CATHODIC ATOMIZATION OF LEAD AND EVOLUTION OF HYDROGEN IN SOLUTIONS OF ALKALI

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Measurements in which the weight loss of the electrode as a result of atomization under varying experimental conditions (concentration of the solution of alkali, potential of polarization) is determined are important for determining the nature of the cathodic atomization and disintegration of lead during its polarization in solutions of alkalis. In [1] the atomization of lead was studied according to the decrease in the weight of the cathode in solutions of certain salts of the alkali metals and in 0.04 and 4 N solutions of alkalis. On the basis of the relationship found between the increase in the rate of atomization and the activity of water in the solution of the electrolyte (in the interval 0.87-1), it was concluded in [1] that atomization is associated with a breakdown of volatile hydride compounds of lead, formed during the evolution of hydrogen. The explanation of the atomization of lead by the decomposition of hydride compounds is contradicted by the low solubility of hydrogen in it and its low adsorption on it [2]. In [3] the atomization of lead was investigated according to weight loss in solutions of sulfuric acid with additions of salts of the alkali and alkaline earth metals. In this case no atomization was detected in pure solutions of acids. According to [3] the atomization of lead is associated with a decomposition by water of the alloys of lead with the alkali and alkaline earth metals, formed during cathodic polarization. This explanation agrees with the conclusion on the cause of atomization, drawn earlier by Haber, Bredig, and Sack [4, 5] on the basis of a comparison of the cathodic atomization of lead and spontaneous atomization in water of alloys of lead with an alkali metal, produced by fusion of the components. In [6] the overvoltage of hydrogen was compared with the cathodic insertion of alkali metals.

As was shown in [7], the atomization of lead in solutions of alkalis occurs under our conditions at potentials of -2.2 to -2.3 V (normal hydrogen electrode), at which substantial amounts of the alkali metal are accumulated on the cathode, equivalent to an amount of electricity 10^{-2}-10^{-1} C/cm^2.

In this article we discuss the dependence of the rate of atomization and disintegration of lead (according to the weight loss of the electrode) on the polarization potential; a comparison is cited with the data obtained by the methods of chronopotentiometry and with polarization measurements. The purification of the solution was described in [8]. A lead rod, produced by drawing molten lead (purity 99.999%) into a Teflon capillary with an inner diameter of 1.5 mm, was used as the electrode. Each measurement was performed on a new portion of the electrode, for which part of the Teflon capillary surrounding the electrode and part of the rod serving as the electrode were successively removed. The working surface of the electrodes was close to 0.2 cm^2. The time of cathodic polarization under conditions of atomization of lead was 2 min. After atomization, the lead sponge was removed from the electrode with filter paper; the electrode was washed and then dried in a drying oven at 50-75°C. The weight loss of the lead cathode was determined by weighing. The weight of the investigated electrodes was equal to about 1-1.5 g.

Figure 1 presents the dependence of the logarithm of the weight loss of a lead cathode P (g/cm^2 · min) on the polarization potential. The measurements were performed in a 10 N solution of KOH. As can be seen, the logarithm of the weight loss of the lead cathode increases approximately linearly with increasing negative potential.

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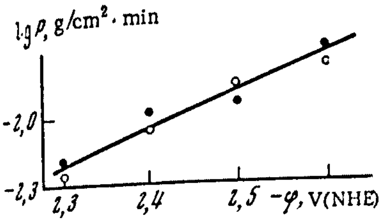

Fig. 1. Dependence of the logarithm of the weight loss of a lead cathode P on the polarization potential in 10 N KOH (two series of experiments).

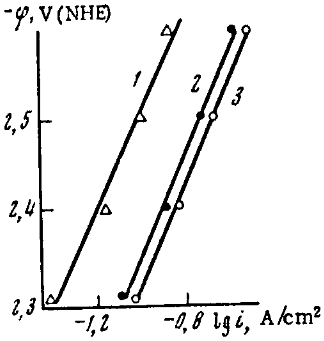

Fig. 2. Dependence of the logarithm of the current i on the polarization potential in 10 N KOH (average values of the current from two series of experiments are given): 1) calculated discharge current of potassium ions, calculation performed according to Eq. (1) under the condition that n = 1; 2) calculation performed under the condition that n = 2; 3) current that can be registered by an ammeter.

If we consider that one atom of the alkali metal corresponds to the atomization of one atom of lead (at high negative potentials KPb and K_2Pb can be formed), then according to the formula

$$i = pnF/A_{Pb}t$$

(where n = 1, p is the weight loss of lead during atomization during the experiment; F is Faraday's number; A_{Pb} is the weight of a gram atom of lead; t is the time of atomization), the current i used for the introduction of potassium ions with the formation of an intermetallic compound is calculated. The intermetallic compound is rapidly decomposed by water [9], resulting in atomization and the formation of a sponge. The amount of alkali metal penetrating into the surface layer of the electrode in a definite time is calculated according to the anodic chronopotentiogram [7].

The values of the discharge current of ions of the alkali metal, calculated according to weight loss (Fig. 2, curve 1) are approximately half the values of the current that can be registered, equivalent to the rate of evolution of hydrogen (Fig. 2, curve 3). If we consider that atomization is caused by decomposition of the compound K_2Pb (n = 2), then the dependence of φ on log i is expressed by curve 2 (Fig. 2). Curves 2 and 3 practically coincide. Consequently, if the last assumption is correct, it can be concluded that at high cathodic potentials hydrogen is liberated on lead practically only according to the new electrochemical mechanism of "hyperactivation" [10], in which chemical interaction of the intermetallic compound with water and the recombinations of hydrogen atoms into a molecule [11, 12] are faster steps than insertion. Actually, the difference of the mechanism of the evolution of hydrogen from strong alkali solutions on mercury (the Tafel constant b is equal to 0.06 V [11]) and on lead ($b \simeq 0.5$ V) (Fig. 2) consists of the fact that discharging and insertion of alkali metal ions into lead, in contrast to mercury, does not proceed without hindrance under these conditions; the rate of this electrochemical step of the total process is low in comparison with the rate of the subsequent chemical decomposition of the intermetallic compound by water. This overvoltage is associated with the necessity of breakdown of the crystal lattice of the solid metal, which is not the case when an alkali metal is inserted into mercury.

The indicated slope of the curves of the potential vs the logarithm of the current density pertains to lead electrodes with a new surface. We should mention that on lead electrodes with a changed surface layer (previously subjected to cathodic polarization and atomization) the slope decreases to about 0.2 V. The insertion of an alkali metal into lead with a developed surface proceeds more readily than into a new electrode. On the other hand, the evolution of hydrogen according to the usual electrochemical mechanism with discharging of a proton from a water molecule as the slow step, characterized by the constant b = 0.12 V, is not observed under our conditions because the overvoltage of the evolution of hydrogen according to this mechanism increases with increasing content of the alkali metal in the intermetallic compound, and consequently, with increasing negative potential [13].

Our experimental demonstration of the accumulation of substantial amounts of alkali metal on the electrode at high cathodic potentials [7] and the relationships between the weight loss of lead and rate of evolution of hydrogen demonstrated in this article are evidence that the atomization is associated with the cathodic insertion of the alkali metal and is the result of breakdown of alloys of lead with an alkali metal by water. The decomposition is accompanied by an equivalent evolution of hydrogen.

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