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Abstract

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STUDY OF THE MECHANISM OF RECTIFYING ACTION ON AN OXIDIZED ZIRCONIUM ELECTRODE

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At present the rectifying action of oxide films on valve metals is associated either with the existence of a p—n junction in the film ([1,2]), or with the presence of a space charge in the oxide film and with processes occurring at the oxide–electrolyte boundary ([3–9]).

The assumption that a p—n junction exists in the oxide film is refuted by the experiments of Smith ([10]), Vermilyea ([11]), and L. Young ([6]). The latter, however, do not take into account the influence of the electrolyte on this phenomenon. Schmidt ([12,13]) relates the appearance of conductivity in the oxide film under cathodic polarization to the penetration of protons from the electrolyte into the film and to the formation in it, in this way, of a sufficient concentration of carriers. From the concept of the existence of a space charge in the film and of a barrier at the oxide–electrolyte boundary it follows that a change in the potential at this boundary should substantially affect the electrophysical properties of the film as a whole. Despite the great importance of information on the dependence of the resistance of films on the potential at the oxide–electrolyte boundary for elucidating the mechanism of rectifying action, such data have not been obtained up to the present time.

The commonly used method for studying the influence of a change in potential on the properties of the electrode–solution boundary by imposing polarization on the electrode cannot be applied here, since, when current passes through the film, it is impossible to separate the change in potential at the oxide–solution boundary from the ohmic voltage drop in the film. It is also necessary to take into account that, in the overall change in the electrode–solution potential difference, which reaches hundreds of volts under anodic polarization, the relative contribution of the change in potential at the oxide–solution boundary is small and cannot be measured with sufficient accuracy.

In order to isolate the component of the total electrode–solution potential drop that is of interest to us and that pertains to the oxide–solution boundary, in the present work we investigated the dependence of the resistance R and capacitance

Fig. 1

Figure 1: Fig. 1

C of an oxidized zirconium electrode on the potential of the oxidation-reduction medium. In this case it may be assumed that the change in the electrode–solution potential will correspond to a change in the oxide–solution potential, since the ohmic voltage drop in the film iR can be neglected when measuring the potential with an instrument having a small current consumption.

An electrode in the form of a wire of diameter 1 mm and length 2.5 mm made of iodide zirconium (99.8 Zr, 0.02% Si, Al and Fe, 0.01% Be) was subjected to anodizing at 0° with a current of 260 μA/cm^2 in a 0.2 N solution of H_2SO_4. The film thickness δ was calculated from the values of the capacitance C, measured in 0.2 N H_2SO_4 at a frequency of 400 Hz, by the formula

$$\delta = \frac{\varepsilon}{4\pi C}.$$

The dielectric constant ε was taken to be equal to 20 ([14,15]). The reproducibility of the film thickness measured by this method was 5-10%. To vary the electrode-solution potential, the following systems were used: Fe^{2+}/Fe^{3+} at pH 1.4, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ at pH 8.4, and J^-/J_3^- at pH 1.5. In choosing the systems we were guided by the fact that they are highly reversible ([16–18]), and the transition from the oxidized form to the reduced one is accompanied only by electron transfer. By varying the concentration ratios of the oxidized and reduced forms from 1 : 0.001 to 0.001 : 1, while keeping the total salt concentration equal to 0.5 N, it was possible to change the system potential by 0.3 V.

The resistance and capacitance of the electrode were measured with an AC bridge at an amplitude of 10 mV and frequencies from 400 to 5000 Hz on films of thickness 500, 1000, and 1500 Å. The results obtained from the series connection circuit R and C were recalculated for a circuit with their parallel connection, which corresponds to a greater extent to the equivalent circuit of an oxidized zirconium electrode. The film does not immediately come into equilibrium with the solution; therefore measurements of capacitance and resistance were begun after 5-hour thermostating at +30°. In this case the potential of the oxidized zirconium electrode was equal to the potential of a platinum electrode immersed in the same solution. The potentials were measured with a pH-E-M type electrometer with a current consumption of $5 \cdot 10^{-15}$ A/div relative to an Hg/Hg_2SO_4 electrode in 0.2 N H_2SO_4.

Fig. 1. Dependence of the resistance (curves A) and capacitance (curves B) on the oxidation-reduction potential of the medium in the Fe^{2+}/Fe^{3+} system: 1 –at a frequency of 400 Hz, 2 –at a frequency of 1000 Hz, 3 –at a frequency of 2500 Hz, 4 –at a frequency of 5000 Hz.

Figure 2

Figure 2: Figure 2

Figure 1 gives the dependence of resistance and capacitance on the potential set by the Fe^{2+}/Fe^{3+} system at frequencies of 400, 1000, 2500, and 5000 Hz for an electrode with an oxide film of 1090 Å. It follows from Fig. 1 that, when the potential is shifted from +0.85 to +0.57 V relative to the normal hydrogen electrode, the resistance of the film at 400 Hz falls by a factor of two, while the capacitance increases by 10%. In addition, the C–φ curves at frequencies of 400 and 1000 Hz have a maximum, and the R–φ curves a minimum at $\varphi = 0.69$ V, which corresponds to equal concentrations of oxidant and reductant $(0.25\,N)$.

Figure 2 presents the dependence of the resistance and capacitance of the same electrode on the potential set by the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system for a film of 1090 Å at frequencies of 400, 1000, 2500, and 5000 Hz. When the potential is shifted in the negative direction by 0.4 V, at 400 Hz the capacitance of the film first increases by 10% and, after passing through a maximum, reaches its initial value; the resistance in this case falls by a factor of two, passing through a minimum at $\varphi = 0.47$ V, i.e., at the point of equal concentrations of the oxidized and reduced forms.

With increasing frequency, the amplitudes of the extrema on the C–φ and R –φ curves decrease, and at 5000 Hz they practically disappear both in the Fe^{2+}/Fe^{3+} system and in the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system. On films of thickness 500 and 1500 Å, dependences analogous to those shown in Figs. 1 and 2 were obtained.

The curves R–φ and C–φ shown in Figs. 1 and 2 have two characteristic features: an increase in capacitance and a decrease in resistance upon transition

toward less positive values of the potential and the presence of extrema at points corresponding to equal concentrations of oxidant and reductant in the solution. The presence of extrema in the curves of Figs. 1 and 2 is apparently due to the fact that the systems Fe^{2+}/Fe^{3+} and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, reversible on metals, lose their reversibility when the electrochemical process is carried out on a semiconductor, which may be connected with the difficulty of transfer of electrons from the electrode to ions, the concentration of which in the semiconductor is small.

With increasing concentration of the oxidant and reductant, the resistance caused by the slowness of the electrochemical process decreases.

Fig. 2. Dependence of resistance (curves A) and capacitance (curves B) on the oxidation-reduction potential of the medium in the system $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$:
1 –at a frequency of 400 Hz, 2 –at a frequency of 1000 Hz,

3 –at a frequency of 2500 Hz, 4 –at a frequency of 5000 Hz

This leads to the appearance of minima in the R–φ curves at points with equal concentrations of oxidant and reductant. The maxima in the C–φ curves are probably due to the presence of a pseudocapacitance associated with the course of the electrochemical process. The disappearance of the extrema in the C–φ and R–φ curves at high frequencies confirms the conclusion made above as to their nature.

In addition to the common features, some differences are observed in the behavior of the oxidized zirconium electrode in the Fe^{2+}/Fe^{3+} and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ systems. In the C–φ and R–φ curves in the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ system, the extrema have a larger amplitude and disappear at lower frequencies than in the Fe^{3+}/Fe^{2+} system. This indicates the greater reversibility of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system. In addition, at high frequencies the resistance and capacitance of the electrode in the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system are practically independent of potential, in contrast to the Fe^{2+}/Fe^{3+} system, where the resistance of the electrode decreases and the capacitance increases on going to less positive values of the potential.

A twofold decrease in the resistance of the film in the Fe^{2+}/Fe^{3+} system and a 10% increase in capacitance, equivalent to a decrease in the film thickness by the same amount, when the potential is shifted in the negative direction by 0.25 V, indicate that the principal resistance of the film is concentrated in the layer in contact with the electrolyte.

The conclusion that the resistance of the film depends substantially on the potential is even more strongly confirmed by comparison of the resistance values of the oxidized zirconium electrode at different potentials set by different oxidation-reduction systems, under conditions most favorable for the electrochemical process, i.e., in solutions with a concentration of the oxidized and reduced forms equal to $0.25\,N$.

It was found that at potentials of 0.72, 0.54, and 0.77 V, set by the systems Fe^{2+}/Fe^{3+}, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, J_3^-/J^-, the resistance of a film 1000 Å in ···

is, respectively, $4.7 \cdot 10^5$ and $0.5 \cdot 10^5$, $0.2\ \text{V} \cdot 10^5$ ohms, i.e., the resistance of the film decreases by a factor of 9 when the potential is decreased by 0.25 V.

The experimental results presented in this work confirm the conclusion that there is a nonuniform distribution of carriers in the film and that the oxide-electrolyte boundary has a substantial influence on the electrophysical properties of the film as a whole; they also indicate that the rectifying action of the oxide film is associated with an increase in the concentration of current carriers in the layer of the film in contact with the electrolyte when the potential is shifted in the negative direction.

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