PHYSICAL CHEMISTRY

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1962

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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CATHODIC INCORPORATION OF ALKALI METALS INTO ELECTRODES IN AQUEOUS SOLUTIONS

(Presented by Academician A. N. Frumkin, 12 III 1962)

There have long been indirect indications in the literature that some cations are capable of discharging on solid electrodes at potentials considerably more positive than their equilibrium potentials. This can occur if the cation being discharged is capable of forming an intermetallic compound with the material of the cathode. Thus, for example, in works (^{1}, ^{2}), in studying the cathodic loosening of lead in the presence of Na^+ ions, the authors suggested that the mechanism of loosening may be connected with the intermediate formation of an intermetallic compound or alloy of lead with sodium. The loosening potential is approximately 1 V more positive than the equilibrium potential of Na^+ in the same solution.

In recent years the concept of the electrochemical formation of intermetallic compounds of a whole series of alkali and alkaline-earth metals has been used to explain the loosening and dissolution of a lead cathode (^{3}), as well as the formation of a loose cathodic zinc deposit (^{4}). The interaction of the electrode surface with an alkali metal has also been used to explain a new phenomenon—cathodic superactivation of aluminum (^{5}). Reports in the literature (^{6}) that at times the same loosening and dissolution of the cathode was obtained in acid solutions can be explained by the fact that in these cases traces of salts of alkali metals were present in the acid solutions (extracted, for example, from the glass of the vessels). Under conditions of limiting currents of hydrogen-ion diffusion, the cations of these salts are concentrated at the cathode.

During cathodic polarization of certain metals (aluminum, lead) that form compounds with alkali metals, in alkaline solutions, bends were found on the hydrogen overvoltage curves and changes of potential with time at high current densities (^{7}, ^{3}). A rise of potential with time at high current densities was also observed on metals of another type (iron, nickel) (^{8}). In addition, in the case of silver and iron, irreversible changes with time in the capacitance of the double layer were noted (^{9}, ^{8}). These phenomena have not received a complete explanation. The aim of our work was to investigate the cathodic incorporation

Fig. 1. Hydrogen overvoltage on zinc; dots—in 1 *N* KOH, circles—in 1 *N* tetramethylammonium hydroxide

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of alkali metals into electrodes; in addition, we wished to clarify the influence of this process on the electrochemical and physical state of the electrode. We studied lead, zinc, and silver. Many compounds of lead with alkali metals are known (see, for example, (10)). Zinc forms compounds stable at room temperature, for example with potassium KZn_{13} (11). Metallurgical alloys of silver with alkali metals, except lithium, are not known; therefore earlier indications of the possibility of the electrochemical formation of sodium compounds with silver (12) have recently not been taken into consideration (10).

In our work the following methods were used: measurements of overvoltage, capacitance, decay of potential with time, electron-microsco-

chemical, electronographic, and the method of diffusion through a polarized membrane.

Measurement of the hydrogen overvoltage on Pb, Zn, and Ag in 1-10 *N* alkali solutions was carried out in glass or Teflon vessels. In rapid measurements after holding the electrode at comparatively low potentials, overvoltage curves are obtained with a slope coefficient not exceeding 0.13 V. At sufficiently negative potentials, whose value depends on the nature of the electrode and on the nature and concentration of the alkali cations, the hydrogen overvoltage increases with time, after which the overvoltage curve has a larger slope and hysteresis is observed. In tetramethylammonium hydroxide solutions, strong cathodic polarization of zinc does not increase the hydrogen overvoltage with time and does not distort the course of the curve (Fig. 1).

Fig. 1. Hydrogen overvoltage on zinc; dots—in 1 *N* KOH, circles—in 1 *N* tetramethylammonium hydroxide

In alkali solutions free from oxygen, the stationary potential of lead and silver electrodes after strong cathodic polarization becomes considerably (by 0.2-0.3 V) more negative than the equilibrium value. Such a shift of the potential from equilibrium cannot be explained by a polarization decrease in the concentration of the ions determining the potential. Evidently, the stationary potential is determined, on the one hand, by the rate of hydrogen evolution and ionization of traces of oxygen, and on the other by the rate of oxidative decomposition of the compound formed under strong cathodic polarization.

When measuring the double-layer capacitance of lead and silver in alkaline solutions, upon reaching the same negative potentials an irreversible change in the state of the surface is likewise observed. The capacitance increases with time, and when the potential is lowered the capacitance changes in a complex manner

Fig. 2. Dependence of capacitance on potential

Figure 2: Fig. 2. Dependence of capacitance on potential

(Fig. 2).

Electron-microscopic investigation showed that after prolonged cathodic polarization in alkaline solutions at a sufficiently high potential, the surface of the silver electrode is loosened (Fig. 3, see insert, p. 1062). The nature of the alkali cation affects the quantitative aspect of these processes.

Fig. 2. Dependence of capacitance on potential

All the phenomena described, both those known earlier (for example, sputtering of cathodes) and the new ones, should be explained by one and the same process —cathodic insertion of alkali metals into the electrode metal with the formation of intermetallic compounds. The conditions under which this process proceeds depend on the nature of the cation; they become more difficult in going from lithium to cesium and, especially, to tetra-substituted ammonium. Loosening and sputtering of the electrode

at constant potential is caused by decomposition of the intermetallic compound in the film under the bubble, where polarization is hindered (13) and the negative potential rapidly decreases because of hydrogen evolution. The capacitance of the electrode, measured with alternating current, is higher on the intermetallic compound, and also increases as a result of surface roughening. Apparently, the hydrogen overvoltage at high current densities is higher on the intermetallic compound than on the original metal, at least in the case of zinc and silver. When the current density is decreased, it falls not only in accordance with the Tafel equation for an unchanged surface, but also because of decomposition of the compound, as well as an increase in the electrode surface during roughening of the metal. At low current density the surface is gradually smoothed (14). The hydrogen overvoltage in alkalis is probably also affected by the specific adsorption of cations*.

The hysteresis phenomena observed by us in measurements of hydrogen overvoltage, capacitance, and potential-decay curves may be connected with the high overvoltage of formation and decomposition of intermetallic compounds and with appreciable diffusion of alkali metals into the depth of the electrode. The high overvoltage of the process of intermetallic-compound formation is indicated, in particular, by the slowness of the rise in hydrogen overvoltage at high current densities.

The shifted stationary potential (or the large delay on the potential-decay curve) is maintained by slow decomposition of the compound and its diffusion from the interior of the electrode. There are indications in the literature (16) of the experimental and theoretical possibility of increasing the diffusion coefficient of metals in solid intermetallic compounds by several orders of magnitude in comparison with ordinary diffusion coefficients in solid solutions and self-diffusion. We therefore attempted to detect the formation of bulk compounds between alkali metals and the metals of our electrodes by carrying out diffusion of alkali metals through thin (30–40 μ) membranes of Zn and Ag. Glass apparatuses were used, analogous to those employed in electrochemical studies of hydrogen diffusion through metallic membranes. On one side of the membrane there was an alkaline solution and cathodic polarization was carried out for 24 hours at a current density of the order of 10^{-2} A/cm^2, while on the other side there was water or a weak KCl solution and the pH of this solution was measured.

The experiments showed that, in the case of zinc membranes, the pH on the "diffusion" side shifts in 24 hours from 6.1 to 9–9.5. Roughening of the electrode surface, observed with the aid of an electron microscope, in the case of zinc under certain conditions is detected not only on the "polarization" side but also on the "diffusion" side of the membrane. When $(CH_3)_4NOH$ is present on the "polarization" side, these processes do not occur on the "diffusion" side. Thus, diffusion of the entering metal in the crystal lattice (possibly in regions of its disturbances, defects) undoubtedly plays a role in the phenomena described.

A detailed presentation of the experimental material and a discussion of the mechanism of each process will be given in subsequent articles. Here we wished to emphasize that the introduction of alkali and alkaline-earth metals into electrodes, especially those having a high hydrogen overvoltage, is an important and widespread phenomenon, playing a major role in the kinetics of many cathodic processes and in the corrosion of cathodes occurring both in alkaline and in initially neutral and acidified solutions. This introduction occurs at potentials 1–1.5 V more positive than the equilibrium—

* A number of works (15) are devoted to the influence of adsorption of alkali-metal cations on the kinetics of electrochemical processes.

···of the potential of the given alkali metal and, consequently, cannot be explained by the formation of solid solutions, but is due to the formation of intermetallic compounds with a large free energy.

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Received
9 III 1962

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