SIMULATION OF CONCENTRATED MARANGONI CONVECTION IN ELECTROCHEMICAL SYSTEMS

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We investigate the nonlinear closed mathematical model of three-dimensional concentrated Marangoni convection, such as is developed at the boundary separating an electrolyte from a liquid-metal cathode.

The mathematical modeling of convection-type hydrodynamic structures at the boundary between a liquid and a liquid is currently undergoing extensive development. A large number of studies [1] have been devoted to the linear analysis of surface instability. In a number of papers [2, 3], use is made of the small-parameter method, in conjunction with asymptotic methods, to study the formation of steady-state convective structures in the region of weak supercriticality. The fluctuating nature of instability generation lies at the very basis of the mathematical modeling of interphase Marangoni convection. Its very physical nature is associated with the directed flows of heat or mass through interphase boundary, closing the positive feedback loop between interphase tension and the convective flows.

The existence of Marangoni instability is valid also in electrochemical systems in which a directed flow of a mass of electroactive particles is set up out of an electrolyte in the direction of a liquid-metal electrode. Electrochemical systems with liquid-metal electrodes serve as possible potential technological sources for a number of metals, as well as systems by means of which these metals can be refined. The study of surface hydrodynamic regimes is therefore urgent, since it is these regimes that significantly accelerate the exchange of mass. As demonstrated by experimental research [4, 5], at the boundary between the electrolyte and the liquid-metal cathode-polarized electrode, given specific values for the applied emf, we observe an interphase Marangoni convection in the form of three-dimensional circulation cells 10^{-3} m in dimension, covering the interphase surface. The initial theoretical analysis of the Marangoni convection of an electrochemical system is to be found in [6], and it is continued in [7, 8], where the methods of linear stability analysis yielded dispersion relationships and the region of electrochemical potentials determining the Marangoni instability.

However, a significant limitation of the model developed in [6] involves the derivation of the boundary conditions at the reaction surface in linear approximation, preventing the execution of a nonlinear analysis.

In the present paper we investigate the nonlinear closed model of three- dimensional concentrated Marangoni convection within a bounded geometry. We simulated the electrochemical system "electrolyte-liquid-metal cathode" by means of two incompressible nonmixing liquids separated by a plane infinitely thin interphase boundary (Fig. 1). We investigated the process of cathode ion deposition on a uniform liquid-metal substrate (electrochemical refining [4]). It was assumed that the electroactive particles (EAP) are contained in large quantities in the electrolyte which provides small currents within the electrochemical system and for the macroscopic electrical neutrality of the electrolyte all the way to the dual electric layer. Approximation of the diluted solutions made it possible to eliminate the release of heat and the influence exerted by volumetric forces near the reaction surface. We neglected the boundary effect at the solid walls in the approximation of the developed reaction surface. We assumed the diffusion kinetics to be the limiting stage of the electrochemical reaction. The Navier–Stokes incompressibility equations were made part of the mathematical model, for each of the bases and the convective diffusion of the EAP:

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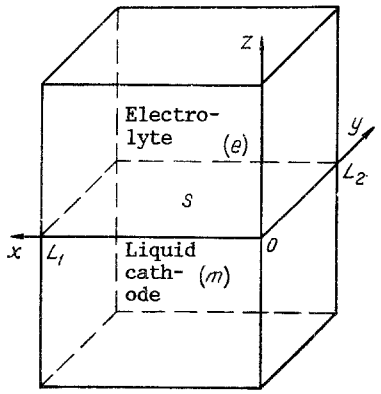

Fig. 1

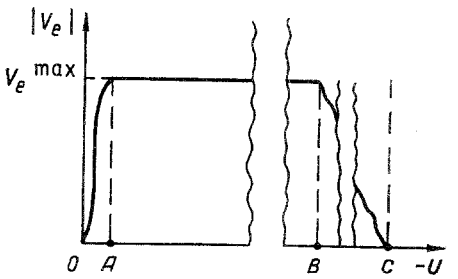

Fig. 2

Fig. 1. Diagram of the electrochemical system: s, phase separation surface.

Fig. 2. The structuring of the instability region: 0C) instability region; 0A) circulation cell velocity deceleration region; AB) region of developed Marangoni convenction with high-cell velocities; BC) circulation cell quantization region.

$$\frac{\partial \mathbf{V}_e}{\partial t} + \mathbf{V}_e(\nabla \mathbf{V}_e) = \nu_e \Delta \mathbf{V}_e(x,\ y,\ z,\ t),\ \ \mathrm{div}\,\mathbf{V}_e = 0,$$
$$\frac{\partial C_e}{\partial t} + \mathbf{V}_e(\nabla C_e) = D_e \Delta C_e(x,\ y,\ z,\ t), \tag{1}$$
$$\frac{\partial \mathbf{V}_m}{\partial t} + \mathbf{V}_m(\nabla \mathbf{V}_m) = \nu_m \Delta \mathbf{V}_m(x,\ y,\ z,\ t),\ \ \mathrm{div}\,\mathbf{V}_m = 0,$$

where subscript e represents the electrolyte and m represents the liquid-metal cathode.

The following boundary conditions were specified at the walls (x = 0; L_1 and y = 0; L_2) in the form of mass flows equal to zero and the normal velocity components, as well as in the form of attenuation of the velocity at some distance from the boundary (z = $\pm\infty$) and the concentration field in the form $C_e(x, y, z, t) = C_{0_e}$ with z = $+\infty$.

The boundary conditions of adhesion, phase slippage without penetration, the condition of electrochemical reaction, and a balance of tangential momentum components were all specified at the reaction surface z = 0. The detailed derivation of these last three boundary conditions was accomplished in [8]. They are of the following form:

$$\delta_e \frac{\partial C_e}{\partial z} = (\exp(-\kappa U) - 1)\, C_e(x,\ y,\ z,\ t),\ z = 0, \tag{2}$$

$$\eta_e \left(\frac{\partial V_{z_e}}{\partial x} + \frac{\partial V_{x_e}}{\partial z}\right) - \eta_m \left(\frac{\partial V_{z_m}}{\partial x} + \frac{\partial V_{x_m}}{\partial z}\right) = -\frac{\partial \sigma}{\partial U}\frac{\partial U}{\partial C_e}\frac{\partial C_e}{\partial x}, \tag{3}$$

$$\eta_e \left(\frac{\partial V_{z_e}}{\partial y} + \frac{\partial V_{y_e}}{\partial z}\right) - \eta_m \left(\frac{\partial V_{z_m}}{\partial y} + \frac{\partial V_{y_m}}{\partial z}\right) = -\frac{\partial \sigma}{\partial U}\frac{\partial U}{\partial C_e}\frac{\partial C_e}{\partial y},\ z = 0.$$

Approximation of the small currents made it possible to neglect the Ohmic losses leading to the heating of the electrochemical system. However, such idealization is possible only in the finite interval of polarization values, which leads to a modification of the boundary condition (2) with expansion of the coefficient in the right-hand side into a series and to a finite-number limitation of the terms:

$$\delta_e \frac{\partial C_e}{\partial z} = \sum_{p=1}^{r} (-1)^p \frac{(\kappa U)^p}{p!} C_e(x,\ y,\ z,\ t),\ z = 0. \tag{4}$$

The number r is determined from an approximation of the volt-ampere characteristic at the limit currents. The value of the current fluctuation was initially calculated in the saturation region

$$(\Delta i / i_{\mathrm{lim}}) = 1 - \exp(\kappa \Delta U). \tag{5}$$

The quantity ΔU is determined by the noise level of the system formed by the object and the regulator. The range in kU is found from the expression

$$0 < |\kappa U| < \left|\ln\left(\Delta i / i_{\text{lim}}\right)\right|. \tag{6}$$

The accuracy in the approximation of the last term of the series is determined as follows:

$$\left|\frac{(-\kappa U)^r}{r!}\right| < \exp|\kappa \Delta U| - 1. \tag{7}$$

For each specific system it is possible to determine the value of r (7).

A linear analysis of the stability of model (1) was undertaken by the Fourier analysis method [1, 6, 8, 9] for three-dimensional perturbations of the normal velocity components, of the rotation and of the perturbation of the linear concentrated profile. Linearization was accomplished by substitution of the indicated perturbations into (1) in the form

$$A_{z_n}(x,\ y,\ z,\ t) = A_n(z)\, F_n(x,\ y) \exp(p_n t), \tag{8}$$

where

$$F_n(x,\ y) = \begin{cases} \cos(k_{x_n} x)\cos(k_{y_n} y) & \text{for } V_{z_e},\ V_{z_m},\ S_e, \\ \sin(k_{x_n} x)\sin(k_{y_n} y) & \text{for } \omega_{z_e},\ \omega_{z_m}. \end{cases}$$

Having equated to zero the determinate of the stability matrix [1], we found the dispersion relationship which links the time constant p_n, the wave vector k_n and the parameters of the system:

$$\left(\eta_e \sqrt{k_n^2 + (p_n/\nu_e)} + \eta_m \sqrt{k_n^2 + (p_n/\nu_m)}\right)\left(\frac{C_{o_e} k_n^2}{D_e}(1 - \exp(\kappa U)) \times\right. \tag{9}$$

$$\times \left(-\frac{\partial \sigma}{\partial U}\ \frac{\partial U}{\partial C_e}\right)\left(\frac{D_e(k_n - b_{e_n})}{p_n} - \frac{D_e \nu_e}{\nu_e - D_e}\frac{1}{p_n}\left(\sqrt{k_n^2 + (p_n/\nu_e)} - b_{e_n}\right) + \right.$$

$$\left. + (\gamma_1(U) + \delta_e b_{e_n}) p_n \left(\frac{\eta_e}{\nu_e} + \frac{\eta_m}{\nu_m}\frac{\sqrt{k_n^2 + (p_n/\nu_e)} - k_n}{\sqrt{k_n^2 + (p_n/\nu_m)} - k_n}\right)\right) = 0,$$

where

$$\gamma_1(U) = \left(-1 + \frac{(-\kappa U)^r}{r!}\right);\quad b_{e_n} = \sqrt{k_n^2 + (p_n/D_e)}.$$

Its asymptotic for small $|p_n/k_n{}^2 D_e|$ (the case of weak supercriticality) has the following appearance:

$$p_n = \frac{RT}{n^* F}\frac{(\exp(-\kappa U) - 1)}{4\delta_e(\eta_e + \eta_m)}\left(-\frac{\partial \sigma}{\partial U}\right) - 2 D_e k_n \left(k_n + \frac{\gamma_1(U)}{\delta_e}\right). \tag{10}$$

The marginal solution ($p_n = 0$) determined the critical value of U_c, corresponding to the onset of Marangoni instability:

$$8(\eta_e + \eta_m) D_e k_n (\gamma_1(U_c) + \delta_e k_n) = \frac{RT}{n^* F}(\exp(-\kappa U_c) - 1)\left(-\frac{\partial \sigma}{\partial U}\right)\Big|_{U = U_c}. \tag{11}$$

The nonlinear analysis was carried out in the region of weak supercriticality in one of the proposed instability modes. Boundary condition (2), after expansion of the coefficient in the right-hand side over the perturbations in concentration, acquired the following form:

$$\delta_e \frac{\partial S_e}{\partial z} = \gamma_1(U) S_e + B_1(U) S_e^2 + B_2(U)\ S_e^3,\ z = 0, \tag{12}$$

where

$$B_1(U) = \frac{1}{2}\frac{\exp(-\kappa U)}{C_{o_e}}\frac{\kappa^{r-1} U^{r-1}}{(r-1)!};\quad B_2(U) = \frac{1}{6}\frac{\exp(-3\kappa U)}{C_{o_e}^2}.$$

The coordinate portion $S_e(x, y, z, t)$ was determined through linear analysis of stability. Having eliminated the integral term in the solution of the nonuniform diffusion equation with the aid of boundary condition (3), modified for the perturbations, from (12) we derived the following equation:

$$\delta_e \sum_{n=1}^{\infty} \left(k_n C_{e_n}(t) + \frac{p_n}{2k_n D_e} C_{e_n}(t) \right) \cos k_{x_n} x \cos k_{y_n} y = \tag{13}$$

$$= -\sum_{n=1}^{\infty} \left(\gamma_1(U) - \frac{1}{2k_n D_e} \frac{RT}{n^* F} (\exp(-\kappa U) - 1) \frac{1}{4(\eta_e + \eta_m)} \times \right.$$

$$\left. \times \left(-\frac{\partial \sigma}{\partial U} \right) \right) \cos k_{x_n} x \cos k_{y_n} y + \sum_{d,p=1}^{\infty} B_1(U) C_{e_d}(t) C_{e_p}(t) \cos k_{x_d} x \cos k_{y_d} y \times$$

$$\times \cos k_{x_p} x \cos k_{y_p} y - \sum_{\alpha,\beta,\gamma=1}^{\infty} B_2(U) C_{e_\alpha}(t) C_{e_\beta}(t) C_{e_\gamma}(t) \cos k_{x_\alpha} x \times$$

$$\times \cos k_{y_\alpha} y \cos k_{x_\beta} x \cos k_{y_\beta} y \cos k_{x_\gamma} x \cos k_{y_\gamma} y.$$

Let us note that in approximation of the slowly changing amplitudes $b_{e_n} = \sqrt{k_n^2 + (p_n/D_e)}$ (13) is expanded with the linear-term limitation:

$$b_{e_n} \simeq k_n \left(1 + \frac{1}{2} \frac{p_n}{k_n^2 D_e} \right). \tag{14}$$

Since in linear analysis of stability we made use of the exponential dependence on time, it was assumed that in the region of weak supercriticality the operator relationship was satisfied, namely:

$$p_n C_{e_n}(t) \simeq \frac{d}{dt} C_{e_n}(t). \tag{15}$$

Condition (13), after substitution of (15), became fundamental for the derivation of the equation for the evolution of the order parameter. It was assumed that in the region of weak supercriticality one of the modes with $(k_n)_{min} = k_f \neq 0$ become unstable. The procedure for the derivation of the equation for the order parameter with a single unstable mode is well known [10]. After a number of algebraic transformations, associated with the adiabatic exclusion of the rapidly relaxing variables, the equation for the unstable mode assumed the form

$$\frac{df(t)}{dt} = \left(\frac{2D_e k_f \kappa}{\delta_e} \frac{(-\kappa U_c)^{r-1}}{(r-1)!} + \frac{RT}{n^* F} \frac{(\exp(-\kappa U_c) - 1)}{4\delta_e (\eta_e + \eta_m)} \right) (U - U_c) f(t) - \tag{16}$$

$$- \frac{3 \exp(-3\kappa U_c) D_e k_f}{16 \delta_e C_{o_e}^2} f^3(t).$$

Since the coefficient for f^3 in (16) is negative, a normal bifurcation situation was achieved [11]. The steady-state soltuion for f(t) is given by:

$$f_{st} = \pm C_{o_e} \left(\frac{32\kappa(U - U_c)}{3\exp(-\kappa U_c)} \frac{(-\kappa U_c)^{r-1}}{(r-1)!} + \frac{RT}{n^* F} \frac{4(U - U_c)}{3 D_e k_f (\eta_e + \eta_m) \exp(-2\kappa U_c)} \right)^{\frac{1}{2}}. \tag{17}$$

The unstable mode in the perturbation of concentration, which functions in the role of the order parameter, is stabilized as a consequence of the nonlinearity of boundary condition (2). The bifurcation transition from one node into two described by Eq. (16), demonstrated the mechanism for the formation of the first convective regime. The three-dimensional skeleton of the regime in approximation of weak supercriticality is determined by relationships (8). The steady-state solution (17), with the aid of boundary conditions (3), made it possible to find the characteristics of the stabilized Marangoni convection (distribution of the normal component of velocity and the distribution of the EAP):

$$V_{z_e}(x, y, z) = -\frac{k_f \left(\frac{\partial \sigma}{\partial U} \frac{\partial U}{\partial C_e} \right)\Big|_{U = U_c + \Delta U}}{2(\eta_m + \eta_e)} f_{st} z \times$$

$$\times \exp(-k_f z) \cos k_{x_f} x \cos k_{y_f} y;$$

$$V_{z_m}(x, y, z) = -\frac{\nu_m}{\nu_e} V_{z_e}(x, y, z);$$

$$C_e(x, y, z) = \frac{C_{o_e}}{\delta_e} (1 - \exp(\kappa U_c)) z + C_{o_e} \exp(\kappa U_c) + f_{st} \exp(-k_f z) \times$$

$$\times \cos k_{x_f} x \cos k_{y_f} y + \frac{C_{o_e}(1 - \exp(\kappa U_c))}{\delta_e D_e} \frac{k_f}{2(\eta_m + \eta_e)} \times \tag{18}$$

$$\times \left(\frac{\partial \sigma}{\partial U} \frac{\partial U}{\partial C_e} \right)\Big|_{U=U_c+\Delta U} f_{st} \left(\frac{z^2}{4} + \frac{z}{4k_f} + \frac{1}{8k_f^2} \right) \exp(-k_f z) \cos k_{x_f} x \cos k_{y_f} y.$$

This study made it possible to structure (Fig. 2) the region of Marangoni instability, as opposed to [6] for systems of bounded geometry. At the edges of the instability region (near the equilibrium polarization and about the potential of zero change) there exists intervals in the generation of large-scale surface structures with slow internal velocities. The developed Marangoni convection corresponds to the regime of high convective-structure velocities with $k_n = (\delta_e)^{-1}$. Moreover, it becomes clear from an analysis of relationship (11) that, when $U \lesssim 0$, we are dealing with two unstable modes. The results of this simulation qualitatively explain the experimental data [4, 12], which demonstrate the growth in the number of cell structures under potentiostatic conditions with a change in the concentration polarization from the boundaries of the instability region to its center.

Let us note that the value of k_n specifies the spatial distribution of the forming structure in nonunique fashion:

$$k_n = \pi \sqrt{(n_1/L_1)^2 + (n_2/L_2)^2}, \text{ where } n_1,\ n_2 = 0,\ 1,\ 2,\ \ldots \tag{19}$$

The realization of a total or three-dimensional cellular structure with an arbitrary relationship between L_1 and L_2 calls for additional study.

Mathematical simulation of a two-phase system with nonlinear boundary closure is achieved in the region of weak supercriticality, given the assumption of slowing changing amplitudes. Subsequent analysis of developed Marangoni convection in electrochemical systems with liquid electrodes can be accomplished in the following ways. Of interest is a study of the supercriticality region with several unstable modes, following the diagram in [10]. However, the study of all possible hydrodynamic surface regimes is extremely difficult from an analytical standpoint. Among the promising directions we have the invariant-group methods, while for technological objects of complex geometry we have the methods of numerical analysis.

In conclusion, we will estimate the velocities of liquid motion in a regime of stabilized Marangoni convection for the process of cathodic mercury ion deposition on a mercury cathode from an aqueous solution. The fundamental calculation parameters are the following: $T = 290$ K, $\delta_e = 10^{-5}$ m, $L_1 = 10^{-1}$ m, $L_2 = 10^{-1}$ m, $r = 19$, $n^* = 2$, $\eta_e = 10^{-3}$ Pa·sec, $\eta_m = 1.6 \cdot 10^{-3}$ Pa·sec, $\partial\sigma/\partial U = -0.22(U + 0.5)$, $\kappa = 77.5$ V^{-1},

$$|\bar{V}_e| = -\frac{\left(-\frac{\partial \sigma}{\partial U} \frac{\partial U}{\partial C_e}\right)\Big|_{U=U_c+\Delta U}}{2(\eta_m + \eta_e)} \left(\frac{32\kappa(U - U_c)}{3\exp(-3\kappa U_c)} \frac{(-\kappa U_c)^{18}}{18!} + \right.$$

$$\left. + \frac{RT}{n^* F} \frac{4(U - U_c)}{3 D_e k_f \exp(-2\kappa U_c)} \frac{1}{(\eta_e + \eta_m)} \right)^{\frac{1}{2}} \exp(-1) \simeq 5.4 \cdot 10^{-2} \text{ m/sec}$$

$$|\bar{V}_m| \simeq 5.4 \cdot 10^{-3} \text{ m/sec}.$$

It should be noted that the quadricellular structure corresponds to large-scale hydrodynamic instability where there are slow internal velocities. There regions of transition to developed Marangoni convection for this system (Fig. 2): 0A) $7.3 \cdot 10^{-2}$ V; BC) $1.9 \cdot 10^{-2}$ V.

The three-dimensional circulation cells with $n_1 = n_2 = 2250$ correspond to the regime of developed Marangoni convection for the given relationship between L_1 and L_2.

NOTATION

$V_e(V_{x_e}, V_{y_e}, V_{z_e})$, $V_m(V_{x_m}, V_{y_m}, V_{z_m})$, field of velocities in the electrolyte and liquid-metal cathode phase, respectively (m/sec); $C_e(x, y, z, t)$, field of electroactive particle concentrations (EAP) in the electrolyte phase (mole/m^3); ν_e and ν_m are coefficients of kinematic viscosity for the electrolyte and electrode, respectively (m^2/sec); η_e and η_m are co-

efficients of dynamic viscosity for the electrolyte and electrode (Pa·sec); C_{0_e}, volumetric EAP concentration; $\kappa = (n^*F/RT)$; n^*, cation change; F, Faraday constant (96,487 Coulombs per gram equivalent); R, universal gas constant [8.31 J/(K·mole)]; T, mean reaction surface temperature (K); $U = (RT/n^*F)\ln\left(\frac{C_s}{C_{0_e}}\right)$, concentrated overvoltage (V); $\gamma_1(U) = \left(-1+\frac{(-\kappa U)^r}{r!}\right)$; δ_e, thickness of EAP diffusion layer (m); σ, interphase tension (J/m^2); ΔU, internal noise level (V); ω_e (ω_{x_e}, ω_{y_e}, ω_{z_e}), ω_m (ω_{x_m}, ω_{y_m}, ω_{z_m}), rotation field in the electrolyte and the electrode, respectively; p_n, time constant (sec^{-1}); $k_n = \sqrt{k_{x_n}^2 + k_{y_n}^2}$, wave vector ($1/m^2$); $k_{x_n} = \pi n/L_1$; $k_{y_n} = \pi n/L_2$; L_1, L_2, horizontal dimensions of electrode surface (m); $b_{e_n} = \sqrt{k_n^2 + p_n/D_e}$; ; f(t), unstable concentration perturbation mode; $\nabla = \left(\frac{\partial}{\partial x}; \frac{\partial}{\partial y}; \frac{\partial}{\partial z}\right)$; $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

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