THE INFLUENCE OF THE BRANCHED ELECTRODEPOSIT MORPHOLOGY ON THE TRANSPORT PHENOMENA DURING THIN-LAYER ELECTROCHEMICAL DEPOSITION (ECD)

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Abstract

A numerical study of the role of the electrodeposit geometry on the electroconvective motion in a thin electrodeposition cell is presented. The transport phenomena are described in terms of evolutionary two-dimensional Nernst-Planck equations for cation and anion concentrations, the Poisson equation for the electric field and Navier-Stokes equations for the laminar fluid flow. The simulations are performed for different geometries of the cathodic electrodeposit in order to emphasize its influence on the electrically driven convection. The predicted concentration, electrostatic potential and flow patterns are in qualitative agreement with typical electrodeposition experiments.

Keywords: electrodeposition, dendritic growth, ion transport, numerical simulation.

1.Introduction

In recent years, considerable advance was achieved in the understanding of ECD through analysis and physical and numerical experiments [1]-[6]. Most of the previous ECD studies consider linear fixed electrodes, but the development of the cathodic electrodeposit has a certain influence on the hydrodynamic motion in the vicinity of the electrodes [2]. The present work focuses on the role of the electrodeposit geometry on the transport processes in a thin-layer ECD cell. The simulations correspond to the "top view" model, the results obtained in the case of the "side view" model being presented elsewhere [7].

2. Theoretical and computational model

The mathematical model describing the ions transport in the electrochemical cell in the "top view" model comprises a set of classical PDE [4]:

$$\frac{\partial C}{\partial t} = \frac{1}{Pe_C} \nabla^2 C + \frac{1}{M_C} \nabla(C\nabla\Phi) - \vec{v}\nabla C, \tag{1}$$

$$\frac{\partial A}{\partial t} = \frac{1}{Pe_A}\nabla^2 A - \frac{1}{M_A}\nabla(A\nabla\Phi) - \vec{v}\nabla A, \tag{2}$$

$$\nabla^2\Phi = -\frac{1}{Po_C}C + \frac{1}{Po_A}A, \tag{3}$$

$$\frac{\partial\vec{v}}{\partial t} + \vec{v}\cdot\nabla\vec{v} = -\nabla p + \frac{1}{Re}\nabla^2\vec{v} - \nabla\Phi(Ge_C C + Ge_A A), \tag{4}$$

$$\nabla\cdot\vec{v} = 0, \tag{5}$$

where C_i is the dimensionless concentration of ionic species i (i = C and A, standing for cations and anions, respectively); $\vec{v}$, p, and Φ are the dimensionless fluid velocity, pressure, and electrostatic potential, respectively. The dimensionless parameters which appear in Eq. 1-4 are defined in Table 1.

Table 1. Definition and values of dimensionless parameters

Parameter	Reynolds	Migration	Peclet	Poisson	Electrical Grashof
Definition	$Re = \dfrac{x_0 u_0}{\nu}$	$M_i = \dfrac{x_0 u_0}{\mu_i \Phi_0}$	$Pe_i = \dfrac{x_0 u_0}{D_i}$	$Po_i = \dfrac{\varepsilon\,\Phi_0}{x_0^2 C_0 z_i e}$	$Ge_i = \dfrac{e z_i C_0 \Phi_0}{\rho_0 u_0^2}$
Value in simulations	10.	19.62 (cations) 12.06 (anions)	100.	0.0443	0.16

The quantities z_i, μ_i, and D_i are, respectively, the number of charges per ion, mobility, and diffusion constants of the ionic species i; e is the electronic charge, ε is the permitivity of the medium and ν is the kinematic viscosity. Φ_0, C_0, x_0, u_0 and ρ_0 are reference values of the electrostatic potential, concentration, length, velocity and fluid density, respectively. A Boussinesq-type approximation was used for the fluid density: $\rho = \rho_0(1 + \alpha\Delta C + \beta\Delta A)$, where $\alpha = (1/\rho_0)\partial\rho/\partial C$ and $\beta = (1/\rho_0)\partial\rho/\partial A$; ΔC and ΔA are the local variations of the cation and anion concentrations that are responsible for the density variation $\Delta\rho = \rho - \rho_0$. The considered initial conditions are a linear profile for the electrostatic potential between $y=0$ (cathode) and $y=L$ (anode), and a constant value $C_0 = C_C = C_A$ for the concentration of the initial electrolyte. The boundary conditions on the electrodes are [4]:

$$\Phi(x,y) = -\frac{kT}{z_C e\Phi_0}\ln[C(x,y)], \quad \frac{\partial C(x,y)}{\partial\vec{n}} = 0, \quad \vec{N}_{An}(x,y) = 0 \tag{6}$$

at the cathode, and $\Phi(x,y) = 1 - \dfrac{kT}{z_C e\Phi_0}\ln[C(x,y)], \quad C(x,y) = A(x,y), \quad \vec{N}_{An}(x,y) = 0$ \hfill (7)

at the anode, where $\vec{N}_{An}(x,y) = -\dfrac{1}{M_A}A\nabla\Phi - \dfrac{1}{Pe_A}\nabla A + \vec{v}A$ is the anion flux, $\vec{n}$ is the normal to the boundary, k is the Boltzmann constant and T is the absolute temperature. The boundary conditions on the side walls are $\partial C/\partial\vec{n} = \partial A/\partial\vec{n} = 0, \ \partial\Phi/\partial\vec{n} = 0$. The system (1)-(5) together with the corresponding initial and boundary conditions is solved using the finite element partial differential equation solver FreeFEM [8].

3. Results and Discussions

The anion and cation concentrations, the electrostatic potential, the velocity field and the stream function are computed for a unit square domain situated in the horizontal plane (*x,y*) of an ECD cell. The validation of the code is performed using the same geometry and values of the parameters as reported in [3] and [4] (see Table 1). The agreement between our results, presented in figures 1.a-c and 2a-c, respectively, and figures 8.a,d,e from [3] and 8.b-d from [4], respectively, is excellent.
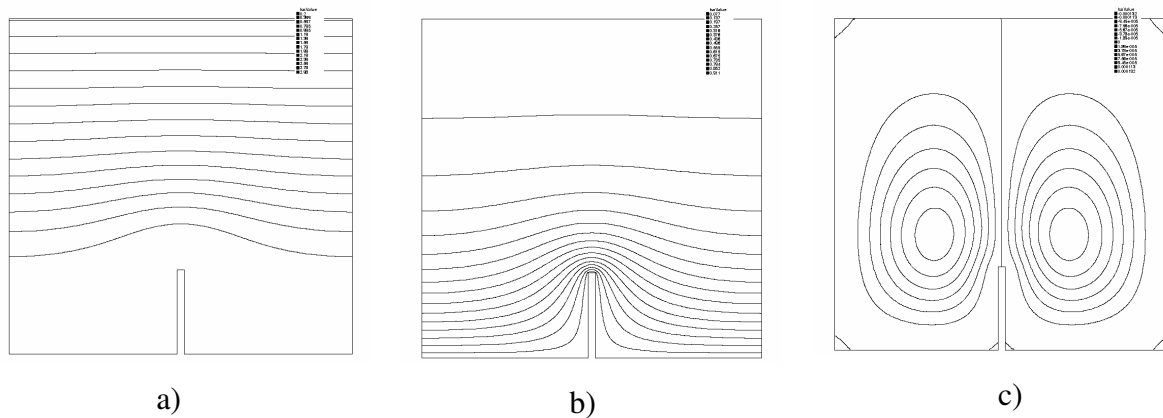

a)　　　　　　　　　　b)　　　　　　　　　　c)

Fig. 1 Validation case: Steady state isovalues for (a) anion concentration, (b) electro-static potential and (c) stream function for the values of parameters given in Table 1.
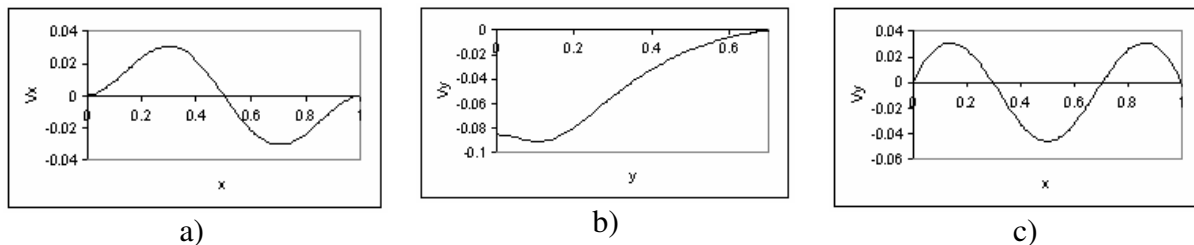

a)　　　　　　　　　　b)　　　　　　　　　　c)

Fig. 2 a) Velocity component V_x along a horizontal line at y = 0.6; b) Velocity component V_y as a function of the distance of the tip along a vertical line passing through the tip; c) Velocity component V_y along a horizontal line at y = 0.6.

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The profiles of anion concentration, electrostatic potential and stream function obtained for a branched deposit, consisting of 5 tips, are presented in Fig. 3. The results are in qualitative agreement with the experimental results reported in [2] and [5].
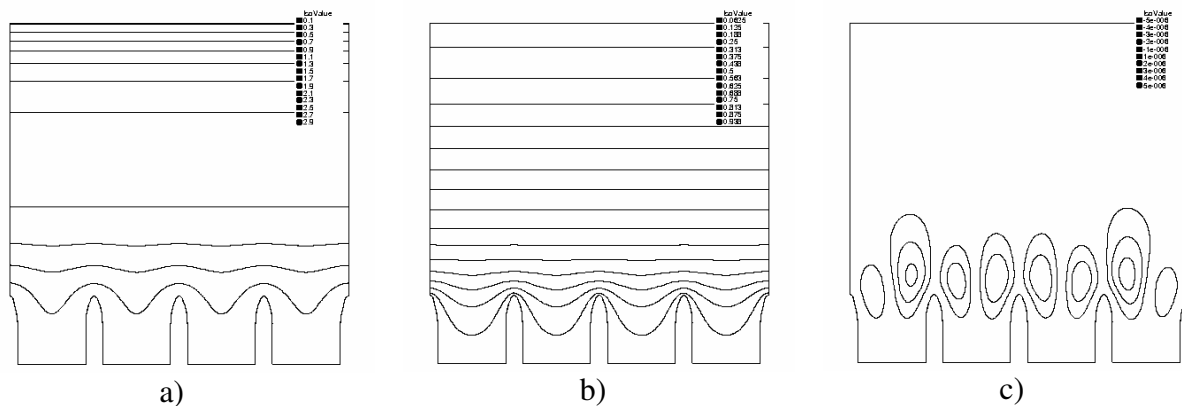

a)   b)   c)

Fig. 3 Isovalues for (a) anion concentration, (b) electrostatic potential and (c) stream function for a branched cathodic electrodeposit.

4. Conclusions

In this paper we presented an extension of the numerical results from [3] and [4], by taking into account the branched geometry of the cathodic electrodeposit in an ECD cell. We have calculated concentration, velocity patterns and stream function profiles for the two-dimensional problem restricted to the horizontal (x,y) plane of the cell (top view). The results obtained are in good agreement with typical electrodeposition experiments reported in literature [2],[5] and represent a more realistic description of the transport phenomena during the electrodeposition process in a thin-layer cell.

References

[1] J.-N.Chazalviel, Phys.Rev A **42**, 7355 (1990)

[2] J. Huth et.al., Phys. Rev. E **51**(4), 3444 (1995)

[3] G. Marshall, P. Mocskos, Phys. Rev. E **55**(1), 549(1997)

[4] G. Marshall et.al., Phys. Rev. E **59**(2), 2157(1999)

[5] C. Leger et.al., Phys. Rev. E **61**(5), 5452 (2000)

[6] J. Newman, *Electrochemical Systems*, J.Wiley & Sons, New York (2004)

[7] P. Barvinschi, A. Neculae, Analele UVT, seria Fizica **47**, 25(2005)

[8] http://www.freefem.org