HYDROGEN OVERPOTENTIAL ON SILVER AT LOW CURRENT DENSITIES

I. EFFECT OF COMPOSITION OF SOLUTION

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The effect of the solution composition on the hydrogen overpotential has been investigated. The method used enabled measurements to be carried out down to 10^{-8}-$10^{-8.5}$ A/cm^2. It was shown that the reduction of the hydroxyl ion on a silver cathode may be normal ($\alpha = {}^1/_2$) and barrierless ($\alpha = 1$). The effect of the composition of solution, in general, corresponded to the theory of slow discharge [11] for a positively charged electrode surface. The stoichiometric number, determined from the polarization curve, close to the equilibrium potential, was unity. The adsorption of hydrogen on the silver electrode was small (this was shown by the method of potential drop after switching off the current). On the basis of the obtained results, it may be proposed that the stage determining the kinetics is a slow discharge without barrier with subsequent rapid electrochemical desorption, taking place with an increase in potential to the normal value.

The hydrogen overpotential on silver in acid solutions has been studied in many works. Loshkarev and Ozerov [2] first observed the region with a low Tafel constant of b = 60 mV. Measurements in a wide range of current densities [3-10] showed the presence of two portions on the polarization curve with gradients 100-130 and 50-70 mV. A satisfactory explanation of this fact has not been forthcoming up to the present time. Bockris and his coworkers [6] explained the transition from the gradient of 100 mV to a gradient of 60 mV by a considerable change in the ψ_1 potential with change in electrode potential close to the zero charge point. However, this explanation was based on old unreliable data for the potential of zero charge for silver. Modern investigations [11-13], carried out by various methods, show that the zero point for silver in a sulfate solutions is at a potential of −0.7 V (normal hydrogen electrode), and in a chloride solution is more negative. Therefore, the change in gradient of the polarization curves takes place more than 0.5 V more positive than the zero charge point, so that the proposed explanation is clearly untenable. Antoniou and Wetmore [8] accepted as the slow stage the surface migration of adsorbed atoms on the basis of the stoichiometric number, determined in the investigation, of 1. Together with this, such a stoichiometric number may also occur with a slow discharge and subsequent rapid electrochemical desorption [14, 15], which was not considered by the authors. In addition, the authors rejected the slow discharge, on the basis of calculations with a kinetic equation true only in a particular case.

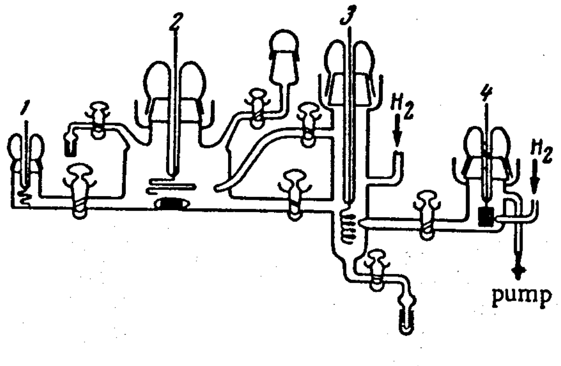

Fig. 1. Cell for polarization measurements: 1) anode; 2) auxiliary cathode; 3) investigated electrode; 4) hydrogen electrode.

In the literature there are data on the effect of the composition of solution on the overpotential [4, 6], indicating that, in those cases when this effect is in general observed, it will be stronger in the region with b = 120 mV than in the region with b = 60 mV, but these data do not enable us to draw clear conclusions on the mechanism of the process. The average data from several electrodes used in the quoted works do not enable the small effects, sometimes comparable with the scatter in the values of overpotential for measurements on different samples, to be cleared up. In the present work, we tried to avoid conditions which cause this scatter.

METHOD

Measurements were carried out in a cell of pyrex glass shown in Fig. 1. The investigated electrode was a silver

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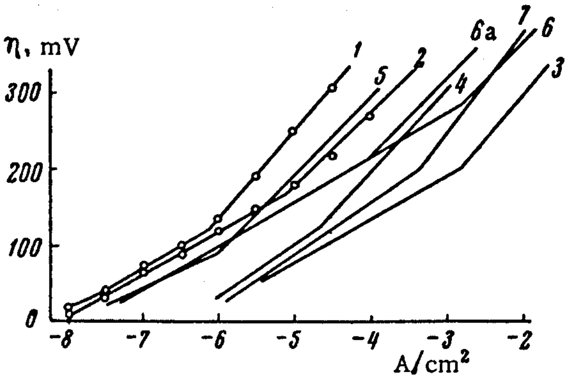

Fig. 2

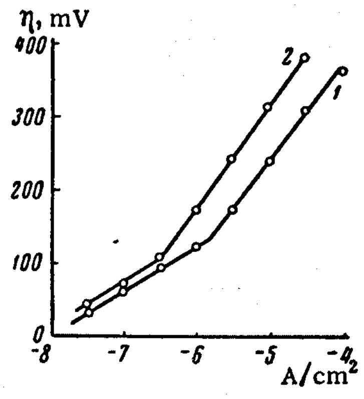

Fig. 3

Fig. 2. Polarization curve for evolution of hydrogen on silver: 1) 0.1 N H_2SO_4, our data; 2) 0.1 N HCl, our data; 3) 1.0 N H_2SO_4 according to [8]; 4) 0.2 N H_2SO_4 according to [7]; 5) 1.0 N H_2SO_4, according to [9]; 6 and 6a) 0.4 and 0.1 N HCl according to [6]; 7) 0.1 N HCl according to [10].
Fig. 3. Polarization curves: 1) 0.1 N H_2SO_4; 2) 0.01 N H_2SO_4.

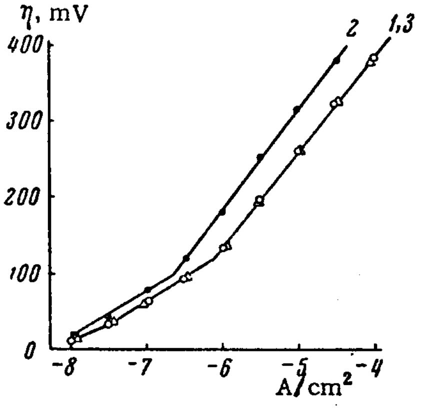

Fig. 4

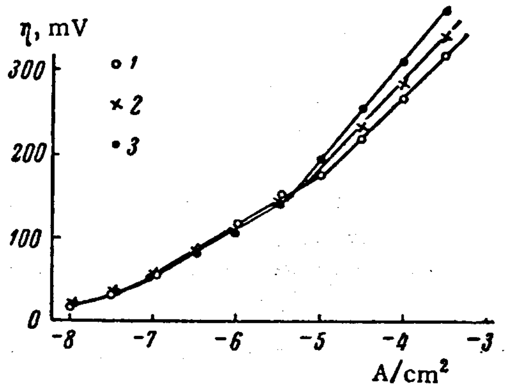

Fig. 5

Fig. 4. Polarization curves in the following solutions: 1) 0.1 N H_2SO_4 + 1.0 N K_2SO_4; 2) 0.01 N H_2SO_4 + 1.0 N K_2SO_4; 3) 0.1 N H_2SO_4 + 1.0 N K_2SO_4.
Fig. 5. Polarization curves in the following solutions: 1) 0.1 N HCl; 2) 0.033 N HCl; 3) 0.01 N HCl.

wire of diameter 0.3 mm and apparent surface area of about 1.3 cm^2. The reference electrode was platinized platinum in the same solution saturated with hydrogen. The advantages of the method used by us are as follows: 1) the possibility of treating the solution with an auxiliary cathode with intensive mixing and a current of hydrogen. This enables a high degree of purification of the solution, in particular from dissolved oxygen; 2) one and the same studied electrode can be used successively in solutions different in composition and well purified.

The overpotential was measured with a valve potentiometer LP-5. At the highest current density, the potential was maintained constant for 20-25 min and at other current densities for 5 min. The cell was placed in an air thermostat. The temperature was maintained with an accuracy of ± 0.2°C. The solutions were prepared from triply distilled water, triply distilled hydrochloric and doubly distilled sulfuric acids. The potassium salts of these acids of cp grade were doubly recrystallized with bidistillate and roasted at 700°C. The vessel and the cell were washed with sulfuric acid in a mixture with perhydrol and afterwards with triply distilled water. The measurements were carried out in a hydrogen atmosphere, which was obtained electrolytically with subsequent standard purification, and, in addition, passage through activated carbon, cooled with liquid nitrogen and washed with the same solution as in the cell. During the passage of hydrogen through the cell, a repeated alternating evacuation with a vacuum pump and filling with hydrogen was used. The solution was poured into the compartment with the auxiliary cathode. The time and regime of the preliminary electrolysis was chosen in relation to the composition of the solution, during which an increase in the length of electrolytic purification of the solution had no effect on the results of the measurements.

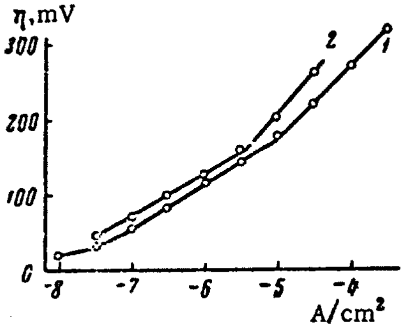

Fig. 6

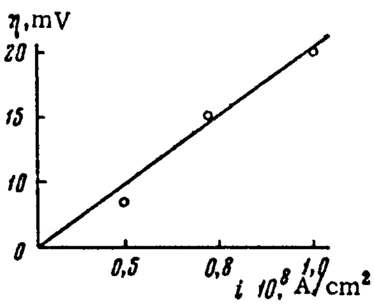

Fig. 7

Fig. 6. Polarization curves in the following solutions: 1) 0.1 N HCl; 2) 0.01 N HCl+ 0.09 N KCl.

Fig. 7. Polarization curve for near the equilibrium potential.

A silver wire of 99.99% purity was prepared in a solution of alkali and in a solution of nitric acid, after each operation being washed with hot bidistilled water. Then the electrode was polished with fine glass powder elutriated in water [11]. As a result of such a treatment, the roughness factor was 2-3 [16]. After polishing, the electrode was held in boiling tridistilled water for 15-20 minutes and was then placed in the cell. The observation of the method described above enabled measurements of overpotential at current densities to $10^{-8.0}$-$10^{-8.5}$A/cm^2.

EXPERIMENTAL RESULTS

As the first experiments showed, a change in composition of solution had an effect on the overpotential but the effect was small. In addition, some divergence was observed in the data in the same solution on different electrodes – the circumstance often encountered during operation with solid electrodes. Therefore, we carried out measurements on one electrode in solutions of varying composition. During the measurements, the state of the surface of the electrode could change, particularly in dilute solutions. Therefore, after measurements with each new solution, we verified that the state of the electrode in its behavior in one and the same solution was unchanged.

Figure 2 gives typical curves in sulfuric and hydrochloric acids in comparison with literature data. The agreement with the results of various investigators is completely satisfactory, the agreement being closest with the results of [6, 9]. The indicated shape of the curves with gradients 100-120 mV for the upper and 59-61 mV for the lower portions was observed by us in approximately 100 independent experiments. Figures 3 and 5 give the curves in solutions of sulfuric and hydrochloric acid and Figs. 4 and 6 in solutions of the same acids with additions of the corresponding potassium salts. On each of these figures, the data obtained from one and the same electrodes are given and the state of its surface was shown to be unchanged by periodic control in the corresponding 0.1 N acid.

In solutions of both acids, the stoichiometric number was measured for the process corresponding to the portion with a gradient of 60 mV, on approaching the equilibrium potential. It was equal to unity. The exchange current was determined by extrapolation of the lower portion of the polarization curve, $(\partial\eta/\partial_i)_{i\to 0}$, from the linear part of the polarization curve close to the equilibrium potential. The good observation of linearity is shown in Fig. 7.

DISCUSSION

In the literature it is indicated [11, 12, 13, 16] that the zero charge point for silver is at a potential of –0.7-–0.8 V (normal hydrogen electrode) in neutral sulfate and chloride solutions. Our measurements were carried out in a potential region from 0 to –0.4 V (normal hydrogen electrode), i.e., considerably more positive than the potential for the zero charge. The theory of slow discharge of hydrogen gives the following equation for the overpotential [1]:

$$\eta = a + \frac{1-\alpha}{\alpha}\psi_1 - \frac{1-\alpha}{\alpha}\frac{RT}{F}\ln[\mathrm{H_3O^+}] + \frac{RT}{\alpha F}\ln i. \qquad (1)$$

In equation (1), two members depend on the composition of the solution – one of them contains the concentration of hydrogen ions in an explicit form, and the other, $(1-\alpha)\alpha^{-1}\psi_1$, depends on the total concentration of the electrolyte. For a positively charged surface of the electrode, the dependence of ψ on the total concentration of electrolyte is expressed by the equation [1]

$$\psi_1 \simeq \text{const} - \frac{RT}{F} \ln c. \qquad (2)$$

Substituting (2) in (1), we find that the overpotential on a positively charged electrode is

$$\eta = a' - \frac{1-\alpha}{\alpha} \frac{RT}{F} \ln c - \frac{1-\alpha}{\alpha} \frac{RT}{F} \ln [H_3O^+] + \frac{RT}{\alpha F} \ln i. \qquad (3)$$

In solutions of pure acid c corresponds with $[H_3O^+]$ and the total effect of the increase in overpotential with a tenfold decrease in concentration of acid is 118 mV. This effect was observed by us for the portion with high b in solutions of both of the pure acids. However, the overpotential increases somewhat less than follows from theory: in sulfuric by 75-80 mV (Fig. 3) and in hydrochloric 45-50 mV (Fig. 5). It may be proposed that the decrease in the effect is caused by specific adsorption of anions which displace the ψ_1 potential in a negative direction. The considerably more positive zero charge point may be expected from the increased surface activity even of such weakly adsorbed anions as sulfate.

The surface concentration of anions changes more slowly than the general concentration and therefore the effect connected with the structure of the double layer may not appear fully. The chloride ion possesses a greater specific adsorption, in connection with which its influence on the ψ_1 potential is more marked. The specific adsorption of the chlorine anion on silver is marked [11] – the chloride displaces the zero charge point in a negative direction in comparison with the sulfate.

A change in pH with the same general concentration of anion (addition of salt) causes an increase in overpotential for the part with the greater gradient. From the theory of slow discharge [1] it follows that, in similar conditions, the overpotential is increased by 59 mV per unit pH (it changes only the second member in equation (1)). In our experiments in sulfuric acid with an addition of sulfate, the effect corresponds to the theoretical value of 55-58 mV, and in acid solutions of chloride it is somewhat less at 45 mV. Thus, the influence of the composition of the solution on the upper portion of the polarization curve corresponds, in general, to the theory of slow discharge for positively charged electrode surface.

The part of the polarization curve with a gradient of 60 mV either does not change its position with change in composition of solution (in the case of pure hydrochloric acid) (Fig. 5), or is displaced no more than 8-10 mV in other cases (Figs. 3, 4, 6). Therefore, in contrast to the part with the gradient of 120 mV, the change in composition of solution, in the limits of experimental error, has no effect on the process corresponding to the lower portion. The small displacement of this portion may be connected with a change in the surface state. In particular, we observed in the more dilute solutions of acid a slow increase in overpotential with time. In decinormal acid this phenomenon is absent.

The obtained data enable a mechanism to be established for the evolution of hydrogen on silver. First of all it should be noted that the evolution of hydrogen at various potentials may have a different mechanism, as is indicated by the inflexion on the Tafel curve and the two portions with different gradients lying in fairly large ranges of current density (the part with b = 60 mV extends for 2 or $2^1/_2$ orders). The explanation of the inflexion and the gradient 60 mV, which is given in the literature, cannot be considered correct as was indicated above. The obtained experimental material in the present work may be examined from the point of view of the theory of barrier-less processes [17-18]. From the theory it follows that the barrier-less process may be observed if the region of transition from $\alpha = 1$ to $\alpha = {}^1/_2$ lies above the equilibrium potential of the system.. In contrast to the relationships with a normal discharge, the activation energy for the barrier-less process (discharge or electrochemical desorption) is equal to the heat of the elementary act of the reaction. The kinetic relationships, describing this type of electrode reaction have characteristic properties: the gradient of the polarization curve is 60 mV, the overpotential is independent of the concentration of discharging particles and is independent of the value of the ψ_1 potential. This is connected with the fact that in conditions for the barrier-less process, the transfer coefficient $\alpha = 1$, which leads to complete compensation of the opposing effects influencing overpotential. The portion with a gradient 60 mV obviously corresponds to the barrier-less process since the change in composition of solution and concentration of discharging particles practically does not change its position. With increase in current density, the barrier-less process transfers to the normal process. From an analysis of the influence of the composition of solution, it may be proposed that the portion with a gradient 120 mV is the slow stage of discharge or the electrochemical desorption

$$H_3O^+ + e^- \rightarrow H_{ads} + H_2O \qquad (a)$$

$$H_{ads} + e^- + H_3O^+ \rightarrow H_{2\,ads} + H_2O\,. \qquad (b)$$

As is well known, during the slow electrochemical desorption, a high superequilibrium concentration of hydrogen is probable on the electrode surface. In order to verify this possibility of accumulation of hydrogen, we investigated the fall in potential after switching off the current. In the logarithmic region and from the initial straight line portion of the oscillogram, the electrode capacity consists of 60-80 $\mu F/cm^2$ on various electrodes (the divergence may be explained by a difference in the roughness factor).

The indicated values practically coincide with the capacity at the same potential determined by Leikis [11, 16] by the alternating current method in weakly acid, neutral, and alkaline solutions of sulfate, i.e., in conditions where evolution of hydrogen was considerably less or even thermodynamically impossible. The impedence measurements of Leikis and Alexandrova [19], carried out in the conditions of our experiments (upper branch of the polarization curve), also led the authors to the conclusion that the value of the adsorption capacity was small. Thus, the electrode capacity practically agrees with the double layer capacity on silver, which indicates the low adsorbability of hydrogen in acid solutions. This gives us a basis for proposing that the slow discharge is the stage determining the kinetics of the reactions for the portion with a gradient of 120 mV. An analagous mechanism for this region of potentials was proposed in the work of Cerescher and Mehl [20] on the basis of potentiostatic measurements, and also in [21]. The gradient of 60 mV was earlier based on a barrier-less process proceeding in this region of potentials. In principle, this gradient may determine the chemical reactions of first order on the surface of the electrode but this possibility is refuted by the value of the stoichiometric number found by us as unity. As was shown by Frumkin [14], the experimentally determined stoichiometric number ν is 1 both for the slow electrochemical desorption and for slow discharge with subsequent rapid electrochemical desorption. Thus, on the basis of the indicated value it is impossible to make a choice between these two stages. The electrode capacity in the region of the barrier-less process determined by us from the logarithmic part of the decrease in potential is also close to 60 $\mu F/cm^2$. Remembering that adsorption of hydrogen practically does not occur it may be considered that the barrier-less electrochemical desorption is not very probable.

The gradient of 60 mV could result from the electrochemical desorption at low degrees of coverage of the surface by hydrogen if the adsorption itself occurs without activation, i.e., the true value $\alpha = 0$ and the apparent value $\alpha = 1 + \alpha = 1$ [22]. But in this case, the dependence of overpotential on composition of solution should be the same as for the normal discharge of desorption. Therefore this explanation is not acceptable.

Thus, the most probable mechanism should be considered as the slow barrier-less discharge with subsequent rapid electrochemical desorption, transferring with increase in potential to normal discharge.

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