

**NUMERICAL SOLUTION FOR THE TRANSPORT EQUATIONS  
IN THIN-LAYER ELECTRODEPOSITION USING  
A FINITE ELEMENT METHOD**

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**Abstract**

A realistic model describing the ionic transport by diffusive, migratory and convective motion in thin-layer electrodeposition is analyzed. The model equations (Nernst-Planck, Poisson and Navier-Stokes) are written in terms of some dimensionless quantities. Ionic concentration, velocity pattern and stream function profiles are calculated using a finite element method. Numerical results are compared with experimental ones and very good agreement is obtained.

**Keywords:** electrodeposition, ion transport, numerical simulation.

**1. Introduction**

Electrochemical deposition (ECD) of ramified deposits in thin-layer cells is a paradigmatic model for studying growth pattern formation. In a typical thin-layer experiment, when the electric circuit is closed, the cations and anions move toward the cathode and anode respectively. Because of ion depletion near the cathode and ion enhancement near the anode two zones develop, one with low metal ion concentration (low density) near the cathode and another one with high ion concentration (high density) near the anode. This unstable configuration generates a density current flow at both electrodes: at the cathode the fluid ascends toward the top plate and at the anode the fluid descends towards the bottom. These currents generate a gravity driven vortex tube or roll at each electrode, rotating in the same sense, expanding one toward the other and invading the center of the cell. Simultaneously, in the narrow depleted region near the cathode a local space charge develops, giving rise to the destabilization of the cathode and triggering the growth of a deposit. The deposit develops like a three-dimensional array of thin metallic filaments. Each filament allows fluid to penetrate its tip and to be ejected from sides, forming a toroidal vortex ring driven by the electric force. In the plane of the growth, this vortex ring reduces to a pair of counter-rotating

vortices. The real fluid motion near the deposit results from the interaction of gravity driven vortex tubes and electrical driven vortex rings.

In an attempt to describe particular aspects of the previous scenario, various mathematical models in one and two dimensions have been proposed [1] – [3]. In this paper we present a global three dimensional model that includes all the relevant ion transport mechanisms: diffusion, migration, and convection driven by Coulombic and buoyant forces. In our treatment we follow the ideas developed in [4] and introduce some dimensionless parameters governing the dynamics. The 3D model can be solved as two 2D models, one in a horizontal plane (top view) and the other in a vertical plane (side view). The present work analyze only the vertical plane model and the numerical results are compared with experimental measurements reported in [5].

## 2. Theoretical and computational model

The mathematical model describing the ions transport in the electrochemical cell comprises a set of classical PDE including the Nernst-Planck equations for transport of ions, the Poisson equation for the electric potential, and the Navier-Stokes equations for the fluid motion [4], [6]. The nondimensionalized system of equations is:

$$\frac{\partial C}{\partial t} = \frac{1}{Pe_C} \nabla^2 C + \frac{1}{M_C} \nabla(C \nabla \Phi) - \bar{v} \nabla C, \quad (1) \quad \frac{\partial A}{\partial t} = \frac{1}{Pe_A} \nabla^2 A - \frac{1}{M_A} \nabla(A \nabla \Phi) - \bar{v} \nabla A, \quad (2)$$

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

$$\frac{\partial \bar{v}}{\partial t} + \bar{v} \cdot \nabla \bar{v} = -\nabla p + \frac{1}{Re} \nabla^2 \bar{v} + \left( \frac{1}{Fr} + Gg_C \Delta C + Gg_A \Delta A \right) \frac{\bar{g}}{g} - \nabla \Phi (Ge_C C + Ge_A A), \quad (4)$$

$$\nabla \cdot \bar{v} = 0, \quad (5)$$

where  $C_i$  are the dimensionless concentration of ionic species  $i$  (for a binary electrolyte such as  $ZnSO_4$ ,  $i = C$  and  $A$ , standing for zinc and sulfate ions respectively);  $\bar{v}$ ,  $p$ , and  $\Phi$  are the dimensionless fluid velocity, pressure, and electric potential respectively and  $\bar{g}$  is the gravitational acceleration. The dimensionless parameters which appear in Eq. 1-4 are defined as shown in Table 1. The quantities  $z_i$ ,  $\mu_i$ , and  $D_i$  are, respectively, the number of charges per ion, mobility, and diffusion constants of the ionic species  $i$  ( $z_i$  and  $\mu_i$  are signed quantities, being positive for cations and negative for anions);  $e$  is the electronic charge,  $\varepsilon$  is the permittivity of the medium and  $\nu$  is the kinematic viscosity.  $\Phi_0, C_0, x_0, u_0$  and  $\rho_0$  are

reference values of the electric potential, concentration, length, velocity and fluid density, respectively. A Boussinesque-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  $\beta = (1/\rho_0)\partial\rho/\partial A$ ;  $\Delta C$  and  $\Delta A$  are the local variations of the cation and anion concentrations that are responsible for the variation  $\Delta\rho = \rho - \rho_0$  of the local density in solution. The values of the dimensionless numbers corresponding to the real experimental conditions can be obtained associating a typical reference length  $x_0$  with the cell gap  $d$ , and estimating the characteristic potential drop over this length scale,  $\Phi_0$ , assuming an ohmic approximation. For a potentiostatic experiment in a rectangular geometry,  $\Phi_0 = Vd/L$ , where  $V$  is the potential across the cell length,  $L$ . For a galvanostatic experiment in a rectangular geometry we can take  $\Phi_0 = jd/[C_0ez(\mu_C + \mu_A)]$ , where  $j = I/wd$  is the average current density through the cell cross section [4].

**Table 1.** Definitions and values of dimensionless parameters

Dimensionless parameter	Definition	Real value	Value in simulation
Reynolds	$Re = \frac{x_0 u_0}{\nu}$	0.0025	0.0025
Froude	$Fr = \frac{u_0^2}{x_0 g}$	$4 \times 10^{-7}$	$4 \times 10^{-7}$
Migration	$M_i = \frac{x_0 u_0}{\mu_i \Phi_0}$	0.1164 (cations) 0.0754 (anions)	0.1164 (cations) 0.0754 (anions)
Peclet	$Pe_i = \frac{x_0 u_0}{D_i}$	3.676 (cations) 2.358 (anions)	3.676 (cations) 2.358 (anions)
Poisson	$Po_i = \frac{\varepsilon \Phi_0}{x_0^2 C_0 z_i e}$	$0.0115 \times 10^{-8}$	0.068
Electrical Grashof	$Ge_i = \frac{ez_i C_0 \Phi_0}{\rho_0 u_0^2}$	$1.536 \times 10^{14}$	$1.536 \times 10^8$
Gravity Grashof	$Gg_i = \frac{x_0 C_0 g \alpha_i}{u_0^2}$	$8 \times 10^5$	$8 \times 10^5$

We have solved simultaneously the system (1)-(5) using the finite element partial differential equation solver FreeFEM [7]. The computational domain is a rectangle in the  $(y,z)$  plane. The mesh size used in this work is  $400 \times 20$ , our numerical results are verified to be grid-independent; the dimensionless time step is  $10^{-2}$ . The considered initial conditions are a linear profile for the electric 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. If one assume ideally fast electrochemical transfer kinetics, the boundary conditions on the electrodes sides can be expressed as equilibrium conditions across the two double layers:

$$\Phi(y, z) = -\frac{kT}{z_c e \Phi_0} \ln[C(y, z)], \quad \frac{\partial C(y, z)}{\partial \vec{n}} = 0, \quad N_{A\vec{n}}(y, z) = 0 \quad (6)$$

at the cathode, and  $\Phi(y, z) = 1 - \frac{kT}{z_c e \Phi_0} \ln[C(y, z)], \quad C(y, z) = A(y, z), \quad N_{A\vec{n}}(y, z) = 0$

(7)

at the anode, where  $N_{A\vec{n}}(y, z)$  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 horizontal walls are  $\partial C / \partial \vec{n} = \partial A / \partial \vec{n} = 0, \quad \partial \Phi / \partial \vec{n} = 0$ .

### 3. Results and Discussions

The presented numerical results are obtained for a growthless evolutionary process in the vertical plane ( $y, z$ ) of an ECD cell. The geometrical and physical parameters are taking the same values as reported in [5] for real experiments performed in galvanostatic regime and using an aqueous  $ZnSO_4$  solution. The experimentally controlled parameters are  $d=0.25$  mm,  $j=40$  mA/cm<sup>2</sup>,  $L=17$  mm,  $C_0=0.2$  M/dm<sup>3</sup>. As reference values we have used  $x_0=d=0.25$  mm,  $u_0=10$   $\mu$ m/s, and  $\Phi_0=0.04$  V. In Table 1 are presented the values of dimensionless parameters corresponding to the experimental data and reference values. Due to computer limitation and numerical stability we have used in our simulations smaller values for  $Ge_i$ , and higher values for  $Po_i$  than the real ones.

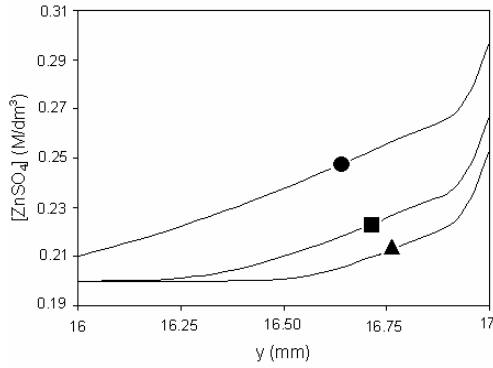


Fig. 1. Side view model simulation for ion concentration at mid-depth as a function of distance from anode for  $t= 20$  sec ( $\blacktriangle$ ),  $40$  sec ( $\blacksquare$ ) and  $110$  sec( $\bullet$ ).

The calculated ionic concentration at mid-depth as a function of distance from the anode is shown in Fig.1 at three moments ( $t=20$ s;  $40$ s;  $120$ s). The profiles of the ionic concentrations and their gradients are similar to the experimental ones (see Fig.3b in Ref.[5]).

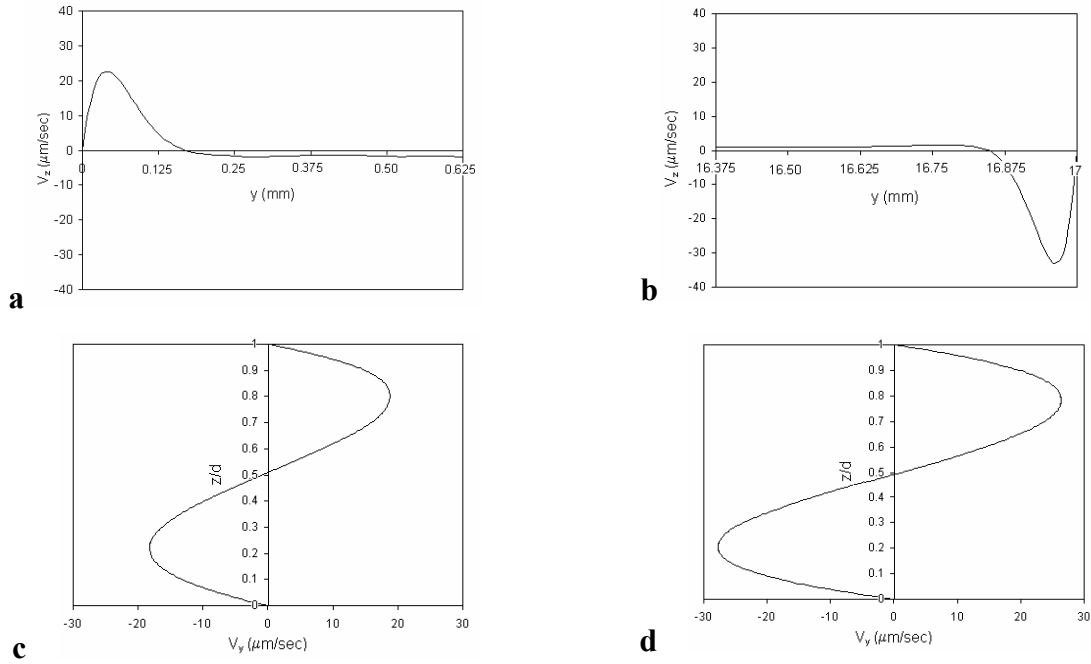


Fig. 2 Side view model simulation of velocity component  $v_z$  as a function of distance from cathode (a) and anode (b) at  $t = 120$  sec. Calculated velocity component  $v_y$  as a function of height near the cathode (c) and the anode (d) at the same time.

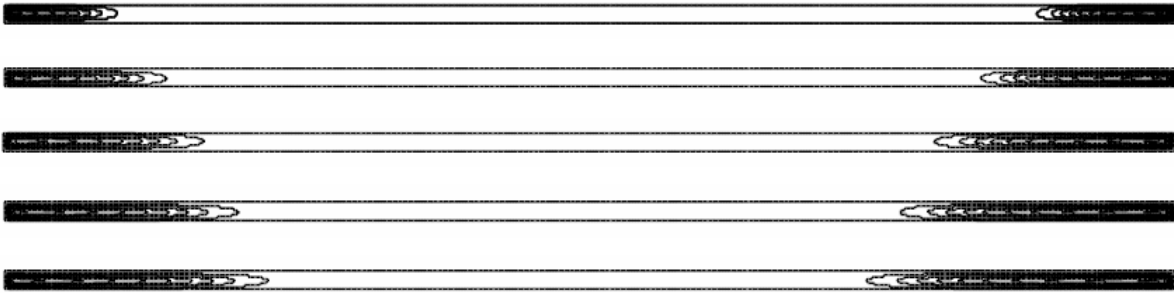


Fig. 3 Side view model simulation of the stream function contour lines for  $t = 200, 400, 600, 800$  and  $1000$  sec (time increasing downwards) showing the cathode (left) and anode (right) vortex evolution before their collision.

Figure 2 shows simulated velocity components at  $t=120$ s:  $v_z$  at mid-depth of the cell as a function of distance from the cathode (Fig.2a) and from the anode (Fig.2b),  $v_y$  as a function of height near the cathode (Fig.2c) and near the anode (Fig.2d), respectively. The simulated profiles and velocity values are very similar to the experimental results reported in [5] (see Figs.4c-f in this reference). Figure 3 presents stream function contours at different moments, showing the space-time evolution of cathode and anode vortex rolls.

The region entrained by the buoyancy-driven convection grows over time and invades the cell from both ends. After the collision, the fluid is entrained in a single long vortex, not shown here. The sequence in Fig.3 shows that the anode vortex is slightly larger than the cathode one, which is in accord with the velocity simulations (see Figs.2a-d). To characterize

the evolution of the cathodic and anodic convective rolls, the size of each vortex can be determined numerically as a function of time. Experiments revealed two regimes: at early times the convection rolls grow as  $t^{4/5}$  and for longer times the roll sizes grow as  $t^{1/2}$ . As shown in Fig.4, our simulation confirms very clearly the long time regime.

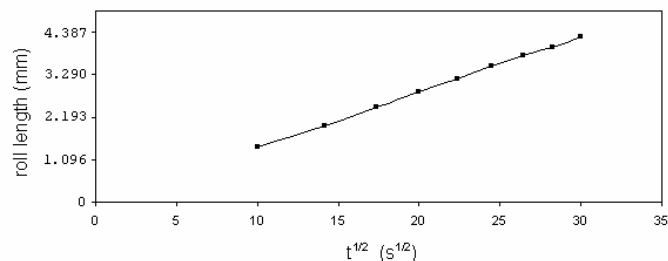


Fig. 4 Size of the convection rolls as a function of the square root of time.

#### 4. Conclusions

In this paper we have presented a physical model that describes the diffusive, migratory, and convective motion of ions in a thin-layer electrodeposition cell. The model includes the Nernst-Planck, Poisson, and Navier-Stokes equations. A Boussinesq-type approximation is used to describe the dependence of mass density on ion concentration. The equations are written in terms of some dimensionless quantities and the solutions of the model are analyzed in these terms. Using the PDE solver FreeFEM we have calculated concentration, velocity patterns and stream function profiles for the two-dimensional problem restricted to the vertical ( $y,z$ ) plane of the cell (side view). The results obtained are in very good agreement with typical electrodeposition experiments reported in literature. The presented model is suitable to describe the most important features of ionic transport in thin-layer electrodeposition and the numerical results gives us the support to extend the actual treatment to the simulation of other situations of interest to this topic.

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