CATHODIC ELECTROCHEMICAL DISPERSION OF LEAD

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The literature [1-4] describes the dispersion of lead during cathodic polarization in solutions containing ions of alkali and alkali-earth metals. According to some authors [1-3], this phenomenon is due to decomposition of the intermetallic compounds formed between lead and an alkali metal during cathodic polarization, while others [4] hold that it is caused by formation of metastable lead hydrides during cathodic hydrogen evolution at the lead. The latter explanation is contradicted by the low energy of hydrogen adsorption on lead and by experimental data indicating that there is no dispersion of lead in solutions containing no alkali–metal ions [3]. It has been suggested that the dispersion of lead during cathodic polarization must be regarded as resulting from the decrease in the surface tension of metals as the cathodic potential increases. The data in the literature show that there is as yet no unanimity of opinion with respect to the factors responsible for the dispersion of lead and certain other metals at high cathodic potentials.

Electrocapillary measurements at mercury [5] and estimates made from the equation $\Delta\sigma = -1/2C(\varphi - \varphi_a)^2$, where $\Delta\sigma$ is the decrease in surface tension, C is the capacitance of the double layer, which is assumed to be constant (20 F/cm^2), φ_a is the zero-charge potential of lead, and φ is the polarization potential, have shown that the decrease in surface tension at dispersion potentials does not exceed $\Delta\sigma$ = 200-250 erg/cm^2. As was demonstrated by Likhtman et al. [7], spontaneous dispersion of a solid into colloidal particles with an average diameter of 10^{-6} to 10^{-5} cm as a result of a decrease in free surface energy is possible only when σ is reduced to one and several tenths erg per square centimeter. The decrease in the surface tension of the metal therefore cannot explain the observed dispersion of lead during cathodic polarization, but, on the other hand, the role of this decrease in the phenomenon in question must obviously be taken into account.

Investigations that showed alkali metals to be injected into hard electrodes [8-9] at cathodic potentials below their dispersion potential also indicated that there is a relationship between the cathodic dispersion of lead and the introduction of an alkali metal into it. Kudryavtsev et al. [10] also pointed out the existence of a relationship between the dispersion of metals and the introduction of alkali and alkali-earth metals into them.

In the present investigation, we employed chronopotentiometry to study the injection of an alkali metal into a lead electrode in 10 N NaOH solution at high cathodic potentials. The solution was made up from analytically pure alkali and subjected to additional purification by electrolysis. The amount of alkali metal introduced into the lead Q_A (C/cm^2) was calculated from the duration of the potential change in the $\varphi(t)$ curve after termination of cathodic polarization and simultaneous application of an anodic current ($i_A = 2.5 \cdot 10^{-4}$ A/cm^2). The voltage drop between the end of the measuring capillary of the comparison electrode and the cathode introduced no noticeable error into the potential measurement. The working surface of the lead electrode was bounded with Teflon.

When we investigated the dependence of Q_A on the polarization potential φ (Fig. 1), we found that the amount of alkali metal introduced into the lead increased abruptly at potentials of between −2.1 and −2.2 V (n.h.e.). Figure 2 shows an anodic oscillogram recorded after polarization of a lead cathode in 10 N NaOH at −2.2 V for 5 min. The amount of alkali metal injected was about $4 \cdot 10^{-2}$ C/cm^2. Rapid dispersion of the lead, which could be observed visually in transmitted light, occurred in 10 N NaOH solution at −2.3 V. The solution turned black after brief cathodic polarization at −2.3 V. Slight dispersion also took place at a lower cathodic potential if polarization was conducted over a longer period.

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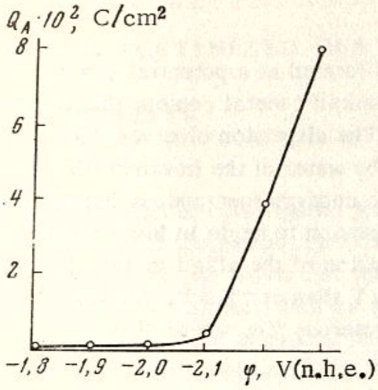

Fig. 1

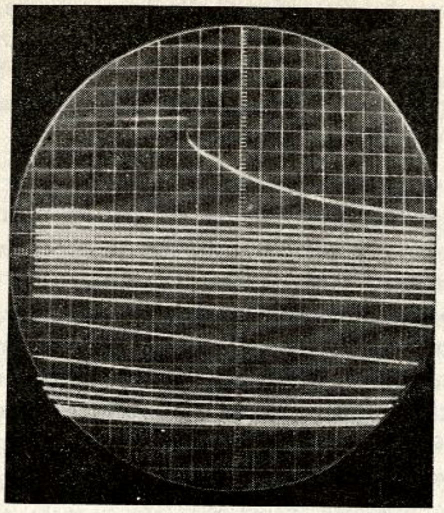

Fig. 2

Fig. 1. Amount of alkali metal injected into lead cathode as a function of cathodic polarization potential (with cathodic polarization time of 5 min and anodic current density of $2.5 \cdot 10^{-4}$ A/cm²).

Fig. 2. Chronopotentiogram of anodic decomposition of intermetallic compound formed between lead and alkali metal ($i_A = 2.5 \cdot 10^{-4}$ A/cm²; the sweep marker is 10 sec along the x axis and 0.1 V along the y axis).

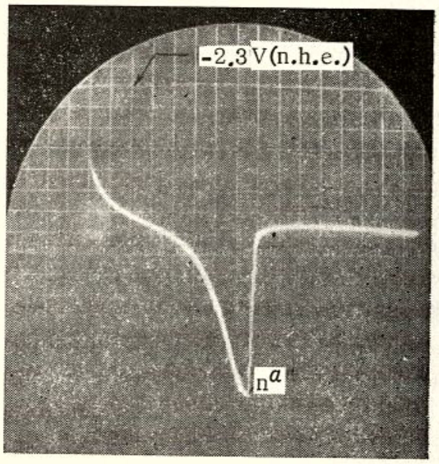

Fig. 3. Rise in potential at lead after discontinuation of anodic current of $5 \cdot 10^{-3}$ A/cm² at point a (−0.85 V); the sweep marker is 10 sec along the x axis and 0.1 V along the y axis.

Sponge lead was formed on the electrode surface after prolonged exposure to a dispersion potential of −2.3 V. The increase in the amount of alkali metal in the electrode Q_A under these conditions was also related to its accumulation in the sponge lead. When the sponge was removed from the cathode, the amount of alkali metal injected at the dispersion potential decreased, although remaining considerable. The development of sponge lead on the cathode surface can be attributed to the prolonged alkali−metal injection and the dispersion of the cathode. During anodic oxidation, the substantial amounts of alkali metal injected diffuse from the deeper layers toward the surface of the electrode metal. When polarization at $\varphi = -2.3$ V was discontinued and a large anodic current was applied ($i_A = 5 \cdot 10^{-3}$ A/cm²), almost all the alkali metal located at the cathode surface before the current was switched off had time to dissolve before a potential close to the equilibrium potential of lead was reached.

After the anodic current was switched off (point a in Fig. 3) near the equilibrium potential of lead, a spontaneous shift in potential to −1.65 V (n.h.e.) occurred, indicating diffusion of the alkali metal from the surface layer of the cathode. Depending on the amount of alkali metal injected into the lead and on the instant at which the anodic current was discontinued, the potential shift could take place at a different rate and to a different level than shown in Fig. 3. The oscillogram (Fig. 3) characteristically exhibited a potential lag in the current-free and anodic branches near −1.7 V (n.h.e.). This potential can probably be regarded as the equilibrium potential of the intermetallic compound formed between the alkali metal and lead, which has the composition Na_2Pb_3 (8 wt. % Na) [1].

In interpreting the acceleration of alkali−metal injection into the lead (starting at −2.2 V) and the concomitant dispersion of the cathode, consideration must be given to the fact that these processes take place at very large negative potentials. Formation of an alloy between an alkali metal and a hard metal is possible only when the former is injected into the electrode lattice, the rate of the process depending on the vacancy concentration at the electrode surface [8, 9]. A low equilibrium vacancy concentration in the crystal lattice and at the surface of the electrode metal causes discharge of alkali−metal ions at the hard metal surface to be impeded. On the other hand, it is well known that formation of alkali–metal amalgams proceeds rapidly at liquid mercury, in which the vacancy concentration and convection are large, and there is hence always a free volume near the surface. It can be assumed that the energy of the alkali–metal ions in the double-layer field becomes adequate for direct penetration (introduction without preliminary formation of single vacancies in the surface layer) of these ions into the crystal lattice as the cathodic potential is increased.

Moreover, it can be surmised that the intermetallic compound formed at a potential $\varphi = -2.3$ V as a result of direct penetration of alkali–metal ions into the lead has so high an alkali–metal content that it can undergo chemical decomposition by water [11], leading to dispersion of the lead. The dispersion observed during more prolonged polarization at $\varphi = -2.2$ V can also be attributed to decomposition by water of the intermetallic compound formed with time. Alloys containing 4.5-8 wt. % sodium have been shown to undergo spontaneous dispersion in water [1]. It is characteristic that longer cathodic polarization is required for dispersion to begin in less concentrated alkali solutions at a potential of −2.3 V, which may be due to slower accumulation of the alkali metal. Dispersion in less concentrated alkali solutions (1-5 N) is substantially more rapid at −2.4 V than at −2.3 V. Microscopic examination of the surface of a lead cathode that has undergone dispersion shows numerous pits, where dispersion and decomposition were probably most severe.

The experimental proof given above of the accumulation of substantial amounts of alkali metal in the surface layer of a lead cathode at dispersion potentials is thus in conformity with the hypothesis that the main factor responsible for the dispersion of lead is chemically decomposition by water of its intermetallic compound with a large amount of alkali metal.

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