fz_3 D_1 c_1}{RT} \nabla \phi \right],$$

$$z_1 c_1 + z_2 c_2 + z_3 c_3 = 0$$

where $c_1$, $D_1$, and $z_2$ are the concentration, diffusion coefficient, and charge of ions of the $k$-th type ($k=1$ for electroactive metal cation, $k=2$ for supporting electrolyte cation, and $k=3$ for the common anion); $\phi$ is the potential in the solution; $t$ is the time; $F$ is the Faraday’s constant; $R$ is the gas constant; and $T$ is the temperature of solution.

In system of equations (1), the migration term in the transport equation for the electroactive component ($c_1$) is omitted. This is allowable at a high concentration of indifferent electrolyte (Volgin and Davydov, 2006), i.e. at

$$c_2 \gg c_1$$

(2)

where subscript $b$ corresponds to the bulk electrolyte solution.

Passing to the dimensionless variables, diameter of spherical particles $d_{sph}$ is taken as a unit length, $RT/F$ is taken as a unit potential, $c_1$ is taken as a unit concentration, and $d_{sph}^2/D_1$ is taken as a unit time. A new variable, which characterizes the concentration on inactive ions, is introduced:

$$C_q = C_2 - C_2^s + C_3 - C_3^s$$

(3)
Then, system of equations (1) can be written as follows:

$$
\frac{\partial C_i}{\partial \tau} = D_i \frac{\partial^2 C_i}{\partial z^2} + D'_i \frac{\partial C_i}{\partial z} - \Phi_i = 0
$$

(4)

where $C_i$ is the dimensionless concentration of ions of the $k$-th type and $\tau$ is the dimensionless time;

$$
D_i = \frac{D_k D_1 (z_i - z_k)}{D_1 (z_i - z_k) D_k}
$$

To solve the above system of equations, it is necessary to determine the shape and sizes of computational region and prescribe the corresponding boundary conditions. Here, a unit cell with triangular cross-section is taken as a computational region (Volgin et al., 2012); the lower boundary of the cell corresponds to the growing metal deposit surface ($Z = Z_{\text{bottom}}$), and the upper boundary ($Z = Z_{\text{top}}$) is offset by a certain distance (about $d_{\text{dep}}$) from the outer boundary of colloidal crystal mask, so that the concentration and potential on it are independent of the lateral coordinates (Figures 1d, 1e).

The boundary conditions for system of equations (5) can be written as follows.

$$
\Delta C_i = 0
$$

$$
\Delta C'_i = 0
$$

$$
\Delta \Phi = 0
$$

(5)
\[ \frac{\partial C_s}{\partial t} = \frac{\partial D_s}{\partial x} = \frac{\partial \Phi}{\partial x} = 0 \] (6)

On the upper boundary of computational region:

\[ C_1 |_{x=x_{top}} = C_1', \quad C_4 |_{x=x_{top}} = 0, \quad \Phi |_{x=x_{top}} = \Phi' \] (7)

On the lower boundary of computational region (the metal deposit surface):

\[ \frac{\partial C_1}{\partial Z} |_{Z=Z_{bottom}} = -I_0 e^{-(\alpha-\alpha)z} - C_1 e^{\alpha\Phi \Phi} \] (8)

Here, \( \Phi \) is the potential on the outer boundary of diffusion layer.

Substituting (9) into boundary conditions (6) – (8), we obtain the boundary value problem for the concentration of electroactive cations:

\[ \Delta C_1 = 0 \]

Thus obtained mathematical model was used to simulate the metal electrodeposition through a colloidal crystal mask.

3. Results and discussion

The numerical solution of boundary value problem (10) was performed by the finite element method. The mesh parameters were chosen so that the calculated results were independent of the mesh step and the number of nodes (Figure 2).

In the calculations, the dimensionless potential on the outer boundary of diffusion layer (the resistance of bulk electrolyte solution was ignored, because the electrode potential on the outer boundary of diffusion layer rather than a voltage was imposed) was taken to be 1 and 5; the diffusion layer thickness was taken to be 100; the number of particle layers, 3. The computational region thickness was taken to be 4 (this provided uniform distributions of concentration and current density over the outer boundary of computational region). The dimensionless exchange current density was taken to be 0.05. It was determined as a ratio of the exchange current density to the limiting current density, which was calculated by the diameter of spherical particles. The diameter of particles is rather small; therefore, the limiting current density is rather high and the dimensionless current density is much smaller than unity. A ratio between the concentration of supporting electrolyte and the concentration of electroactive ions was taken to be 10. All diffusion coefficients were taken to be \( 10^{-9} \) m²/s; the ion charges, +1 and -1.

Figure 2 shows the distributions of concentration of electroactive ion over the growing deposit surface for various instants of time (various deposit thickness).
Figure 2: (a, c) A mesh of finite elements and (b, d) the distribution of concentration of electroactive ion at a dimensionless imposed voltage $\Phi = 5$: (a) and (b) $Z_{\text{bottom}} = 0$ (corresponds to the onset of metal deposition); (c) and (d) $Z_{\text{bottom}} = 1.32$ (corresponds to the instant of time when the deposit front is located in the plane passing through the centers of spherical particles of the second layer).

Figure 3 gives the variations in the current density during the filling of colloidal crystal pores with metal deposit at various imposed voltages.

Figure 3: Dependences of dimensionless current on the deposit thickness: (1) $\Phi = 5$, (2) $\Phi = 1$, (3) a relative area of the pores.

The simulated dependences of the current on the deposit thickness agree with the experimental data: the current decreases with decreasing electroactive surface area. A relative amplitude of current oscillations depends on the ratio of an average current density to the limiting current density for the electrode through a colloidal mask: a relative amplitude of current oscillations decreases when an average current approaches the limiting value.

4. Conclusions

The proposed mathematical model of transport processes in the metal electrodeposition through colloidal crystal mask is based on the quasi-steady-state approximation. The kinetics of metal ion reduction is taken
into account by the Butler-Volmer equation. Under the assumption of a plane front of growing metal deposit, the dependences of an average current density (deposit growth rate) on the thickness of deposited metal layer (time) were obtained. These dependences agree with the literature data. In particular, the model enables us to obtain the quantitative dependences between the thickness of deposited metal layer, the operating conditions, and the current density.

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References
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