STATIONARY STATES OF DISTRIBUTED ELECTROCHEMICAL SYSTEMS AND THEIR STABILITY

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Abstract

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V. P. SMILGA and Yu. A. CHIZMADZHEV

STATIONARY STATES OF DISTRIBUTED ELECTROCHEMICAL SYSTEMS AND THEIR STABILITY

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The literature contains descriptions of self-oscillatory phenomena in certain electrochemical systems during the passage of current ([1–6]). To elucidate the mechanism of these phenomena, it is necessary to investigate the question of the stationary states of distributed systems and their stability.

Let us consider the problem of the distribution of potential in a one-dimensional distributed system, a model of which, as in ([6]), may be a tube of length $2l$, filled with electrolyte, on the walls of which an electrochemical reaction $j(\varphi)$ takes place. The tube is polarized from both ends. The potential distribution is described by the equation ([7])

$$\chi r_0 \frac{d^2\varphi}{dx^2} - j(\varphi) = 0, \tag{1}$$

where χ is the electrical conductivity, r_0 is the radius of the tube, and the coordinate x is measured from the left end of the tube. In ([6]), the stationary states of equation (1) were investigated for the case of a constant polarizing potential φ_1 applied to the ends of the tube. The calculations were carried out for a definite form of the function $j(\varphi)$. Below we shall present an investigation of the case of a prescribed potential φ_1 for an arbitrary function $j(\varphi)$ of prescribed current, and also the most general case of a prescribed relation between current and potential. We begin with the consideration of a prescribed potential

$$\varphi = \varphi_1, \quad x = 0; \qquad \varphi = \varphi_1, \quad x = 2l.$$

From the symmetry conditions of the problem with respect to the plane $x = l$, it follows that $d\varphi/dx = 0$ at $x = l$. Let us denote the potential at the point $x = l$ by φ_l. From physical considerations it is clear that $j(\varphi) > 0$ everywhere, except, possibly, at the point $\varphi = 0$. The general solution of the problem has the form

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

$$\frac{l}{\chi r_0} = F(\varphi_l) = \int_{\varphi_l}^{\varphi_1} \frac{d\varphi}{\left[\int_{\varphi_l}^{\varphi} j(t)\,dt\right]^{1/2}}. \tag{2}$$

Depending on the form of the function $j(\varphi)$, the solution $F(\varphi_l)$ will be represented by a curve from the family of functions shown in Fig. 1. The behavior of $F(\varphi_l)$ at zero is determined by the character of the function $j(\varphi)$ as $\varphi \to 0$. If $j(0) \neq 0$ or $j \sim \varphi^n$, where $n < 1$, then $F(0)$ is finite (curves a and b). If $j(\varphi)$ has no decreasing portions, then curve b is realized. It can be shown that a function of type a is possible only when decreasing portions are present in the curve $j(\varphi)$. If $j(\varphi)$ as $\varphi \to 0$ is proportional to φ^n, where $n \geq 1$, then $F(\varphi_l)$ becomes infinite at zero (curves v and g). It can be shown that case v corresponds to a polarization characteristic with decreasing portions.

Let us consider the case $n < 1$ (curves a and b). In case b, for $l < l_{\text{cr}}$ the stationary state lies in the region $\varphi_l < \varphi < \varphi_1$. For $l > l_{\text{cr}}$ the entire tube is divided into two regions: the first—the working region—is equal to l_{cr}; the second, equal to $(l - l_{\text{cr}})$, is characterized by the fact that no current passes through it and the potential

for $x > l_{\text{cr}}$ is equal to zero. Thus, for any l there exists a stationary state of the system. In case a, for $l > l_{\text{cr}}$ there are no stationary states in the system.* In electrochemical problems $n = 1$, so curves b and c can be realized, i.e., the function $F(\varphi_l)$ tends to infinity as $\varphi_l \to 0$. This leads to the fact that for any l there exists a stationary state. Case c, which is realized when there are falling portions on the curve $j(\varphi)$, is characterized by a peculiar dependence of the potential distribution on the length of the tube. For $l \neq l_{\text{cr}}$ the potential distribution is a continuous function of the length l: as the length increases, φ_l decreases and the entire distribution shifts downward. However, when l passes through l_{cr}, the value φ_l, as well as the entire potential distribution, changes discontinuously, as shown in Fig. 2. The shaded region is forbidden.

Fig. 1

Fig. 2

Curves that lie in this region are never realized. The potential $\varphi(x)$, for any value of l, is a continuous function of the coordinate x.

Fig. 3

Figure 3: Fig. 3

Figure 3 shows the polarization characteristic $j(\varphi)$. The tube is polarized by the potential φ_1 at the point $x = 0$. For a given l, the potential in the middle of the tube is equal to φ_1, and along the tube the region of the polarization curve lying between $j(\varphi_l)$ and $j(\varphi_1)$ is realized. As l increases, the potential φ_1 shifts continuously to the left until the length l reaches l_{cr}. With a further increase of l, the working region of the polarization curve changes discontinuously, jumping over the shaded segment in Fig. 3. Approximation of a real polarization characteristic satisfying the condition $j(0) = 0$ by the linear function $j = K(\varphi_0 - \varphi)$ is equivalent to a transition from curve c to curve a. With such a replacement we lose an entire class of solutions and arrive at the conclusion that for $l > l_{\text{cr}}$ stationary solutions are absent.

Fig. 3

The stationary distribution requires additional investigation for stability. For the case $j = K(\varphi_0 - \varphi)$ and a prescribed potential, the stability criterion obtained in ([6]) was

$$\sqrt{\frac{K}{\chi r_0}}\, l < \frac{\pi}{2}.$$

This stability criterion coincides with the condition for the existence of stationary solutions for the case $j = K(\varphi_0 - \varphi)$. In other words, the stationary distribution under the conditions specified above is stable. The conclusion made in ([6]) about instability is invalid for $j(\varphi) > 0$. Investigation of a number of specific functions $j(\varphi)$,

* This disappearance of stationary solutions is analogous to the so-called "thermal explosion" studied in the chemical kinetics of homogeneous systems ([8]).

satisfying the condition $j(0) = 0$ and $j(\varphi) > 0$, showed that the stationary state at a prescribed polarizing potential is stable.

Let us pass to the case of a prescribed polarizing current $\chi\varphi'_{x=0} = -i_0$, when $j(\varphi) = K(\varphi_0 - \varphi)$. As in the case of a prescribed potential, from the requirement $j(\varphi) > 0$ we obtain that a stationary state on the descending branch exists only when $\sqrt{\frac{K}{\chi r_0}}\, l < \frac{\pi}{2}$. The disappearance of solutions, as was emphasized above, is connected with an approximation and has no physical meaning. The potential satisfies the time-dependent equation

Fig. 4

Figure 4: Fig. 4

$$C\frac{\partial\varphi(x,t)}{\partial t} = \chi r_0 \frac{\partial^2\varphi(x,t)}{\partial x^2} - j(\varphi). \tag{3}$$

As usual, we represent the solution in the form

$$\varphi(x,t) = \varphi(x) + \gamma\varphi_1(x,t),$$

where $\varphi_1(x,t)$ is the deviation from the stationary state, and γ is a small parameter. The function $\varphi_1(x,t)$ satisfies the equation

$$\frac{C}{\chi r_0}\frac{\partial\varphi_1}{\partial t} = \frac{\partial^2\varphi_1}{\partial x^2} + k^2\varphi_{1s}, \qquad k^2 = \frac{K}{\chi r_0}$$

and the boundary conditions $\varphi_1'(0,t) = 0$, $\varphi_1'(l,t) = 0$. Let $k^2 = \text{const}$. Then $\varphi_1 = \psi(t)\cdot\text{const}$, or $\varphi_1 = \text{const}\cdot e^{\lambda t}$, where $\lambda = \dfrac{k^2\chi r_0}{C} > 0$. Consequently, in the constant-current regime the state on the descending branch is unstable. However, prescribing the current at the inlet of the tube does not yet fix the state on the descending branch. As in the case of an equipotential system, the presence of an N-shaped characteristic leads to a nonuniqueness of the potential at a prescribed current.

Fig. 4

We shall now prove that instability can arise only on the descending branch. Separating the variables in equation (3):

$$\begin{gathered} \varphi_1(xt) = u(x)v(t), \qquad v(t) = v(0)e^{\lambda t}, \\ u'' - \left[\frac{dj}{d\varphi} + \lambda\right]u = 0, \qquad C = \chi = r_0 = 1. \end{gathered} \tag{4}$$

Multiplying the equation by u and integrating from 0 to l, we obtain

$$\lambda\int_0^l u^2\,du = -\int_0^l \frac{dj}{d\varphi}u^2\,dx - \int_0^l {u'}^2\,dx,$$

whence it follows that $\lambda > 0$ when $dj/d\varphi < 0$ and when

$$\int_0^l \left|\frac{dj}{d\varphi}\right| u^2\,dx > \int_0^l {u'}^2\,dx.$$

Finally, let us consider the case when a relation between the current and the potential is prescribed at the ends of the tube:

$$\frac{E - \varphi(0)}{R} = -\chi \left. \frac{d\varphi}{dx} \right|_0,$$

where E is the e.m.f. of the battery, and R is the resistance of the external circuit. Let $j = K(\varphi_0 - \varphi)$. If $E > \varphi_0$, the solution exists in the region $l^* < l < \pi/2k$, where l^* is the root of the transcendental equation shown in Fig. 4. For $E < \varphi_0$, the admissible l are limited by the inequality $l < l^*$. To investigate stability it is necessary to find λ from equation (4)

$$u'' + \alpha^2 u = 0, \qquad \alpha^2 = k^2 - \lambda$$

and the boundary conditions

$$u'_{x=l} = 0, \qquad u_{x=0} = \varkappa R u'_{x=0}.$$

The equation for determining α has the form:

$$\operatorname{ctg} \alpha l = \varkappa R \alpha.$$

The solution is unstable if $\lambda > 0$, i.e. $\alpha < k$. From Fig. 4 it is seen that for $E > \varphi_0$ one can find $\alpha < k$ in the region where solutions exist, whereas in the case $E < \varphi_0$ no such α exists and the solutions are stable. However, for $E > \varphi_0$ the stationary state ceases to be unique, as in the exponential case. Thus, in the cases analyzed above, the distributed character of the system does not lead to the appearance of oscillatory solutions.

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Institute of Electrochemistry
Academy of Sciences of the USSR

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REFERENCES

[1] M. Thalanger, M. Volmer, *Zs. phys. Chem.*, **150**, 401 (1930).
[2] J. Butler, *Disc. Farad. Soc.*, **1**, 122 (1947).
[3] E. A. Aikazyan, *ZhFKh*, **33**, No. 5 (1939).
[4] A. G. Bagramyan, *Electrodeposition of Metals*, 1950.
[5] A. Ya. Gokhshtein, A. N. Frumkin, *DAN*, **132**, No. 2 (1960).

[6] Yu. A. Chizmadzhev, *DAN*, **124**, 142 (1959).
[7] A. N. Frumkin, *ZhFKh*, **23**, 1477 (1949).
[8] D. A. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics*, 1948.

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