DEPENDENCE OF THE STEADY POTENTIAL OF AN INTERMETALLIDE ON THE SOLUTION COMPOSITION

I. G. Kiseleva, N. N. Tomashova, B. N. Kabanov, and V. D. Meshko

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Our study [1] of cathode and anode charging curves for Ag, Cd, Pb, and Zn in alkali solutions revealed steps at potentials of about −1.3 V. The presence of steps was attributed to electrochemical processes associated with cathodic incorporation of alkali-metal ions into the metal of the cathode to form an intermetallide, and with anodic decomposition of this compound. The potential corresponding to the average of the cathode and anode step potentials is taken as the equilibrium potential of the corresponding intermetallide.

To verify that the intermetallide potential is the equilibrium potential with respect, for example, to the reaction

$$Na^+ + 3Pb = NaPb_3 - e^-,$$

it was necessary to study how the potential changes with the solution composition. This is the aim of the present work.

Owing to structural limitations, incorporation of an alkali metal into the pure cathode metal is very slow against the background of hydrogen evolution [2]. If cathodic polarization is not very prolonged, a small amount of intermetallide is formed and rapidly decomposes after the cathodic polarization is halted. The equilibrium of the system intermetallide-solution is more advantageously studied on electrodes from a previously prepared alloy of the cathode and alkali metals. Owing to the presence of a considerable reserve of the compound and the high rate of reactive diffusion of the alkali metal in the alloy (decomposing due to evolution of hydrogen), in this case the intermetallide is continuously replenished and the potential remains stable for several days without an external current.

Several intermetallides: $Na_{15}Pb_4$, Na_5Pb_2, NaPb, $NaPb_3$ [3] can be obtained by thermal fusion of lead and sodium. The most interesting of these is the compound readily obtained on lead during its cathodic polarization in alkali, i.e., by cathodic incorporation. The intermetallide $NaPb_3$ is apparently such a compound, because its potential, like that of the intermetallide usually formed during incorporation, is −1.3 V [2, 4]. *

The intermetallide was obtained by the procedure in [2]. Judging from the potential, the composition of the alloy on the electrode surface changes with time. The freshly prepared alloy, with a 1 : 3 atomic ratio of Na to Pb, has a potential in the range from −1.7 to −1.6 V, which is rapidly displaced towards more positive values (Fig. 1, curve 1). If the alloy is kept for several days at room temperature, it rapidly acquires a potential of −1.3 V which remains stable with time; this potential corresponds to the phase $NaPb_3$ (Fig. 1, curve 2) and is probably due to gradual transition of the alloy to the equilibrium state as a result of crystallization and increased uniformity of sodium distribution. After more prolonged residence of the alloy in air, for example, about a month, the potential of the electrode in the first half an hour or so after immersion in the solution is close to that of lead (from −0.5 to −0.6 V) but then exhibits a negative shift, reaching the steady value of −1.3 V (Fig. 1, curve 3). It may be assumed that in the first period the electrode potential is determined by contact between the solution and the electrode's outerlayer, which is without sodium and consists of spongy lead and plumbic oxide. The surface layer of lead has fine pores and the change in potential from a value in the range from −0.5 to −0.6 to −1.3 V is evidently due to the slow penetration of the electrolyte through these air-filled pores and to the appearance of an $NaPb_3$-solution boundary within the electrode. This assumption is confirmed by the fact that the steady potential of such an electrode changes very slowly with the solution composition: in the micropores of the layer of lead, the solution composition remains unchanged for tens of minutes, despite the change in the solution outside the electrode. The

*Formation of an intermetallide with a different composition (with a potential of about −1.5 or −1.0 V) is only rarely observed [1].

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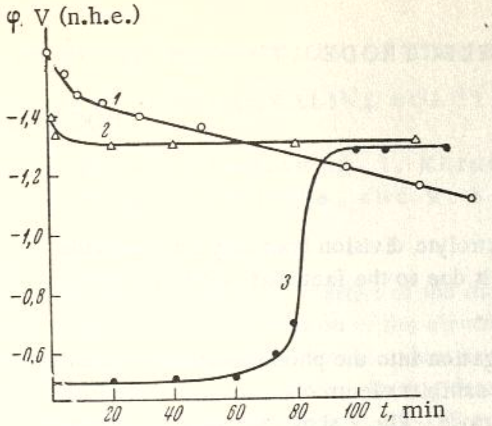

Fig. 1. Time dependence of the potential of an alloy obtained by thermal fusion of lead and sodium in 1 N NaOH. 1) Freshly prepared alloy; 2) alloy kept without contact with the solution for several days; 3) alloy kept for a month.

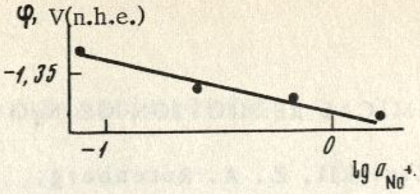

Fig. 2. Intermetallide potential versus logarithm of the activity of sodium ions in a solution with pH 13.

period required to establish the potential can be reduced by cathodic polarization of the alloy. After cathodic polarization for 20 min at $\varphi = -1.25$ V, the intermetallide potential (−1.3 V) is established instantaneously and remains constant for a considerable period. This might be due to the increased wettability of the lead at high cathodic polarization at increased distance from the zero-charge potential [5], equal in the case of lead to −0.65 V [6], and of the accompanying accelerated penetration of the electrolyte through the pores of the lead layer to the intermetallide.

The effect of the solution composition on the intermetallide potential was studied in NaOH solutions of different concentration, and in an NaOH solution with added Na_2SO_4, at a constant solution pH. The alkali was subjected to cathodic purification before use. Sodium sulfate was recrystallized twice in doubly distilled water. The measurements were performed in hydrogen. The comparison electrode was a mercury oxide electrode in an alkali solution of the same concentration as the investigated solution. The potentials were related to a normal hydrogen electrode.

Figure 2 plots the intermetallide potential versus the logarithm of the activity of sodium ions in the solution at pH 13. A similar dependence on a_{Na^+} is obtained with a change in the pH (in pure NaOH solutions, from 0.1 to 2.3 N). It will be seen from Fig. 2 that a tenfold increase in the activity of the sodium ions leads to a positive shift of 60 mV. This dependence implies that the electrode equilibrium potential is due to the to the fact that an electrochemical process with 1 sodium ion per 1 electron takes place at the boundary between the intermetallide and the solution. The spontaneous decomposition of the intermetallide in the alkali solution may be represented as two conjugated but independent reactions, taking place at the same potential:

$$NaPb_3 \rightleftarrows Na^+ + e^- + 3Pb, \tag{1}$$

$$2H_2O \rightarrow H_2 + 2OH^- - 2e^-. \tag{2}$$

Reaction (1) is reversible and can take place in both directions at a rate much greater than (2). Hence the potential of spontaneous decomposition of the intermetallide must be practically equal to the equilibrium potential, determined by an equation which, in the case of (1), can be written as:

$$\varphi = \varphi_0 + (RT/F) \ln a_{Na^+},$$

where φ_0 is the steady potential of the intermetallide and a_{Na^+} is the activity of the sodium ions in the solution; this was confirmed experimentally (Fig. 2).

LITERATURE CITED

1. I. G. Kiseleva, N. N. Tomashova, and B. N. Kabanov, Zh. Fiz. Khimii, 38, 1188 (1964).
2. B. N. Kabanov, I. G. Kiseleva, I. I. Astakhov, and N. N. Tomashova, Élektrokhimiya, 1, 1023 (1965); D. P. Aleksandrova, I. G. Kiseleva, and B. N. Kabanov, Zh. Fiz. Khimii, 38, 1493 (1964).
3. M. Hansen and K. Anderko, Structures of Binary Alloys [Russian translation], Metallurgizdat, Moscow (1962).
4. R. Kremann and P. V. Reininghaus, Z. Metallkunde, 12, 273 (1920).
5. A. N. Frumkin, A. V. Gorodetskaya, B. N. Kabanov, and N. I. Nekrasov, Zh. Fiz. Khimii, 3, 351 (1932).
6. K. V. Rybalka and D. I. Leikis, Élektrokhimiya, 3, 1135 (1967); B. Kabanov, S. Filippov, L. Banyukova, Z. Iofa, and A. Prokof'eva, Zh. Fiz. Khimii, 13, 341 (1939).

ELECTROCHEMICAL REDUCTION OF N_2O AT A LEAD ELECTRODE

V. V. Eletskii, Z. A. Rotenberg, and Yu. V. Pleskov

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In the investigation of the photoelectric effect at the metal–electrolyte division boundary nitrous oxide (N_2O) is frequently used as acceptor for solvated electrons [1, 2]. This is due to the fact that, while it interacts with solvated electrons, N_2O is in practice not discharged on mercury.

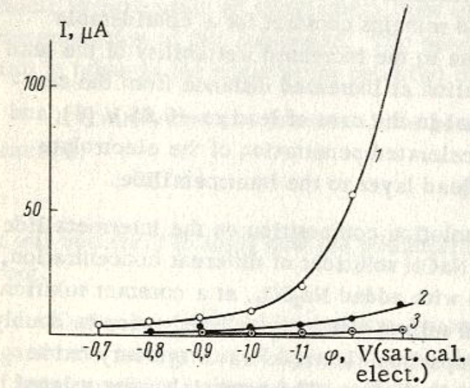

Fig. 1. Variation of current with potential on lead in 0.1 N solution of KF: 1) solution saturated with N_2O; 2) solution saturated with hydrogen; 3) amalgamated lead electrode and solution saturated with N_2O.

During an investigation into the photoelectric effect on lead we discovered that N_2O exhibits electrochemical activity with respect to the lead electrode. Fig. 1 shows the $i-\varphi$ curve for lead in 0.1 N KF solution saturated with N_2O (Curve 1). Curve 2 shows the same relationship for lead in the same solution saturated with hydrogen. Curve 3 was taken in a solution of KF saturated with N_2O on an amalgamated lead electrode. As seen from Fig. 1 N_2O is reduced on lead (in contrast to mercury). It can be supposed that by analogy with the reactions of N_2O in solution with a solvated electron [3] the reduction of N_2O at the electrode proceeds according to the following mechanism: $N_2O + e^- \rightarrow N_2 + O^-$, $O^- + H_2O \rightarrow OH + OH^-$; $OH + e^- \rightarrow OH^-$.

This reaction should be taken into account particularly when interpreting data on the photoelectric effect at a lead anode with N_2O as acceptor.

LITERATURE CITED

1. G. S. Barker, A. W. Gardner, and D. C. Sammon, J. Electrochem. Soc., 113, 1182 (1966).
2. Yu. V. Pleskov and Z. A. Rotenberg, J. Electroanalyt. Chem., 20, 1 (1969).
3. F. Dainton and G. Peterson, Proc. Roy. Soc., A267, 443 (1962).

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 5, No. 4, p. 469, April, 1969. Original article submitted August 28, 1968.