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Abstract

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On the Adsorption of Iodine Ions on Platinum and Its Influence on the Process of Hydrogen Ionization

(Presented by Academician A. N. Frumkin, 15 IV 1960)

Anions, adsorbing on an electrode surface, exert a substantial influence on the rate of electrode processes, in particular on the rate of evolution and ionization of hydrogen. Depending on the nature of the metal of which the electrode is made, the ions Cl^-, Br^-, and J^-, forming adsorption layers of different structure, may either increase the overvoltage of the process or decrease it ([1–4]). In the latter case, an increase in the residence time of the electrode in solutions containing Br^- and J^- anions leads to an even greater slowing of the process ([3]). In papers ([5–8]) it was found that, with time, the bond of the anion with the metal surface becomes stronger, as a result of which the bond energy of hydrogen with the surface decreases.

In the present work the influence of anion adsorption on smooth platinum was studied; moreover, in contrast to what was done in paper ([3]), measurements of the ionization rate were carried out with an electrode on which Br^- and J^- had been preliminarily adsorbed, in a solution of $1\,N\,H_2SO_4$ that no longer contained anions. Such a method, the use of which is possible owing to the great strength of adsorption of Br^- and J^- anions by platinum, has certain advantages. Thus, it permits adsorption to be carried out at a potential φ independent of the magnitude of the overvoltage η at which measurements of the process rate are performed.

In the present work the apparatus and procedure described in paper ([9]) were used; however, the preliminary treatment of the electrode was carried out somewhat differently. Before each experiment the electrode was brought to a certain standard activity. Then the activated electrode was immersed in a solution of $1\,N$ HBr or in $1\,N$ KJ + $0.1\,N\,H_2SO_4$, previously purified by adsorption on a large platinum gauze and saturated with hydrogen, and was kept in it at a definite potential. After this the poisoning solution was drained off, the cell and electrode were washed with bidistillate (in the case of poisoning in KJ, until the wash waters gave a negative reaction with starch for iodine), the system was purged with hydrogen, purified and hydrogen-saturated $1\,N\,H_2SO_4$ was forced into the cell, and the anodic polarization curve was recorded in a hydrogen atmosphere at an electrode rotation rate of 5000 rpm.

The influence of the time of poisoning of the electrode by iodine and bromine

Fig. 1 and Fig. 2 graphs

Figure 1: Fig. 1 and Fig. 2 graphs

anions on the rate of the ionization reaction of molecular hydrogen was studied. The electrode was kept for 2, 4, 8, 16, and 24 hours in a solution of $1\,N$ KJ + $0.1\,N$ H_2SO_4 in a hydrogen atmosphere, after which polarization curves were recorded on it. The results obtained are presented in Fig. 1. As can be seen from Fig. 1, the maximum on the polarization curve, expressing the rate of the process of hydrogen ionization i as a function of the overvoltage η, decreases as the time of poisoning of the electrode increases. After 24-hour poisoning of the electrode, the maximum on the curve disappears and the current up to potentials of 0.6-0.7 V becomes practically equal to zero, which indicates

of the complete suppression of the hydrogen ionization process on such an electrode. The potential at which the poisoning of the electrode was carried out has a definite effect on the rate of the hydrogen ionization process. The electrode was kept in a solution of $1\,N$ KJ + $0.1\,N$ H_2SO_4 for 2 hours, at potentials 0.27; 0.17; 0.07; −0.09; −0.13; −0.23 V (relative to the normal hydrogen electrode) in a hydrogen atmosphere. The experimental results are given in Fig. 2. As can be seen from Fig. 2, after poisoning the electrode at $\varphi = -0.23$ V it becomes very inactive with respect to hydrogen ionization. A decrease in the negative

Fig. 1. Dependence of the activity of the electrode with respect to the hydrogen ionization reaction on the duration of its poisoning in a solution of $1\,N$ KJ + $0.1\,N$ H_2SO_4 in an H_2 atmosphere:
1 −2 hours; 2 −4 hours; 3 −8 hours; 4 −16 hours; 5 −24 hours.

Fig. 2. Dependence of the activity of the electrode on the potential at which it was poisoned in a solution of $1\,N$ KJ + $0.1\,N$ H_2SO_4 in an H_2 atmosphere for 2 hours. The electrode was poisoned:
1 −at $\varphi = +0.27$ V; 2 −$\varphi = +0.17$ V; 3 −$\varphi = +0.07$ V; 4 −$\varphi = -0.09$ V; 5 −$\varphi = -0.13$ V; 6 −$\varphi = -0.23$ V.

poisoning potential (down to −0.09 V) leads to the preservation by the electrode of a certain activity. With increasing positive poisoning potential of the electrode, its activity with respect to hydrogen ionization increases.

The data obtained on electrodes poisoned by bromine ions are of an analogous character. The sharp decrease in the rate of the molecular hydrogen ionization reaction as a function of the residence time of the electrode in the poison solution, and the almost complete suppression of the process after 24-hour poisoning of the electrode, indicate a decrease with time in the number of active centers on the electrode surface at which the H_2 ionization process takes place.

The dependence of the rate of the hydrogen ionization process on the potential at which the poisoning of the electrode was carried out is of an unexpected

Fig. 3 and Fig. 4: polarization curves

Figure 2: Fig. 3 and Fig. 4: polarization curves

character. Indeed, as the anodic potential increases, the activity of the poisoned electrode with respect to hydrogen ionization increases, despite the fact that the amount of adsorbed anions, according to the data of N. A. Balashova [10], increases. The low activity of the electrode poisoned at negative potentials can be explained by the fact that, under these conditions,

apart from the adsorption of anions on the electrode surface, no changes occur, and a small amount of adsorbed substance is sufficient to passivate the electrode. In the case of poisoning at more positive potentials, along with the increase in anion adsorption there occurs, apparently, some renewal of the electrode surface due to slight dissolution of platinum in the presence of halogen ions. This can explain the comparatively high activity of the electrode with respect to the hydrogen ionization reaction after its poisoning at more positive potentials.

When polarization measurements are carried out on curves obtained with electrodes previously kept for some time in a solution of

Fig. 3. Polarization curve recorded on an electrode kept in a solution of $1\,N$ KJ + $0.1\,N$ H_2SO_4 for 4 hours in an H_2 atmosphere.

Fig. 4. Polarization curves recorded on an electrode kept in a solution of $1\,N$ KJ + $0.1\,N$ H_2SO_4 for 4 hours in an H_2 atmosphere: $1, 3$—in an N_2 atmosphere; $2, 4$—in an H_2 atmosphere.

KJ (Fig. 3), at φ = 0.6-0.7 V, a sharp rise in current is observed, which continues up to 0.09-1.0 V; then there is a slight drop in current, and at $\varphi = 1.2$ V the current again increases. The second rise in current is higher than the first. At more anodic potentials the current decreases somewhat and then begins to increase again at $\varphi = 1.6$ V. The rise in current at φ = 0.6-0.7 V is not connected with the dissolution of platinum in H_2SO_4 in the presence of J^-, as was initially assumed, since analysis for platinum by the method described in work [12] gave no positive results, although, as indicated above, it is quite probable that traces of platinum pass into solution.

The first wave corresponds to the oxidation of J^- to free iodine (the normal potential of the process is $\varphi^0 = 0.53$ V), and the second—to the oxidation of J_2 to JO_3^- at $\varphi = 1.19$ V, which is confirmed by direct experiments. If the electrode is kept at potentials $\varphi = 0.95$ V (or $\varphi = 1.2$ V), and then the solution is poured off and analyzed, free iodine (or JO_3^-) can be detected in it.

However, the height of the waves on the polarization curves is associated not only with iodine oxidation processes, but also with the participation of hydrogen in the electrode process. In order to determine whether hydrogen takes part in the electrode process, a series of curves was recorded in a nitrogen atmosphere. The electrode was treated in the usual manner in $1\,N$ KJ + $0.1\,N$ H_2SO_4 for

4 hours, washed free of KJ, transferred to a solution of 1 N H_2SO_4 saturated with nitrogen, after which a polarization curve was recorded with continuous nitrogen purging through the cell. When necessary, hydrogen was introduced into the cell and the curve was then recorded in a hydrogen atmosphere. As can be seen from Fig. 4, the magnitude of the current on curve 1, recorded in a nitrogen atmosphere, is almost half the magnitude

of the current in curve 2, recorded in a hydrogen atmosphere. If hydrogen was admitted into the cell during the recording of the curve (at $\varphi = 1.2$ V; see Fig. 4, curves 3, 4), the current also increased appreciably. The amount of electricity expended in removing from the electrode one and the same amount of iodine in a hydrogen atmosphere is almost twice as large as in a nitrogen atmosphere.

With prolonged treatment by an anodic current, the electrode is gradually freed of iodine and restores its initial activity with respect to the ionization of hydrogen. The results described were obtained on a disk electrode, as well as on electrodes in the form of a massive plate and a mesh.

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