OVERVOLTAGE AND MECHANISM OF THE CATHODIC INSERTION OF ALKALI METALS INTO SOLID ELECTRODES

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The rate and mechanism of the cathodic insertion of an alkali metal into the electrode metal were studied. Measurements were conducted in 1 and 10 N NaOH on pure lead and on a preliminarily produced (by electrolysis or fusion) compound of lead with sodium. In the case of lead that was not subjected to preliminary cathodic treatment, the exchange current i_0 is of the order of 10^{-10} A/cm^2, while on the alloy or cathode-treated lead, $i_0 = 10^{-3}$ A/cm^2. Such a great change in the value of i_0 is explained by the fact that the rate of insertion increases with the number of vacancies in the lattice of the metal near the electrode surface. The number of vacancies may be large in the presence of a structure of the alloy or a large number of defects in the structure of the electrode metal. In accord with this, factors acting upon the state only of the electrode surface, for example, the adsorption of As, Hg, and Te on it, polishing and etching of the electrode, have little effect upon the rate of insertion.

It has repeatedly been proposed that cathodic formation of surface compounds of the alkali metals with metals of solid electrodes may play a role in various electrochemical processes [1-3].

The discharging of alkali metal cations with the formation of intermetallic compounds with the solid metal of the cathode according to a reaction of the type

$$B^+ + e + m\,\mathrm{Me} = \mathrm{BMe}_m \tag{1}$$

(where Me represents such metals as silver, cadmium, aluminum, zinc, lead, while B^+ represents the alkali metal ion) has recently been studied in [4-7] and has been called cathodic insertion of the alkali metal into the electrode.

For a study of the principles of insertion into solid electrodes, we investigated the dependence of the rate of reaction (1) on the potential and the structure of the electrode material. It was established that on a fresh lead electrode, the process of insertion proceeds very slowly: after brief cathodic polarization of the electrode, the anodic chronopotentiogram φ versus t, taken on an oscillograph at constant current density (charging curve), possesses no lag (Fig. 1, curve c). The anodic lag, due to the decomposition of the compound formed, can be detected only after prolonged cathodic polarization (Fig. 1, curves b and c). Information on the rate of the cathodic reaction (1) can also be obtained using data on the increase in the hydrogen overvoltage with time [6]. Actually, if we assume that the reaching of the limiting value of the hydrogen overvoltage involves the formation of one monolayer of the compound BMe_m, then we can evaluate the average rate of insertion on a fresh electrode. This assumption naturally permits us to evaluate only the order of magnitude of the reaction rate. According to our data, the hydrogen overvoltage on lead in 1N NaOH reaches the limiting value after cathodic polarization for 30-60 min (Fig. 2). The same duration of cathodic polarization requires that in the subsequent anodic polarization, the lag on the charging curve be equivalent to approximately one monolayer of the intermetallic compound. The average current density

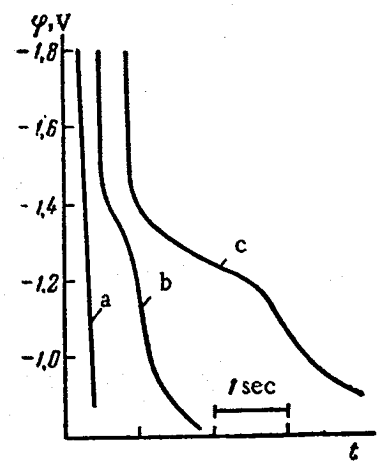

Fig. 1. Anodic φ, t curves on Pb in 1 N NaOH at $i_A = 5 \cdot 10^{-5}$ A/cm², taken after cathodic polarization at $i_k = 1 \cdot 10^{-3}$ A/cm² within a time t_k: a) 1 min; b) 15 min; c) 30 min.

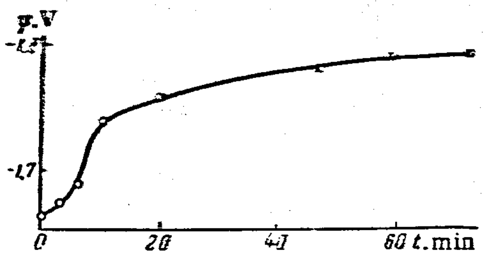

Fig. 2. Increase in hydrogen overvoltage on lead in 1 N CsOH at constant current density $i_k = 3 \cdot 10^{-3}$ A/cm².

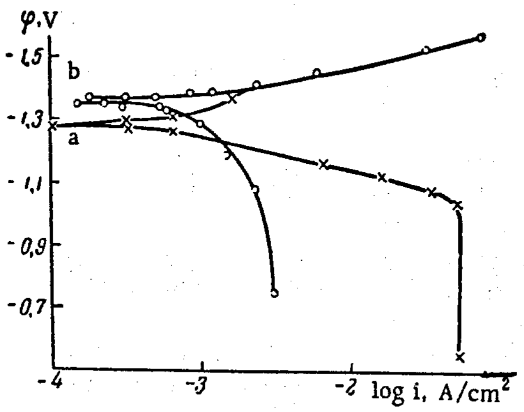

Fig. 3. Polarization curves: a) fresh alloy of lead with sodium in 1 N NaOH; b) partially depleted alloy in 10 N NaOH (the initial alloy b contained somewhat more Na than the alloy a).

of the insertion of an alkali metal into pure lead at $\varphi = -1.3$ V, calculated from this with the aid of slight extrapolation, is equal to approximately 10^{-10} A/cm².*

We measured the rate of reaction (1) by a direct method on a preliminarily produced compound of lead with sodium. Two variations of such measurements were performed: on an electrode of metallic lead after preliminary cathodic polarization and on an electrode of an alloy of lead with sodium. The alloy was produced by direct fusion of lead with 3.5-10% metallic sodium in a steel crucible in a an atmosphere of argon. The lead was drawn into glass capillaries. Thus, the alloy was produced in the form of rods from 1 to 5 mm in diameter, which served as electrodes. The measurements were conducted on the end or on a portion of the side surface freed of glass. On an alloy in 1 N and 10 N NaOH solutions, the φ, log i curves were taken by the usual method. Measurements showed that the exchange current of reaction (1) on the alloy was of the order of 10^{-3} A/cm², while the potential without the current was about −1.3 V (normal hydrogen electrode); the slope of the φ, log i curves was b = 0.1 V (Fig. 3). Here are cited the curves obtained on two different electrodes. It is difficult to obtain well expressed cathodic and anodic curves on the same electrode, since in the case of a large degree of depletion of the alloy in sodium, the cathodic curve obtained is better expressed, while the anodic curve is better expressed in the case of a low degree of depletion.

For an electrode of pure metallic lead, the dependence of the rate of the reaction of anodic decomposition of the intermetallic compound on the potential was found from the series of charging curves. For this purpose, the lead electrode was subjected to cathode polarization for 40 min; then on the lead "developed" by this method, the cathodic polarization was replaced by anodic polarization of a definite magnitude. The charging potential corresponding to a given value of the anodic current was found according to the oscillographic anodic charging curve φ versus t. In the following experiment, the anodic current was increased, while the potential of the lag on the φ versus t curve was shifted toward more positive values. By varying the anodic current density within the interval 10^{-2}-10^{-4} A/cm², we obtained a series of values of the potential of the anodic lags. The φ versus log i curve was constructed according to the data (Fig. 4). In this case also, the value of the exchange current of reaction (1) was about 10^{-3} A/cm². Thus, even considering the fact that the assumption made in evaluating the rate of the cathodic reaction (1) on fresh lead is very rough, it may be stated that the rate of the reaction on a fresh lead electrode is several orders of magnitude lower than on preliminarily-cathode-polarized lead or on an alloy of lead with sodium.

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* The rate of insertion cannot be measured directly in this case on account of the rapid evolution of hydrogen at these potentials.

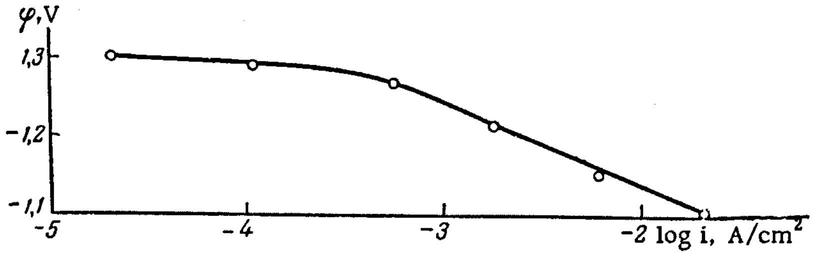
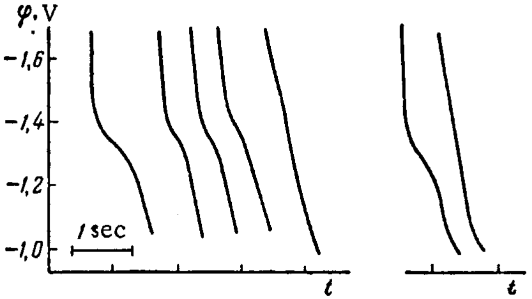


Fig. 4. Anodic polarization curve of a "developed" lead electrode in 9 N NaOH.



a b

Fig. 5. Anodic potential versus time curves: a) t_k = 90 min; b) t_k = 20 min.

In contrast to the formation of liquid amalgams, the discharging of alkali metal ions in our case occurs on a solid metallic surface. The primary formation of an intermetallic compound in the surface layer of a solid electrode should involve great difficulties, since the alkali metal atoms should be inserted into the crystal lattice of the electrode metal. Since the crystal lattice of the metal is close packed, and the intermetallic compounds of lead with sodium, just like most other intermetallic compounds, are formed according to the substitutional type, the elementary event of formation of an intermetallic compound may occur only in a case when there is a vacancy in the surface layer of the lattice of the electrode metal, into which the discharging sodium ion is inserted. Thus, the rate of the process of discharging of alkali metal ions on an electrode, with the formation of an intermetallic compound, should be determined by the number of vacancies in the surface layer of the electrode metal. The number of vacancies on the surface depends on the rate of their formation on the surface and on the rate of their delivery from the deeper layers of metal.

Lead is a metal with a low melting point and comparatively high coefficient of self-diffusion, which recrystallizes at room temperature. Hence, it is not very probable that there will be excess vacancies within the crystalline range of an undeveloped lead electrode at room temperature in comparison with the thermodynamic equilibrium value. The basic "suppliers" of vacancies in this case should be the surface, the grain boundaries, and dislocations. The diffusion of an alkali metal deep into the electrode at room temperature occurs chiefly along the grain boundaries. The discharging of alkali metal ions evidently does not occur uniformly over the entire electrode surface, but occurs primarily at the sites of emergence of dislocations and grain boundaries of the metal upon the surface. The discharged alkali metal ions may diffuse along the grain boundaries into the electrode,* and also, more slowly, within the grain. As a result of this, as well as the presence of a certain "equilibrium" number of vacancies, creating the possibility of insertion of the alkali metal, the surface may gradually become coated with a layer of an intermetallic compound.

As was mentioned above, as the electrode surface becomes coated by the intermetallic compound, there is an increase in the hydrogen overvoltage. Probably after the entire surface has become coated, the overvoltage reaches its limiting value. Upon further polarization of the electrode, the layer of the intermetallic compound on the surface of the metallic grain gradually is thickened, and there is simultaneously a more rapid penetration of the compound into the electrode along the grain boundaries. If the intermetallic compound in cathodic polarization were formed not only in a monoatomic surface layer, but also pentrated into the close-lying layers of the metal, and then were subjected to anodic decomposition on the surface, then on the electrode surface, as well as within a small volume close to the surface (primarily along the grain boundaries and close to the undecomposed phase of the

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*We have found [8] that the diffusion coefficient of cadmium along the grain boundaries in zinc is of the order of 10^{-12} cm^2/sec. Probably the diffusion coefficient of Na along the grain boundaries in zinc is of approximately the same order of magnitude.

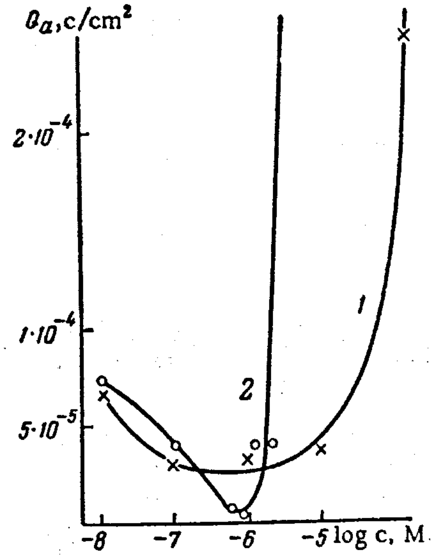

Fig. 6. Dependence of the length of the anodic lag on lead on the concentration of As_2O_3 (1) and HgO (2) in 1 N NaOH.

intermetallic compound remaining within the electrode), there is a superfluous number of vacancies. It is precisely such an electrode that is "developed". In view of the excess number of vacancies, the process of discharging of alkali metal cations on it, with the formation of an intermetallic compound, is facilitated. As a result, the rate of the process proves to be increased by several orders of magnitude.

The electrode may remain in such a "developed" state for only a limited time, until the superfluous vacancies have diffused to the sites of their drainage, after which the electrode reacquires the properties (for example, hydrogen overvoltage on it) characteristic of the original metal, and not of the compound [5]. As a result, the rate of process (1) again becomes very small.

The following experiments confirm the proposed mechanism of the insertion process. The electrode was polarized for 20 or 90 min, after which the anodic φ versus t curve was taken. Immediately thereafter, the electrode again was subjected to cathodic polarization for 0.5 sec, and the anodic φ versus t curve was again taken, again brief cathodic polarization, etc. It was found that after 20 min polarization, the lag corresponding to anodic decomposition of the compound is obtained only on the first φ versus t curve (Fig. 5, curve b). After 90 min polarization and brief cathodic polarizations, not one, but several anodic curves with gradually decreasing lengths of the lag can be taken (Fig. 5, curve a). This is explained by the fact that the rate of diffusion of sodium from within the electrode is insufficient to guarantee the presence of one large lag at $\varphi = -1.3$ V and a given anodic current density. However, the layer of the compound on the surface has time to be partially reduced in 0.5 sec of cathodic polarization on account of the discharging of sodium ions and the diffusion of sodium from within the electrode.

The anodic process of decomposition of the intermetallic compound formed is characterized by the fact that both in a "developed" lead electrode and in an electrode from an intermetallic compound prepared by fusion, the sodium atoms diffuse from within the electrode to the surface through a layer of the intermetallic compound. It is known that such diffusion should proceed considerably more rapidly than the diffusion of these atoms into the pure electrode metal [9]. As it follows from the results of our experiments, actually reaction (1) proceeds on a fresh lead electrode (but not on the alloy) several orders of magnitude more slowly in the cathodic direction than in the anodic direction on a "developed" electrode.* Analogous results are obtained with other electrode metals and other alkali metals [5, 6].

The results of our investigations thus showed that the "equilibrium" vacancies, generated on the surface of a metallic electrode or diffusing from within it, may guarantee the occurrence of the process of insertion only at a very low rate, of the order of 10^{-10} A/cm^2.† Insertion may occur at an appreciable rate only in the presence of a large number of superfluous vacancies in comparison with the "equilibrium" concentration, which may be delivered to the surface from the deeper layers of the electrode. A characteristic feature of the process of insertion con-

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*On an alloy with a certain deficiency of alkali atoms, both processes proceed rapidly. Moreover, on lead the rate of diffusion of the alkali metal within the solid phase is great, as a result of which an amount of electricity, for example, of more than a coulomb may be passed through one direction at a current density of about 10^{-2} A/cm^2, without appreciable concentration polarization in the solid phase.

† From this it follows that on electrodes with a low rate of insertion of alkali metals, not only is the equilibrium concentration of surface vacancies low, but the frequency of their appearance is low. Since the basic means of appearance of surface vacancies is the removal of one atom from the flat surface of the crystal lattice of electrode metal, then our results are an indirect experimental indication that the exchange current on an electrode whose surface contains no defects (dislocations, grain boundaries, steps of growth, etc.), should be exceptionally small, for example, less than 10^{-10} A/cm^2 for lead.

sequently is the fact that the rate of insertion is determined primarily by the state of the metal in the volume (close to the surface), which is unusual in electrochemistry. Of course, factors that affect only the state of the surface play some role in this case too. However, their effect cannot be compared with the effect obtained on account of structural changes. Anodic polishing and etching activate the surface and only slightly facilitate insertion [5]. The presence of arsenic, mercury, and tellurium on the electrode surface also influences the rate of insertion into Pb, Ag, and Cd. Their action depends on their concentration in solution. When introduced into solution in amounts of 10^{-8}-10^{-6} mole/liter, they somewhat slow down insertion, while in larger amounts they promote insertion (Fig. 6).

The great rate of insertion of an alkali metal in the presence of a large amount of mercuric hydroxide in solution is explained by the fact that at potentials more negative than the reversible potential for mercury ions there is a rapid joint deposition of mercury and the alkali metal, and a new phase is formed—an amalgam of the alkali metal. Consequently, the basic hindrance of the process due to the presence of an ordered crystal lattice, into which the atom of the alkali metal should penetrate, is eliminated.

Arsenic and tellurium in large quantities facilitate insertion because in their presence, just as in the presence of mercury ions, an intermetallic compound of the alkali metal not with the cathode metal, but with arsenic or tellurium may be formed at the moment of their deposition, i. e., coprecipitation, for example, of $AsNa_3$ or $TeNa_2$ may occur. Moreover, triple compounds of the type of AsNaZn may be formed here [10].

Thus, the rate of the process of insertion of an alkali metal into the electrode is determined by the number of vacancies in the crystal lattice of the cathode metal close to the surface. Factors affecting the state only of the electrode surface, for example, adsorption of poisoners, polishing, and etching, have little effect upon the rate of the process.

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