ON THE QUESTION OF THE OVERVOLTAGE OF HYDROGEN ON PLATINUM

1960

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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ON THE QUESTION OF THE OVERVOLTAGE OF HYDROGEN ON PLATINUM

(Presented by Academician A. N. Frumkin, 26 IV 1960)

It is known from the literature ([1]) that, at small overvoltages, the rate of electrochemical evolution of hydrogen in acid solutions on active electrodes made of noble metals and, in particular, of platinum is determined by the Tafel equation

$$\eta_{\mathrm{H2},i} = a + b \lg i \tag{1}$$

with a slope b close to 29 mV (room temperature). Such a value of the slope may be connected with the retardation of the stage of recombination of hydrogen atoms discharged on the electrode surface into an H_2 molecule ([2]). According to another point of view, developed initially for the case of a palladium cathode, in this region of potentials the rate of the process is limited mainly by the diffusion of molecular hydrogen from the cathode surface into the bulk of the solution ([3]). In this case the surface concentration of hydrogen increases in comparison with the concentration in the bulk and, in accordance with the Nernst equation

$$\varphi = \varphi_0 + \frac{RT}{nF} \cdot \ln \frac{C^2_{\mathrm{H}^+}}{P_{\mathrm{H2}}}, \tag{2}$$

the cathode potential shifts in the negative direction. With increasing current density the diffusion component of the total overvoltage η_d reaches a limiting value equal to 30-60 mV, which corresponds to an increase in the surface concentration of hydrogen by 1-2 orders of magnitude.

We have undertaken an attempt to verify the correctness of the indicated point of view by direct experimental determination of the concentration of hydrogen near a working platinum microcathode by the method of oscillographic polarography. If, during cathodic polarization, hydrogen accumulates in the near-electrode region of the solution, then, with a sufficiently rapid shift of the electrode potential in the positive direction, a peak of anodic oxidation of this hydrogen, proportional to its concentration, should be observed on the cathodic-anodic polarograms. The proportionality coefficient can be determined experimentally in experiments at elevated hydrogen pressures.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Two series of experiments were carried out. In one of them anodic polarograms were recorded (rate of potential application to the electrode $a \ll 10$ V/sec) on a Pt electrode in 1 N solutions of H_2SO_4, $HClO_4$, and HCl, saturated with hydrogen under a pressure $P_{H2} \leq 440$ atm., from potentials $\varphi_{initial} = 0$ relative to the hydrogen electrode in the same solution. In the other, analogous i–φ curves were recorded at atmospheric hydrogen pressure from various potentials $\varphi_{initial} < 0$ (n.h.e.). The work was carried out in two-electrode cells without separation of the cathodic and anodic spaces. The surface of the electrodes tested varied within the limits 0.01–0.08 cm^2.* A large platinized platinum electrode was used as the auxiliary electrode. The experimental procedure provided for anodic activation of the electrode, its polarization at a specified $\varphi_{initial}$ for 1 sec. (which, as a rule, was sufficient for the establishment of stationary concentrations near the electrode), and recording of anodic

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* The surface area of the electrodes was estimated from the magnitude of the limiting diffusion current of hydrogen ionization ([4]).

and cathodic-anodic polarograms up to the potential of oxygen evolution (or chlorine, in the case of HCl). In addition, reverse-scan curves were recorded.

Fig. 1. Anodic oxidation of hydrogen on Pt in 1 N H_2SO_4 under a pressure $P_{H2} = 65$ atm. Rate of potential application $\alpha = 10$ V/sec. I–forward scan, $\varphi_{initial} = 0$ (V, hydrogen scale); II–reverse scan.
$S_{Pt} = 0.0156$ cm^2

Fig. 2. Curve of anodic polarization of Pt in 1 N H_2SO_4, $P_{H2} = 1$ atm. I–forward scan, $\varphi_{initial} = 0$ (hydrogen scale); II–reverse scan.
$S_{Pt} = 0.0156$ cm^2

In Fig. 1, as an example, a polarogram is presented (forward and reverse scans, $\alpha = 10$ V/sec, holding at $\varphi = 1450$ mV for 0.075 sec), recorded in 1 N H_2SO_4 at $P_{H2} = 65$ atm. It can be shown that the current maximum observed on the forward-scan curve (as, indeed, on the reverse-scan curve as well),

is associated with the ionization of hydrogen dissolved in the near-electrode layers of the solution, and not adsorbed on the surface or incorporated into the surface layer of the metal. The quantity of electricity required to shift the electrode potential to the potential of the maximum may, at least, exceed by an order of magnitude the value equivalent to removal from the surface of a

Fig. 3. Curve of anodic polarization of Pt in 1 N H_2SO_4, $P_{H2} = 1$ atm. I–forward scan, φ = −77.7 mV (n.h.e.); II–reverse scan. $S_{Pt} = 0.0156$ cm^2

Figure 3: Fig. 3. Curve of anodic polarization of Pt in 1 N H_2SO_4, $P_{H2} = 1$ atm. I–forward scan, φ = −77.7 mV (n.h.e.); II–reverse scan. $S_{Pt} = 0.0156$ cm^2

monolayer of hydrogen (the adsorption of hydrogen on Pt apparently does not exceed this value (5)); moreover, it depends on α. The height of the maximum (i_{max}) on the polarograms is proportional to $\alpha^{1/2}$ and to the bulk concentration of hydrogen (C), and consequently also to the pressure P_{H2}. At $\alpha = 10$ V/sec.

Fig. 3. Curve of anodic polarization of Pt in 1 N H_2SO_4, $P_{H2} = 1$ atm. I–forward scan, φ = −77.7 mV (n.h.e.); II–reverse scan. $S_{Pt} = 0.0156$ cm^2

$$i_{max} = 3.8 \cdot P_{H2} \text{ mA/cm}^2, \tag{3}$$

where P_{H2} is expressed in atm. Calculation of i_{max} from the Ševčík-Randles equation (6)

$$i_{max} = K \cdot n^{3/2} \cdot \alpha^{1/2} \cdot D^{1/2} \cdot C, \tag{4}$$

where K is a constant,* n is the number of electrons participating in the reaction, and D is the diffusion coefficient for various α and P_{H2}, gives values close, in order of magnitude, to those obtained experimentally. The decrease in current after the maximum is reached follows the diffusion law

$$i = \frac{A}{\sqrt{\tau}} + B, \tag{5}$$

where A and B are constants, and τ is time. The values of B, calculated from the polarograms, are close to the values of the limiting diffusion currents of hydrogen ionization.

The form of the i-φ curves obtained in the second series of experiments depends strongly on φ . As is seen from Fig. 2, at $\varphi \geq 0$ (correspondingly, $i \geq 0$) the oscillogram is a somewhat distorted curve of the dependence of the capacitance of the Pt electrode on potential, with a characteristic separation of the regions of hydrogen and oxygen adsorption and with maxima of pseudocapacitance

* The numerical value of K calculated for the case of a solid electrode was used (7).

in the region of hydrogen adsorption ([5,8]). At sufficiently large α the current magnitude over the entire investigated potential range is practically independent of the rotation rate of the electrode or of stirring of the electrolyte. However, displacement of φ_{isx} in the negative direction ($i_{isx} < 0$) causes the appearance on

the polarogram of a current maximum, analogous to that observed at elevated hydrogen pressures (Fig. 3). The height of the maximum depends on φ_{isx}, pH, α, and the duration of the preliminary cathodic polarization, but

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Fig. 4. Dependence of the hydrogen overvoltage on Pt in 1 N H_2SO_4 on the logarithm of the current density i_{isx}.

η_{H_2} is the total overvoltage; η_d is the diffusion component of the total overvoltage, calculated from equations (3) and (2).

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does not depend on the nature of the acid. The height of the maximum and the rate of current decay after the maximum decrease sharply with intensive stirring of the electrolyte or rotation of the electrode.

The aggregate of the data obtained makes it possible to assert that the method of oscillographic polarography on a Pt microelectrode in an acidic medium can be applied to the determination of not too small concentrations of hydrogen both in the bulk of the solution and near the surface of the working Pt cathode. In Table 1, the overvoltage values $\eta_{H_2} (= \varphi_{\text{isx}})$ measured in one of the experiments are compared with the values of P_{H_2} and η_d calculated from equations (3) and (2). The dependence between η_{H_2} and η_d and the cathodic current density is presented in semilogarithmic coordinates in Fig. 4.

Table 1

η_{H_2}, mV	33.7	35.4	44.4	56.4	65.4	77.7	87.9	104.4	152.7	179.7
η_d, mV	32.0	35.9	42.1	46.6	47.2	48.6	50.2	51.3	51.4	49.9
P_{H_2}, atm	12	16	26	37	39	44	49	53	54	48

From Fig. 4 and Table 1 it is seen that the overvoltage of hydrogen on the investigated Pt electrode up to potentials $\eta_{H_2} \simeq 40$ mV has a purely diffusional nature ($\eta_{H_2} = \eta_d$). With further displacement of the potential in the negative direction, η_d reaches a limiting value ([3]), and then, judging from the data we obtained, decreases somewhat. Possibly this is explained by more intensive stirring of the solution near the electrode surface by bubbles of the hydrogen being evolved.

We express our gratitude to I. E. Bryksin for developing and fabricating the oscillographic polarograph used in this work.

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Received
11 IV 1960

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