The hodograph is the sum of a straight line intersecting the real axis in the coordinate origin under an angle of 45° and of a quadratic parabola. All other curves presented in Fig. 1 were obtained by analysis of the limiting behavior of the impedance and admittance components as described above.

For more complicated circuits containing several reactive elements, this analysis also does not pose any particular difficulties. The expressions for Z' and Z'' represent rational fractions having polynomials in integer powers of $\omega$ and $\sqrt{\omega}$ in the numerator and denominator, so that the limits can always be found. It must be noted that the terms with the highest powers of $\omega$ are of interest to us when seeking the limit for $\omega \to \infty$, while terms with the lowest powers of $\omega$ are of interest when seeking the limit for $\omega \to 0$; hence, it is not necessary to completely write out any particularly cumbersome expressions.

The impedance hodographs for complicated equivalent circuits proposed to describe the electrode process in solid electrolytes [5] are reported in Figs. 2 and 3. A dashed line shows the shape of the hodograph when the individual parts of the circuit have highly different relaxation times. In equivalent circuits only containing resistances, capacitances, and Warburg impedances, the angles of intersection of the hodograph and its individual parts with the axis of abscissas are 90 or 45°. When the experimental plot shows other angles between the hodograph and the real axis, this can imply either that the equivalent circuit contains an impedance with arbitrary phase angle [1] or that the process being examined cannot at all be adequately described in terms of an equivalent circuit consisting of simple elements.

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# INTERACTION OF LITHIUM WITH ALUMINUM DURING THE CATHODIC INCORPORATION OF LITHIUM FROM NONAQUEOUS SOLUTIONS


I. G. Kiseleva, L. A. Alekseeva,
G. L. Teplitskaya, and B. N. Kabanov



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Reliably identified solid interaction products in the lithium–aluminum system are phases $\alpha$ and $\beta$ [1]. The $\alpha$-phase represents a solid solution of lithium in aluminum containing up to 5.5 atom % of lithium at 15°C, while the $\beta$-phase is an intermetallic compound LiAl with a homogeneity range from 45 to 56 atom % of lithium [2].

Literature data are contradictory with respect to compounds richer in lithium. Various workers reported information about compounds having the compositions $Li_2Al$ [2, 3], $Li_9Al_4$ [4], and $Li_3Al_2$ [4-6]. However, the existence of compounds $Li_2Al$ and $Li_9Al_4$ has been disputed in later papers [5, 6]. Only one compound having the composition $Li_3Al_2$ (60 atom % of lithium) was found to exist in [6] when phase formation in the lithium–aluminum system was investigated in the range of lithium concentrations over 50%.

Considering the promising application of lithium–aluminum alloys as electrodes in heavy-duty power sources, a number of papers concerning the electrochemical production of compounds in the lithium–aluminum system have appeared recently. It has been shown in this work that solid solutions of lithium in aluminum and the compounds LiAl [7-9] and $Li_3Al_2$ [6] are formed at the cathode during cathodic polarization of aluminum in molten lithium salts.


Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow.


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TABLE 1. Data of X-Ray Phase Analysis of Samples Obtained at 0.1 V

| Line No. | Our data | | Literature data [14] | | Literature data [15] | | Phase |
|---|---|---|---|---|---|---|---|
| | $I/I_1$ | $d$, Å | $I/I_1$ | $d$, Å | $I/I_1$ | $d$, Å | |
| 1 | 100 | 3,656 | 75 | 3,65 | | | LiAl |
| 2 | 10 | 2,334 | | | 100 | 2,33 | Al |
| 3 | 70 | 2,240 | 100 | 2,26 | | | LiAl |
| 4 | 15 | 2,024 | | | 40 | 2,02 | Al |
| 5 | 30 | 1,917 | 75 | 1,92 | | | LiAl |
| 6 | 5 | 1,587 | 60 | 1,58 | | | LiAl |
| 7 | 10 | 1,457 | 60 | 1,46 | | | LiAl |
| 8 | 9 | 1,431 | | | 30 | 1,43 | Al |
| 9 | 20 | 1,296 | 100 | 1,30 | | | LiAl |
| 10 | 60 | 1,222 | 75 | 1,22 | 30 | 1,219 | LiAl, Al |
| 11 | 4 | 1,124 | 75 | 1,12 | | | LiAl |
| 12 | 5 | 1,075 | 75 | 1,07 | | | LiAl |
| 13 | 3 | 1,007 | 85 | 1,01 | | | LiAl |
| 14 | 5 | 0,930 | | | 4 | 0,928 | Al |

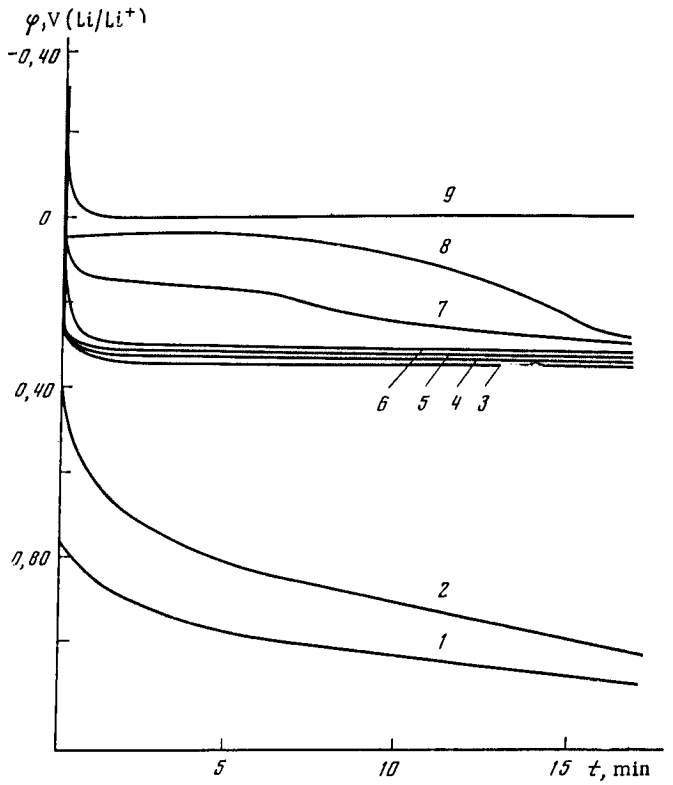


Fig. 1. Open-circuit potential variation of electrodes after prior cathodic polarization of the aluminum to potentials (against the $Li/Li^+$ electrode) and for times of polarization of: 1) 0.75 V, over 120 min; 2) 0.35 V, 30 min; 3) 0.25 V, 90 min; 4) 0.15 V, 7 min; 5) 0.25 V, 30 min; 6) 0.0 V, 30 min; 7) -0.3 V, 5 min; 8) -0.25 V, 75 min; and 9) -0.35 V, 30 min. Polarization was conducted in lithium perchlorate solutions (0.5 N: curves 2 and 6 to 9; 1.0 N: curves 1 and 3 to 5) in propylene carbonate at 22°C.

An interaction of lithium with aluminum cathodes also occurs in solutions. Indications for such an interaction in aqueous solutions had been obtained in studies of the cathodic superactivation of aluminum [10, 11]. Later [12] an interaction of lithium ions with an aluminum cathode in aqueous $Li_2SO_4$ solution was demonstrated by chronopotentiometry and flame photometry. The interaction products were not identified in these papers. Formation of a mixture of different compounds of lithium with aluminum was found when lithium was deposited onto aluminum from nonaqueous solution [13].

In the present work we have studied the cathodic incorporation of lithium into aluminum from propylene carbonate solutions of lithium perchlorate. The phases produced during the incorporation were examined by chronopotentiometry and x-ray phase analysis.

The measurements were performed with aluminum electrodes (of 99.99% purity) in the shape of wire (diameter 0.12 cm) or foil (thickness 80 $\mu$m). Cathodic incorporation of lithium into aluminum was conducted from 0.5 and 1.0 M lithium perchlorate solutions in propylene carbonate. For solution preparation we used twice recrystallized salt dried for 30 h at temperatures of 120-140°C and a pressure of 2-5 mm Hg. Propylene carbonate was distilled with a fractionating column under reduced pressure (2-5 mm Hg) in argon atmosphere. As reference electrode we used a silver–silver chloride electrode in 1 M lithium perchlorate solution in propylene carbonate saturated with lithium chloride. In the paper, the values of potential are stated relative to the $Li/Li^+$ electrode, which has a potential of -2.85 V against the silver–silver chloride electrode. The measurements were conducted at room temperature in a cell with separate cathode and anode compartment. The aluminum electrodes were polarized cathodically under potentiostatic conditions (potentiostats P-5848 and P-5827M). The chronopotentiograms were recorded with a KSP-4 potentiometer.

The compound obtained after cathodic polarization was identified with a DRON-2,0 instrument. We used $K_\alpha$ emission of cobalt; the $\beta$-line was filtered out with an iron filter. The wavelength of the Co-$K_\alpha$ emission was assumed to be 1.7902 Å.

Figure 1 shows plots of electrode potential against time at open circuit after cathodic polarization of aluminum in lithium perchlorate solutions which had lasted different lengths of time (from 5 min to 2 h) and involved different potentials (from 0.75 to -0.35 V vs. the $Li/Li^+$ electrode). The potential decay curves have different shape, depending on the cathodic polarization potential: either a monotonic potential shift in the direction of more positive values (curves 1 and 2) or termination in a well-defined plateau (curves 3 to 6 and 9), or a decay in steps (curves 7 and 8). At potentials more positive than 0.35 V, a solid solution of lithium in aluminum is produced. Its potential depends on the conditions of cathodic polarization (the level and duration). After the end of cathodic polarization, the potential of the solid solution is gradually shifting in the direction of positive values (curves 1 and 2). The plateaus in the potential decay curves obtained at open circuit which are grouped together in the potential range of 0.31 to 0.35 V (curves 3 to 6) are obtained after electrode polarization to potentials of 0.0 to 0.2 V and correspond to formation of intermetallic LiAl compound ($\beta$-phase) on the electrode surface. This was ascertained by x-ray phase analysis of samples obtained by incorporation of lithium into aluminum foil at a potential of 0.1 V. The results obtained when measuring the radiograms are reported in Table 1.

One can see from the data reported that the phase composition of the sample examined corresponds to a mixture of two phases. The chief part of the sample consists of the intermetallic compound LiAl; it is present in the mixture in an amount of about 70%. The other, weaker lines belong to aluminum.

According to literature data, an equilibrium potential of 0.290 to 0.375 V results for the LiAl phase obtained by smelting of the elements [9, 13], the diffusion of lithium deposited onto aluminum from molten electrolyte [6], and from nonaqueous electrolyte [13], as well as from lithium incorporation from molten electrolyte [8, 9]. The potentials found for the LiAl phase in the present work are 0.310 to 0.350 V, in good agreement with the values reported in the literature.

The incorporation reaction yielding LiAl phase can be expressed by the following equation:

$$Li^+ + e^- + Al = LiAl.$$

The free energy change calculated for this reaction from the equilibrium potential (relative to the potential of the $Li/Li^+$ system) is 33 to 36 kJ/mole.

Another two intermediate phases can be obtained by polarizing aluminum to more negative potentials, according to the arrests in the potential decay curves at open circuit (curves 7 and 8). We did not perform x-ray phase analysis of these compounds, but one can say concerning their composition that they contain more

lithium than the $\beta$-phase; the equilibrium potentials of these phases are approximately 0.150 and 0.040 V. Such values had not been obtained previously for equilibrium potentials of phases in the Li/Al system. A compound richer in lithium than the $\beta$-phase had also been detected in [6], but its equilibrium potential, of 0.015 to 0.020 V, does not coincide with any of the two potentials found in the present work. It is not impossible, therefore, that all three of the intermetallic compounds reported in the work of different authors [2-6] exist in this region. In this case, evidently, the potential of 0.150 V should correspond to the compound $Li_3Al_2$, the potential of 0.040 V to the compound $Li_2Al$, and the potential of 0.015 to 0.020 V [13] to the compound $Li_9Al_4$.

It must be said in conclusion that the results of chronopotentiometric and x-ray phase studies have shown that phase formation during cathodic incorporation can be more differentiated and allows one to separately obtain the $\alpha$- and $\beta$-phase and also to exclude formation of undesired phases, in contrast to phase formation occurring during lithium deposition and its subsequent diffusion into aluminum, which yields a mixture of all compounds possible in the system [13].

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