ACTIVATION ENERGY FOR CATHODIC INTRUSION OF AN ALKALI METAL

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The overvoltage for intrusion of alkali metal cations into solid cathodes is very great [1]. Discharge of alkali metal cations on mercury occurs at a rapid rate although, judging from the free energy for formation of the intermetallic compounds with the alkali metals, one might expect that the overvoltage for discharge of alkali metals on mercury would be greater than on silver, cadmium, lead, and the others on which intrusion of the alkali metals has been studied. The difference in the rates of intrusion into solid metals and into mercury is connected with the aggregate states of the electrodes. In the case of the solid cathode the intrusion reaction rate, in distinction from the majority of other electrochemical reactions, is determined not so much by the rate of charge transfer occurring directly on the electrode surface as by the rate of appearance of favorable structural features in the surface layer of the lattice of the cathode metal [2].

A decisive role is played by the concentration of atomic vacancies in the crystalline lattice at the surface of the metal and near the surface. According to the vacancy mechanism for the intrusion process, the elementary act of the formation of the intermetallic compound can occur only if the alkali metal cation discharges in the vicinity of an atomic vacancy [1].

A study of the temperature dependence of the intrusion rate at constant overvoltage, and thereby a determination of the real activation energy for the process [3], was necessary for further development of ideas on the mechanism of intrusion of alkali metals into solid cathodes.

Measurements were conducted in the temperature range 10-70°C in 1 N NaOH on electrodes of type SV lead and of a lead-sodium alloy with an average composition corresponding to the compound $NaPb_3$. The method of purifying the solution and preparing the lead-sodium alloy has been described earlier [1, 4]. A mercury-mercurous oxide electrode in the same basic solution served as the reference electrode. Values of the potentials with respect to the normal hydrogen electrode were calculated.

Curves of the dependence of the overvoltage (η) on the logarithm of the current density (log i) were recorded for the alloy. Measurements were conducted on fresh electrodes and on electrodes from which part of the sodium had been extracted by passage of an anodic current (2 h, 10^{-3} A/cm^2). The electrode potentials at zero current in these two states were −1.5 and −1.4 V (N. H. E.), respectively, at 20°C. In order to maintain a constant composition of intermetallic compound at the surface of the electrode, the anodic and cathodic overvoltage curves were recorded at the same time by alternate anodic and cathodic polarization.

In Fig. 1 are shown η, log i curves taken on fresh alloy. Similar curves were taken on a depleted electrode. From these data, the dependenence of log i on 1/T was plotted (Fig. 2), and the activation energy was determined. The value of i at an overvoltage of 20 mV* was used for the calculation.

This method of determining the activation energy for the intrusion process can be successfully applied only in the case of a prepared alloy. Since intrusion of an alkali metal cation into an untreated metallic surface occurs at a very high overvoltage, it is impossible to record η, log i curves for intrusion on such electrodes. Measurement of the current density is hindered by hydrogen evolution. Thus the average intrusion rate into pure lead can be determined approximately from the quantity of dissociated intermetallic compound Q_a measured from the oscillographic φ, t curves after the intrusion process has been conducted at constant potential for a certain length of time. With a short cathodic polarization time, when the forming compound has not penetrated deeply into the cathode but remains concentrated in a surface layer, practically the whole amount of the intermetallic compound formed during cathodic polarization Q_c can be dissociated by the imposition of anodic polarization.

* Curves with the same slopes are obtained with $\Delta\eta$ = 15 and 10 mV for both cathodic (i_c) and anodic (i_a) currents.

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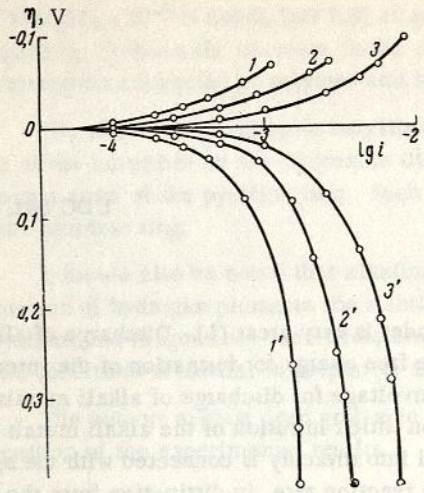

Fig. 1. Overvoltage curves on fresh $NaPb_3$ alloy in 1 N NaOH; 1 and 1') 20°; 2 and 2') 40°; and 3 and 3') 70°C.

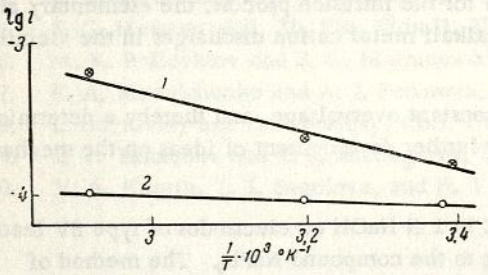

Fig. 2. Temperature dependence of the rate of cathodic intrusion of sodium: 1) in fresh alloy; 2) in depleted alloy.

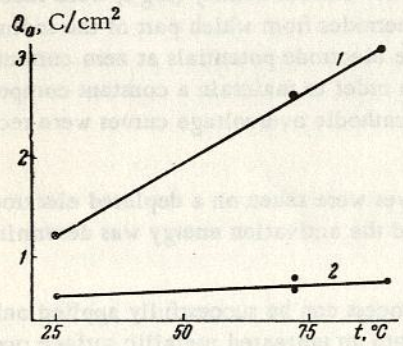

Fig. 3. Dependence of the amount of sodium extracted during anodic polarization on the temperature t_a of the anodic process: 1) t_c = 60 min; 2) t_c = 15 min.

TABLE 1

Cathode metal	E_1, kcal/mole
Pb	~7
Alloy ($NaPb_3$):	
fresh	6.8
depleted	2.3

The temperature dependence of Q_a after 60- and 15-min cathodic polarizations is shown in Fig. 3. In all cases the cathodic polarization was conducted at 8°C. After the 60 min cathodic polarization, Q_a grows with an increase in the decomposition temperature, since sodium is extracted from a greater depth when diffusion is accelerated. After the 15-min cathodic polarization, Q_a does not depend on the temperature. This means that in this case diffusion at 25°C has already resulted in a practically complete extraction of sodium from the cathodic metal; i.e., the amount of anodically dissociated compound Q_a is approximately equal to the amount of compound formed cathodically Q_c in a given time τ and is proportional to the average intrusion rate. From the dependence of Q_a on the temperature at constant τ, then, one can make a rough estimate of the intrusion activation energy. The dependence of intrusion into pure lead was determined by this method (Fig. 4). Values of the activation energy E calculated from the dependences of log i on 1/T and log (Q/τ) on 1/T are shown in Table 1.

The values of E obtained are very small and depend on the state of the crystalline lattice. The properties of the metallic lattice in the fresh and depleted states are different. This difference consists, for example, in a different vacancy concentration. Lead must have the smallest concentration, since this low-melting metal recrystallizes easily at room temperature, and its vacancy concentration would rapidly tend to a low equilibrium value. The equilibrium vancancy concentration in the alloy is usually higher than in the pure metal, because vacancies form more easily in places adjacent to foreign atoms [5]. In $NaPb_3$, therefore, the vacancy concentration should be greater than in the pure metal. There is an excess of vacancies in the anodically depleted alloy compared with the fresh alloy, because Na^+ leaves the crystalline lattice during anodic polarization, forming a vacancy.

Judging from the values of the activation energy obtained in our experiments, intrusion is easiest in the lattice of the depleted alloy with a high vacancy concentration (E = 2.3 kcal/mole), and most difficult in the lattice with a low concentration (E = 7 kcal/mole).

For diffusion in metals with face-centered cubic lattices, the vacancy mechanism is known to be the most probable. The dependence of the intrusion process on the vacancy concentration therefore implies dependence of the intrusion on diffusion processes, and that the intrusion activation energy values found should correspond to diffusion activation energies. It is well known that the diffusion activation energy under the vacancy mechanism is equal to the sum of the energy of vacancy formation and the activation energy for vacancy motion. An excess of vacancies strongly affects the diffusion process in this way.

In our case an increase in the vacancy concentration was achieved by extracting part of the Na contained in the alloy during the passage of an anodic current. It may be assumed that, with a sufficiently high excess vacancy

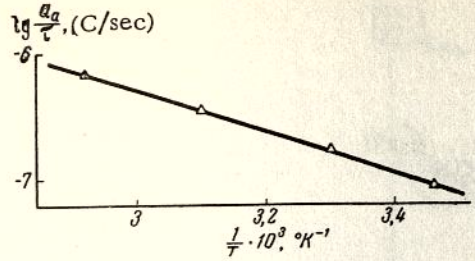

Fig. 4. Temperature dependence of the rate of formation of intermetallic compound during cathodic polarization of Pb.

concentration, diffusion in the alloy is determined essentially by the vacancy mobility. Therefore the activation energy found for this case (2.3 kcal/mole) represents the activation energy for vacancy motion. For a fresh alloy with a smaller vacancy concentration, the diffusion activation energy is considerably greater. Assuming that it is determined in this case by the sum of the vacancies' formation energy and their kinetic energy, one can find the ratio of the vacancy formation energy to the diffusion activation energy. It turns out to be 0.33. A similar ratio was found for Ag, Cu, and Al [6].

The anodic η, log i curves (Fig. 1) obtained for the alloy have a shape typical of diffusion-limited processes. In our case the diffusion limitation is due to the lagging of the rate of sodium diffusion from the depth of the alloy behind its dissolution rate at the electrode surface in the electrolyte during anodic polarization. The sodium diffusion coefficient in the alloy was calculated from the diffusion currents. For this calculation, the formula for nonsteady-state diffusion was used [7]:

$$i = nF\sqrt{Dc^0} / \sqrt{\pi t},$$

where t is the time for a given current (i) to be established, and the concentration c^0 corresponds to the composition of $NaPb_3$. The diffusion coefficient at 20°C turned out to be $4 \cdot 10^{-11}$ cm^2/sec. This value of the diffusion coefficient may be compared with the known limiting value for self-diffusion of lead ($2 \cdot 10^{-12}$ cm^2/sec) [8]. Sodium thus diffuses an order of magnitude faster in lead than does lead in lead.

On the basis of the dependence of the activation energy for intrusion of an alkali metal on the state of the crystalline lattice of the electrode metal into which the intrusion occurs, and according to the assumptions we have made, it has been found that the reason for the large overvoltage for intrusion is the limiting vacancy concentration in the near-surface layer of the solid cathode and the slowness of the diffusion processes in the electrode.

LITERATURE CITED

1. B. N. Kabanov, I. G. Kiseleva, I. I. Astakhov, and N. N. Tomashova, Élektrokhimiya, 1, 1023 (1965).
2. I. I. Astakhov, Diss., In-t Élektrokhimii, AN SSSR, Moscow (1965).
3. M. I. Temkin, Zh. Fiz. Khimii, 22, 1081 (1948).
4. I. G. Kiseleva, N. N. Tomashova, and B. N. Kabanov, Zh. Fiz. Khimii, 38, 1188 (1964).
5. R. P. Johnson, J. Phys. Chem., 110, 149 (1924).
6. S. D. Gertsriken, Dokl. Akad. Nauk SSSR, 98, 211 (1954).
7. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, Kinetics of Electrode Processes [in Russian], Izd. MGU, Moscow (1952).
8. B. Okkerse, Acta Metallurgica, 2, 551 (1954).