PHYSICAL CHEMISTRY

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1961

SovietRxiv

Abstract

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KINETICS OF CATHODIC PROCESSES ON SEMICONDUCTOR ELECTRODES WITH PARTICIPATION OF VALENCE-BAND ELECTRONS

(Presented by Academician A. N. Frumkin, 10 IV 1961)

The theory of cathodic processes on semiconductors has been developed as applied to the case in which conduction electrons participate in the process ([1]). There is known, however, a group of cathodic processes that proceed with consumption of valence-band electrons ([2–5]). Without considering here the conditions under which valence electrons can participate in the cathodic process ([3]), let us examine how their participation affects the form of the kinetic equations. In doing so we shall proceed from the results obtained in ([1]).

Let us first analyze the case in which the fraction of participation of valence electrons in the reaction is equal to unity. This case has already been discussed in ([6]). Here we shall consider it from another point of view and, on the basis of this consideration, discuss the case of joint participation in the reaction of electrons of both bands ([4]). For simplicity, we shall assume that surface states are absent ([1]). In addition, we shall take the ψ_1-potential to be equal to zero. Let η_g be the shift of the potential in the Helmholtz part of the double layer when a current of density i passes; $\Delta\varphi_{os}$ the shift of the potential in the space-charge layer in the semiconductor; Δq the change of charge on the ionic plate when current passes. If η is the measured overvoltage, then

$$\eta = \eta_g + \Delta\varphi_{os}. \tag{1}$$

In a first approximation it is assumed, as in ([1]), that the state of the electrode surface does not change upon polarization.

As is known,

$$i = i_0(C/C_0)e^{-\alpha\eta_g F/RT}. \tag{2}$$

Here i_0 is the exchange-current density; C is the concentration of electrons on the semiconductor surface under polarization, C_0 the same at $i = 0$; the

remaining symbols have their usual meaning. Equation (2) describes a process whose rate is determined by the rate of one of the stages of the electrochemical reaction. This means that the passage of current does not disturb the electronic equilibrium in the semiconductor. For elucidating the fundamental aspect of the question, this simplified representation is sufficient.

In ([1]), C and C_0 are treated as concentrations only of conduction electrons. Formula (2), however, has a more general meaning and is applicable also when valence electrons participate in the process. Taking C and C_0 to be the total concentrations of electrons on the surface, we obtain $C \cong C_0$, since under conditions usual for electrochemical reactions the total concentration of electrons on the electrode surface practically does not change.

From (2) we have

$$\eta_{\text{g}} = \frac{RT}{\alpha F} \ln \frac{i_0}{i}. \tag{3}$$

Keeping (1) in mind, we obtain

$$\eta - \Delta\varphi_{\text{oz}} = \frac{RT}{\alpha F} \ln \frac{i_o}{i}, \tag{4}$$

whereas from (2) one can obtain, taking C and C_0 to be the concentrations of conduction electrons, the equation

$$\eta + \frac{1-\alpha}{\alpha} \Delta\varphi_{\text{oz}} = \frac{RT}{\alpha F} \ln \frac{i_o}{i}. \tag{5}$$

The i_o in formulas (4) and (5) are not equal, since at $\eta = 0$ the concentrations of the electrons participating in the reaction are not equal.

As $i \to 0$, as shown in (1),

$$\eta = -\frac{RT}{nFi_o}\, i. \tag{6}$$

When valence electrons participate in the reaction, however, such a dependence relates not η and i, but η_{g} and i, as follows from (3). Therefore

$$\eta - \Delta\varphi_{\text{oz}} = -\frac{RT}{nFi_o}\, i. \tag{7}$$

Comparison of (4) and (5), as well as of (7) and (6), shows that it is easier to shift the equilibrium of a reaction involving valence electrons (i.e., to obtain a potential differing from the equilibrium one) than the equilibrium of a reaction involving conduction electrons. The reason for this is that, when valence

electrons participate in the reaction, its rate can increase only as a result of a decrease in the activation energy upon a change in the potential jump in the Helmholtz layer. Therefore η_g in this case must be greater than when conduction electrons participate (at the same i/i_o), when, in addition to the decrease in activation energy, an accelerating effect is also produced by an increase in the concentration of the reactant—the conduction electrons. Since a larger η_g corresponds also to a larger $\Delta\varphi_{oz}$, η will be larger in the case of consumption of valence electrons. It is essential that the relation between $\Delta\varphi_{oz}$ and η_g also depends on whether the surface of the semiconductor is degenerate or not. For a nondegenerate surface, $\Delta\varphi_{oz}$ is considerably greater than η_g and constitutes the main part of the total overvoltage. Therefore, as follows from (1), (4) or (7) and the relation between η_g and $\Delta\varphi_{oz}$ (1), the polarizability under these conditions is very high. For a degenerate surface, $\Delta\varphi_{oz}$ is comparable with η_g; therefore from the same equations (1) and (4) or (7), and the corresponding relation between η_g and $\Delta\varphi_{oz}$ for a degenerate surface (1), it follows that the polarizability will be much smaller than in the first case, which will lead to a sharp decrease in the slope of the overvoltage curve. Thus, for example, for a hole semiconductor whose surface, in the absence of an external current, has an enriched layer, the cathodic overvoltage curve in the case of consumption of valence electrons has a step with a height approximately equal to the width of the forbidden band (a region with a small slope in the enriched-layer region is replaced by a region with a larger slope upon transition to the nondegenerate region; after the Fermi level has moved from below upward through the entire forbidden band, degeneracy again sets in, which leads to a decrease in the slope). This qualitative conclusion (with the use of the corresponding relations between η_g and $\Delta\varphi_{oz}$ given in (1), one can also obtain a quantitative result) agrees with the conclusions obtained in (6) by another method.

Let us now consider the case in which both valence electrons and conduction electrons participate in the reaction. We shall assume the surface of the semiconductor to be nondegenerate. In this case equation (2) remains valid; however, it is difficult to determine the concentrations of electrons entering the reaction from both bands. Therefore it is desirable to obtain a kinetic equation,

containing the experimentally determined quantity—the fraction of valence electrons in the total current (4).

Let us denote the valence-electron current by i , and the conduction-electron current by i . Obviously,

$$i + i = i. \tag{8}$$

Let

$$i /i = x. \tag{9}$$

Let us first consider the case of small currents ($i \ll i_0$). If it is assumed that the currents i and i are independent of one another, i.e., that the reaction consuming conduction electrons proceeds independently of the reaction consuming valence electrons, then, according to (6) and (7),

$$-\frac{RT}{nF}\frac{i}{i_0} = \eta\,; \qquad -\frac{RT}{nF}\frac{i}{i_0} = \eta. \tag{10}$$

Here i_0 is the exchange current of the reaction involving valence electrons, and i_0 is the exchange current of the reaction involving conduction electrons. Obviously,

$$i_0 + i_0 = i_0. \tag{11}$$

Equations (8), (10), and (11) form a system whose solution, taking (9) into account, gives the desired expression:

$$-\frac{RT}{nF}\frac{i}{i_0} = \frac{\eta\,(\eta - \Delta\varphi\ )}{\eta - \Delta\varphi\ (1-x)}. \tag{12}$$

An analogous assumption concerning the independence of the course of the reactions consuming valence electrons and conduction electrons in the region $i \gg i_0$ leads, in accordance with (4) and (5), to the expressions

$$i = i_0\, e^{-\alpha F\eta\,/RT}; \qquad i = i_0\, e^{-F\Delta\varphi\ /RT} e^{-\alpha F\eta\,/RT}. \tag{13}$$

Solving (13) together with (8) and (11) gives

$$i = i_0 \frac{e^{-F\Delta\varphi\ /RT} e^{-\alpha F\eta\,/RT}}{1 - x\left(1 - e^{-F\Delta\varphi\ /RT}\right)}. \tag{14}$$

It should be emphasized that the results obtained are valid only in the absence of a diffusion limitation for the conduction electrons participating in the reaction.

The features described above are most clearly manifested during the polarization of Si in alkaline solutions (7). The self-dissolution current of Si in $10\,N$ KOH, measured from the rate of hydrogen evolution, is $\sim 10^{-3}$ A/cm^2; the stationary potential is ~ -300 mV relative to the hydrogen electrode in the same solution. A cathodic current of $\sim 10^{-4}$ A/cm^2 shifts the potential of p-Si by 100 mV instead of by tenths of a millivolt, as should be expected in the case of consumption of conduction electrons (1). On n-Si a current of $2\text{–}3\cdot 10^{-4}$ A/cm^2 shifts the potential by $\sim$ 200 mV instead of by several millivolts. Such high overvoltages are difficult to explain as drops in an oxide film, since Si in this potential region dissolves actively and therefore there cannot be an oxide film

of high resistance on it. These facts qualitatively correspond to the picture of a reduction process with consumption of valence electrons described above. The possibility of participation of valence electrons in the reaction of water reduction on Si is ensured by the large difference between the normal potentials of the processes of Si dissolution ($E_0 = -1.7$ V) and water reduction.

According to (3), there is a direct correspondence between this difference and the probability of participation of valence electrons in the reaction. It should be noted that,

The data presented for the Si cathode can also be explained by assuming that Si interacts chemically with the solution, and that this leads to a discrepancy between the observed overvoltages and the self-dissolution current. Apparently, the available experimental data refute neither the one nor the other hypothesis.

The authors express their gratitude to Prof. V. I. Veselovskii, N. A. Aladzhalova, T. I. Borisova, and V. M. Novakovskii for participating in the discussion of the work.

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Received
4 IV 1961

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