ZERO-CHARGE POTENTIALS OF ALLOYS OF LEAD WITH SODIUM

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During cathodic polarization of metals in solutions containing alkali metal cations, the latter react with the metal of the cathode. The reaction has a cathodic incorporation mechanism and leads to formation of intermetallides of alkali metals with the cathode metal and of solutions of these compounds in the cathode metal [1, 2]. This may be accompanied by a considerable change in the mechanical and electrochemical properties of the cathode [3]. It is known, for example, that incorporation leads to a change in the kinetics of cathodic reactions [1]. In particular, reduction of the NO_3^- anion [4] and acetone [5] are markedly accelerated, which might be due to displacement of the zero charge potential of the cathode metal when alkali metal is incorporated. In the case of mercury, experimental research has revealed how the zero charge potential [6] and the electron work function [7, 8] change with an alkali metal admixture.

When alkali metals are incorporated into solid electrodes, the change in the zero charge potential may evidently be more rapid than for mercury, because the surface concentration of the alkali in the liquid metal increases less rapidly than in a solid metal owing to convective removal of alkali metal into the bulk of the cathode from the liquid metal surface. Our aim is to compare the zero charge potentials of pure lead and sodium-containing lead.

The zero charge potentials were determined by measuring the impedance with an R-568 bridge. The measurements were performed on pure lead (99.9998%) electrodes and lead–sodium electrodes. The alloys were obtained by fusing lead and sodium in argon [9]. The sodium content of the lead was 1 at.% or 30 at.%. The latter alloy is the β-phase of $NaPb_3$ [10].

The special difficulty of studying alloys by measuring the impedance is that constancy of the surface layer of the electrode must be ensured. The surface concentration may be increased by incorporation of sodium from the solution, or reduced by the anode process and chemical reaction of the sodium in the alloy with water [11]. It follows from [12] that the surface concentration of sodium increases rapidly at a high (10 N) alkali concentration and in the presence of marked polarization of the electrode (above −2.2 V). To avoid a change in the surface state during recording of the curve, the electrodes were prepared from alloys which had been kept at room temperature for one or two weeks. Owing to the recrystallization which takes place during such residence, to the high rate of diffusion of sodium in the alloy, and to the decrease in the rate of chemical [11] and electrochemical self-solution (during cathodic polarization in alkali the hydrogen overvoltage on lead increases with time [1, 3]), the electrodes apparently acquire the value of a potential without current, the value remaining steady for several hours [14]. We may therefore assume that the sodium concentration on the electrode surface was practically constant during our measurements.

To determine the zero-charge potentials of the alloys, we measured the differential capacitance in dilute alkalis in the potential range from −0.5 to −1.2 V (nhe). Figure 1 plots the double-layer capacitance vs the electrode potential for pure lead and for a lead alloy containing 1% sodium. It will be seen that the potentials of the capacitance curve minimum differ by 0.2–0.22 V. On the curve for lead the minimum is

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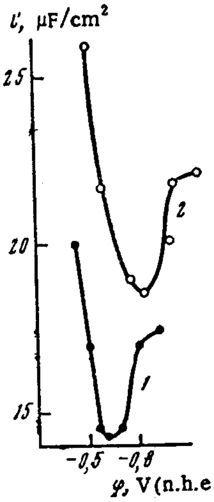

Fig. 1

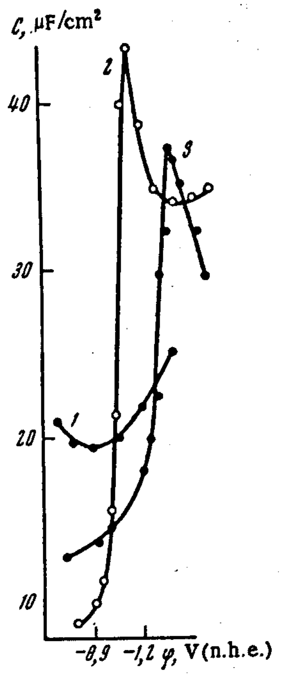

Fig. 2

Fig. 1. Differential capacitance vs potential in 0.01 N Na_2SO_4: 1) Pb; 2) Pb + 1 at.% Na.

Fig. 2. Differential capacitance vs potential: 1) base electrolyte curve for Pb in 1 N Na_2SO_4; 2) for Pb in 1 N Na_2SO_4 saturated with hexyl alcohol; 3) Pb + 1 at.% sodium in the same solution.

observed at − 0.62 V, which coincides with the zero charge of lead determined in [15] for solutions containing no surface-active ions. On the curve for the alloy the minimum is observed at − 0.85 V.*

It was interesting to compare this discrepancy between the zero-charge potentials of lead and the alloy with measurements of the double layer capacitance in solutions containing molecularly adsorbent surface-active substances. For this purpose, measurements were performed in solutions containing hexyl alcohol. Assuming that pure lead and the alloy with a low sodium content have roughly the same capacity to adsorb specifically the same substance, we may expect that displacement of the adsorption−desorption peak will correspond to that of the zero-charge potential [16]. It will be seen from Fig. 2 that in the case of the alloy the desorption peak potential also has a more negative value than in the case of pure lead. The difference ranges from 160 to 180 mV in different experiments. We may thus assume that the zero-charge potentials of pure lead and of the alloy with 1 at.% Na differ by ~0.2 V, i.e., that the zero-charge potential of this alloy is approximately − 0.8 V.

For the alloy with a high (30 at.%) sodium content, determination of the potential from the minimum in a dilute solution is impossible because during measurement, owing to reaction of the sodium, extracted from the alloy, with water [11] the solution concentration in the layer adjacent to the electrode increases; furthermore, owing to electrochemical solution of sodium, it is difficult to distinguish the double-layer capacitance from measurements of the impedance.† Therefore, on such an alloy the measurements were performed only in a 1 N Na_2SO_4 solution saturated with hexyl alcohol.

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*When the capacitance component of the impedance was measured at 1 kHz, the tangent of the phase shift was more than 9 and an increase in the frequency to 10 kHz reduced the capacitance component by only 10%; this enabled us to identify the measured capacitance with the differential capacitance of the electric double layer with an accuracy sufficient for determining the zero charge point.

†Escape of sodium from the alloy in the near-electrode layer of the solution does not lead to marked sodium depletion of the alloy surface owing to rapid diffusion of sodium in the alloy [13].

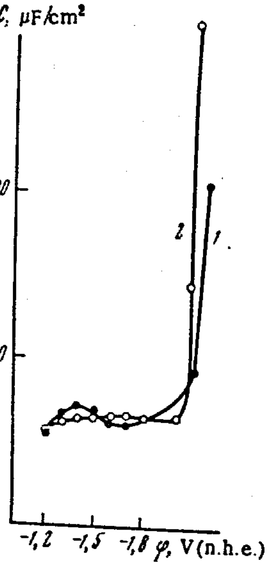

Fig. 3

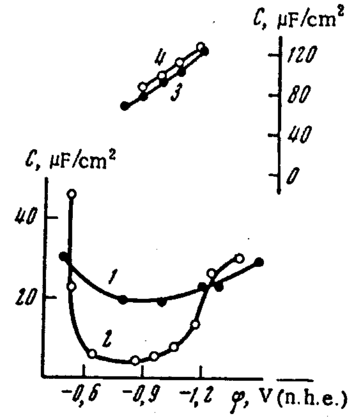

Fig. 4

Fig. 3. Differential capacitance vs potential for an electrode of an alloy of the composition Pb + 30 at.% sodium: 1) 1 N Na_2SO_4; 2) 1 N Na_2SO_4 saturated with hexyl alcohol.

Fig. 4. Differential capacitance vs potential: 1) Pb in 1 N Na_2SO_4; b) Pb in 1 N Na_2SO_4 saturated with isoprene; 3) Pb + 30% Na in 1 N Na_2SO_4; 4) Pb + 30% Na in 1 N Na_2SO_4 saturated with isoprene.

In the potential range investigated the adsorption properties of the alloy with a high sodium content differed markedly from those of pure lead and the alloy with 1% Na; hexyl alcohol is not adsorbed on $NaPb_3$ in the range from −1.2 V to −2.0 V, which is indicated by the absence of a fall in capacitance when alcohol is added to the solution (Fig. 3, curves 1, 2). Accordingly, in the case of $NaPb_3$ at these potentials no hexyl alcohol desorption peak is observed.* Another surface-active substance, isoprene, behaves in the same way. As on pure lead, on the alloy with 1% Na, isoprene markedly reduces the double-layer capacitance of the electrode and is therefore adsorbed (Fig. 4, curves 1, 2), but on $NaPb_3$ the capacitance is not reduced (Fig. 4, curves 3, 4).

The absence of adsorption of alcohol and isoprene means that the surface charge of the electrode in this potential range is high. With increasing sodium content, the zero-charge potential of the electrode is evidently markedly displaced toward negative values. The absence of a decrease in the capacitance when the negative value of the potential increases as far as −2.0 V enables us to assume that the zero-charge potential of $NaPb_3$ has a more negative value – at least −2.5 V.

LITERATURE CITED

1. B. N. Kabanov, I. I. Astakhov, and I. G. Kiseleva, Uspekhi Khimii, 34, 1813 (1965).
2. B. N. Kabanov, I. G. Kiseleva, I. I. Astakhov, and N. N. Tomashova, Élektrokhimiya, 1, 1023 (1965).
3. D. P. Aleksandrova, I. G. Kiseleva, and B. N. Kabanov, Zh. Fiz. Khimii, 38, 1493 (1964).
4. B. N. Kabanov, N. N. Tomashova, and I. G. Kiseleva, Élektrokhimiya, 6, 612 (1970).
5. M. G. Smirnova, V. A. Smirnov, and L. I. Antropov, Tr. Novocherkassk. Politekhn. In-ta, 79, 43(1959).
6. V. A. Smirnov and L. I. Antropov, Dokl. Akad. Nauk SSSR, 113, 1098 (1957).
7. V. B. Lazarev, Yu. I. Maslov, and G. A. Sharpataya, Élektrokhimiya, 6, 820 (1970); V. B. Lazarev and Yu. I. Maslov, Élektrokhimiya, 3, 294 (1967).

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*The high values of the capacitance on $NaPb_3$ are due to the fact that these electrodes have rougher surfaces. The increase of the capacitance at −2.0 V is not due to the presence of a desorption peak. It is also observed in the absence of hexyl alcohol (Fig. 3, curve 1) and is apparently due to the marked increase in the rate of cathodic incorporation and anodic removal of sodium [12].

8. S. D. Levina, L. A. Korob, and G. E. Kalenchuk, Élektrokhimiya, 6, 1334 (1970).
9. B. N. Kabanov, I. G. Kiseleva, I. I. Astakhov, and N. N. Tomashova, Élektrokhimiya, 1, 1023 (1965).
10. M. Hansen and K. Anderko, The Constitution of Binary Alloys, McGraw-Hill (1958).
11. N. N. Tomashova, I. G. Kiseleva, and B. N. Kabanov, Élektrokhimiya, 7, 438 (1971).
12. A. I. Chernomorskii, I. G. Kiseleva, and B. N. Kabanov, Élektrokhimiya, 6, 429 (1970).
13. N. N. Tomashova, I. G. Kiseleva, I. I. Astakhov, and B. N. Kabanov, Élektrokhimiya, 4, 471 (1968).
14. I. G. Kiseleva, N. N. Tomashova, B. N. Kabanov, and V. D. Meshko, Élektrokhimiya, 5, 466 (1969).
15. K. V. Rybalka and D. I. Leikis, Élektrokhimiya, 3, 383 (1967).
16. É. S. Sevast'yanov and D. I. Leikis, Izv. Akad. Nauk SSSR, Ser. Khim., 450 (1964).