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Abstract

Full Text

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STUDY OF SELF-OSCILLATIONS IN SYSTEMS FREE OF PASSIVATION BY MEANS OF A SOLID ELECTRODE

As was reported, in electrolytic systems free of passivation and having a falling characteristic, periodic undamped current oscillations were discovered ($^{1-3}$) and their theory was given (^{3}). The objects of experimental studies of these self-oscillations have until now been stationary or growing dropping mercury electrodes; the results of the studies are in complete agreement with the theory. The theory that has been constructed does not connect the principal properties of the self-oscillations with any single type of electrode, and requires only that the near-electrode layer be renewed in one way or another, so that the system as a whole can remain in a quasistationary state. In the case of a mercury electrode this is ensured by natural tangential oscillations of small amplitude of the mercury surface (^{1}), which, without substantially affecting the distribution of concentration at the electrode surface, limit the thickness of the near-electrode layer in which the main change of concentration to its value in the bulk of the solution takes place. A similar renewal mechanism can be obtained on a cylindrical electrode with circular vibrations. In the present work, for the purpose of further testing the theory, the task was set of eliminating tangential oscillations, replacing them by another method of renewing the near-electrode layer.

Fig. 1. Current self-oscillations at constant voltage. Copper disk rotating electrode in $6 \cdot 10^{-3}$ M $K_2S_2O_8$, $\omega = 15$ rev/sec; oscillation amplitude $1.61 \cdot 10^{-4}$ A, frequency 10 Hz.

In earlier work, for recording stationary polarization curves of electroreduction

Figure 2

Figure 2: Figure 2

of anions, an amalgamated disk rotating electrode was successfully used (^{4})*. The copper disk rotating electrode used in the present work for the study of self-oscillations was not amalgamated, which fully ensures the required absence of spontaneous oscillations of the surface.

In confirmation of the theory (^{3}), the form and properties of the periodic undamped self-oscillations obtained in this way (Fig. 1) coincide with the form and properties of the self-oscillations previously obtained on a dropping mercury electrode (^{1}). As follows from the theory (^{3}), for the normal course of the oscillatory process it is necessary that the jump of the system from the state with a high rate of consumption of the substance consumed at the electrode to the state with a low rate of consumption be preceded by the predominance of the rate of consumption over the rate of delivery of the substance to the electrode surface. Conversely, the jump from low consumption to high must be preceded by the predominance of the rate of delivery over the rate of consumption. The corresponding break points a and b (break downward and break upward) are indicated in Fig. 2 for a fixed voltage v applied to the circuit of the system. The circuit consists of the electrolyte with polarizable and auxiliary electrodes. The series resistance of the circuit r is composed of the electrolyte resistance and the external resistance. The curves $i_a = c_a\vec{p}(\varphi)$ and $i_b = c_b\vec{p}(\varphi)$ express the dependence of the current i on the potential φ for values of the near-electrode concentration realized in the states of the system a and b. The points a and b are determined by the tangency of i_a and i_b with the straight line $ir + \varphi = v$. As v is decreased, the positions of the points a and b change until they merge at the point D, corresponding to the limiting position of the cycle of oscillations. The geometric loci of these points are indicated in Fig. 2 by the branches AD and BD. The curves $i_{01}(\varphi)$ and $i_{02}(\varphi)$ are the dependences of the stationary currents on φ, corresponding to two thicknesses of the near-electrode layer $l_2 < l_1$, at a constant concentration $\bar{c}$ in the bulk of the electrolyte (calculated from formula $(3)^3$ for $G_1 = 0.14$, $G_2 = 0.20$, and $\bar{c} = 7$).

Fig. 2. Change in the region of self-oscillations with a change in the thickness of the near-electrode layer

Let us determine how the region Δv, in which self-oscillations occur, depends on l. The necessary condition indicated above, in the case l_1, reduces to the requirement that the points a and b be located on different sides of the curve i_{01}. The boundaries of the region Δv_1 in which this condition is satisfied are given

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* See also the diploma thesis of Yu. M. Povarov, Moscow University, 1958.

Fig. 3

Figure 3: Fig. 3

by the values of v corresponding to the points of intersection of i_{01} with AD (the left boundary) and with BD (the right). The region Δv_2 for the other layer thickness l_2 is determined analogously. A comparison of the two results shows that the boundaries of the region Δv depend substantially on the thickness of the near-electrode layer.

This conclusion finds direct confirmation in the experimental results of Fig. 3a, b, c, d, where oscillograms I—v are shown, recorded at a low rate of voltage decrease (from right to left), $v = 0.25$ V/sec, and at different electrode rotation rates (respectively $\omega = 5$; 8; 15; 29 rev/sec; with increasing ω, l decreases (5)). In agreement with the theory, a decrease in the thickness of the near-electrode layer is accompanied by a displacement of the region Δv and by the disappearance from it of those sections of the voltage axis on which the amplitude of the self-oscillations is small (Fig. 3a–c). With a further decrease of l, the region Δv degenerates (Fig. 3d); the single jump of the current in Fig. 3d represents a transition of the system from one state to another, caused by the voltage decrease, followed by the arrival of the system in a stationary state.

It should be noted that the dependence of the region Δv on l is, in essence, the dependence of Δv on the position of the curve of stationary states $i_0(\varphi)$, which is also determined by the concentration in the bulk of the solution $\bar{c}$. Usually $\bar{c}$ remains

constant in a series of experiments with different l. The dependence of the region Δv on c at constant l and r is established by the same reasoning, if it is taken into account that i_0 increases in proportion to $\bar{c}$; the constancy of r is then ensured by introducing an additional external resistance as the resistance of the electrolyte decreases. By simultaneously changing l and $\bar{c}$, one can partially or completely (at large l) compensate their influence on Δv.

Owing to the high steepness of the branch AD, the displacement δv of the left boundary of the region Δv can be used to estimate the resistance of the system r (see Fig. 2): $r \simeq \delta v / \delta I$, where δI is the corresponding displacement of the change in the stationary

Fig. 3. Experimental study of self-oscillations at different thicknesses of the near-electrode layer. Copper disk rotating electrode, $2\lambda = 1.9$ mm; second electrode—a platinum plate; $3.7 \cdot 10^{-3}\,M$ $K_2S_2O_8$ (the beginning of oscillogram is shifted relative to the others to the left by 0.04 V)

(limiting) current of the left boundary. Comparison of the oscillograms in Figs. 3a and 3 gives $\delta v = 0.09$ V, $\delta I = 40$ μA, and $r = 2.2 \cdot 10^3$ Ω. For comparison, let us calculate the resistance of the system by another method. In the present case (Figs. 1 and 3) no external resistance is introduced, and r is determined by the resistance of the electrolyte into which a disk electrode of radius λ is immersed. Solving the corresponding boundary-value problem, it is not difficult to show that, in the limiting-current regime, the voltage drops when current passes through the electrolyte are, at the center and at the edge of the disk:

$$u(0) = \frac{i}{\sigma}\lambda, \qquad u(\lambda) = \frac{2}{\pi}\frac{i}{\sigma}\lambda,$$

where σ is the specific electrical conductivity of the solution, and i is the current density on the disk. Like the dropping electrode, the disk electrode is not equipotential ($u(0)/u(\lambda) = \pi/2$), and therefore the resistance of the system is understood to mean a value lying between r_0 and r_λ, referred to the center and to the edge of the disk, $r_\rho = u(\rho)/I$. Since $I = \pi\lambda^2 i$, $r_0 = 1/\pi\sigma\lambda$ and $r_\lambda = 2/\pi^2\sigma\lambda$. For $3.7 \cdot 10^{-3}\, M$ $K_2S_2O_8$, $\sigma = 1.18 \cdot 10^{-3}$ $\Omega^{-1}\text{cm}^{-1}$. Hence $r_0 = 2.7 \cdot 10^3$ Ω, $r_\lambda = 1.7 \cdot 10^3$ Ω. Thus, $r_\lambda < r < r_0$, which confirms the assumptions used above in calculating r.

In accordance with the theory (3), one also finds such facts (Fig. 3) as the invariance (at fixed v) of the amplitude of self-oscillations when chan-

···the decrease of l and the reduction of the period of the self-oscillations due to shortening that part of it in which the current is small; as l decreases, the ratio p of that part of the period in which the current is large to the entire period increases. An exact derivation of the formula for the frequency (ν) of the self-oscillations (which will be published shortly) shows that, at fixed v, as l decreases, ν changes nonmonotonically—at first it increases, reaches a maximum at $p \approx 1/2$, and then decreases to zero. Individual portions of this dependence can be observed experimentally under those conditions in which, when l is varied within the corresponding limits, the voltage v continues to remain in the region Δv (the latter, as was shown above, shifts with changing l). Under the experimental conditions of Fig. 3, the portion of the dependence corresponding to values $p < 1/2$ is accessible to observation.

The geometrically nonuniform arrangement of different parts of the electrode surface in real systems leads to the occurrence of one and the same stage of the process at different points of the electrode being somewhat spread out in time. However, owing to the mutual influence of different parts of one and the same electrode, the time spread is small, and cases of interference can be observed only at the boundaries of the oscillation region. The nonequipotentiality of the electrode caused by the nonuniformity can be considerably reduced in those cases where the addition to the solution of a substantial excess of an indifferent electrolyte is permissible (systems with K_2PtCl_4, K_2PtCl_6 (4)).

An analysis of the results obtained in the study of self-oscillations in systems free from passivation reveals a feature in the behavior of electrolytic systems having a falling characteristic; it consists in the possibility of very rapid transitions. An example is the transition from a state with a small consumption of substance to a state with a large consumption (a sharp rise of the current on the leading front of the oscillations, Fig. 3). It is accelerated by the fact that recharging of the electrical double layer, associated with a change in the electrode potential, takes place at the expense of electroreduction, the rate of which in a system with a falling characteristic increases when the potential is shifted in the positive direction. Part of the negative electricity consumed in the electroreduction reaction flows off from the metallic plate of the double layer, which acquires a more positive charge in accordance with the more positive potential of the electrode.

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

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