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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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PHYSICAL CHEMISTRY

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ON THE RESONANCE PROPERTIES OF ELECTROCHEMICAL SELF-OSCILLATING SYSTEMS

(Presented by Academician A. N. Frumkin, August 12, 1963)

Various electrochemical self-oscillating systems are known in which the polarization curve exhibits a falling segment ([1],[2]). The presence of a falling segment on the stationary polarization curve is, however, not obligatory ([3],[4]). Moreover, it follows from work ([4]) that electrochemical systems are possible which, in the region where periodic processes are observed, have a positive slope of the stationary polarization curve.

In studying the self-oscillations accompanying the electrodeposition of cadmium in the presence of surface-active substances ([2]), we found that in the region of potentials where periodic processes are observed, the dynamic properties of the system have the following features. The dynamic polarization curve (i.e., the relationship between the electrode potential and the current density when the potential is changed sufficiently rapidly) has a negative slope, the absolute value of which depends on the rate of change of the potential and, as this rate increases, first increases, reaches a maximum, then decreases, and finally the slope becomes positive.

Fig. 1

It may be assumed that, under these conditions, the existence of a maximum slope of the dynamic polarization curve corresponds to the presence of resonance properties in the system.

The aim of the present work was to detect resonance properties in a system with a copper anode immersed in phosphoric acid. The stationary polarization curve

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Fig. 2

Figure 2: Fig. 2

of this system has no falling segment, while the dependence of the slope of the dynamic polarization curve on the rate of change of the potential is the same as that described above.

An electrolytic two-electrode cell, in series with a load resistance, was connected to a source of a sinusoidal signal. This circuit is analogous to the circuit in which a tunnel diode is connected as a voltage amplifier ([5]). It is known that the presence on the current-voltage characteristic of a segment with a negative slope makes it possible to connect the system as a voltage and power amplifier. In contrast to the characteristic of a tunnel diode, the position of the dynamic polarization curve of an electrochemical system depends on the frequency of the input signal. The greatest amplification is attained when the dynamic polarization curve reaches its greatest steepness.

The slope of the load line was chosen to be somewhat steeper than the slope of the falling segment on the dynamic polarization curve having the maximum slope. The change in voltage was observed with the aid of an oscil-

···of an ENO-1 oscillograph; the change in current in the circuit was recorded with an MPO-2 loop oscillograph. As the source of a low-frequency sinusoidal signal, a circuit was used with a slider-type rheostat device connected as a voltage divider. The rheostat slider was set into reciprocating motion by means of a crank mechanism. The internal resistance of the alternating-current source used did not exceed 0.1 ohm; the signal amplitude was chosen within the range 0.03–0.10 V. The anode was vertical, rectangular, with an area of 0.37 cm^2. The cathode was made of copper, with an area of 200 cm^2. To obtain a stable effect, it is desirable to use a nonpolarizable cathode. The electrolyzer was glass, rectangular, with a capacity of 300 cm^3.

Fig. 2

Fig. 1 presents the dependence of the voltage gain of the circuit on the frequency of the input signal. Fig. 2 shows oscillograms of the input signal varying in frequency (the curve with constant amplitude) and the change in the amplitude of the cell current. The signal frequency corresponding to the maximum amplification is the resonance frequency of the electrochemical system. It should be noted that the phase shift between the input signal and the cell current is opposite in sign for frequencies below and above the resonance frequency.

The value of the resonance frequency for the case described (3.9 Hz) corresponds to the frequency interval (from units to hundreds of hertz) characteristic of electrochemical systems whose oscillation mechanism is associated with diffusion processes ([1]).

The results obtained show the possibility of using electrochemical systems as

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voltage and power amplifiers. The resonance phenomenon agrees well with the conclusions of work ([4]), according to which such systems must have order no lower than the second.

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