THE EFFECT OF STRONGLY ADSORBING SUBSTANCES ON THE IONIZATION OF MOLECULAR HYDROGEN ON SMOOTH PLATINUM

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The literature contains few experimental data on the effect of strongly adsorbing substances upon the ionization of molecular hydrogen at the platinum electrode. The effect of Br^- and I^- ions upon this reaction has been studied under conditions where Br^- and I^- adsorption changed with potential [1], or had a constant value which was not controlled [2].

It is the aim of the present work to determine the relation between the degree of surface coverage by strongly adsorbed particles and the rate of H_2 ionization. In [3-7], contrary to [1, 8], no limiting kinetic current for H_2 ionization could be observed in 1 N H_2SO_4. We have made an attempt to see whether the results of [1, 8] could be reproduced when poisoning the electrode with strongly adsorbing substances.

The measurements were carried out at 20 ± 2°C in 1 N H_2SO_4 with a rotating disc electrode of smooth platinum, in the presence of strongly adsorbed iodine, thallium, sulfur, copper, and mercury. Potentials given relative to the reversible hydrogen electrode in the same solution are designated by φ_r. Preparation of the electrode for the experiments, determination of its true surface area, and other experimental details were the same as in [7].

The measurements were organized as follows. Initially a potentiodynamic curve was recorded in 1 N H_2SO_4. Then certain amounts of KI, Tl_2SO_4, $CuSO_4$, or $HgCl_2$ were introduced into the cell. Adsorption of the poison was allowed to occur in hydrogen-saturated solution at $\varphi_r = 0$ V. When the electrode was to be poisoned with sulfur, the hydrogen passing through the cell was first passed through a sodium sulfide solution acidified with sulfuric acid. After a certain period of time the solution containing the poison was poured from the cell, and the whole system was carefully washed with twice-distilled water and with 1 N H_2SO_4.

Then potentiodynamic and polarization curves for H_2 ionization in 1 N H_2SO_4 were measured at different rates of rotation of the electrode. The polarization range of the poisoned electrode was chosen in such a way that during the recording of the polarization curves, desorption of the strongly adsorbed substances would not occur. The starting potential was always $\varphi_r = 0$. The highest anodic potentials for electrodes poisoned with iodine were 0.7 V, with mercury and copper they were 0.4 V, with thallium 0.5 V, and with sulfur 0.4 V. It follows from [9-12] that over this range of φ_r values, desorption of the above substances does not occur. When the polarization curves had been recorded, the surface coverage by the poison was again checked according to the hydrogen region of the potentiodynamic curve in 1 N H_2SO_4.

By way of an example, anodic-polarization curves recorded on a clean and on poisoned electrodes in 1 N H_2SO_4 at 4600 rpm are shown in Fig. 1. The rate of H_2 ionization on poisoned electrodes is lower than that on a clean electrode. The shape of the polarization curves depends on the nature of the poison.

The processes were studied in more detail on electrodes poisoned with iodine and with thallium (Fig. 2). A drop in current is observed on the polarization curve for H_2 ionization when poisoning is by iodine. The measurements were carried out at a constant degree of poisoning of the platinum by iodine; therefore, one of the reasons of this drop may be given by a variation in the surface state upon strengthening of the

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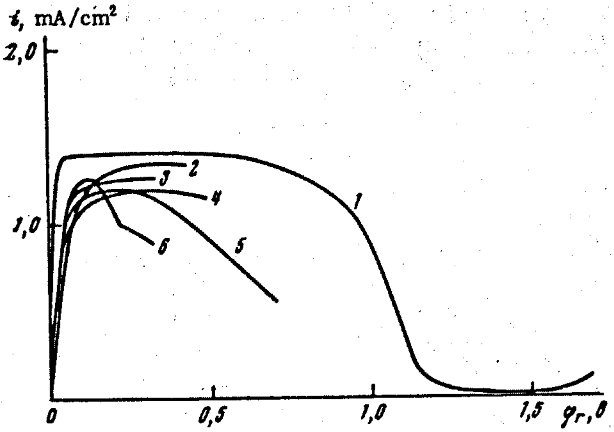

Fig. 1. Anodic polarization curves for the ionization of molecular hydrogen in 1 N H_2SO_4 on a clean Pt electrode (1) and on electrodes poisoned with sulfur (2, $\Delta\theta = 0.61$), mercury (3, $\Delta\theta = 0.61$), thallium (4, $\Delta\theta = 0.60$), iodine (5, $\Delta\theta = 0.76$), and copper (6, $\Delta\theta = 0.60$). The potential scan rate was 100 mV/min. The rate of electrode rotation was 4600 rpm.

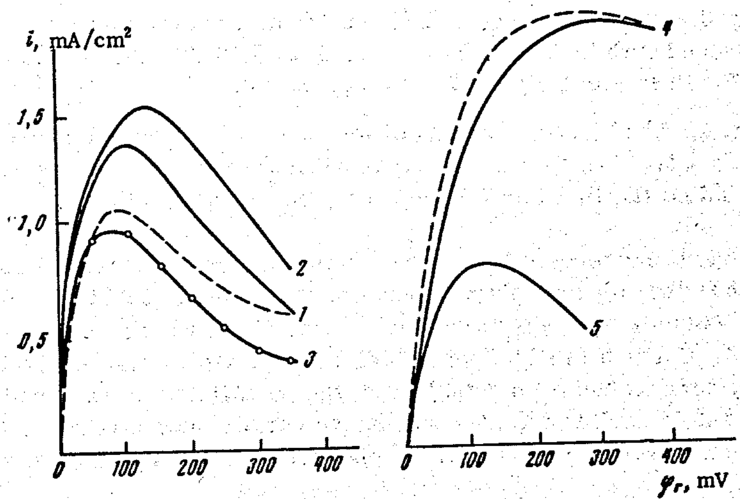

Fig. 2. Polarization curves for H_2 ionization in 1 N H_2SO_4 (1, 3, 4) and in 1 N HCl (2, 5) on electrodes poisoned with iodine (1-3) or thallium (4, 5). With iodine in 1 N H_2SO_4, $\Delta\theta = 0.72$, with thallium $\Delta\theta = 0.55$. The rate of rotation of the electrode was 6600 rpm. The dashed lines are cathodic-polarization curves. Curves 1, 2, 4, and 5 were recorded with a potential scan rate of 100 mV/min.

bond between the adsorbed particles and the platinum as the potential is moved toward the anodic side. Another possibility is the adsorption of sulfate ions which may begin as φ_r increases. Support for the first possibility is provided by the fact that the adsorption of SO_4^{2-} is strongly decreased when platinum is poisoned by iodine [13]. If the drop was due to the adsorption of SO_4^{2-} ions, then one could have expected even earlier inhibition of the reaction in the presence of Cl^- ions. However, the drops on the polarization curves in 1 N H_2SO_4 and 1 N HCl are observed at similar φ_r when the electrode is poisoned with iodine (Fig. 2, curves 1 and 2). The measurements in the presence of HCl were carried out at a somewhat lower surface coverage by I^- because part of the iodine became desorbed when the H_2SO_4 solution was replaced by HCl solution.

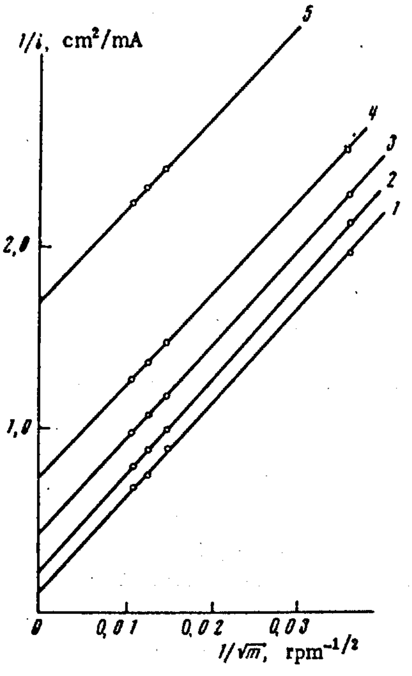

Fig. 3

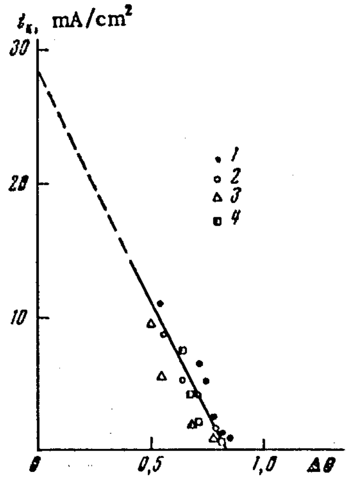

Fig. 4

Fig. 3. The dependence of $1/i_k$ on $1/\sqrt{m}$ when the platinum is poisoned with thallium: 1) $\Delta\theta = 0.49$; 2) 0.56; 3) 0.65; 4) 0.68; 5) 0.77. Base electrolyte: 1 N H_2SO_4, $\varphi_r = 0.3$ V.

Fig. 4. The kinetic currents of ionization of molecular hydrogen, i_k, in 1 N H_2SO_4 as function of $\Delta\theta$ when the platinum was poisoned by iodine (1), thallium (2), mercury (3), or sulfur (4).

In the presence of iodine, hysteresis is observed between curves measured during anodic and cathodic potential scan, which is difficult to explain unless one takes into account strengthening of the Pt–I bond with increasing φ_r. This strengthening also occurs with time, which produces a drop in the rate of H_2 ionization at φ_r = const. Curve 3 in Fig. 2 was obtained after the electrode had been held for 2 h at 350 mV, until a stationary current had been established; the potential then was suddenly changed by 50 mV in the cathodic direction, and at each new φ_r the stationary current was recorded. The stationary currents for H_2 oxidation at $\varphi_r > 50$ mV were lower than those observed when varying φ_r in cyclical fashion at a given rate.

A drop in current is also observed on an electrode poisoned with thallium (Fig. 2, curve 4). However, here the drop in current occurs at lower φ_r when the H_2SO_4 solution is replaced by HCl solution (compare curves 4 and 5 of Fig. 2). In view of this result and also in view of the data on the adsorption of SO_4^{2-} on a thallium-poisoned surface [13] one can conclude that in this case adsorption of the anions is one of the reasons for the drop in current. In the presence of thallium one finds hysteresis (even though this is relatively small) between curves recorded during anodic and cathodic potential scan; the cathodic curve is above the anodic one. This is possibly due to an increasing degree of "ionicity" of the Pt–Tl bond when φ_r shifts toward the anodic side. When other poisons are adsorbed, the anodic and cathodic curves differ little from each other.

Measurements at different rates of rotation m have shown that the i-$\sqrt{m}$ relations on poisoned electrodes were curved but go over into the straight-line plots which are typical for pure diffusion control when the rates of rotation are low. The bending of the i-$\sqrt{m}$ dependences is due to the transition into a region of mixed kinetics.* By way of an example, plots of $1/i$ against $1/\sqrt{m}$ for different degrees of surface coverage by thallium at $\varphi_r = 0.3$ V are shown in Fig. 3. The parallel disposition of the straight lines

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* In the cases studied, there is no reason to assume formation of blocked areas measuring 10^{-3}-10^{-5} cm on the electrode surface (as was done in [14]) in order to explain the experimental data.

indicates that ionization on an electrode having thallium adsorbed is a first-order reaction. Analogous relations were obtained for the other strongly adsorbing substances. By extrapolating these straight lines to $1/\sqrt{m} = 0$ one can obtain values for the kinetic current i_k at a given surface poisoning.

Figure 4 shows values for the kinetic current densities reckoned per unit of true surface area of the electrode, as function of the amount of adsorbed hydrogen that has been displaced by the poison. The latter was calculated from the potentiodynamic curves, and is shown as the ratio between the amount of hydrogen displaced, ΔA_H, and the total amount of hydrogen adsorbed in the absence of poison, A_H: $\Delta\theta = \Delta A_H/A_H$. The relations found between i_k and $\Delta\theta$ are linear, to a first approximation, and differ relatively little for different poisons. It must be noted that in the adsorption of various substances on platinum one finds superequivalent displacement of adsorbed hydrogen [9, 10]. Therefore identical $\Delta\theta$ really correspond to different surface coverages by poison.

It can be seen from Fig. 4 that even at $\Delta\theta = 0.5$, the kinetic current density is appreciably larger than the limiting value of current density obtained in [1, 8]. By extrapolating the straight-line plots of i_k against $\Delta\theta$ to $\Delta\theta = 0$ one can estimate the kinetic current density on a clean electrode. This is about 30 mA/cm². This estimate is not very precise, because one must assume linearity between i_k and $\Delta\theta$ over a wide range of $\Delta\theta$. The i_k value obtained by us for a clean electrode is close to the one reported in [6].

By carrying out measurements and calculations like the ones described above at different φ_r one could in principle construct the $i_k - \varphi_r$ relation for H_2 ionization on an unpoisoned electrode, were it not for the fact that in doing so one would have to make use of too rough an extrapolation of the $i_k - \Delta\theta$ straight-line plots. We have found a strong depression of the H_2-ionization current while significant adsorption of atomic hydrogen is maintained, when silver is deposited on the platinum surface. Here, however, it was not possible to obtain reproducible polarization curves.

It is a conspicuous fact that transition to mixed kinetics occurs only at rather high degrees of poisoning of the platinum. We have carried out measurements when the platinum was poisoned with methanol or glycerol; here a noticeable decrease in the ionization current is also observed at $\Delta\theta \geqslant 0.5$. But, the drop in the H_2-ionization current in 1 N H_2SO_4 takes place at about 0.7 V (curve 1 of Fig. 1), when the surface coverage by adsorbed oxygen is low, and adsorption of SO_4^{2-} ions also is small. Further research is required in order to elucidate the causes of these discrepancies.

It follows from the measurements carried out that H_2 ionization is a first-order reaction when the platinum is poisoned by various contaminants introduced into the solution. The zero reaction order that had been observed in [1, 8] could not even be reproduced on electrodes that had been exposed for a long time to the reducing flame of a blow torch. We have also repeated measurements on electrodes treated in the same way as in [15]. Here the shape of the polarization and potentiodynamic curves of platinum is strongly changed, primarily perhaps because of contamination of the electrode surface by the polishing paper.* We did not find conditions under which in 1 N HCl one could observe zero reaction order.

It is not impossible that the results obtained in [1, 8] will be explained by the presence of impurities in the electrode material itself, which could substantially influence the character of anion or impurity adsorption from the solution on the electrode surface. Unfortunately the electrodes used in that work were not kept, which makes it impossible to definitely elucidate the reasons why the hydrogen-ionization reaction ran so differently on smooth platinum in [1, 8] and in subsequent work, both of ours and of a number of other authors.

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*However, the shape of the curves is not reproducible even after treating the electrode with a mixture of hydrochloric and hydrofluoric acid, where residues of the abrasive material should have dissolved.

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