Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1960

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1960. Vol. 130, No. 6

PHYSICAL CHEMISTRY

G. P. DEZIDEREV and S. I. BEREZINA

LIMITING DIFFUSION CURRENT TO A ROTATING DISK ELECTRODE DURING CATHODIC HYDROGEN EVOLUTION

(Presented by Academician A. N. Frumkin, 4 XI 1959)

As was shown earlier (1), the limiting current densities during cathodic hydrogen evolution on platinum or nickel from sulfuric acid solutions are characterized by the fact that the discharge reaction of the hydrogen ion $H^{+}+e \rightarrow H$ is replaced by the reaction $H_2O+e \rightarrow OH'+H$, the process of hydrogen evolution from the solution alkalized in the near-cathode layer. Alkalization of the electrolyte in the near-electrode layer occurs as a result of the accumulation of non-dischargeable cations, impurities whose concentration in the initial solution is readily calculated from the equation derived by A. N. Frumkin (2). If, for the calculation, we use our experimental data, it turns out that the concentration of impurities of alkali-metal cations in the solution is close to 10^{-8}-10^{-9} N, which corresponds to the approximate spectral determinations carried out by us.

The decrease in the concentration of potential-determining ions in the near-electrode film of electrolyte can be weakened by forced circulation of the electrolyte, which leads to a decrease in the thickness of the boundary layer. If such circulation of the liquid occurs regularly and, consequently, the thickness of the boundary layer changes regularly, the dependence between the limiting current and the total concentration of the solution may prove simpler than in the case of gas evolution in an unstirred liquid.

According to V. G. Levich (3), the simplest case of flow of a solid body by a liquid is obtained when a disk rotates in it. The thickness of the boundary layer is inversely proportional to the square root of the rotational speed of the disk, and the limiting current is inversely proportional to the thickness of the boundary layer. Already the first experimental verification of V. G. Levich’ s theory, carried out by B. N. Kabanov (4), confirmed the existence of a linear dependence between the limiting current and the square root of the rotational speed of the disk. The electrode process studied by B. N. Kabanov (cathodic reduction of oxygen in acidic solutions to hydrogen peroxide) was not complicated by any side phenomena. In the case of cathodic hydrogen evolution on a rotating disk, we are dealing with the formation of gas bubbles and their detachment from the electrode surface. This leads to a complication of the hydrodynamic regime at the electrode surface. It seemed of interest to determine which factor is predominant in this case—the ordered motion of the liquid at the surface of the rotating disk, or the stirring action of gas bubbles detaching from this surface.

Experimental Part

The potentials of a platinum disk cathode 6.00 mm in diameter, rotating at a speed from 1000 to 22,000 rpm, were determined. The compensation circuit was closed $3 \cdot 10^{-3}$ sec. (^{5}) after switching off the polarizing current. This made it possible to measure electrode potentials close to equilibrium ones—the ohmic component of the potential and the overvoltage in this case decay (^{1}). Solutions of sulfuric acid of various concentrations (from 0.0005 to 0.05 N) were subjected to electrolysis; the cathode and anode compartments of the electrolyzer were connected by a wide siphon, and hydrogen was supplied to the cathode compartment. The reproducibility of the measurements was checked repeatedly.

In dilute solutions (0.0005-0.004 N) at low electrode rotation rates, the value of the limiting current can be established directly from the polarization curves —the sharp rise in the potential indicates rather clearly at what current density the character of the electrode reaction changes. In solutions with a higher acid concentration (up to 0.05 N) at high disk rotation rates (10,000–20,000 rpm) it is not possible to establish the position of the potential jump from the polarization curves—besides vigorous gas evolution, heating of the electrolyte in the near-electrode layer with elevated resistance also interferes. In this case the limiting current density i_d can be calculated from the equation relating this quantity to the concentration of potential-determining ions at the electrode C_s, the total concentration C_0, and the applied current density i:

[Figure 1 and Figure 2]

Fig. 1. Dependence of the limiting diffusion current on the concentration of H_2SO_4 at various disk rotation rates.
a–0, *b*–3000, *v*–8000, *g*–15,000, *d*–21,000 rpm.

Fig. 2. Dependence of the limiting diffusion current on the disk rotation rate for dilute H_2SO_4 solutions:
a–0.0005 N, *b*–0.00075 N, *v*–0.001 N, *g*–0.002 N, *d*–0.03 N, *e*–0.004 N.

$$i_d = \frac{C_0 i}{C_0 - C_s}.$$

The value of C_s is determined from the electrode potential measured $3 \cdot 10^{-3}$ sec after switching off the polarizing current, since it had previously been established by various independent methods that during this time interval the electrode reaches an equilibrium state.

With a stationary electrode, the deviation of the i_d–C dependence from linearity begins at H_2SO_4 concentrations of 0.02-0.03 N. In these and more concentrated solutions, near the limiting values of the current density, mixing of the near-electrode liquid by the evolved hydrogen is so strong that i_d increases noticeably and deviates all the more from the straight line the more concentrated the solution. If rotation of the electrode leads to ordering of the motion of the liquid, and the stirring action of hydrogen has a smaller value, then with increasing disk rotation rate we shall observe a gradual straightening of the $i_d - C$ curve. As is seen from Fig. 1, this is precisely what occurs. Increasing the disk rotation rate leads to the creation of a more stable hydrodynamic regime.

Under conditions in which replacement of one electrochemical reaction by another, associated with reaching a possible minimum concentration of potential-determining ions, occurs with comparatively slight gas evolution (for example, in dilute acid solutions at low disk rotation rates), i.e., when the limiting current densities are not very high, we may expect a linear relationship to be observed between i_d and

square root of the disk rotation rate. Our experimental material confirms this: the dependence between the limiting current and the square root of the number of revolutions of the electrode per unit time is expressed by straight lines whose extensions are directed toward the origin of coordinates (Fig. 2). Increasing the acid concentration and the disk rotation rate leads to a strong increase in the values of the limiting current. In this case, the stirring action of hydrogen begins to play a large role. Here it is impossible to create conditions under which the effect of this factor would be negligibly small–as we see from the example of the dependence i_d—C, an increase in the electrode rotation rate to some extent helps to order the hydrodynamic regime, but the corresponding curves nevertheless do not become completely straight. According to our experimental data, the dependence between the limiting current and the square root of the number of revolutions of the electrode per unit time is represented in this case by straight lines that are not directed toward the origin of coordinates (Fig. 3); they intersect the ordinate axis at points corresponding to the limiting currents at a stationary electrode, and in the three solutions of the highest concentrations–even somewhat higher (these are precisely the solutions for which the dependence i_d—C deviates from linearity).

Fig. 3. Dependence of the limiting diffusion current on the disk rotation rate over a wider range of concentrations of H_2SO_4:
a–0.002 N, *b*–0.003 N, *v*–0.005 N, *g*–0.0075 N, *d*–0.01 N, *e*–0.02 N, *zh*–0.03 N, *z*–0.04 N, *i*–0.05 N.

Such a result was to be expected, since upon lowering the disk rotation rate the thickness of the boundary layer will be determined to an ever greater extent by the stirring action of gas bubbles separating from the electrode; for this reason the straight line is directed toward the point corresponding to the limiting current at a stationary electrode. However, as is evident, conditions are possible under which stirring of the electrolyte by gas shifts the limiting currents at the rotating electrode very strongly upward, and the ordering action of the jet impinging on the disk proves insufficient. In this case the straight lines intersect the ordinate axis above the points corresponding to the limiting current at a stationary electrode.

According to the results of the calculations performed, the polarization curves studied in the region of current densities not exceeding the limiting values correspond to the equation for concentration polarization of the form

$$\varphi = \varphi_0 + \frac{RT}{nF} \ln C_0 + \frac{RT}{nF} \ln \left(1 - \frac{i}{i_d}\right).$$

The deviation of the measured potential values from the calculated ones is 4–6 mV.

Chemical Institute
Kazan Branch of the Academy of Sciences of the USSR

Received
22 X 1959

CITED LITERATURE

1. G. P. Dezider' ev, S. I. Berezina, *Izv. Kazansk. fil. AN SSSR*, ser. khim. nauk, issue 3, 41 (1957); Abstracts of reports at the Fourth Conference on Electrochemistry, Moscow, 1956, p. 37; S. I. Berezina, G. S. Vozdvizhenskii, G. P. Dezider' ev, *DAN*, 87, 53 (1951); S. I. Berezina, G. S. Vozdvizhenskii, G. P. Dezider' ev, *ZhPKh*, 25, 994 (1952).
2. A. N. Frumkin, *DAN*, 117, 102 (1957).
3. V. G. Levich, *Physicochemical Hydrodynamics*, Moscow, 1952, pp. 50, 195; V. G. Levich, *ZhFKh*, 18, 335 (1944); 22, 575 (1948).
4. Yu. G. Siver, B. N. Kabanov, *ZhFKh*, 22, 53 (1948).
5. S. I. Berezina, A. Sh. Valeev et al., *ZhFKh*, 29, 237 (1955).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.