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Abstract

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RATE OF IONIZATION OF HYDROGEN ON ACTIVE ELECTRODES

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The investigation whose results are presented here has as its aim the establishment of the regularities determining the current drawn from a gas electrode partially immersed in an electrolyte, under conditions in which the electrode reaction, at not too low gas concentrations in the electrolyte, proceeds so rapidly that activation polarization may be regarded as absent. The results, as will be shown, can be used to explain the values of the current density attained on porous gas electrodes.

The ionization of hydrogen was studied on smooth nickel and platinum electrodes in concentrated aqueous KOH solutions. In order to prevent poisoning of the electrode by impurities in the electrolyte, the volume of the latter was made minimal. The electrode had the shape of a cone with its apex directed downward. When the electrolyte level was changed, the length of the three-phase boundary electrode–electrolyte–gas changed in proportion to the depth of immersion of the electrode, while the area of the electrode–electrolyte interface changed in proportion to the square of the immersion depth. This makes it possible to judge whether the electrochemical process occurred only near the three-phase boundary or over the entire surface of the electrode immersed in the electrolyte.

The nickel electrode was machined from chemically pure nickel and polished. The platinum electrode was made from bright platinum foil. The auxiliary electrode, of funnel shape and closely fitting the glass funnel, was prepared by sintering nickel powder, with subsequent deposition of cadmium oxide in the pores, by a method similar to that used in the manufacture of cadmium electrodes of lamellar alkaline storage batteries.

Table 1

Fig. 1

Figure 1: Fig. 1

Electrolyte height, cm	Area S, cm^2	Length l, cm	Ni 1: $i = \frac{I}{S}$, μA/cm^2	Ni 1: $i_l = \frac{I}{l}$, μA/cm	Ni 2: $i = \frac{I}{S}$, μA/cm^2	Ni 2: $i_l = \frac{I}{l}$, μA/cm	Pt: $i = \frac{I}{S}$, μA/cm^2	Pt: $i_l = \frac{I}{l}$, μA/cm
1.0	1.35	2.51	95.5	51.0	97.6	52.3	101.3	54.1
1.5	3.1	3.75	63.2	52.0	68.5	56.6	65.8	53.9
2.0	5.57	5.03	49.3	54.3	51.5	56.8	52.0	57.2
3.0	12.4	7.53	34.9	57.6	36.7	60.1	37.0	60.3
4.0	22.1	10.6	28.3	59.1	29.2	61.4	29.8	62.7

The measuring cell consisted of the hydrogen electrode under investigation—the anode—and an oxide-cadmium nonpolarizable cathode inserted into a glass funnel with double walls, between which water from a thermostat was passed. The cathode also served as the reference electrode. The gap between anode and cathode was about 1 mm. The measuring cell was filled with purified hydrogen from an electrolyzer or with a mixture of hydrogen and pure nitrogen. The anode, suspended on a nickel wire, could be raised into a quartz tube attached by a ground joint and equipped with a furnace and a thermocouple. The electrolyte solution was subjected to final purification from admi—

and, in particular, from traces of oxygen in the purification cell, after which hydrogen was supplied under pressure to the measuring cell to the required level. Table 1 gives the values of the ratios of the current I to the area of the part of the electrode immersed in the electrolyte, S, and to the length of the three-phase boundary

Fig. 1. Ionization of hydrogen on platinized platinum at 21°, 1 atm H_2, at various KOH concentrations: 1—1N; 2—4N; 3—7N; 4—10N KOH

l, as a function of the depth of immersion of the electrodes. The measurements were carried out at 21° in 10N KOH at a polarization of 0.07 V with a Ni electrode annealed in a hydrogen atmosphere at 400° for 40 min. (Ni1), a Ni electrode electroplated with a nickel layer of 40 μ, annealed in hydrogen at 400° for 20 min. (Ni2), and a Pt electrode annealed in hydrogen at 400° for 20 min. (Pt). From the data of Table 1 it is evident that the current is proportional to the length of the three-phase boundary. The current is practically independent of the electrode material; consequently, electrochemical polarization is absent in the region of the three-phase boundary. In Figs. 1 and 2 the dashed lines show the polarization curves for hydrogen ionization at an electrolyte height in the cell of 40 mm. At small polarizations (up to 20 or 25 mV) the current is almost

Fig. 2

Figure 2: Fig. 2

proportional to the polarization; then it increases more slowly, but no limiting current is observed.

Fig. 2. Ionization of hydrogen on nickel at 75° in $7N$ KOH. 1—1 atm H_2; 2—300 mm Hg H_2

Two different routes may be envisaged for supplying an electrochemically active gas, for example hydrogen, to the place where the electrochemical process occurs: 1) the gas dissolves in the electrolyte and diffuses to the electrode surface; 2) the gas is adsorbed on the electrode surface protruding above the electrolyte and migrates along the surface, or dissolves in the metal and diffuses in it to the electrode-electrolyte boundary. To judge the relative role of these mechanisms, we shall carry out a theoretical calculation of the current under the assumption that only the first of them has practical significance, and compare the results of the calculation with experiment. The calculation will be carried out

for the case of a flat smooth electrode partially immersed in the electrolyte.

Owing to the action of capillary forces, the electrolyte forms a meniscus at the surface of the electrode. Gas diffuses to the electrode surface located under the meniscus film, followed by ionization; the remaining part of the surface behaves as an ideally polarizable electrode, because the concentration of dissolved gas at this surface is very small. Let us place the origin of coordinates at the upper edge of the meniscus and direct the X-axis from the electrode surface perpendicular to it, and the Y-axis along the electrode surface into the depth of the solution, perpendicular to the edge of the meniscus. In calculating the current, we shall make the following simplifications: we shall assume that diffusion occurs parallel to the X-axis, and that the current flows in the direction of the Y-axis. This means that we neglect the quantity $\partial C/\partial y$ in comparison with $\partial C/\partial x$, where C is the gas concentration in the solution, and neglect the quantity $\partial E/\partial x$ in comparison with $\partial E/\partial y$, where E is the electric potential in the solution. It is assumed that electrochemical polarization is absent; therefore the potential jump at the electrode-solution boundary varies with the gas concentration at this boundary, C_1, according to the Nernst formula. The potential of the metallic electrode practically does not depend on y; consequently, E varies with y in accordance with the equality

$$dE = \frac{RT}{nF} d \ln C_1, \tag{1}$$

where n is the number of electrons released upon ionization of one gas molecule. In the case of hydrogen $n = 2$. Let dr denote the ohmic resistance of a film segment of length dy along the Y-axis and of unit length in the direction of the three-phase boundary,

$$dr = \frac{1}{\chi x_0}\,dy, \tag{2}$$

where χ is the electrical conductivity of the solution, and x_0 is the film thickness. Then the linear current density $i_l = I/l$ is determined by the equality

$$i_l = -\frac{dE}{dr}, \tag{3}$$

whence

$$i_l = -\chi x_0 \frac{RT}{nF}\frac{d\ln C_1}{dy}. \tag{4}$$

The amount of gas diffusing per unit time to the electrode surface under the indicated segment of the film is equal to $D\frac{C_0 - C_1}{x_0}\,dy$, where C_0 is the concentration of the saturated gas solution established at the solution-gas boundary. Therefore the increment of the linear current density on this segment is

$$di_l = nFD\frac{C_0 - C_1}{x_0}\,dy. \tag{5}$$

Multiplying equations (4) and (5) and carrying out the integration, taking into account that at $y = 0$, $i_l = 0$, $C_1 = C_0$, we obtain

$$i_l = \sqrt{2RTDC_0\chi\left(\ln\frac{C_0}{C_1} + \frac{C_1}{C_0} - 1\right)}. \tag{6}$$

Let us denote by $\Delta\varphi$ the difference of the equilibrium potentials of the electrode at concentrations C_0 and C_1. This difference is equal to the observed anodic polarization of the electrode.

Since

$$\frac{C_1}{C_0} = e^{-\frac{nF\Delta\varphi}{RT}}, \tag{7}$$

equation (6) gives

$$i_l = \sqrt{2RTDC_0\chi\left(\frac{nF\Delta\varphi}{RT} + e^{-\frac{nF\Delta\varphi}{RT}} - 1\right)}. \tag{8}$$

It follows from equation (8) that at small polarizations i_l is proportional to $\Delta\varphi$, and at large ones to $(\Delta\varphi)^{1/2}$. To carry out calculations by equation (8), we measured the solubility of hydrogen (and also oxygen) in concentrated KOH solutions at various temperatures. The determination of the limiting diffusion currents of hydrogen in concentrated KOH solutions on a rotating disk electrode, carried out at the Department of Electrochemistry of Moscow State University by L. N. Nekrasov and G. B. Magnitskaya, made it possible, using the values of hydrogen solubility and also the viscosity coefficients of the corresponding solutions measured by us, to calculate the values of the hydrogen diffusion coefficient D. The missing value of D for 75° was calculated on the assumption that D is proportional to T/η, where η is the viscosity of the corresponding solution. In Figs. 1 and 2, the values of i_l calculated from equation (8) (solid curves) are compared with the experimental ones. The agreement should be regarded as quite satisfactory, taking into account that the calculation by equation (8) is absolute. It shows that the supply of hydrogen to the three-phase boundary by surface migration or by dissolution in the metal is of no importance.

An equation equivalent to equation (8) is contained in Will's paper (^{1}), which appeared in print after the present work had been completed. Will experimentally confirmed the applicability of the equation to a platinum hydrogen electrode in sulfuric acid solutions. Equation (8) makes it possible to estimate the current density on active porous electrodes. According to Justi (^{2}), the mean pore radius for the hydrogen electrodes he investigated is $\bar{r} = 1.9 \cdot 10^{-4}$ cm, and the number of pores per 1 cm^2 is $N = 7.2 \cdot 10^5$ cm^{-2}. Hence the pore perimeter per 1 cm^2 of electrode area is $p = 2\pi\bar{r}N = 860$ cm^{-1}. From equation (8), in a 7 N KOH solution, at a polarization of 0.1 V, a hydrogen pressure of 3.8 atm, and a temperature of 40°, $i_l = 380$ μA/cm. Hence $i = i_l p = 350$ μA/cm^2. This value is close to the current-density values obtained by Justi on active electrodes (^{2}).

In the case of electrodes containing narrow and wide pores, the relations are more complicated (^{3}). The polarization curves obtained in the reduction of oxygen on smooth silver, gold, and platinum electrodes in 0.5 N KOH at room temperature (^{4}) are similar to the curves in Fig. 1. If oxygen ionization proceeds according to the equation $O_2 + 2H_2O + 4e = 4OH^-$, then $n = -4$. Using the data on the solubility of oxygen and the value of the diffusion coefficient (^{5}) for the indicated solution, we obtain from equation (8), for $\Delta\varphi = -1$ V, $i_l =$ 1.50 mA/cm. Experimentally, the value $i_l = 1.80$ mA/cm was obtained, i.e., a close value. The cited authors note that decreasing the partial pressure of O_2 by a factor of 5 (replacement of oxygen by air) leads to a decrease in i_l by approximately a factor of 2. This agrees with equation (8), according to which i_l is proportional to $C^{1/2}$. The data presented make it possible to consider equation (8) applicable also to the oxygen electrode.

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