ON THE CHANGE IN THE ELECTROCHEMICAL ACTIVITY OF ZIRCONIUM UNDER THE ACTION OF RADIATION

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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When the elements Zr—Al and Zr—Fe were irradiated in a moving electrolyte (3% NaCl) with a beam of high-energy electrons (0.8 MeV) at an intensity of 15 μA/cm^2, a sharp increase in the galvanic-pair current was observed. The current increased immediately after the start of irradiation and exceeded the galvanic-pair current before irradiation by 15-20 times. Subsequently, over the entire course of the experiment (1 hour), the current changed relatively little. After irradiation was stopped, the current fell sharply, almost to its initial value.

Experiments in which only the anode or the cathode was subjected to irradiation showed that the observed effect occurs only when the cathode is irradiated

Fig. 1. Change with time in the galvanic-pair current of Zr—Al (*I*) and Zr—Fe (*II*) in 3% NaCl: *1* —absence of irradiation at room temperature; *2* —absence of irradiation at the temperature arising under irradiation; *3* —during irradiation of the anode (Al or, respectively, Fe); *4* —during irradiation of the cathode (Zr); the arrow indicates the moment irradiation was stopped.

(Zr). When the anode (Al or Fe) is irradiated, the effect is not observed. The results of these experiments are represented by curves 3 and 4 in Fig. 1. For comparison, curves are given for the dependence of the element current on time in the absence of irradiation at room temperature (Fig. 1, curve 1) and at the temperature arising at the metal-electrolyte interface owing to absorption of radiation energy (Fig. 1, curve 2).

Electrodes that had served as anodes in experiments under irradiation underwent considerably greater destruction than in experiments under the same conditions but in the absence of irradiation. Figure 2 (see the insert to p. 80) presents photographs of the surface of aluminum electrodes that had served as ca—

as anodes in a pair with a zirconium electrode under irradiation and in its absence (the duration of the experiments was 1 hour in both cases).

The observed effect cannot be explained as the result of the action of any of the factors that have hitherto been put forward as the principal stimulators of the rate of electrode processes under irradiation. The influence of temperature was studied in control experiments. It proved to be insignificant (Fig. 1, curve 2). Long-lived radiolysis products also cannot be regarded as the principal stimulators, since their steady-state concentration could not exceed 0.001 *N*. This is also indicated by the sharp drop in current after the irradiation is stopped. The anodic polarization due to electrons absorbed by the electrolyte did not exceed 7-8 $\mu A/cm^2$, whereas in the experiment the currents of the elements under irradiation increase to 800 $\mu A/cm^2$ (Zr-Al pair).

It seems possible to us to explain the change in the electrochemical activity of the zirconium electrode under irradiation by those changes in the physical properties of the oxide film on the zirconium cathode which radiation can cause. Most oxide films are typical semiconductors. The latter, as is known, possess the characteristic feature of an extreme sensitivity of their electrical properties to all kinds of external influences. Thus, irradiation in most cases causes a sharp increase in the electrical conductivity of semiconductors. This occurs as a result of the transfer of electrons from the filled band or from impurity levels into the conduction band at the expense of the radiation energy absorbed in the semiconductor. If in our experiments the oxide film on the cathode (ZrO_2) is regarded as a semiconductor, then under the action of irradiation the electrical resistance of such a film will decrease as a result of the appearance of "radiation conductivity" *. If one takes into account that the current of the cell is determined by the rate of the cathodic reaction of oxygen reduction, and assumes that the latter is limited by the high resistance of the semiconductor film on the cathode, then irradiation, leading to the appearance of radiation conductivity in the film, should accelerate the cathodic reaction and lead to a sharp increase in the current of the cell.

At the same time, if one proceeds from the proposed mechanism, one cannot expect irradiation of the anode to lead to a noticeable increase in the current of the cell—this is confirmed by experiment.

Radiation conductivity in a semiconductor arises immediately after the beginning of irradiation and disappears when it is ended. This accounts for the rapid rise of the current at the beginning of irradiation and the sharp drop after it is stopped.

The dependence of the current of the pairs on the radiation intensity was studied theoretically and experimentally. If it is assumed that the principal source of free electrons is the filled band, then, proceeding from the basic concepts of the photoconductivity of semiconductors, the change in the concentration of free electrons in the conduction band can be expressed in the following form:

$$\frac{dn}{dt} = \alpha I - kn^2, \tag{1}$$

where α is the quantum yield, I is the radiation intensity, k is the recombination coefficient, and n is the concentration of electrons in the conduction band. Under steady-state conditions (1) takes the form:

$$\alpha I = kn^2. \tag{2}$$

The left-hand side of the equation represents the quantity of electrons released at radiation intensity I; the right-hand side is the quantity of electrons returning back to the filled band.

* By radiation conductivity we mean conductivity caused by the action of both electromagnetic and corpuscular radiation, by analogy with photoconductivity caused by the action of light.

The current flowing through an irradiated semiconductor placed between electrodes is expressed as follows:

$$i = 2neu\frac{\Delta V}{d}S, \tag{3}$$

where ΔV is the potential difference of the electrodes, S is the area of the electrodes, d is the thickness of the semiconductor, n is the concentration of current carriers of a given sign, u is their mobility, and e is the charge of the carriers. Taking (2) and (3) into account, we obtain:

$$i = \frac{2\Delta VSeu}{d}\sqrt{\frac{\alpha}{k}I}. \tag{4}$$

If it is assumed that the increase in the current of the couple under irradiation is determined mainly by the radiation conductivity in the oxide film-semiconductor, then, denoting the constant quantities entering into (4) by A, we obtain the following dependence of the couple current on the radiation intensity:

$$J_k = I_k^0 + A\sqrt{I},$$

where I_k^0 is the current of the couple in the absence of radiation, and I is the radiation intensity.

Fig. 3. Dependence of the current of the Zr–Al couple in 3% NaCl on the intensity of electron radiation: 1 –calculated curve; 2 –experimental curve

Figure 3 gives curves of the dependence of the current of the Zr–Al couple on the radiation intensity, obtained by calculation* (curve 1) and experimentally

Fig. 3. Dependence of the current of the Zr—Al couple in 3% NaCl on the intensity of electron radiation: 1 —calculated curve; 2 —experimental curve

Figure 2: Fig. 3. Dependence of the current of the Zr—Al couple in 3% NaCl on the intensity of electron radiation: 1 —calculated curve; 2 —experimental curve

(curve 2). As follows from the graphs presented, at relatively low radiation intensities there is satisfactory agreement between the theoretical and experimental curves. The deviation of the experimental curve from the calculated one at higher intensities is apparently due to the presence of anodic polarization, which was not taken into account in the calculations.

In conclusion it should be noted that the question of the influence of short-lived radiolysis products remains open. Further investigation should show whether the increase in the electrochemical activity of the zirconium cathode under irradiation can be attributed entirely to an increase in the conductivity of the semiconductor film, or whether it is also necessary to take into account the action of short-lived radicals as depolarizers.

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* The value of the constant k was found from experimental data for the dependence of J_k on I at one of the values of I.

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