INFLUENCE OF CATIONS ON THE IONIZATION OF MOLECULAR HYDROGEN ON SMOOTH PLATINUM

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The electrochemical oxidation of molecular hydrogen on smooth platinum has been studied over a prolonged period (a review is given in [1-4]). Recently, a number of new results were obtained with electrodes operating in thin films of electrolytes [5,6]. We have not found any published data, however, on the influence of inorganic cations on the ionization of molecular hydrogen on platinum. It was therefore of interest to study the relationship between the nature of the adsorption of a cation and its influence on the process being considered.*

For the study of the kinetics of the ionization of molecular hydrogen on smooth platinum we used a rotating disc electrode. The measurements were made on an assembly developed in the Institute of Electrochemistry of the Academy of Sciences of the USSR, and also on an assembly in which the cell was insulated from the mechanical system by means of a seal containing concentrated sulfuric acid.

The solutions were purified using large Pt/Pt gauzes over a period of several days with cathodic polarization by a current of 2-3 mA. The salts were purified by recrystallizing twice, and the sulfuric acid was vacuum-distilled twice. The solutions were prepared with twice-distilled water. In control experiments to investigate the influence of the degree of purity of the hydrogen on the process being studied, we used hydrogen purified by diffusion through a palladium membrane. No significant differences were observed, however, between these results and the results obtained with electrolytic hydrogen purified by the usual methods.

The electrode was prepared as follows. The electrode was treated with emery polishing paper and wiped with a cloth moistened with ethanol, after which it was washed thoroughly with warm concentrated sulfuric acid and twice-distilled water. Directly before the measurements, the electrode was subjected to repeated cycles in the range of potentials (φ_r) from 0 to 1.45 V in 1 N H_2SO_4 (φ_r is the potential, related to that of a reversible hydrogen electrode in the same solution) at a rate of scanning of the potential equal to 0.5 V/sec. The state of the surface and the purity of the solution were controlled by recording the potentiodynamic curves.

To investigate the influence of the cations studied on the exchange current of adsorbed hydrogen we used impedance measurements. The impedance measurements were made by the method described in [8]. As equivalent scheme modeling the processes at the platinum electrode we used the Dolin-Ershler scheme [9].

The true surface area of the electrodes was calculated from the hydrogen section of the potentiodynamic curve in 1 N H_2SO_4 with the assumption that 210 μC of hydrogen is adsorbed per 1 cm^2 surface area [1]. The roughness factor of the electrodes studied was 2.5-3. The exchange current densities and the values of the capacity of the electrodes, and also the data in Fig. 2, are given for 1 cm^2 of true surface area.

In the experiments we used a P-5827 potentiostat and a PO-5122 model 03 oscillographic polarograph.

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*A preliminary notice of the results obtained was given in [7].

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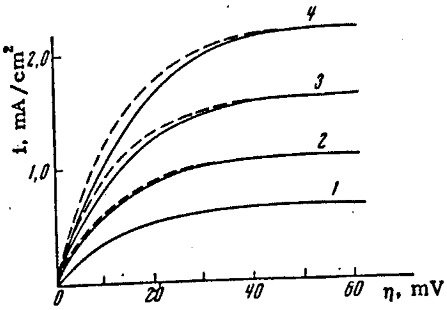

Fig. 1

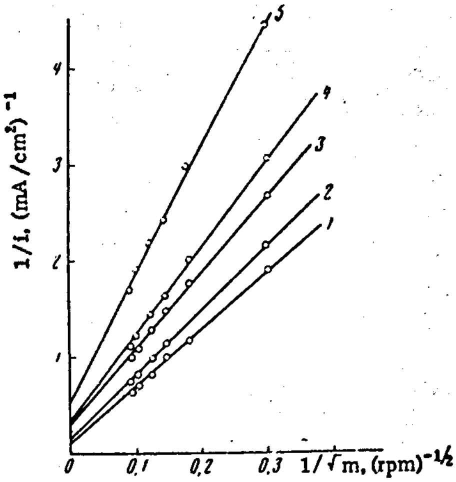

Fig. 2

Fig. 1. Polarization curves for the ionization of molecular hydrogen on smooth platinum in 1 N H_2SO_4 at 1100 (1), 3000 (2), 6400 (3), and 11,400 (4) rpm. The broken line gives the calculated results for the case of purely diffusion control. The rate of application of the potential was 10 mV/min.

Fig. 2. Plot of 1/i against $1/\sqrt{m}$ at overpotentials of 20 (1), 15 (2), 10 (3), 8 (4), and 5 (5) mV in 1 N H_2SO_4.

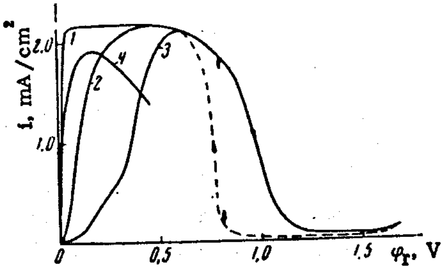

Fig. 3

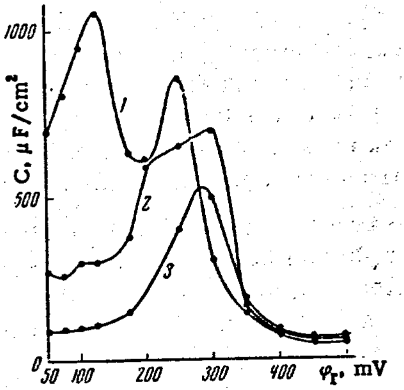

Fig. 4

Fig. 3. Polarization curves for the ionization of molecular hydrogen on smooth platinum in 1 N H_2SO_4 (1), 0.1 N $ZnSO_4$ + 1 N H_2SO_4 (2), 0.1 N $CdSO_4$ + 1 N H_2SO_4 (3), and in 1 N H_2SO_4 for a degree of covering of the surface by thallium ions equal to 0.44 (4). Rate of rotation of the electrode 12,000 rpm. Rate of application of the potential 100 mV/min.

Fig. 4. Dependence of the capacity of the platinum electrode, measured by a series replacement scheme, on potential in 1 N H_2SO_4 (1), 0.1 N $ZnSO_4$ + 1 N H_2SO_4 (2), and 0.1 N $CdSO_4$ + 1 N H_2SO_4 (3) at an alternating-current frequency of 40 Hz.

The measurements showed, in agreement with published data [5,6], that at rates of rotation of the electrode up to 12,000 rpm the polarization curves for the concentration of molecular hydrogen in 1 N H_2SO_4 have clearly defined limiting diffusion current plateaux, the values of the limiting current corresponding strictly to the Levich equation. In measurements with an L-shaped electrode in the range of φ_r values 0.05-0.4 V it was again impossible to go beyond the mixed-kinetics range.

Figure 1 gives the polarization curves in 1 N H_2SO_4, obtained experimentally for low values of φ_r and calculated for the case of purely diffusion control and from the equation

$$\eta = -0.029 \lg \left(1 - \frac{i}{i_d}\right),$$

where η is the overpotential ($\eta = \varphi_r$), and i_d is the limiting diffusion current. It can be seen from Fig. 1 that at high rates of rotation and low values of η the reaction takes place in the mixed-kinetics range. The plots of $1/i$ against $1/\sqrt{m}$ for low values of φ_r (m is the rate of rotation at the electrode) are given in Fig. 2, and show that the ionization of molecular hydrogen is a first-order reaction. The kinetic current density at low values of η can be found by extrapolating the straight lines obtained to $1/\sqrt{m} = 0$. We then constructed the kinetic curve, the slope of which at $\eta = 0$ is equal to the resistance of the reaction $R_i = RT/2Fi_0$, where i_0 is the exchange current for the ionization of molecular hydrogen. The value of i_0 was found to be 4.5 mA/cm². In [6] the value $i_0 \simeq 50$ mA/cm² for $\eta = 50$ mV was obtained by a different method.

We measured the polarization curves for the ionization of molecular hydrogen in 1 N H_2SO_4 with the addition of 0.1 N Cs_2SO_4, $ZnSO_4$, and $CdSO_4$, and also on an electrode on which different quantities of Tl^+ ions had previously been adsorbed. The adsorption of Tl^+ was carried out from a solution of Tl_2SO_4 in 1 N H_2SO_4 at $\varphi_r = 0$, after which the system was washed free from thallium salt solution. The degree of covering of the surface by thallium ions is given as the values of the ratio of the quantity of hydrogen displaced by thallium ions to the quantity of hydrogen adsorbed in 1 N H_2SO_4 at $\varphi_r = 0$. The adsorption of hydrogen in the presence of Tl^+ was found from the potentiodynamic curves.

The polarization curve in the presence of 0.1 N Cs_2SO_4 practically coincided with the polarization curve in 1 N H_2SO_4. The experimental data for the other systems studied are shown in Fig. 3. Zn^{2+} and Cd^{2+} ions suppress the hydrogen ionization current in the initial section of the polarization curve. At $\varphi_r \geq 0.4$ V in the case of Zn^{2+} ions and at $\varphi_r \geqslant 0.6$ V in the case of Cd^{2+} ions, the curves in solutions containing added zinc and cadmium salts coincide with the i, φ_r curve in 1 N H_2SO_4. The potentials at which the retarding action of the cations disappears coincide with the potentials of the practically complete desorption of Zn^{2+} and Cd^{2+} ions from the platinum surface, found by the radioactive tracer method [10-12]. The stronger influence of Cd^{2+} ions on the ionization of H_2 agrees with the higher adsorbability of these ions on a platinum electrode [12].

At $\varphi_r > 0.6$ V in 1 N H_2SO_4 and also in the presence of Zn^{2+} and Cd^{2+} ions, the ionization of H_2 is passivated, due to the adsorption of oxygen and sulfate anions [1]. In the range of φ_r values 1.3-0.6 V, the curves recorded in the anodic and cathodic directions of change in potential show hysteresis. When the electrode potential is kept for a long time in the region of the current drop, the current decreases if the given potential was reached from more cathodic values of φ_r, but increases if the given potential was reached from the anodic side; this is shown by means of the vertical arrows in Fig. 3.

The influence of Tl^+ cations on the ionization of molecular hydrogen differs from the influence of zinc and cadmium ions. Thallium ions produce a greater decrease in the rate of this reaction at more anodic potentials, whereas in the initial range their action is not so marked as the action of Zn^{2+} and Cd^{2+} ions. The measurements in the presence of adsorbed Tl^+ ions were carried out only as far as about 0.5 V in order to avoid the slight desorption of this ion which takes place at more anodic potentials [12].

It is known [1] that in 1 N H_2SO_4 the ionization of adsorbed atomic hydrogen is not the limiting stage in the overall process of H_2 ionization. In actual fact, as shown above, the exchange current of the overall process is equal to approximately 4.5 mA/cm², whereas the exchange current of the discharge stage is about 1 A/cm² [8]. Since in the presence of Zn^{2+} and Cd^{2+} cations the exchange current of the stage involving the discharge and ionization of adsorbed hydrogen is lowered [13], it is necessary to determine whether under these conditions the ionization of adsorbed hydrogen is not limited by the stage of the overall process. For this purpose we carried out impedance measurements in 0.1 N $ZnSO_4$ + 1 N H_2SO_4 and 0.1 N $CdSO_4$ + 1 N H_2SO_4 solutions and calculated the values of the resistance of the stage involving the discharge and ionization of H_{ads}, R_η. Figure 4 shows the relationship between the potential and the capacity, measured by a series replacement scheme at a frequency of 40 Hz. These curves lead to the conclusion that there is a decrease in the H_{ads} exchange current, which is more marked in the presence of Cd^{2+} ions. The calculation of R_η for $\varphi_r = 50$ mV led to values of 0.5 Ω · cm² in the presence of zinc ions and 2.6 Ω · cm² in the presence of cadmium ions. At the same time the calculation of R_i from the initial section of the polarization curve for the ionization of molecular hydrogen at $\varphi_r = 0$ leads to values of 315 and $3.7 \cdot 10^3$ Ω · cm², respectively. Thus, the stage involving the ionization of adsorbed atomic hydrogen is not the limiting stage in the ionization of H_2 in the presence of zinc and cadmium cations.

The data obtained do not contradict the mechanism of H_2 ionization proposed in [6], according to which this process in strongly acidic media takes place chiefly according to the equation: $H_2 \xrightarrow{\text{slow}} (H_2^+)_{ads} + e$;

$(H_2^+)_{ads} \rightarrow 2H^+ + e$. In actual fact, Zn^{2+} and Cd^{2+} cations, which retain part of their charge on adsorption [10-12], by lowering the energy of the bond between $(H_2^+)_{ads}$ and the platinum surface as a consequence of the electrostatic interaction with these particles, should lead to a decrease in the rate of ionization of H_2, as observed experimentally. The state of the adsorbed Tl^+ ions is close to atomic [14], so that their action reduces chiefly to the blocking of part of the electrode surface. Further study is required in order to explain the details of the course of the polarization curves in the presence of Zn^{2+} and Cd^{2+} at low values of φ_r.

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