OVERVOLTAGE OF HYDROGEN ON ALUMINUM AND INTRODUCTION OF AN ALKALI METAL

(UDC 541.138:3:546.11)

A. I. Zak and B. N. Kabanov

Institute of Electrochemistry, Academy of Sciences, USSR

Translated from Élektrokhimiya, Vol. 1, No. 1,
pp. 68-71, January, 1965
Original article submitted September 15, 1964

The characteristics of the overvoltage of hydrogen on aluminum in alkalis—variation of the overvoltage with time, increased slope of the overvoltage curves—are explained by the concept of the introduction of alkali metals into the metal of the electrode and the formation of intermetallic compounds, in this case of aluminum with potassium.

The kinetics of the cathodic liberation of hydrogen in alkalis has received little investigation [1, 2]. The unusual shape of the curves of the hydrogen overvoltage in this case has not yet received any satisfactory explanation. The explanation of the peculiarities of the overvoltage of hydrogen in alkalis on Ag, Cd, Zn, and Pb found recently [3], as well as the explanation that we had given earlier for the phenomenon of hyperactivation of aluminum [2], also permit the understanding of the peculiarities of the overvoltage of hydrogen on aluminum. Hence, we are now reporting on our earlier unpublished results of experiments on the measurement of the overvoltage of hydrogen on aluminum in alkalis [4].

Measurement Procedure. The electrode was aluminum (content of the pure metal 99.9945%, impurities: Mg 0.002%, Si 0.0015%, Fe and Cu 0.0005% each) in the form of a wire with diameters equal to 0.81 mm and 1.62 mm. The aluminum wire was preliminarily annealed at a temperature of 250°C for 1 h in a closed vessel, through which electrolytic hydrogen, subjected to the usual purification, was passed. The solutions of the alkalis were prepared by dissolving the chemically pure alkali, produced by Becker Company (Fe 0.0002%) or Schering, in double-distilled water. The alkaline solution of tetramethylammonium bromide was prepared by prolonged cathodic polarization of a solution of chemically pure tetramethylammonium bromide with separation of the cathode and anode spaces, with an aluminum cathode; anode—platinum. All the measurements except those related to the determination of the gas evolution, were performed in the usual closed electrolytic cell of pyrex glass. The solution was mixed with hydrogen. At large current densities, the solution was mixed with a strong stream of nitrogen, purified by passage through a glass filter and coil immersed in liquid air. In such purification, the nitrogen was cooled, which was compensated for by heating the solution by the passage of current. The scheme of the polarization circuit made it possible to change the current density a set number of times in 0.1 sec. Oxide-mercury electrodes in the same solutions in which the measurements were performed were used as the reference electrodes. In the conversion to normal hydrogen equivalents, 0.07 V was subtracted in the case of a 2.6 M solution of KOH. In measurements of the capacitance and resistance of the reaction on an aluminum electrode, a platinized platinum cylinder was used for the passage of alternating current. The measurements of the capacitance and resistance of the aluminum electrode were performed with an impedance bridge at different frequencies. The rate of self-solution was determined volumetrically in the usual glass instrument with burette.

Experimental Results. In the passage of direct current through an aluminum electrode preliminarily purified in air, just as in the absence of current, the electrode potential varies with time (Fig. 1). The electrode purified in air was rapidly immersed in solution, with the simultaneous application of the corresponding cathode polarization on the electrode. In the case of anodic current, the potential of the aluminum was displaced in the positive

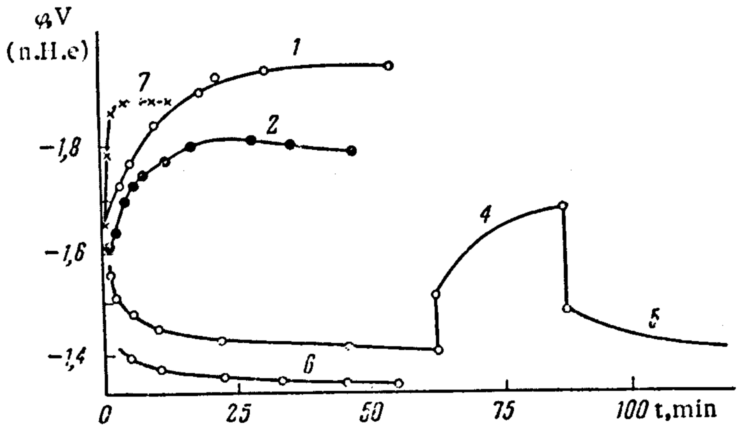

Fig. 1. Variation of the potential of an aluminum electrode with time in 2.6 M KOH: 1) Cathode current 0.5 A/cm^2; 2) without current (Becker Company KOH); 3) without current (less pure KOH); 4) cathode current 0.12 A/cm^2; 5) without current; 6) anode current 0.02 A/cm^2; 7) in 10.4 M KOH, 0.24 A/cm^2 cathode current.

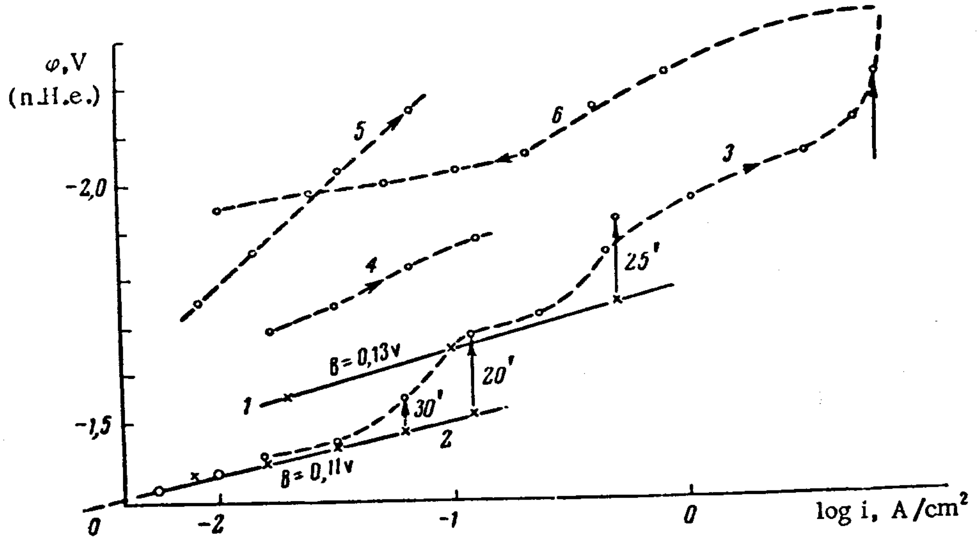

Fig. 2. Potential of the liberation of hydrogen on aluminum: 1) Rapid measurements, purified electrode (crosses); 2) rapid measurements, electrode preliminarily kept without current in solution for 1 h (crosses—measurements according to current, light circles—according to volume of hydrogen); 3-6) potential established with time (dotted curves); arrows—slow changes in the potential with time at constant current density: 1-3 and 6) in 2.6 M KOH; 4) in 5.2 M LiOH; 5) in 0.58 M [$(CH_3)_4NOH$ + $(CH_3)_4NBr$]; 6) after strong cathode polarization (Becker Company KOH).

direction with time (curve 6).* At the same time, the double layer capacitance (measured at 10,000 cps) was reduced from 20 to 10 μF/cm^2. Evidently both effects are related to oxidation of the surface of the aluminum electrode and denote its passivation.

---

*A shift of the potential in the positive direction without current and at low densities of the cathode current, on account of gradual reduction of the overvoltage of hydrogen, may occur when the small admixture of iron present in the metal and in solution accumulates on the surface of the electrode in dispersed form [5]. This was observed (curve 3, Fig. 1) when the admixture of iron in the alkali substantially (by an order or magnitude) exceeded 0.0002%.

The overvoltage on a pure aluminum surface is best expressed by curve 1 (Fig. 2), the points of which were taken at the first moment after immersion of the just purified electrode into the solution. Oxygen adsorbed on the aluminum from the air evidently does not have time to be bonded to the surface strongly enough to cause a great increase in the hydrogen overvoltage [6]. Actually, preliminary purification of the surface of the aluminum electrode in air and its purification with a quartz scraper under the solution give approximately the same electrode potential without current. The double layer capacitance of an electrode preliminarily purified in air corresponds in magnitude to the capacitance of the pure surface of the metal, while it decreases after 10 min, which indicates the formation of an adsorption layer. The constant a of the Tafel' equation for such an aluminum surface purified in air is equal to 0.95 V in 2.6 M KOH.

In the case of cathode currents, the hydrogen overvoltage increased by approximately 0.2-0.3 V in a period of 10 min (Fig. 1, curves 1, 4, 7; Fig. 2, arrows). After strong cathode polarization with a decrease in the current density, the hydrogen overvoltage decreased slowly, and hysteresis was observed (Fig. 2, curve 6). The greater the current density, the more rapid the increase in the overvoltage with time. At current densities above 1 A/cm^2, a considerable rise in the potential occurs during the first seconds and fractions of a second.

Considering the results of [2, 3, 7], we can explain the slow growth of the overvoltage of aluminum in alkali by the slow formation of intermetallic compounds of aluminum with the alkali metals on the surface of the electrode. This also explains the large slope of the overvoltage curve at high current densities, as well as the dependence of this coefficient on the current density. A confirmation of such an explanation is the fact that the limiting (with time) value of the hydrogen overvoltage differs in cases of potassium and lithium ions, i.e., depends on the nature of the alkali cation (see Fig. 2). If no intermetallic compounds were formed here, the hydrogen overvoltage in such strong solutions should not have depended on the nature of the surface of the inactive cations. Moreover, in a 2.6 M solution of KOH, saturated with potassium chloride, the hydrogen overvoltage proved to be 0.1 V higher than in the absence of the salt, which could not have been expected considering the decrease in negative value of the ψ_1-potential, if there were no change in the state of the surface due to the introduction of the alkali metal into the electrode surface.

Thermally produced compounds of aluminum only with lithium: $AlLi$ [8] and perhaps $AlLi_2$ [9], have been described in the literature.

The standard free energies of compounds of aluminum with potassium, calculated on the basis of the approximate values of the equilibrium potentials φ_r, found according to our data on the establishement of the potential under cathode current,* converted to one atom of the alkali metal ($F^0{}_{Al_nK}$), should have values of the order of −22 kcal (on the basis of $\varphi_r = -1.5$ V, normal hydrogen equivalents).† These free energies are smaller in absolute magnitude than for the compounds of cadmium, silver, and lead studied [7], but greater than for other compounds of mercury with sodium. With respect to the kinetics of the formation of a surface compound with potassium, aluminum also occupies an intermediate position.

The high rate of introduction of the alkali metal into aluminum at large cathode current densities makes it necessary to use extremely rapid (oscillographic) methods, if it is desirable to measure the hydrogen overvoltage on the surface of the aluminum itself. On the other hand, it is impossible to obtain a pure aluminum surface, entirely free of adsorbed substances, in alkalis, since although oxygen can be entirely reduced in cathodic polarization in alkali, this can be accomplished only after the entire surface has been coated with the compound of aluminum with the alkali metal.‡ When the alkali metal is removed from the surface by shifting the potential in the

---

*In this case our measurements of the capacitance (converted to a parallel circuit) at low frequencies (2 kc/sec) showed that within the interval of potentials from −1.5 V and above, the capacitance increased rapidly with the potential; an especially great growth of the capacitance is observed beginning with a potential of −1.65 V (33 $\mu F/cm^2$), reaching 500 $\mu F/cm^2$ at a potential of −1.95 V. At 10 kc/sec, the capacitance does not exceed 1.75 $\mu F/cm^2$ within this entire potential interval. The increase in the capacitance with the potential at low frequencies indicates the presence of a "pseudocapacitance" at high potentials, probably due to the presence of a process of introduction of the alkali metal into the electrode at these potentials [3].

†In the calculation, the free energies of the ions and H_2O, as well as the activity coefficient of the alkali, were taken from the tables of Latimer, 1952.

‡The intermetallic compound of aluminum with potassium is more electropositive than both components; hence an oxide film may exist on it at more negative potentials than on the components. The process of reduction of the surface oxide after coating of the surface with the intermetallic compound is evidently explained by a certain decrease in the curve (curves 7 and 2, Fig. 1) after the maximum has been reached.

positive direction, oxygen is immediately readsorbed. In view of the existing kinetic difficulties of the two processes, curve 1 (Fig. 2), close to the curve on pure aluminum, can be obtained by mechanical purification of the surface of the aluminum electrode, and it can even be continued somewhat in the direction of larger current densities.

The electrochemical formation of intermetallic compounds of potassium and aluminum is of interest, since until now it was believed [8, 9] that K formed neither solid compounds nor solid solutions with Al. This shows that the electrochemical method of producing intermetallic compounds under definite conditions is more effective than the thermal method.

LITERATURE CITED

1. S. Glasston, J. Chem. Soc., 123, 1747 (1923); M. D. Zholudev and V. V. Stender, Zh. Prikl. Khimii, 31, 719 (1958).
2. B. N. Kabanov and A. I. Zak, Dokl. AN SSSR, 72, 531 (1950).
3. B. N. Kabanov, D. I. Leikis, I. G. Kiseleva, I. I. Astakhov, and D. P. Aleksandrova, Dokl. AN SSSR, 144, 1085 (1962); D. P. Aleksandrova, I. G. Kiseleva, and B. N. Kabanov, Zh. Fiz. Khimii, 38, 1490 (1964).
4. A. I. Zak, Solution of Aluminum in Cathodic Polarization [in Russian], Dissertation, Moscow (1948).
5. M. Streicher, J. Electrochem. Soc., 96, 170 (1949).
6. S. A. Rozentsveig and B. N. Kabanov, Zh. Fiz., Khimii, 22, 513 (1948); B. N. Kabanov and E. V. Barelko, Zh. Fiz. Khimii, 31, 2501 (1957).
7. I. G. Kiseleva, N. N. Tomashova, and B. N. Kabanov, Zh. Fiz. Khimii, 38, 1188 (1964).
8. W. Pearsons, A Handbook of Lattice Spacing and Structures of Metals and Alloys, London, New York (1958).
9. G. Remy, Course in Inorganic Chemistry [Russian translation], I. Izd. Inostr. Lit., Moscow (1963), p. 621, (Leipzig, 1960).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
