CATHODIC INTRODUCTION OF ALKALI METALS INTO LEAD AT HIGH NEGATIVE POTENTIALS

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In [1-3] the introduction of an alkali metal into lead, during cathodic polarization in alkaline solutions was studied for relatively small negative potentials. At high potentials of cathodic polarization, the rate of cathodic introduction of alkali metal is sharply increased [4] and at potentials more negative than −2.2 V against a normal hydrogen electrode the lead is dispersed.

In the present work, results are described of an investigation of cathodic introduction of sodium into lead at polarization potentials more negative than −2.0 V against a normal hydrogen electrode. The investigation was carried out by a chronopotentiometric method, i.e., by a calculation of the amount of alkali metal introduced from the time to the fall in potential when a constant anodic current is superimposed after the cathodic polarization. The experimental method was described in [3, 4]. The anodic current density was related to the apparent surface area of the electrode and was $2.5 \cdot 10^{-4}$ A/cm².

Figure 1 shows the relationship between the polarization potential φ and logarithm of the amount of sodium introduced into lead, log Q (from calculation from the chronopotentiogram) after 1 min polarization in 1, 2.5, and 10 N NaOH solutions. The potential was gradually displaced in a negative direction by 0.1 V. Measurements in the solution of each concentration began on new lead electrodes. As follows from Fig. 1, this relationship has a linear appearance. Figure 2 gives the similar relationship with a cathodic polarization time of 5 min. The dependence of this for each concentration may be presented by the equation

$$\varphi = A - B \lg Q, \tag{1}$$

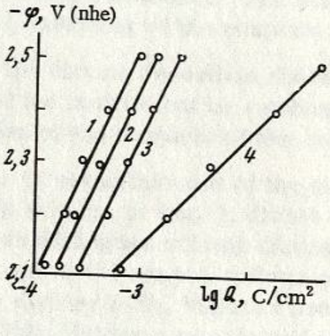

Fig. 1

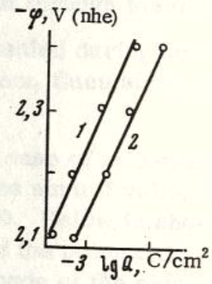

Fig. 2

Fig. 1. Relation between potential of polarization and log of quantity of cathodically deposited alkali metal in lead after 1 min in NaOH solutions of: 1) 1 N, 2) 2 N, 3) 5 N, 4) 10 N.

Fig. 2. Relation between polarization potential and logarithm of the amount of cathodically deposited alkali metal after 5 min: 1) 2 N NaOH, 2) 5 N NaOH.

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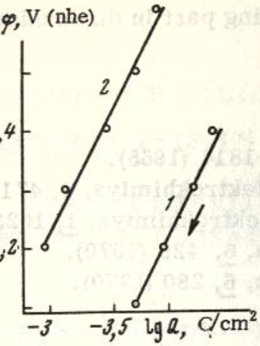

Fig. 3. Relationship between potential of polarization and logarithm of quantity of cathodically deposited alkali metal after 0.5 min in lead in 10 N NaOH: 1) on an electrode previously subjected to dispersion, the potential gradually decreased from −2.4 to −2.1 V; 2) each point obtained on a new lead electrode without preliminary cathodic polarization.

where A and B are constants depending on concentration of solution, time of cathodic polarization and state of electrode surface; Q is the amount of metal depositing at one and the same interval of time which may be descrbed as the mean rate of introduction (in contrast to introduction at less negative potentials [4], in the present case the rate of introduction only slowly decreases with time of cathodic polarization; this indicates that the state of the surface is still far from saturated by alkali metal). As can be seen from Figs. 1 and 2, an increase in quantity of alkali metal on the lead electrode of an order corresponds to an increase in potential of about 0.4−0.5 V and for 10 N solution of NaOH with polarization time of 1 min it is about 0.25 V.

A relationship which is close to proportional is observed between the quantity of cathodically deposited alkali metal and concentration of alkali solution (in the limits from 1 to 5 N). The deviation from this relationship for 10 N solution (Fig. 1, curve 4) and also for proloned cathodic polarization for less concentrated solutions is possible caused by dispersion of the lead and with a change in crystalline structure of the surface layer of the electrode and the formation of sponge lead, leading to additional accumulation of alkali metal [5]. However, in spite of the fact that the formation of sponge lead and the change in surface layer of lead results in an increase in amount of accumulating alkali metal (obviously in a surface treated by preliminary introduction and dispersion further introduction is easier), the semilogarithmic relationship with potential retains its character in the majority of cases. A confirmation that the semilogarithmic relationship is not caused by an increase in the true surface area of electrode with time of experiment and reflects the nature of the process of introduction at high cathodic potentials is the relationship obtained with reverse order of the change in potential on lead which has already been subjected to dispersion (Fig. 3, curve 1) and also the relationship of log Q and polarization φ when a new lead electrode was used for each subsequent polarization (Fig. 3, curve 2).

It should be noted that considerable accumulation of alkali metal with prolonged polarization occurs in lead also at potentials when dispersion has not already set in, which may be explained only by introduction of alkali metal on the smooth surface of the solid cathode.

In order to explain the rapid introduction of alkali metal at high negative potentials, we may propose that with increase in negative potentials the decrease in activation energy of the process becomes sufficient for an increase in the rate of introduction of alkali metal into the crystalline lattice of the lead cathod [5]. The diffusion limitation [1] obviously chahges to a "kinetic" limitation and the character of the relationship for the quantitity of depositing alkali metal after a constant interval of time or the rate of introduction of alkali metal ions (i_{in}) in these conditions will be electrochemical stage (stage of introduction with simultaneous transfer of charge) by the equation

$$i_{\text{in}} = k[c_{\text{Na}^+}]\exp(-\alpha F\varphi / RT), \qquad (2)$$

where φ is the change in potential on the electrode, α is the transfer coefficient, $[c_{\text{Na}^+}]$ is the concentration of ions of alkali metal in the volume of the solution, and k is the rate constant for the process of introduction. This equation agrees with Eq. (1) obtained by us in the experiment. The experiment gave at high cathodic potentials a high gradient for the curves of log Q and φ (0.4-0.5 V) and correspondingly a low value for the coefficient α.

Thus, the semilogarithmic relationship for the rate of introduction and potential, the sharp increase in the rate of introduction of alkali metal at −2.1 V, and the proportionality of the rate of introduction of alkali metal with the concentration of sodium ions in the solution indicate that the introduction of alkali metal at high negative potentials may be described as a process, the slowest stage of which is the electrochemical stage. Its rate was determined by the activation energy for discharge of the ion with simultaneous introduction into the solid cathode.

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