EFFECT OF THE "WORKING" OF CATHODE SURFACE LAYER ON THE RATE OF ELECTROCHEMICAL INTRODUCTION OF ALKALI METALS

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It has been postulated in [1-3] that the introduction of alkali metals into solid cathodes is connected with the presence of vacancies in the surface layer of the cathode metal. Connection between the rate of introduction of alkali metals into cathodes and the structure of their surface layers, and also their history, was established. The introduction of an alkali metal into a cathode, which was not previously subjected to polarization, is slower by a few orders of magnitude than in the case when the cathode was subjected to prolonged cathodic polarization, followed by anodic polarization resulting in decomposition of intermetallic compounds of the alkali metal formed in the surface layer. Thus, the preliminary introduction of the alkali metal into the cathode surface layer has created conditions enhancing the rate of its reintroduction. The effect of such a pretreatment ("working" of a solid metal cathode) has been related to the number and rate of formation of vacancies in the surface layer [1, 2].

It is known that an alkali metal introduced into a solid cathode accumulates in its surface layer, and diffuses deeper into the cathode metal only when the cathodic polarization is prolonged [2]. When a part of the intermetallic compound of the alkali metal is decomposed by anodic current, the concentration of vacancies in the surface layer increases and, hence, the rate of the reintroduction of the alkali metal is increased. The possibility of the formation of a defective crystalline lattice of a metal, when a less electronegative metal is dissolved in it, was discussed in [4, 5]. It should also be taken into consideration that during cathodic polarization defects other than vacancies may be formed or developed, such as microfissures, micropores, and the like, which also would promote the introduction of a foreign metal.

In the present work, we have carried out a more detailed investigation on the effect of a preliminary "working" of lead and cadmium cathodes on the rate of introduction of an alkali metal therein, in particular its dependence on on the duration of the preliminary cathodic polarization* and on the effective degree of the "working". It was of interest to directly determine the introduction rate during the initial stage of polarization by measuring the amount of the alkali metal introduced into the cathode (Q, C/cm^2). This was done by determining the delay period on a chronopotentiogram recorded at a constant density of the anodic current ($2 \cdot 10^{-4}$ A/cm^2) in a range extending to a potential more negative by 20 mV than the equilibrium potential of the cathode metal. The measurements were carried out in 10 N NaOH. The solution was prepared using NaOH of AR grade, and purified by electrolysis for 150 h using a platinum anode and a silver plate cathode. Due to the use of high-concentration solution, we were able to determine the amounts of the alkali metal introduced during brief cathodic polarizations. The duration of the preliminary cathodic polarization ($t_{p.c.}$) was varied from 25 min to 100 min. The alkali metal introduced thereby was subsequently removed by the application of anodic current, and the accompanying changes in the potential were controlled oscillographically. The duration of the reintroduction ($t_{c.}$) was constant in a part of experiments (5 min), and varied from 10 sec to 5 min in the remaining experiments, in which the kinetics of the accumulation of the alkali metal in the cathode was being determined. The amount of the alkali metal introduced was calculated with respect to the visible surface area. The potential of the cathodic polarization was always the same − 1.6 V with respect to the normal

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*During a cathodic polarization, only a minor part of the cathodic current causes the introduction of the alkali metal into the cathode, the rest of the current is actually spent on the liberation of hydrogen.

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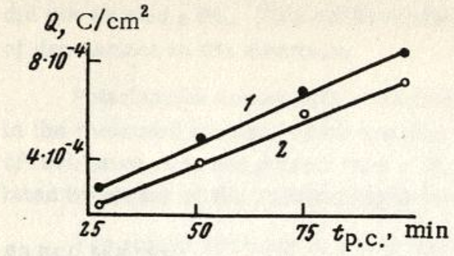

Fig. 1. Dependence of the amount of the alkali metal introduced during a 5 min cathodic polarization on the time of the preliminary polarization: 1) for lead; 2) for cadmium.

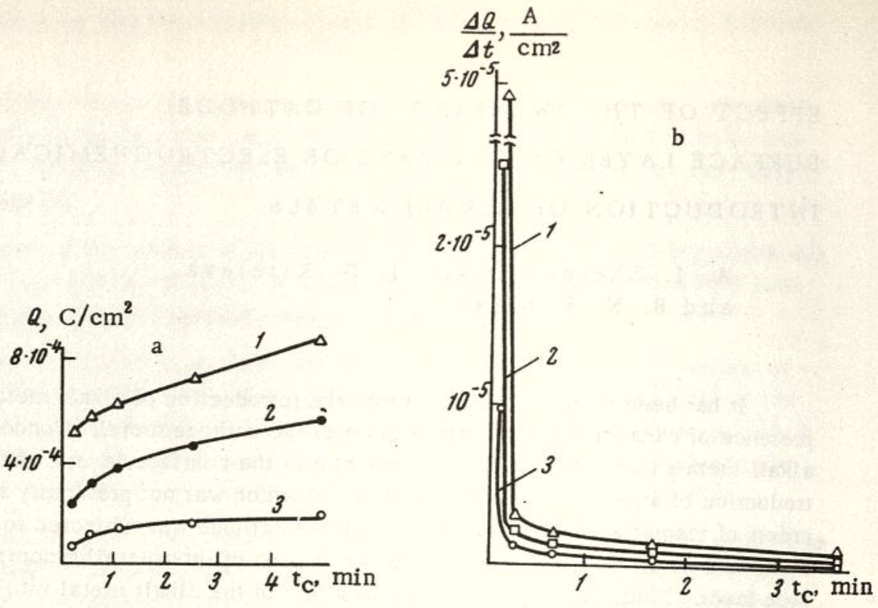

Fig. 2. (a) Curves of the amount of the introduced alkali metal Q; (b) curves showing the decrease in time of the average introduction rate ($\Delta Q/\Delta t$) in the initial period of cathodic polarization; curves 1 and 2 relate to lead electrodes preliminarily cathodically polarized for 100 and 50 min respectively; curve 3 relates to lead electrode not subjected to a preliminary cathodic polarization.

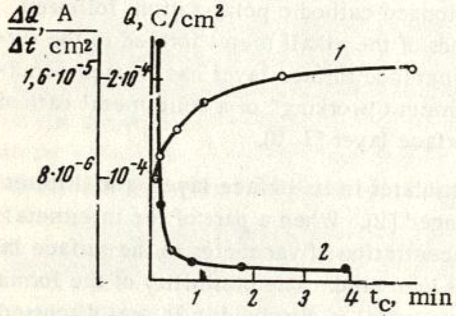

Fig. 3. Curves of the increase in the amount of the alkali metal introduced (1) and the decrease in the calculated average introduction rate (2) in the initial period of polarization, for a cadmium electrode preliminarily cathodically polarized for 20 min.

hydrogen electrode). The lead cathode was made from a wire produced by forcing the metal through a die, the cadmium cathode was prepared from a rolled and tempered metal.

The dependence of Q (t_c = 5 min) on $t_{p.c.}$, for lead and cadmium, is shown in Fig. 1. As can be seen, the amount of the introduced alkali metal linearly increases with the increasing time of the preliminary cathodic polarization. Obviously, the increase in Q in these experiments cannot be ascribed to an increase in the effective electrode surface and to the resulting decrease in the real current density. It can be assumed that changes in the effective surface area of the electrodes were small, as the current densities corresponding to the liberation of hydrogen at the same potential (− 1.6 V after 25 min and 100 min polarization, differed only slightly ($4\cdot 10^{-3}$ and $3.5\cdot 10^{-3}$ A/cm² respectively). *

Figure 2a shows the increase in the amount of the alkali metal introduced into lead after a 5 min cathodic polarization; curves 1 and 2 relate to experiments with a preliminary cathodic polarization at $\varphi_{c.} = -1.6$ V for 100 min and 50 min respectively; in curve 3, each point relates to a lead electrode not subjected to a preliminary "working" (the electrode was kept for 20 min at a potential of − 1.0 V with respect to normal hydrogen electrode). As can be seen, the largest increase in Q occurs during the initial period of cathodic polarization; a further accumulation of the alkali metal proceeds slowly. Figure 2b shows changes in time of the average rate of introduction ($\Delta Q/\Delta t$, A/cm²) calculated from data given in Fig. 2a. For the "worked" electrodes (curves 1 and 2) these values are higher than for the electrode, which was not "worked" (curve 3). In the present work, the shortest polarization time was 10 sec, and the corresponding calculated average introduction rate (current density) at $\varphi_{c.} = -1.6$ V was $5\cdot 10^{-5}$ A/cm² for the lead electrode "worked" for 100 min, and $1\cdot 10^{-5}$ A/cm² for the "unworked" electrode.

The introduction of the alkali metal proceeds at a considerable rate only for a short period. After 1 min, the average density of the introduction current drops to 10^{-6} A/cm². But, in the initial moment, the density of the introduction current must be high. It has been shown in [2], that the exchange current for a deeply "worked" lead electrode in 9 N NaOH is near to 10^{-3} A/cm². The introduction current at $\varphi_c = -1.6$ V, calculated from this value,

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* An increase in the hydrogen overpotential during cathodic polarization, resulting from changes in the properties of the electrode surface upon the introduction of the alkali metal, should be taken into account.

amounts to $10^{-1}-10^{0}$ A/cm^2. Obviously, the introduction current may reach this theoretically calculated value only during a very short time after the current is switched on (a small fraction of a second), until the surface vacancies are filled.

Figure 3 shows the increase in the amount of the alkali metal introduced into a cadmium electrode in the initial period of polarization (curve 1). The electrode was preliminarily polarized for 20 min at $\varphi_c = -1.6$ V. Curve 2 shows the decrease in the calculated average introduction rate ($\Delta Q/\Delta t$, A/cm^2).

Thus, the dependence of the rate of the introduction of an alkali metal into a solid cathode on time can be connected with the occurrence of an increased number of vacancies in the surface layer of the cathode, resulting from decomposition of the previously formed intermetallic compound (cf. [1]). The high rate of introduction of the alkali metal during the intial period of cathodic polarization confirms the assumption about the facilitation of this process by the presence of vacancies in the surface layer. When the vacancies are filled, the introduction rate drops sharply.

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