THE CATHODIC INTRODUCTION OF ALKALI METALS INTO ELECTRODES IN AQUEOUS SOLUTIONS

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There have been indirect statements in the older literature to the effect that certain cations can be discharged at solid electrodes at potentials considerably more positive than their equilibrium potentials. This might happen if the discharged cations were capable of forming intermetallic compounds with the material of the cathode. For example, in studies [1, 2] on the cathodic dispersion of lead in the presence of Na^+ ions, the authors suggested that the dispersion mechanism might be associated with the intermediate formation of an intermetallic compound or alloy of lead with sodium. The dispersion potential was approximately 1 v more positive than the equilibrium potential of Na^+ in the same solution.

In recent years, the conception of electrochemical formation of intermetallic compounds by the whole series of alkali and alkali-earth metals has been used to explain the disintegration and dispersion of a lead cathode [3], and also the formation of a loose cathodic deposit of zinc [4]. Interaction of the electrode surface with alkali metals has also been advanced as an explanation of a new phenomenon, the cathodic superactivation of aluminum [5]. The literature statement [6] that this disintegration and dispersion of the cathode has sometimes been observed with acid solutions can be explained on the assumption that, in these cases, the acid solutions contained traces of alkali metal salts (for example, by extraction from the glass vessel). Under the conditions that the current is limited by diffusion of hydrogen ions, the cations of these salts would concentrate at the cathode.

In the cathodic polarization of certain metals (aluminum, lead) in alkaline solutions, formation of compounds with alkali metals has been indicated by bends in the hydrogen overpotential curves and by changes in potential with time at high current densities [7, 3]. An increase in potential with time at high current densities has also been observed with other types of metal (iron, nickel) [8]. In addition, irreversible changes with time in the capacity of the double layer have been recorded for silver and iron [9, 8]. These phenomena have never been fully explained. The object of the present study was to investigate the cathodic introduction of alkali metals into electrodes and to elucidate the effects on this process of the electrochemical and physical composition of the electrode. We investigated lead, zinc, and silver. It is well known that lead combines with alkali metals (see [10] for example). Zinc forms compounds which are stable at room temperature, such as potassium compound KZn_{13} [11]. Metallurgical alloys of silver with alkali metals, other than lithium, are unknown, so that the earlier suggestion, that a compound of sodium with silver might be formed electrochemically [12], has recently been disregarded [10].

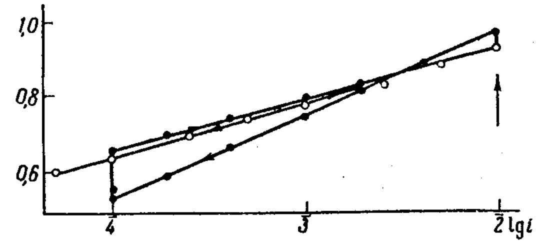

Fig. 1. Hydrogen overvoltage on zinc: dots-in 1N KOH, circles-in 1N tetramethylammonium hydroxide.

We used the following experimental techniques: change in overvoltage, change in capacity, and fall in potential with time, electron microscopy, electronography, and diffusion through a polarized membrane.

Measurements of hydrogen overvoltage at Pb, Zn, and Ag, in 1-10 N alkali, were carried out in glass and teflon vessels. In the case of rapid measurements, after the electrode had been held at a relatively low potential, the overvoltage curves had slope coefficients not exceeding 0.13 v. At sufficiently negative potentials, the value of which depended on the nature of the electrode and on the nature and concentration of the alkali cation, the hydrogen overvoltage increased with time, and the overvoltage curve subsequently had a steep slope and showed hysteresis. However, in tetramethylammonium hydroxide solutions, strong cathodic polarization of zinc did not cause the hydrogen overvoltage to increase with time and did not alter the shape of the curve (Fig. 1).

In alkali solutions, free from oxygen, the stationary potentials of lead and silver electrodes after strong cathodic polarization became considerably more negative (by 0.2-0.3 v) than the equilibrium values. This shift in potential from the equilibrium value could not be explained by a polarization decrease in the concentration of ions determining the potential. It is clear that the stationary potential was determined, on the one hand, by the rate of hydrogen evolution and the ionization of traces of oxygen, and on the other hand,by the rate of oxidative decomposition of the compounds formed by the strong cathodic polarization.

Capacity measurements of the double layer on lead and silver in alkaline solutions, at the same high negative potentials, also showed irreversible changes in the state of the surface. The capacity increased with time and altered in a complex manner when the potential was reduced (Fig. 2).

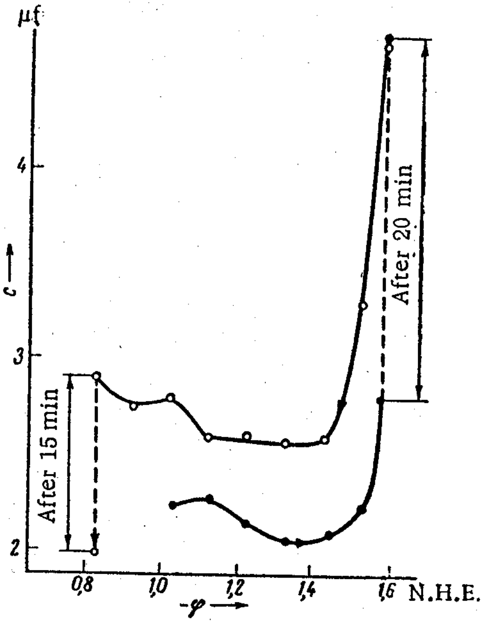

Fig. 2. Relation between capacity and potential.

Investigation by electron microscopy showed that, after prolonged cathodic polarization in alkaline solutions at a high enough potential, the surface of a silver electrode disintegrated (Fig. 3). The nature of the alkali had a quantitative effect on this progress.

All these phenomena, both those known previously (such as the disintegration of cathodes) and the new ones, can be explained in the same way, by the cathodic introduction of alkali metals into the metal of the electrode to form intermetallic compounds. The conditions for carrying out this process depend on the nature of the cation; it becomes more difficult up the series from lithium to cesium, and is particularly so for tetrasubstituted ammonium. Disintegration and dispersion of the electrode at constant potential are caused by decomposition of the intermetallic compound in the film under the bubbles, where polarization is more difficult [13] and the negative potential is readily decreased by hydrogen evolution. The electrode capacity, as measured with alternating current, is higher because of the intermetallic compound and is also increased by the surface disintegration. It is evident that the hydrogen overvoltage, at high current densities, is higher on the intermetallic silver. With a decrease in current density, the overvoltage not only drops in accordance with Tafel's law for a constant surface, but also as the result of decomposition of the compound and the increase in electrode surface produced by disintegration of the metal. The surface gradually becomes smoother at low current densities [14]. The hydrogen overvoltage in alkalies is probably affected by the specific adsorption of the cation*.

The hysteresis phenomena, observed in our measurements of hydrogen overvoltage, capacity, and fall in potential curves, may be associated with the formation of intermetallic compounds at high overvoltages, the decomposition of these compounds, and the diffusion of alkali metals into the interior of the electrode. The process of formation of intermetallic compounds at high overvoltages is indicated, particularly by the slowness of the increase in hydrogen overvoltage at high current densities.

The shift in stationary potential (or the long delay in the fall of the potential curve) also indicates that the compound decomposes slowly and that there is slow diffusion into the interior of the electrode. It is stated in the literature [16] that there are experimental and theoretical grounds for believing that it is possible for the diffusion coefficient of a metal in a solid intermetallic compound to be greater by several orders of magnitude than the normal

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*The effects of alkali metal cation adsorption on the kinetics of electrochemical processes has been discussed in [15].

diffusion coefficient in a solid solution or the coefficient of self diffusion. We therefore attempted to show the formation of some bulk compounds between alkali metals and the metal of our electrodes by studying the diffusion of alkali metals through (30-40μ) membranes of Zn and Ag. We used a glass apparatus, similar to that employed in electrochemical investigation of hydrogen diffusion through metallic membranes. On one side of the membrane was an alkali solution, and this was used to carry out cathodic polarization for a day at a current density of 10^{-2} amp/cm^2; on the other side of the membrane was water or dilute KCl solution, and any change in the pH of this was measured.

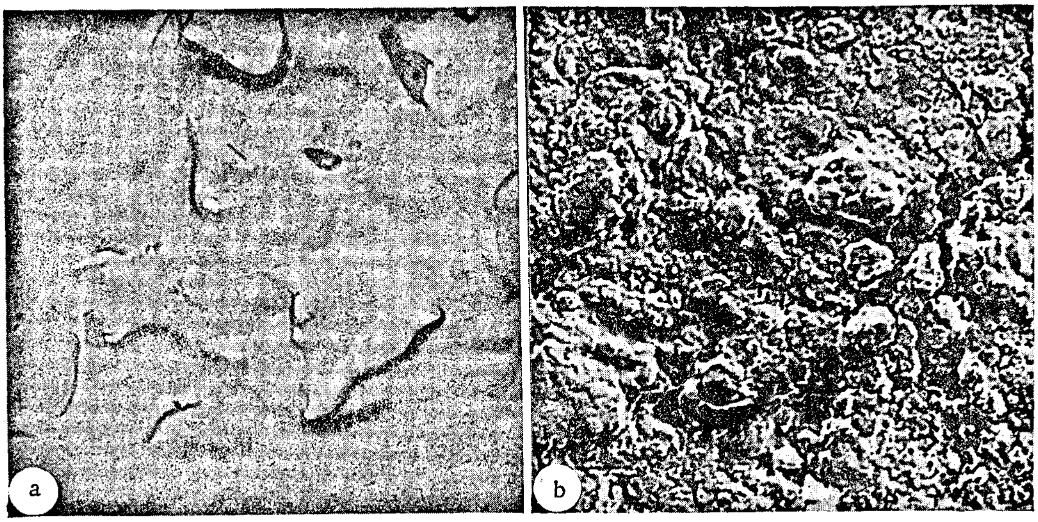

Fig. 3. The disintegration of a silver electrode after polarization in 1N NaOH: a) φ = - 1.1 v (N.H.E.) b) φ = - 1.5 v(N.H.E.)X . 30,000 ×.

Experiments showed that, with a zinc membrane, the pH on the "diffusion" side altered from 6.1 to 9-9.5 in 24 hours. Disintegration of the electrode surface, as observed by an electron microscope, was found to occur under these conditions, not only on the "polarization" side of the membrane but also on the "diffusion" side. When $(CH_3)_4 \cdot NOH$ was used on the "polarization" side, these processes did not occur on the "diffusion" side. Thus, diffusion of the metal introduced into the crystalline lattice (possibly in regions of disturbances or defects) plays some part in the above phenomena.

A detailed account of the experimental material and a discussion of the mechanism of each process will be given in subsequent papers. Here we wish to emphasize that introduction of alkali and alkali-earth metals into electrodes, particularly those with a high hydrogen overvoltage, is an important and widespread phenomenon, it plays a major role in the kinetics of many cathodic processes and in the corrosion of cathodes, both in alkaline and in originally neutral and acid solutions. This introduction occurs at potentials 1-1.5 v more positive than the equilibrium potential of the given alkali metal, and, consequently, cannot be explained by the formation of solid solutions, but depends on the formation of intermetallic compounds of high free energy.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
