FORMATION MECHANISM OF A COMPACT PHASE LAYER OF INTERMETALLIC COMPOUND DURING ELECTROCHEMICAL LITHIUM INCORPORATION INTO ALUMINUM

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It had been shown in [1] that a complicated time dependence is found for the rate of cathodic lithium incorporation into aluminum at a potential of 0.11 V (Li/Li^+). The explanation was offered that the rate-determining step of the process changes as cathodic incorporation proceeds. It was established that first a solid solution of the incorporated metal in the cathode metal is formed on the electrode. At this stage the incorporation rate is limited by lithium diffusion in the aluminum, and decreases with time as $1/\sqrt{t}$. Stability of the process and a constant rate are seen during growth of the layer of intermetallic compound, which occurs without diffusion limitation but is rate-limited by the crystal-chemical reaction

$$Li_{s.sol.} + Al = LiAl.$$

It is the aim of the present work to examine the intermediate stage of incorporation where the process changes from solid-solution formation to the formation of a phase of intermetallic compound. We studied the effect of potential on the shape of the cathodic current—time (i_c vs. t_{cp}) curves, and the effect of cathodic prepolarization time on the shape of the polarization (E vs. i) curves for incorporation.

The measurements were made in 1 M lithium perchlorate solutions in propylene carbonate at a temperature of 25°C using electrodes made of 0.17 cm diameter aluminum wire (99.99% pure aluminum). The measuring procedure and purification of propylene carbonate and lithium perchlorate have been described before [2]. Reference electrode was a silver—silver chloride electrode in 1 M lithium perchlorate solution in propylene carbonate saturated with lithium chloride. The values of potential are reported relative to the Li/Li^+ electrode; its potential is −2.88 V against the silver—silver chloride electrode in the test solution.

Figure 1 shows plots of the rate, i_c, of the cathodic process against time, t_{cp}, at different polarization potentials between +0.33 and −0.27 V (against the Li/Li^+ electrode).* The shape of the i_c vs. t_{cp} curves for cathodic incorporation substantially depends on potential. The region of the initial incorporation period comprising sections a, b, and c, which we have termed the induction period, is diffuse when cathodic polarization is weak. A long time of cathodic polarization is needed in this case in order to attain a steady process (curves 1 and 2 of Fig. 1A). The rate changes more rapidly and drastically during the initial period of the incorporation process when cathodic polarization is strong. Thus, when the potential of cathodic polarization is moved from +0.28 V to +0.03 V (curves 2 to 8 of Fig. 1), section c where the rate of the process rises becomes steeper (the slope changes by a factor of10,000), and the current in the maximum rises from 0.225 to 7.7 mA/Cm².

It had been suggested previously that the formation and growth of nuclei of the intermetallic compound should be very important for the kinetics of the initial period of lithium incorporation into aluminum. The shape and potential dependence of the i_c vs. t_{cp} curves reported in Fig. 1 are in harmony with this suggestion. Thus, the departure from linearity of plots of incorporation rate against $1/\sqrt{t}$ (in the region of section *a*) which had been demonstrated in [1] can be explained in terms of the nucleation of crystals of intermetallic compound in the layer of solid solution already formed, more precisely at its interface with the

*It was seen by chronopotentiometry that free lithium phase is not formed on aluminum up to a potential of −0.27 V.

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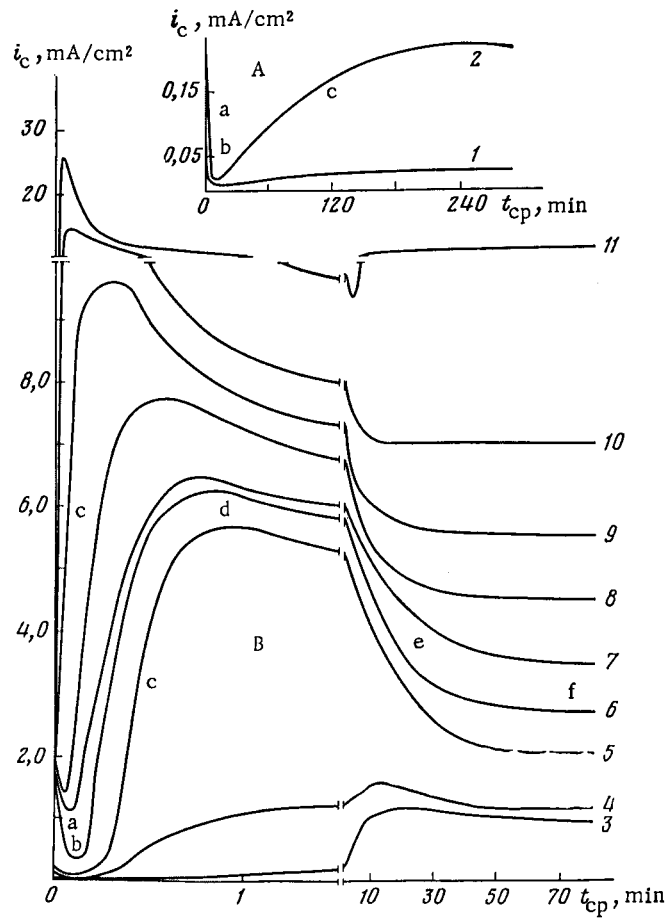

Fig. 1. Plots of the rate, i_c, of cathodic lithium incorporation into aluminum against polarization time, t_{cp}, at 25°C in 1 M lithium perchlorate solution in propylene carbonate at different cathodic polarization potentials. Part A: 1) +0.33 V, 2) +0.28 V; part B: 3) +0.18 V, 4) +0.15 V, 5) +0.13 V, 6) +0.10 V, 7) +0.08 V, 8) +0.03 V, 9) −0.02 V, 10) −0.07 V, and 11) −0.27 V (nle).

electrolyte solution. We recall that the curves shown in Fig. 1 refer to a process conducted under potentiostatic conditions, and that the activity of lithium at the electrode/electrolyte interface should remain constant at all stages of incorporation. The drop in incorporation rate which is seen at the start of the process is due to decreasing rate of lithium transport from the surface to the interior of the cathode metal. The activity coefficient of lithium in compound LiAl is smaller than that in a solid solution having the same lithium concentration. Therefore, nucleation of crystals of the compound LiAl has the effect that the lithium concentration increases substantially while its activity in the surface layer remains unchanged. Hence the incorporation rate ceases to fall with beginning nucleation (section b).

The ensuing increase in process rate (section c) corresponds to the stage of nucleus growth. It is known [3] that owing to the high diffusion rate, incorporation into the intermetallic compound LiAl is much faster than that into solid Li solution in Al. Therefore, practically only the part of surface occupied by intermetallic compound is working area of the electrode when solid solution and intermetallic compound (the growing nuclei) coexist on the electrode surface. The fraction of surface taken up by the intermetallic compound increases as the nuclei grow, and the process rate increases accordingly. The rate increase can be assumed to end when the layer of intermetallic compound has become continuous. Based on these ideas concerning the initial stage of crystallization of the intermetallic compound one can estimate its layer thickness and the number of nuclei which have formed and grown to the thickness of the continuous layer. Assuming that the total current flowing in section c

TABLE 1. Calculated Values for Layer Thickness and for the Number of Nuclei Which Have Grown to Form the Continuous Layer of Intermetallic Compound, as Functions of the Cathodic Polarization Potential

E_{cp}, V	Layer thickness $\delta \cdot 10^4$, cm	Number of nuclei $N/cm^2 \cdot 10^{-4}$	Amount of charge Q, mC/cm^2	Layer formation time, sec	Average rate i_{av}, mA/cm^2
+0,28	5	0,10	2500	13500	0,185
+0,18	2,4	0,4	1200	1230	0,975
+0,15	1,9	0,7	920	580	1,586
+0,13	0,4	15	200	55	3,64
+0,10	0,37	18,5	180	42	4,28
+0,08	0,35	20	170	39	4,35
+0,03	0,35	20	170	33	5,15
−0,02	0,27	35	130	18	7,22
−0,07	0,06	700	30	4	7,5
−0,27	0,04	1500	20	1,5	13,3

is used to form intermetallic compound LiAl we can find the amount of intermetallic compound formed here from the amount of charge that has been passed in this section. The thickness of the continuous layer at a given potential is found on the assumption that the density of intermetallic compound LiAl is 1.725 g/cm^3 [4] and that the resulting layer is uniform, i.e., that the roughness of the intermetallic compound/Al interface is insignificant. Over the potential range from +0.28 to −0.27 V, the thickness of the primary continuous layer of intermetallic compound which is formed on the electrode by nucleus growth is $5 \cdot 10^{-4}$ to $4 \cdot 10^{-6}$ cm (Table 1). The potential dependence of layer thickness arises since different numbers of nuclei of the LiAl crystals are formed at different potentials, and it is the growth of these nuclei which leads to formation of a continuous layer of intermetallic compound on the electrode. This layer becomes continuous when the crystals growing from the nuclei merge. At small distances between the nuclei (when they are numerous), layer continuity is attained at small crystal diameter, and the layer obtained is thin. Conversely, when few nuclei exist, the grown sections of intermetallic compound will merge into a continuous layer only after attaining a large size. In this case the primary continuous layer of intermetallic compound is thicker. Thus, from the thickness of the continuous layer one can determine the original number of nuclei of the LiAl crystals. The thickness of the fully grown continuous layer of intermetallic compound should be approximately one half of a crystallite side or, in other words, one half of the distance between nuclei. Such a calculation using the results of our experiments has shown that the number of nuclei gradually increases from 10^6 to 10^{10} per cm^2 (Table 1) when the cathodic polarization potential is varied from +0.28 to −0.27 V.

One can see from the data of Table 1 that for more negative cathodic polarization potentials E_{cp}, more crystallization sites (N/cm^2) are formed on the electrode surface and a lower thickness (δ) of the layer of intermetallic compound is attained at the time when the electrode surface is fully covered. More intense nucleation and crystal growth of the intermetallic compound at more negative values of the potential of cathodic incorporation can be accepted as proof for the mechanism offered here to explain the formation and growth of the layer of intermetallic compound during the incorporation of alkali metal into the solid cathode.*

According to [1], once the entire electrode surface has been covered with intermetallic compound, further incorporation should occur at constant rate. However, one can see from Fig. 1 that a constant rate is attained by the process, not right after the rate has ceased to grow but following some rate decrease the size of which depends on polarization condi-

*J vs. t curves similar to the curves obtained in [1] and reported here in Fig. 1 have been observed previously, particularly in [5] when depositing silver at 275°C from $NaNO_3$–KNO_3 melt onto platinum, and also when depositing silver onto platinum and graphite, and mercury onto graphite, from aqueous solutions. In this work the increase in process rate is attributed to diffusion-limited rate of growth of the nuclei of new silver phase on the electrode surface. It is possible that in the case of silver on platinum, the silver atoms interact with the cathode material forming a solid solution before they begin to crystallize as an independent phase, and the descending branch at the beginning of the J vs. t curves (which was not analyzed there) might reflect just this process.

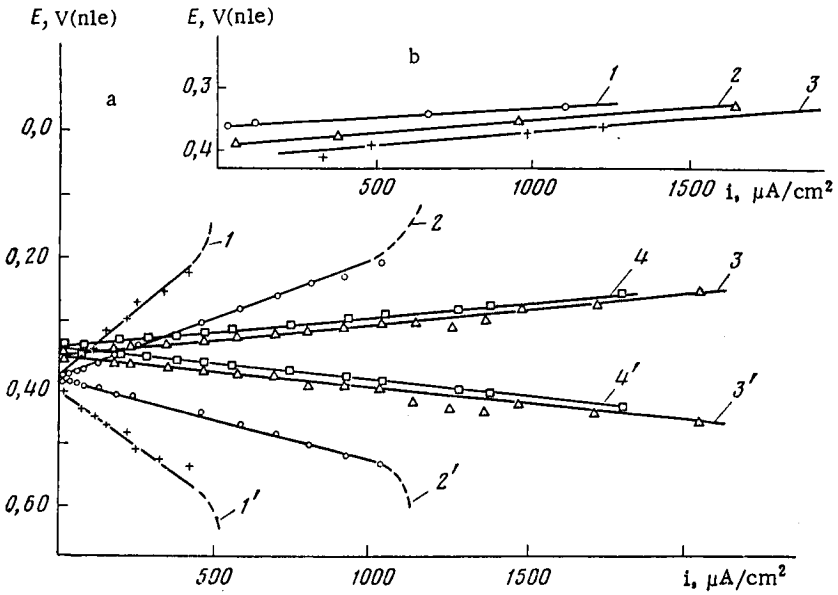

Fig. 2. Part a: Galvanostatic polarization curves of the Al electrode recorded in 1 M $LiClO_4$ solution in propylene carbonate following cathodic prepolarization at E_{cp} = +0.28 V for periods of: 1) and 1') 60 min, 2) and 2') 90 min, 3) and 3') 150 min, 4) and 4') 420 min. Part b: Replotted polarization curves when correction was made for the true working area, for periods of cathodic prepolarization of: 1) 150 min, 2) 90 min, and 3) 60 min.

tions. A possible reason for rate decrease at this stage of incorporation is changing geometry of the intermetallic compound/metal interface where the intermetallic compound LiAl crystallizes. It is possible, too, that the rate decreases since phase growth of the intermetallic compound into the cathode metal is slower than that along the surface.

In order to obtain additional information on the process associated with the ascending part of the i_c vs. t_{cp} curve (section c) it was of interest to examine the electrochemical behavior of the electrode in the time interval corresponding to this section. To this end we recorded steady-state and high-speed polarization curves for incorporation following different periods of cathodic polarization. The times of cathodic prepolarization at potential E_{cp} = +0.28 were 60, 90, 150, and 420 min when recording steady-state polarization curves. Each pair of polarization curves was recorded at a new electrode and in a new solution sample. The curves were recorded in the direction from low to high current densities while alternating between cathodic and anodic polarization. These curves are presented in Fig. 2. One can see from the figure that the slope of the polarization curves depends on the time of prior cathodic polarization, i.e., on the point in ascending section c in the t_c vs. t_{cp} curve where the polarization curve was recorded. The slope decreases for longer cathodic prepolarization, i.e., when approaching the end of section c, and then it ceases to depend on cathodic prepolarization time. One can also see in Fig. 2 that the equilibrium potential of the intermetallic compound shifts to more negative values with increasing cathodic prepolarization time. Compound LiAl is known to have a wide homogeneity range. According to data of [6], the lithium concentration in it can vary between 45 and 56 atom %. With increasing incorporation time the lithium concentration in the intermetallic compound evidently will approach the upper limit, and this is the reason for higher negative values of the phase's equilibrium potential.

For uniform coverage of the electrode surface by intermetallic compound, the fraction of surface taken up by intermetallic compound at a certain time t in curve section c (Fig. 1) should be proportional to the length of the curve segment from the minimum to the point corresponding to time t. The calculation shows that for periods of cathodic prepolarization, t_{cp}, of 60, 90, and 150 min at E_{cp} = +0.28 V, the electrode surface is covered to 14, 20, and 45%, respectively, by a layer of intermetallic compound. When the value of current is re-

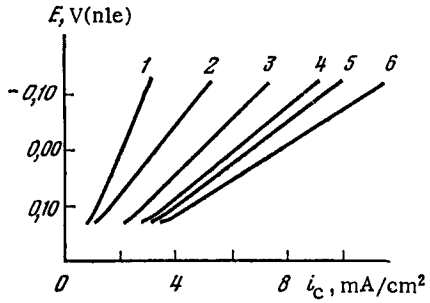

Fig. 3. Fast polarization curves recorded after cathodic prepolarization of the Al electrode in 1 M $LiClO_4$ solution in propylene carbonate at E_{cp} = +0.13 V, as functions of the time of cathodic polarization: 1) 1 min, 2) 3 min, 3) 5 min, 4) 10 min, 5) 30 min, and 6) 240 min. Potential sweep rate was 80 mV/sec.

ferred to the fraction of surface covered with intermetallic compound, then all polarization curves take on a slope approximately corresponding to that of the fourth case (compare curves 1, 2, and 3 of Fig. 2b with curve 4 of Fig. 2a), where almost the entire electrode surface is covered with a continuous layer of intermetallic compound. Here the slope of the polarization curve becomes smallest, and ceases to depend on the time of prior cathodic polarization when this is further increased. This shows that the decrease in slope of the polarization curves which is found to occur as more charge is passed through the electrode, is due to an increase in the working part of electrode surface owing to spread of the phase of intermetallic compound LiAl over the electrode surface.

In harmony with what we have said, the fast cathodic polarization curves which we recorded at a potential sweep rate of 80 mV/sec over the potential range from +0.13 to −0.02 V also show a decrease in slope with increasing time of cathodic prepolarization (Fig. 3). The observation that the slope of the polarization curves decreases for larger amounts of charge passed in section c provides support for the mechanism discussed above, according to which section c reflects the process where the electrode surface becomes covered with a layer of intermetallic compound.

Thus, we have obtained new data advancing the concepts for the formation and growth of a layer of intermetallic compound during cathodic alkali-metal incorporation into solid cathodes. Our measurements have shown that in terms of these concepts, the electrolysis conditions (the potential and time of cathodic polarization) substantially influence phase formation of the intermetallic compound during cathodic lithium incorporation into aluminum from nonaqueous $LiClO_4$ solution, particularly during the initial period. This influence can be traced, both at the stage of nucleation and at the stage of nucleus growth. The number of evolving nuclei and the thickness of the continuous layer of compound LiAl vary as functions of the cathodic polarization potential. From the position of the point on the i_c vs. t_{cp} curve that corresponds to time t, one can tell which stage of cathodic incorporation is in progress at the particular time t, viz., formation of solid solution, nucleation of intermetallic compound, coverage of the electrode surface by intermetallic compound, or vertical growth of the layer of intermetallic compound.

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