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Abstract

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THE INFLUENCE OF THE SEMICONDUCTING PROPERTIES OF OXIDE FILMS ON THE ELECTROCHEMICAL BEHAVIOR OF METALS IN ELECTROLYTES UNDER THE ACTION OF ULTRAVIOLET LIGHT

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V. I. Veselovskii established that oxide films exert a considerable influence on the electrochemical behavior of metals when they are irradiated with ultraviolet light (1). However, the author observed and studied photoelectrochemical effects only during the occurrence of anodic processes.

We have found that for some metals photoelectrochemical phenomena are observed exclusively in the region of cathodic polarization. Further investigations showed that the character of the photoelectrochemical processes is closely connected with the type of conductivity of the oxide films present on the surface of the metals under study. Table 1 gives the results

Table 1

Influence of ultraviolet radiation on the change in the potential of a metal/oxide-film electrode in aqueous electrolyte solutions

Metal/oxide	Type of oxide conductivity according to lit. data	Electrolyte	Electrode with natural oxide film: stationary electrode potential,* V, without u.v. irradiation, V_{dark}	Electrode with natural oxide film: stationary electrode potential,* V, under irradiation, V_{light}	Electrode with natural oxide film: potential change, V, $\Delta V = V_{\text{light}} - V_{\text{dark}}$	Electrode with thickened** oxide film: polarization potential, V	Electrode with thickened** oxide film: V_{dark}	Electrode with thickened** oxide film: V_{light}	Electrode with thickened** oxide film: $\Delta V = V_{\text{light}} - V_{\text{dark}}$
Zn/ZnO	n	0.1 N NaOH	−1.360	−1.360	0	+2.00	−0.710	−0.712	−0.002
Zn/ZnO_2	n	0.1 N NaOH	−0.592	−0.710	−0.118	+10.00	−0.100***	−0.712	−0.612
Ta/Ta_2O_5	n	0.5 N Na_2SO_4	−0.145	−0.370	−0.125	+12.00	−0.430	−1.230	−0.800
Ti/TiO_2	n	0.1 N NaOH	−0.461	−0.735	−0.274	+3.00	−0.105	−0.500	−0.395
Ti/TiO_2	n	0.5 N Na_2SO_4	−0.138	−0.345	−0.207	+6.00	+0.238	−0.865	−1.103
Ni/NiO	p	0.1 N NaOH	−0.135	+0.076	+0.211	+0.80	+0.210	−0.275	−0.485
Cu/Cu_2O	p	0.1 N NaOH	−0.253	−0.240	−0.013	−0.45	−0.131	+0.108	+0.239

Metal/oxide	Type of oxide conductivity according to lit. data	Electrolyte	Electrode with natural oxide film: stationary electrode potential,* V, without u.v. irradiation, V_{dark}	Electrode with natural oxide film: stationary electrode potential,* V, under irradiation, V_{light}	Electrode with natural oxide film: potential change, V, $\Delta V = V_{\text{light}} - V_{\text{dark}}$	Electrode with thickened** oxide film: polarization potential, V	Electrode with thickened** oxide film: V_{dark}	Electrode with thickened** oxide film: V_{light}	Electrode with thickened** oxide film: $\Delta V = V_{\text{light}} - V_{\text{dark}}$
Cd/CdO	*n*	0.1 N NaOH	−1.240	−0.388	+0.852	+2.00	−0.250	−0.022	+0.228
Cd/CdO	*n*	0.1 N NaOH					−0.980	−0.950	+0.030

* The potential values are given relative to the saturated calomel electrode.

** The thickened film was obtained by polarizing the specimens at the indicated potential, in the same solution in which the measurements were carried out; the duration of polarization was determined by the time until a constant current density was established.

*** The indicated potential is not stationary, but was measured immediately after the end of anodic treatment.

of our experiments on the study of the influence of ultraviolet irradiation on the potentials of a number of metals located in dilute electrolytes and bearing an oxide film on their surface. The data of Table 1 show:

1) The direction of the shift of the metal potential under the action of u.v. irradiation depends on the type of conductivity of the oxide film on its surface. For *n*-

for semiconductors the potential tends to shift in the negative direction; for

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

p-semiconductors, conversely, in the positive direction. 2) Thinning of the film leads to an enhancement of the noted effect. The exception

Fig. 1. Magnitude of the photoeffect as a function of potential for various metals during their polarization in electrolytes: for Ta in 0.5 *N* Na_2SO_4, for the other metals in 0.1 *N* NaOH.
1—Ni; 2—Cu; 3—Cd; 4—Zn; 5—Ti; 6—Ta; 7—Zr

Fig. 2. Effect of ultraviolet irradiation on the polarization of Ta/Ta_2O_5 in 0.5 *N* Na_2SO_4. 1—dark current; 2—photocurrent; $3'$, $3''$, $3'''$—photocurrent during the reverse run of the polarization curve

is the Cd/CdO electrode. According to literature data, cadmium oxide belongs to *n*-semiconductors, but ultraviolet irradiation shifts its potential not in the negative, but in the positive direction. At the same time, an increase in the film thickness leads to a decrease in the positive value of the photo-

effect, instead of its increase, as should have occurred, according to the data cited, in the case of *p*-semiconductors. Preliminary experiments showed that a change in the oxygen concentration in the solution has a noticeable effect on the magnitude and character of the photoeffect. This compels the supposition that the shift of potential under the action of UV radiation is connected with a change in the adsorption capacity of the oxide film with respect to oxygen and, possibly, water molecules.

Using the potentiostatic method, we studied the influence of UV irradiation on the processes of cathodic and anodic polarization of the metals listed in Table 1. It was found that, for metals having an oxide film of the *n*-type on their surface, ultraviolet irradiation facilitates the course of the anodic process and has practically no effect on the cathodic process. In the case of an oxide film of the *p*-type, we have the opposite picture. Figure 1 shows the magnitudes of the photoeffects and the regions of their manifestation for all the metals tested. We see that the exception to the rule set forth above is again cadmium, for which effects are observed in both the cathodic and anodic regions. The reason for this behavior of Cd requires further investigation.

The behavior of copper is very distinctive. As is seen from Fig. 1, it has two waves of the photoeffect. The beginning of each wave (under conditions of successive polarization from more negative potentials to more positive ones) corresponds to the potential of the reaction: for the first wave, the formation of cuprous oxide:

$$2\mathrm{Cu} + 2\mathrm{OH}^- \rightleftarrows \mathrm{Cu_2O} + \mathrm{H_2O} + 2\bar{e},$$

for the second wave, the formation of cupric oxide hydrate:

$$\mathrm{Cu_2O} + 2\mathrm{OH}^- + \mathrm{H_2O} \rightleftarrows 2\mathrm{Cu(OH)_2} + 2\bar{e}.$$

The results presented undoubtedly indicate that even very thin oxide films formed on metals in electrolytes exert an influence on the electrochemical behavior of metals, and that not only the presence of the film but also the type of its conductivity is of importance. Consequently, metallic oxides display their semiconductor properties even in very thin layers. Obviously, this factor should be taken into account in corrosion and electrochemical investigations. An analogous conclusion was drawn in work ([2]).

Analysis of the data obtained makes it possible to state that the observed photoelectric effects are connected not only with an increase in the electrical conductivity of the semiconductor oxide layer but, chiefly, with facilitation of the course of the electrochemical reaction at the electrolyte–oxide interface. This follows already from the fact that irradiation effects occur for most films only either in the cathodic or in the anodic region of polarization (see Fig. 1), whereas an increase in electrical conductivity should manifest itself identically, irrespective of the direction of the current flowing.

A similar conclusion also follows from consideration of the curve of the photoelectrochemical current for a tantalum electrode (see Fig. 2).

It has been established ([3]) that the thickness of the film (d) on a tantalum electrode in 0.5 N $\mathrm{Na_2SO_4}$ increases proportionally to the applied voltage (V), and, consequently, $V/d = \mathrm{const}$. The simplest calculation gives, for the present case, $I_\phi = \mathrm{const}$, but this does not correspond to the experimental curve, which shows that with increasing film thickness the photocurrent I_ϕ changes its magnitude. The indicated curve consists of 3 sections. Section I is not considered, since film formation at this initial moment of its formation proceeds under somewhat peculiar conditions and requires special discussion beyond the scope of the present article. In section II we have an increase of the photocurrent with increasing film thickness. This increase can be explained if one proceeds

from the conditions for facilitation of the surface electrode reaction by the arriving current carriers.

Then

$$I_\phi = e n_d^{\tilde{z}} \alpha, \tag{1}$$

where e is the electron charge in amperes; n_d is the total number of current carriers formed in a film of the given thickness under the action of irradiation of the specified intensity; α is the coefficient of surface utilization of these carriers.

From the general laws of absorption of radiation energy it follows that

$$n_d = n(1 - e^{-\mu d}), \tag{2}$$

where d is the film thickness; n is the total number of carriers formed upon complete absorption of the radiation energy; μ is the absorption coefficient.

Assuming that for very thin films $\alpha \approx \text{const}$, and passing from the film thickness to the voltage, instead of equation (1) one may write:

$$I_\phi = An(1 - e^{-BV}), \tag{3}$$

where A and B are constants for the given irradiation intensity. Equation (3) is analogous to the equation given by Young[4]. However, unlike Young, who obtained a very large scatter of data for thicker films and believed that in this region $I_\phi = \text{const}$, we always observed a decrease in I_ϕ, as is shown by segment III of curve 2 in Fig. 2. We explain this by the fact that equation (3) is valid only as long as the film thickness does not exceed the layer of principal absorption ($d_{\max}$) of the ultraviolet radiation. With further thickening of the oxide, a layer d_1 with a large ohmic resistance appears, which leads to a decrease in the field strength in the layer $d_{\max}$, and consequently also to a decrease in I_ϕ. This can be expressed by the equation

$$I_\phi = k\eta V, \tag{4}$$

where η is a coefficient showing the fraction of the voltage drop in the layer $d_{\max}$. It is easy to show that $\eta \to 0$, and the rate of decrease of η is greater than the rate of increase of V. This accounts for the descending character of the curve in segment III. The law governing the change of η with film growth has not yet been determined by us.

The difference between curves $3'$, $3''$, $3'''$ and curve 2 consists in the fact that for each of these curves we have $d = \text{const}$, with $d''' > d'' > d'$. The course of these curves clearly shows that the photocurrent is related to the field strength in the film. It should also be noted that the shape of curves $3'''$ and $3''$ differs from that of $3'$, which is essentially a straight line. Obviously, this is connected with the fact that curves $3'$, $3''$, $3'''$ originate from different segments of curve 2 and, consequently, in film $3'$ there is no layer d_1, which is present in films $3'''$ and $3''$.

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