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Abstract

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CONVECTIVE INSTABILITY IN AN ELECTROCHEMICAL SYSTEM

During the electroreduction of persulfate anions on a mercury drop electrode, A. Ya. Gokhshtein and A. N. Frumkin (1) discovered undamped spontaneous oscillations of the potential of the drop and of the current flowing through the drop. Experiments showed that these oscillations occur on the falling branch of the polarization characteristic in the presence of tangential motions of the mercury surface. Suppression of the latter leads to stabilization of the stationary passage of current. The mercury drop electrode as a dynamical system possesses an infinite number of degrees of freedom, since the potential and the ion concentration are not constant along the surface. However, it follows from experiment (1) that the amplitude of the potential oscillations along the surface, which cause mechanical oscillations of the mercury drop, is small in comparison with the amplitude of the oscillations of the mean potential (Fig. 1). This makes it possible to consider the problem of oscillations of the mean quantities by means of a model with a finite number of degrees of freedom. It was shown earlier (2) that a first-order model, in the presence of a single-valued polarization characteristic, does not describe self-oscillatory phenomena. Therefore we shall consider the mercury drop electrode in the presence of tangential motions as a second-order system. The choice of dynamical variables involves a certain degree of arbitrariness and requires explanation.

Let us introduce a spherical coordinate system whose origin is placed at the center of a drop of radius a. The distributions of ion concentrations and of potential, invariant with respect to rotations about the z-axis (see Fig. 2), will depend on the radius r and the angle θ, measured from the z-axis in the plane of the drawing. We divide the whole volume of the solution into three regions: the outer plate of the diffuse double layer, lying within $a < r < a + \delta$; the electroneutral region of variable concentration $a + \delta < r < a + d$; and the main volume of the solution with constant concentration $r > a + d$. As is known (3), in the stationary state the current of the electrochemical reaction of reduction of persulfate anions may be expressed through the concentration of the reacting substance by the formula

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

$$j = c_s f(\varphi_{\text{met}} - \varphi_s). \tag{1}$$

The period of the observed oscillations $\tau \sim 10^{-2}$ sec is much greater than the relaxation time of the double layer $\tau_\delta \sim 10^{-6}$ sec. Such a ratio of times shows that processes in the region of the double layer do not play an essential role in the origin of the oscillations. Therefore we shall use equality (1), regarding the double layer as inertia-free. Thus, as one dynamical variable we choose the concentration of anions c_s at $r = a + \delta$. For what follows it is convenient, using the smallness of δ in comparison with d, to regard the region of the double layer as a surface and to introduce the effective surface concentration of anions Γ, which is related to the volume concentration c by the relation

$$\Gamma = \int_a^{a+\delta} c(r)\, dr.$$

It is easy to see that Γ satisfies the inequality $\Gamma \ll c_s\delta$. As the second dynamic variable it is convenient to choose the potential jump $\varphi = \varphi_{\text{met}} - \varphi_s$, where φ_{met} is the potential of the metallic plate of the double layer, and φ_s is the potential on the sphere of radius $a + \delta$, depending on the angle θ.

Let us write the equations that describe the behavior of the quantities φ and Γ in time. The law of conservation of charge for the circuit shown in Fig. 2 has the form:

$$\frac{E - \varphi_{\text{met}}}{R} = C_0 \int \frac{\partial(\varphi_{\text{met}} - \varphi_s)}{\partial t}\, ds + \int j\, ds, \tag{2}$$

where R is the resistance of the external circuit, E is the applied voltage, and C_0 is the capacitance of the double layer per 1 cm^2. On the left-hand side of the equation is written

Fig. 1

Fig. 2

the total current flowing through the circuit, which is equal to the sum of the integral capacitive current and the integral current of the electrochemical reaction. We shall assume that the surface area of the drop does not change with time.

Let us further assume that $\varphi_s \ll \varphi_{\text{met}}$. Then equation (2) can be rewritten in differential form as

$$\frac{\partial \varphi}{\partial t} = \frac{E-\varphi}{RC} - \frac{K}{C}\,[\varphi_0 - \varphi]\Gamma, \tag{3}$$

if the polarization characteristic in the region of the descending branch is approximated by the linearly decreasing function $j = K_0[\varphi_0 - \varphi]\Gamma$ and the capacitance of the drop C is introduced.

Let us write the conservation law for the number of anions, taking into account the tangential electrocapillary motion of the surface $^{(4)}$, in the form

$$\frac{\partial \Gamma}{\partial t} = I_{\text{diff}} - \frac{1}{nF} j(\varphi, \Gamma) - \text{div}_s(\Gamma \mathbf{v}_\tau). \tag{4}$$

According to this equation, the surface concentration of anions increases due to diffusion from the bulk, decreases due to the reaction current, and also changes under the action of tangential transport, which is described by the surface divergence $\text{div}_s(\Gamma \mathbf{v}_\tau)$. If the change of concentration along the surface of the drop is small, then

$$\text{div}_s(\Gamma \mathbf{v}_\tau) \simeq \Gamma\ \text{div}_s(\mathbf{v}_\tau),$$

and equation (4) can be rewritten in the form

$$\frac{\partial \Gamma}{\partial t} = I_{\text{diff}} - \frac{1}{nF} j(\varphi, \Gamma) - \Gamma\ \text{div}_s(\mathbf{v}_\tau). \tag{5}$$

Let us consider the case in which the stationary state φ^0, Γ^0 is unique. If it is unstable, then, according to the conclusions of the theory of oscillations $^{(5)}$, the occurrence of a periodic process may be expected. Thus,

the question of the possibility of oscillations reduces to the question of the stability of the stationary state. The stability of the latter is determined by the sign of expression (5)

$$\sigma = \left[-\frac{1}{RC} - \frac{1}{C}\frac{\partial j}{\partial \varphi}\right]_{\varphi^0, \Gamma^0} + \left[\frac{\partial I_{\text{diff}}}{\partial \Gamma} - \frac{1}{nF}\frac{\partial j}{\partial \Gamma} - \text{div}_s(\mathbf{v}_\tau)\right]_{\varphi^0, \Gamma^0}. \tag{6}$$

It should be especially noted that all quantities in (6) must be evaluated in the stationary state.

Using the known [4] expression for the surface divergence $\text{div}_s(\mathbf{v}_\tau) = \frac{2v_0(\varphi)}{a}\cos\theta$, where $v_0(\varphi)$ is the velocity at the equator, we obtain the expression for σ:

$$\sigma = \frac{1}{C}\left(-\frac{1}{R} + K\Gamma^0\right) + \left[\frac{\partial I_{\text{diff}}}{\partial \Gamma} - \frac{K}{nF}(\varphi_0 - \varphi^0) - \frac{2v_0}{a}\cos\theta\right]. \qquad (7)$$

The plus sign of $v_0(\varphi)$ corresponds to motion from bottom to top.

The stationary state is unique only when $\left|\frac{1}{R}\right| > K\Gamma^0$. The first term in formula (7) is negative. Consequently, the stationary state can turn out to be unstable only in the case when the expression in square brackets is positive. The first term in the square brackets, which corresponds to diffusion from the bulk, is negative. Indeed,

$$\frac{\partial I_{\text{diff}}}{\partial \Gamma} = \frac{\partial I_{\text{diff}}}{\partial c_s}\frac{\partial c_s}{\partial \Gamma} \sim \frac{\partial}{\partial c_s}\left[D\,\frac{c_0 - c_s}{d}\right]\frac{1}{\delta} = -\frac{D}{d\delta} < 0.$$

The second term, corresponding to the reaction, is also negative. The last, convective term becomes positive when $\theta > \pi/2$.

Thus, from formula (7) a number of conclusions follow:

1. Instability can arise only in the region of the falling characteristic.
2. For instability to arise, in addition to this, the presence of sufficiently intense tangential motion is necessary.
3. In the absence of tangential motion, the stationary state on the falling characteristic in the region of uniqueness is stable, and self-oscillations are impossible.
4. Diffusion, in contrast to convection, promotes stabilization of the stationary state. The order of magnitude of the tangential velocity that can lead to instability can be roughly estimated. From formula (7) we have:

$$v_0 > v_{\text{cr}} = \frac{aD}{d\delta} \sim 10^{-1}\ \text{cm/sec}. \qquad (8)$$

5. From formula (8) it follows that, as the droplet diameter increases, the onset of instability is hindered, which agrees with the results of experiments [1].
6. From the formulas obtained it is clear that the critical velocity v_{cr} and the critical radius a_{cr} depend on the applied voltage, which agrees with the experimental data [1].
7. In experiment [1] the surface oscillations are more strongly expressed in the shielded part of the electrode. This is in agreement with the theoretical conclusion, from which it follows that instability arises when $\theta > \pi/2$.
8. The period of oscillations in such a system should be of the order $T \sim RC$. The accuracy of this estimate is not great, but the calculated value $T \sim 100$ Hz agrees well with experiment: 60 Hz $< T <$ 175 Hz.

The physical mechanism of the oscillation process can be represented as follows. Let us take the system out of the stationary state φ^0, Γ^0 by imparting to it a small increment $+\Delta\varphi$. This will lead to a decrease in the reaction current j, and

of the current in the external circuit $\dfrac{E-\varphi}{R}$. However, in the region of multivaluedness the reaction current decreases more strongly than the current in the external circuit. This causes a drop in potential. As a result of this process the concentration increases, which leads to an increase in the reaction current j. The presence of two degrees of freedom in the system leads to the fact that the reaction current and the potential overshoot the steady state by $-\Delta\varphi$, and then begin to fall. In the presence of sufficiently intense convective motion the amplitude of these oscillations begins to increase, and the system enters the region of the ascending characteristic, which plays the role of a limiter of the oscillation amplitude. The form of the oscillations may be quite complex, differing significantly from sinusoidal.

Finally, one may express certain considerations concerning the character of the potential distribution along the drop during the oscillation process. Denoting by φ_θ and Γ_θ small deviations from the averages, computed along the surface, we rewrite equations (4) and (5) in the form

$$C\frac{\partial \varphi_\theta}{\partial t} = \left(-\frac{1}{R} - \frac{\partial j}{\partial \varphi}\right)\varphi_\theta - \frac{\partial j}{\partial \Gamma}\Gamma_\theta,$$

$$\frac{\partial \Gamma_\theta}{\partial t} = -\frac{\partial j}{\partial \varphi}\varphi_\theta - \frac{\partial j}{\partial \Gamma}\Gamma_\theta + \frac{\partial I_{\text{diff}}}{\partial \Gamma}\Gamma_\theta - \frac{\partial \operatorname{div}_s(\Gamma \mathbf{v}_\tau)}{\partial v}\,dv - \frac{\partial \operatorname{div}_s(\Gamma \mathbf{v}_\tau)}{\partial \Gamma}\Gamma_\theta \qquad (9)$$

and investigate their stability. It is easy to see that the "local" stability is determined by the same expression σ as the stability on the average, whence it follows that macroscopic oscillations must be accompanied by a redistribution of potential along the surface. It follows from (9) that the rate of change of the local potential has different signs (Fig. 1) for positive and negative φ_θ.

The theory developed is based on the semi-quantitative theory of polarographic maxima and cannot lay claim to quantitative agreement with experiment. The principal result of the work is the identification of the special role of tangential motions in the onset of instability in an electrochemical system.

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Note: Figure translations are in progress. See original paper for figures.

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