THE RATE OF IONIZATION OF HYDROGEN ON ACTIVE ELECTRODES

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(Presented by Academician A. N. Frumkin, April 18, 1963)
Translated from Doklady Akademii Nauk SSSR, Vol. 152, No. 3,
pp. 658-661, September, 1963
Original article submitted April 18, 1963

The studies reported here were aimed at establishing the factors which determine the current that can be drawn from a gaseous electrode partially immersed in a liquid when the concentration of gas in the electrolyte is low and the electrode reaction proceeds so rapidly that activated polarization can be neglected. It will be shown that our results can be used to obtain an understanding of the current densities developed with porous gas electrodes.

Study was made of the ionization of hydrogen on smooth nickel and platinum electrodes immersed in concentrated aqueous KOH solutions. The volume of electrolyte was held at a minimum in order to avoid poisoning the electrode by contaminating substances. The electrode was constructed in the form of a cone set with the vertex pointing downward. Alteration of the level ofthe electrolyte changed both the length of the three-phase electrode–electrolyte– gas boundary and the area of the electrode–electrolyte interface, the first being proportional to the depth of immersion and the second proportional to the square of this depth. In this way it was possible to determine whether the electrochemical process proceeded over all of the immersed surface of the electrode or only in the immediate neighborhood of the three-phase boundary.

The nickel electrode was turned from chemically pure metal and polished. The platinum electrode was prepared from bright platinum sheet. The concial-form auxilliary electrode was firmly affixed to a glass funnel; it was prepared from baked nickel powders and had had cadmium oxide precipitated into its pores by a method similar to that employed in the preparation of cadmium electrodes for nonlaminar alkali storage batteries.

Height of electrolyte cm	Area, S, cm^2	Length, l, cm	Ni 1		Ni 2		Pt	
			$i=\frac{I}{S}$, μ-amp/cm^2	$i_l=\frac{I}{l}$, μ-amp/cm	$i=\frac{I}{S}$, μ-amp/cm^2	$i_l=\frac{I}{l}$, μ-amp/cm	$i=\frac{I}{S}$, μ-amp/cm^2	$i_l=\frac{I}{l}$, μ-amp/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 working cell contained the test hydrogen electrode (anode) and a nonpolarized cadmium oxide cathode, the latter set into a double-walled glass funnel through which water from a constant temperature bath was passed. This cathode also served as a reference electrode. The clearance between the anode and cathode was about 1 mm. The cell could be filled with either purified electrolytic hydrogen or a mixture of hydrogen and purified nitrogen. The anode was suspended on a nickel thread and could be raised and lowered in a quartz tube equipped with a furnace and a thermocouple which was set on a ground joint. The electrolytic solution was carefully freed of traces of oxygen and other contaminants in a purifying cell and then forced to the desired height in the measuring cell by adjusting the hydrogen pressure. The dependence of the ratio of current strength, I, to immersed area, S, of the electrode, and of the ratio of current strength to length of three-phase boundary, l onthe depth of immersion is shown in the table. These measurements were carried out at 21° in 10 N KOH under polarization at 0.07V using a Ni electrode which had been baked for 40 min at 400° in an atmosphere of hydrogen (Ni 1), a Ni electrode which had been galvanically covered with a nickel layer 40 μ deep and then baked for 20 min at 400° in hydrogen (Ni 2), and a Pt electrode which had been baked for 20 min at 400° in hydrogen (Pt). The data of the table make it clear that the current strength was proportional to the length of the three-phase boundary. The current strength was practically

independent of the material of which the electrode was constructed and there was, therefore, no electrochemical polarization in the neighborhood of the boundary. The dotted curves of Figs. 1 and 2 are polarization was low but increased slowly beyond 20 or 25 mV, without however approaching a limiting value.

There are two conceivable mechanisms for the transfer of the electrochemically active gas (hydrogen) to the site of an electrochemical reaction: 1) the gas might dissolve in the electrolyte and then diffuse to the electrode surface, or 2) the gas might adsorb on the portion of the electrode which projects above the electrolyte and then move to the electrode-electrolyte interface either by migration along the surface or by dissolution in the metal and internal diffusion. Theoretical calculations were made of the current strength to be expected if only the first of these two mechanisms were of practical significance and the results obtained compared with the experimental data with a view to determining the relative weights of the mechanisms. The calculations will be reproduced below for the case of a smooth compact electrode partially immersed in an electrolyte.

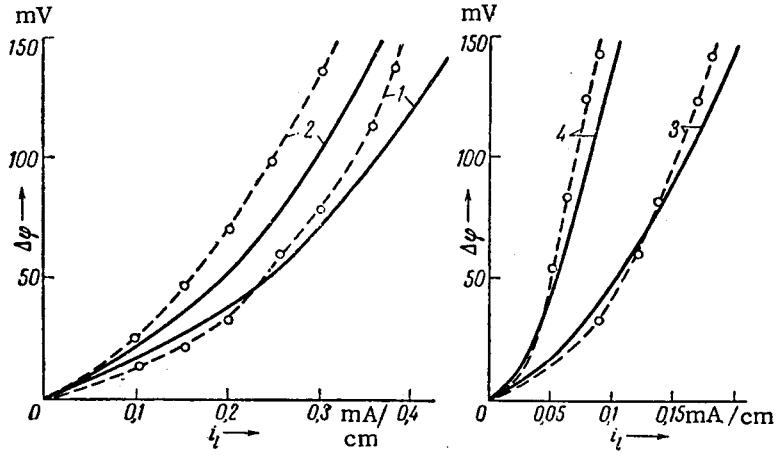

Fig. 1. Hydrogen ionization on platinized platinum at 21° and a 1 atmos pressure of H_2; concentration of KOH: 1) 1N; 2) 4N; 3) 7N; 4) 10N KOH.

The electrolyte forms a menicus at the electrode surface under the action of the capillary forces. Gas diffuses to that portion of the electrode surface which underlies the menicus and there undergoes ionization, while the remainder of the electrode surface functions as an ideally polarized electrode with an extremely low concentration of dissolved gas. We will now introduce a system of coordinates with the origin at the upper edge of the menicus, the X-axis perpendicular to the electrode surface, and the Y-axis in the solution parallel to the surface and at right angles to the meniscus edge. The calculation of the current strength will be simplified by assuming that diffusion is parallel to the X-axis and current flow parallel to the Y-axis. That is to say that $\partial C/\partial y$ is neglected in comparison with $\partial C/\partial x$ (C is the concentration of gas in the solution) and $\partial E/\partial x$ neglected in comparison with $\partial E/\partial y$ (E is the electrical potential in solution). It is further assumed that there is no electrochemical polarization, so that the Nernst Equation can be used to calculate the potential drop at the electrode-solution interface in terms of the gas concentration, C_1, at this interface. Since the potential of the metallic electrode is almost independent of y, it follows that the variation of E with y can be represented by the equation

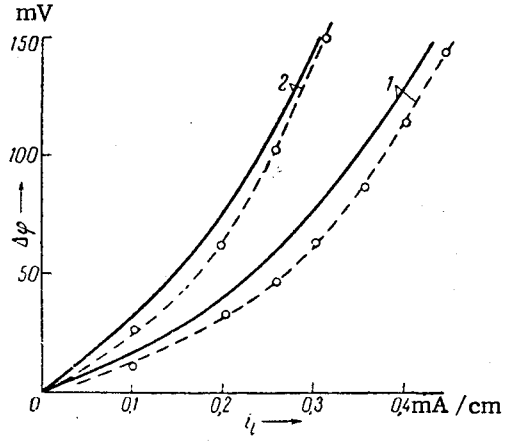

Fig. 2. Hydrogen ionization on nickel at 75° in 7 N KOH: 1) 1 atmos H_2; 2) 300 mm Hg H_2.

$$dE = \frac{RT}{nF} d \ln C_1, \qquad (1)$$

n being the number of electrons liberated per gas molecule ionized, 2 in the case of hydrogen. Representing by dr the ohmic resistance of a film sector of length dy measured along the Y-axis and length unity measured along the three-phase boundary, one has

$$dr = \frac{1}{\varkappa} \frac{dy}{x_0},$$

$\varkappa$ being the electrical conductivity of the solution and x_0 the film depth. The linear current density $i_l = \frac{I}{l}$ will then be determined through the equation

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

from which it follows that

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

The quantity of gas diffusing to the electrode surface under this film in unit time will be equal to $D\frac{C_0 - C_1}{x_0} dy$, C_0 being the concentration of the saturated gas solution which developed at the solution-gas interface. The increase of linear current density over this sector will then be

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

Multiplying (4) and (5) and then integrating with the conditions y = 0, i_l = 0, $C_1 = C_0$, one obtains

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

Let $\Delta\varphi$ be used to designate the difference of the reversible electrode potentials at concentrations C_0 and C_1. This difference is equal to the observed anodic polarization of the electrode.

Since

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

Eq. (6) will give

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

It follows from Eq. (8) that i_l will be proportional to $\Delta\varphi$ when the polarization is low and proportional to $(\Delta\varphi)^{\frac{1}{2}}$ when the polarization is high. The solubilities of hydrogen and oxygen in concentrated KOH solutions were measured with a view to carrying out calculations through Eq. (8). Determinations of limiting hydrogen diffusion currents in concentrated KOH solutions were made with the rotating disc electrode by L. N. Nekrasov and G. B. Magnitskaya working in the Department of Electrochemistry of the MGU. These measurements made it possible to calculate the coefficient of diffusion, D, of hydrogen from our own determinations of the coefficients of viscosity of these solutions. The missing value of D at 75° was estimated by assuming D to be proportional to T/η, η being the coefficient of viscosity of the solution in question. Figures 1 and 2 give comparisons of i_l values which had been calculated through Eq. (8) (full curves) and measured experimentally. The agreement achieved here must be considered as quite satisfactory in view of the fact that the values obtained with Eq. (8) are absolute. This is indication that no significance attaches to the transfer of hydrogen to the three-phase interface through surface migration or dissolution in the metal.

An equation equivalent to (8) is found in a paper of Will [1] which appeared after the present work had been completed. Will showed experimentally that this equation is applicable to the platinized hydrogen electrode in sulfuric acid solution. Equation (8) can be used to estimate the current density on the active porous electrode. The data of [2] show that the hydrogen electrodes used by Justi had a mean pore radius, $\bar{r}$, of $1.9 \cdot 10^{-4}$ cm and contained $7.2 \cdot 10^5$ pores per 1 cm^2(N). It follows from these figures that the pore perimeter per 1 cm^2 of electrode surface was $p = 2\pi\bar{r}N = 860\ cm^{-1}$. For a 7 N KOH solution under 0.1 V polarization at 40° with a hydrogen pressure of 3.8 atmos, Eq. (8) gives i_l = 380 μA/cm. It follows that $i = i_l p$ = 350 μV. This is close to the current densities obtained by Justi for the active electrodes of [2].

The relations for electrodes containing both narrow and wide pores are more complex [3]. Polarization curves similar to those of Fig. 1 have been obtained for the reduction of oxygen on smooth silver, gold, and platinum electrodes in 0.5 N KOH at room temperature [4]. If the ionization of oxygen proceeds through the chemical equation $O_2 = 2H_2O + 4e = 4OH^-$, n = -4. Using the data on the solubility of oxygen and the value of the coefficient of dif-

fusion of oxygen taken from [5] and setting $\Delta\varphi = -1$ V Eq. (8) gives $i_l = 1.50$ mA/cm. The experimental value was quite close to this, namely $i_l = 1.80$ mA/cm. The above authors note that a 1 : 5 reduction of the partial pressure of O_2 resulting from replacement of oxygen by air led to an approximate 1 : 2 reduction in i_l. This is consistent with Eq. (8) which shows i_l to be proportional to $C^{\frac{1}{2}}$. On the basis of these data it can be assumed that Eq. (8) is applicable to the oxygen electrode.

The authors wish to express their thanks to N. A. Aladzhalova, B. N. Kabanov, and P. D. Lukovtsev for valuable suggestions concerning experimental procedures.

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