

THE SECONDARY LITHIUM-ALUMINIUM ELECTRODE AT ROOM TEMPERATURE

II. KINETICS OF THE ELECTROCHEMICAL FORMATION OF THE LITHIUM-ALUMINIUM ALLOY

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Summary

The kinetics of the electrochemical formation of lithium-aluminium alloy was studied by voltammetric, potentiostatic, and pulse galvanostatic techniques in 1M LiClO₄-propylene carbonate solutions.

It was established that the rate of formation of Li-Al alloy up to a thickness of 30 μm is controlled by the dynamics of the interaction between the two metals. The rate constant for this process was found to be a function of the applied potential with values between 10⁻⁶ and 10⁻⁷ cm/s.

A diffusion coefficient of lithium into aluminium equal to 2.4 × 10⁻¹¹ cm²/s was also determined from the initial decay of the potentiostatic transients.

Values of the exchange current density (*i*₀), 2.5 mA/cm² at 20 °C, and of the apparent activation energy (Δ*H*₀), 4.3 kcal/mol, for the process of lithium incorporation into the β-phase of lithium-aluminium were found from micropolarization measurements.

1. Introduction

The underpotential deposition of metals (UPD) on foreign substrates has been studied extensively in recent years [1]. Accurate thermodynamic analysis of UPD is restricted, however, to ideally polarizable metal substrates. During alloying of the deposited metal with the substrate this stringent condition is evidently no longer valid. It was recently shown [1, 2] that for quasi-equilibrium states, as is the case of alloy formation on single or polycrystalline substrates, it is also possible to analyse the experimental data acquired during UPD.

Kabanov *et al.* [3] were the first to point out the substantial role of electrochemical incorporation as a stage between the electrocrystallization of the metal and the formation of liquid or solid metal solutions. According to

these authors [4] the role of the overall process of incorporation can be determined by three equations, depending on the limiting step:

(a) electrochemical incorporation;

(b) diffusion of the incorporated element in the growing layer of the intermetallic compound;

(c) chemical affinity between the metals.

For the case of a fast electrochemical step (high exchange current density), and when the rate determining step is the diffusion in the solid state, Astakhov [5] derived an analytical expression relating the charge, Q , consumed for the formation of the intermetallic compound in an electrolyte solution with a concentration, a_M^{n+} , at a potential of incorporation, E :

$$Q^2 = 2L_1 C_M (RT \ln a_M^{n+} - nFE + \mu^0 - \mu)t \quad (1)$$

resp.

$$Q = K_1 t^{1/2} \quad (2)$$

where t is the time of deposition, L_1 is a kinetic factor, C_M is the concentration of the atoms M , μ is the chemical potential of the inserting metal, and K_1 is a constant.

Equations (1) and (2) reveal that the relationships between Q and t and also between the constant K_1 and the electrode potential E are quadratic.

$$K_1^2 \sim E \quad (3)$$

Astakhov [5] further derived expressions for the case when the rate determining step is the chemical affinity between the metals. In this case the relationships between Q and t and the potential (E) are linear with another constant ($K_2 = dQ/dt$).

$$Q = \frac{L_2}{T} (RT \ln a_M^{n+} - nFE + \mu^0 - \mu)t \quad (4)$$

$$Q = K_2 t \quad (5)$$

$$K_2 \sim E \quad (6)$$

where L_2 is a kinetic factor.

The mechanism developed by Kabanov *et al.* [3-5] was recently applied by Melendres [6] to the case of incorporation of lithium into aluminium in a melt of LiCl-KCl. It was shown that the rate of lithium incorporation can be limited either by the diffusion of lithium in the lithium-aluminium alloy or by the chemical affinity between the metals, depending on the atomic concentration of Li in the alloy.

From the linear dependence of the current on the potential Alexeeva *et al.* [8] assumed that the alloying between the lithium and the aluminium in aprotic solutions is limited by the chemical affinity between the metals.

The purpose of this paper is to acquire more data on the kinetics of the alloying process between lithium and aluminium, and to assess the rate

determining step over a wider range of potentials in the underpotential region and at various states of charge, when using organic solvents and, more specifically, in propylene carbonate (PC).

2. Experimental

The Al electrodes for the experiments were prepared from 2 cm long lengths of 2 mm aluminium wire (99.99%) isolated by a layer of epoxy resin and pressed in a Teflon holder. The free aluminium surface was polished mechanically in a dry box continuously flushed by pure argon. The reference and counter electrodes were made from lithium wire held within a glass tube [9]. The lithium reference electrode was placed in a Luggin capillary, the tip of which was 1 mm from the edge of the test electrode. The ohmic drop, R_{Ω} , in the solution (1M LiClO₄/PC), measured according to ref. 10 was 1.5 ohm cm² at 20 °C. The temperature of the cell could be maintained at any point between -30 and +30 °C to better than ±0.2 °C.

The micropolarization measurements were performed by the pulse galvanostatic method described in ref. 10.

The 1M LiClO₄ test solution was prepared from propylene carbonate (Merck for synthesis) dried over molecular sieves, and LiClO₄ (Merck, p.a.) dried under vacuum at 200 °C for 48 h. The solution was additionally dried over lithium strips to reduce the water content to 20 ppm.

Results and discussion

3.1. Voltammetric measurements

In the study of the underpotential alloying of cadmium with silver, Bort *et al.* [2] demonstrated that the potentiodynamic method is appropriate for the determination of the rate of the metal deposition.

Figure 1 shows a typical $I-E$ curve of the reduction/oxidation reaction of lithium on the aluminium electrode, recorded at a scanning rate of 5 mV/s in the potential range below the equilibrium Li/Li⁺ potential. The anodic oxidation (dissolution) of lithium produced a well-defined peak having an area depending on the amount of lithium deposited during the cathodic reaction.

In this case, however, the efficiency of the anodic dissolution of lithium from aluminium is less than 100%, due to the so-called "retention capacity", as proposed by Besenhard [11]. Cycling the electrode could increase the current efficiency to almost 100%, but control of the electrode surface state would be lost.

As seen from Fig. 1, the change in the voltage scanning direction from cathodic to anodic results in a hysteresis in the voltammogram. As proposed earlier [7, 12] this hysteresis can be attributed to a nuclei formation process and the growth of a new phase, a phenomenon which will be considered below.

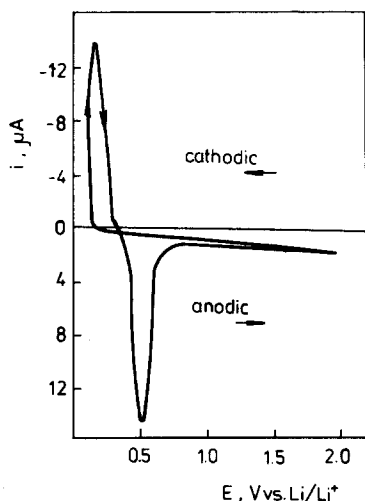


Fig. 1. Current/voltage characteristic for the reduction/oxidation reaction of Li on Al in a 1M LiClO_4/PC solution, $v = 5 \text{ mV/s}$.

3.2. Potentiostatic measurements

The incorporation of lithium in aluminium from fused LiCl-KCl electrolyte was first studied by Melendres [6] using the potentiostatic method. This technique is convenient also for the study of lithium deposition on aluminium at room temperature (in PC solutions, for example) in view of the 100% efficiency of the cathodic reaction [13]. Consequently, the integration of the experimental potential-time curves enables the amount of lithium consumed in the formation of the lithium-aluminium alloy to be determined. A typical potentiostatic transient recorded at 160 mV positive to the Li/Li^+ reference electrode is shown in Fig. 2.

All potentiostatic transients are similar, irrespective of the magnitude of the applied underpotential. A steep, initial decay is followed by a fast rise to a plateau of almost constant current. These three stages of the current-time curves are denoted as I, II and III in Fig. 2. Similar potentiostatic curves have also been reported by Carpio and King [7] for the deposition of Li on Al from melts and by Baranski and Fawcett [14] from PC solutions of LiBr and LiI .

The time dependence of the electric charge (Q) consumed during the incorporation of lithium in aluminium at various underpotentials is shown in Fig. 3. The charge is calculated by integrating the potentiostatic curves for the time interval during which the Li-Al alloy is formed. This corresponds to the electrical charge consumed during stage III, since that consumed during stages I and II is negligible by comparison. The effect of stages I and II is reflected by the intercept of the plots on the abscissa in Fig. 3 which shows that Q is proportional to t over a wide range of underpotentials, with electrical charge in the range between 0.2 and 6 C/cm^2 . This result leads to the conclusion that the rate of formation of up to $30 \mu\text{m}$ of the lithium-

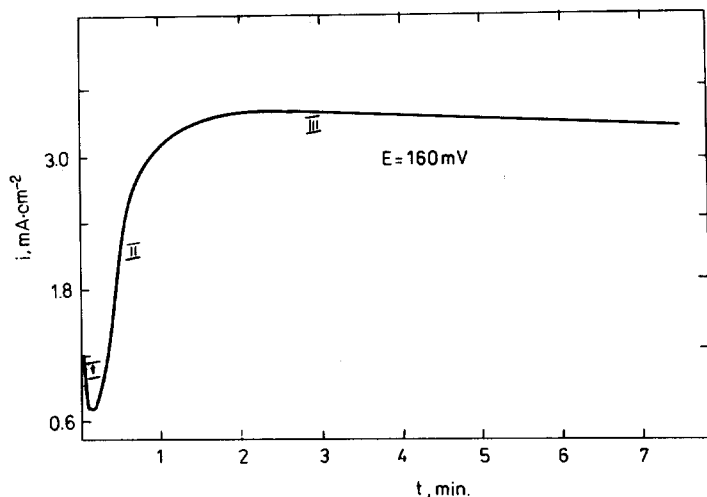


Fig. 2. Typical current vs. time curve at constant potential for the electrochemical formation of the Li-Al alloy. $E = 160 \text{ mV}$ (vs. Li/Li^+). $S = 0.033 \text{ cm}^2$.

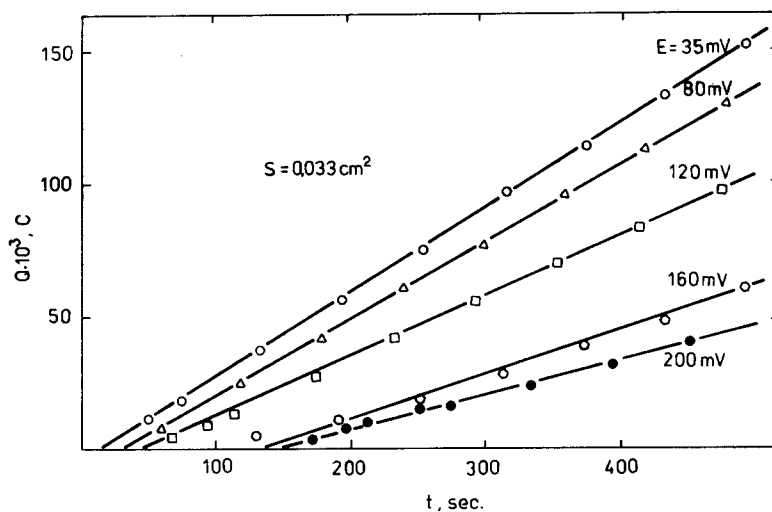


Fig. 3. Charge vs. time curves for the incorporation of lithium into aluminium at various potentials (vs. Li/Li^+) in the potential region of the β -phase of Li-Al.

aluminium alloy from PC solutions is controlled by the dynamics of the interaction of the two metals, in accordance with eqns. (4) - (6). As can be seen from the plots in Fig. 3, decreasing the underpotential of lithium incorporation (or increasing the overpotential of the lithium-aluminium alloy formation) accelerates the process.

The rate of change in thickness of the lithium-aluminium layer (K) at different potentials is given by:

$$K = \frac{\partial l}{\partial t} = \frac{\partial Q V_m}{\partial t F}, \quad \text{cm/s} \quad (7)$$

where l is the thickness of the alloyed layer and V_m is the molar volume of the 50 at.% lithium-aluminium alloy ($\rho = 1.76 \text{ g/cm}^3$, $M = 34$).

Figure 4 shows how K , between 10^{-6} and 10^{-7} cm/s, is the linear function of potential which eqn. (6), derived assuming reaction limited kinetics, predicts.

These results indicate that the kinetics of the formation of the Li-Al in aprotic electrolyte solutions does not differ significantly from that reported for fused salts [6, 7].

Changes in the current with time over the first two stages illustrated in Fig. 2 were also examined. Analysis of the first stage of these curves revealed that the initial deposition of lithium on aluminium was controlled by slow diffusion, probably indicating the formation of the α -phase. This process was studied by analysing the initial potentiostatic transients in the potential range where only the α -phase is formed ($E = 420$ and 380 mV). These were compared with similar plots recorded at potentials in the β -phase formation range (e.g., 160 mV).

As seen in Fig. 5 the $i-t^{-1/2}$ plot at 160 mV almost coincides with that at 380 mV. This confirms the assumption that the first stage of β -phase formation is accompanied by diffusion of lithium into the aluminium substrate and the formation of the α -phase. Since, at potentials more negative than the equilibrium potential of the β -phase, and at constant temperature, the lithium concentration in the α -phase does not vary, the $i-t^{-1/2}$ plots at these two potentials should be similar. The lower slope of the plot at

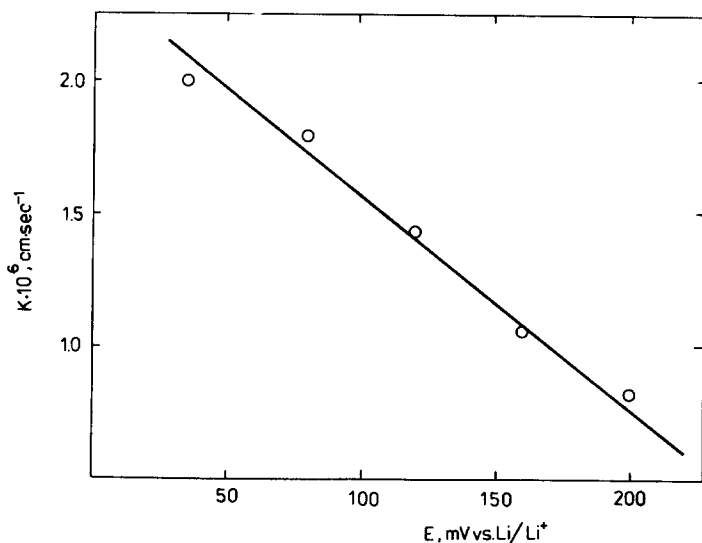


Fig. 4. The rate constant (K) vs. the electrode potential (E) for the process of formation of the β -phase of Li-Al.

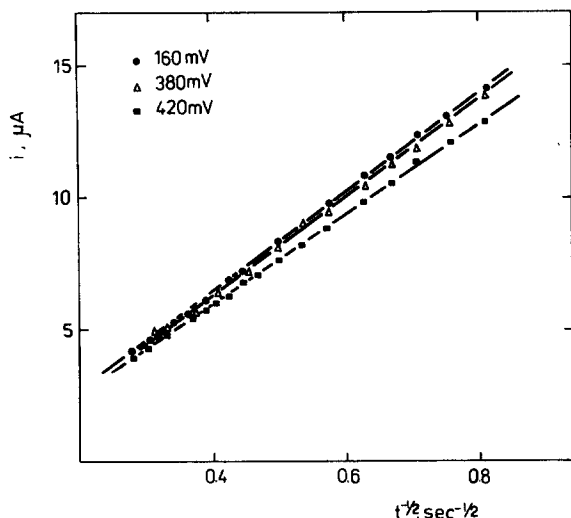


Fig. 5. Current vs. $(\text{time})^{-1/2}$ for the incorporation of lithium into aluminium during α -phase formation at different potentials (vs. Li/Li^+). \bullet , 160 mV; \triangle , 380 mV; \blacksquare , 420 mV.

420 mV is probably due to the reduced concentration of lithium in the α -phase [17].

The diffusion coefficient of lithium in aluminium for the formation of the α -phase can be determined from the $i-t^{-1/2}$ relation shown in Fig. 5 using the equation of Cottrell [16]

$$i(t) = FS(C_s - C_0) \left(\frac{\tilde{D}}{\pi t} \right)^{1/2} \quad (8)$$

The concentration (C_s) is the saturation concentration of lithium in the α -phase at 20 °C (= 2.6 at.% [28]) divided by the molar volume of pure aluminium (= 10 cm³/mole). The initial lithium concentration (C_0) was assumed to be zero.

The experimental value of \tilde{D} was 2.4×10^{-11} cm²/s and is at least 3 orders of magnitude lower than that for lithium in the β -phase of lithium-aluminium, determined previously at the same temperature [14, 15]. Approximately the same difference in the values of \tilde{D} was reported for the diffusion of lithium into aluminium and into the β -phase of lithium-aluminium at 415 °C [17, 18], which increases confidence in the current findings at 20 °C.

The second stage of the potentiostatic transient shows a steep increase in the current. The experimental $i-t$ plots in this stage can best be described by:

$$i = K_3 t^\alpha \quad (9)$$

where α varies from 0.5 to 3, and K_3 grows with the overvoltage of the

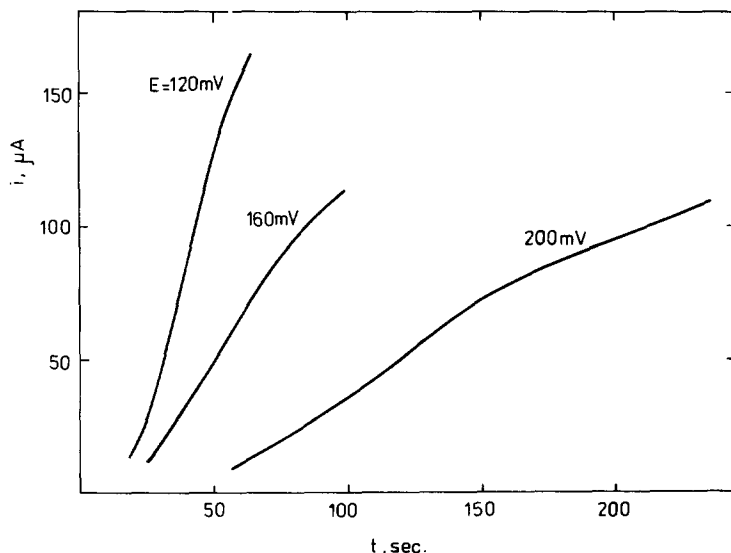


Fig. 6. Current vs. time for stage II of the process of formation of the β -phase of Li-Al at different potentials (vs. Li/Li⁺).

β -phase of lithium-aluminium (Fig. 6). Potentiostatic relations of this type are characteristic of phase formation (nucleation) and growth and have been demonstrated experimentally and theoretically for various cases of metal electrodeposition on foreign substrates [19 - 23].

In accordance with the assumptions of other authors [6, 7], the observed experimental relationships expressed in eqn. (9), and the hysteresis in the potentiodynamic curves shown in Fig. 1, are most likely associated with the processes of nucleation and growth of the β -lithium-aluminium phase. Such a potentiostatic transient might, however, also be due to the presence of oxide films on the aluminium substrate [6, 14]. The second stage in the transients (Figs. 2 and 6) will be investigated further and reported in a subsequent paper.

3.3. Exchange current of the process

In the study of the kinetics of the alloying of Li with Al it was assumed that the exchange current for this process is sufficiently high. According to recent measurements [24] the exchange current density (i_0) in PC solutions varies from 15 to 20 mA/cm² and is strongly affected by the nature of the anion, decreasing by a factor of 3 when the ClO₄ anion was substituted by Br⁻ [14]. On the other hand, Garreau *et al.* [24] reported that, in dioxalane solutions of LiClO₄, i_0 is almost one order of magnitude lower than in PC solutions of LiClO₄. This substitution, however, has no effect on the overall process, *i.e.*, the rate of the latter is similarly controlled by the reactions in the solid phase, and consequently the cycling of the lithium-aluminium electrode is not affected.

The value of i_0 was determined (Fig. 7) by the pulse galvanostatic technique at 20 °C on an Li–Al electrode formed at 160 mV against Li/Li⁺ with a charge of 2 C/cm² in a 1M LiClO₄/PC solution. The experimental value, $i_0 = 2.5$ mA/cm², remained constant during storage of the electrode in the solution for 100 h, and it is close to the minimum value reported by Baranski and Fawcett [14] for LiBr solutions in PC. A similar value for the exchange current density was determined for a pure lithium electrode in the same solution by the extrapolation of Tafel plots [26]. Recently, Garreau *et al.* [15], using electron spectroscopy for chemical analysis (ESCA), established that the lithium–aluminium electrode in PC solutions is covered by surface films. Evidently, as we showed earlier [26], the kinetics at the phase boundary are affected by the thickness of this film. This makes it possible to conclude that the difference between the value of the exchange current density found by us and those reported by Garreau [24], as well as its dependence on the nature of the anion and the solvent reported in refs. 14 and 24, are due to the different thickness and nature of the passive films. Such films are rapidly formed during the incorporation of lithium into aluminium.

The temperature dependence of the exchange current density between –30 and +30 °C is given in Fig. 8. The apparent activation energy (ΔH_0) of this process is 4.3 kcal/mol and is very close to that reported earlier [27] for the deposition of alkali metals on mercury from organic solutions. It is, however, lower than the value of ΔH_0 estimated by the same authors [14] for the process of Li incorporation into Al from LiBr solutions in PC.

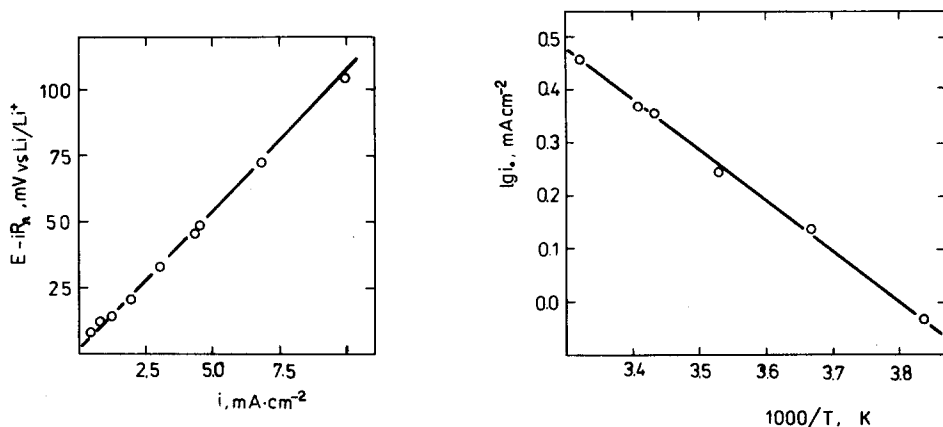


Fig. 7. Micropolarization plot of the Li–Al electrode in 1M LiClO₄/PC. $T = 20$ °C. The Li–Al alloy was formed at $E = 160$ mV (*vs.* Li/Li⁺) with $Q = 2$ C/cm².

Fig. 8. Exchange current density *vs.* temperature for the incorporation of lithium into the lithium–aluminium electrode. The alloy was formed at $E = 160$ mV (*vs.* Li/Li⁺) with $Q = 2$ C/cm².

List of symbols

Q	Charge used for Li-Al incorporation into Al ($C\text{ cm}^{-2}$)
L_1	Kinetic factor when the diffusion in the solid state is the r.d.s.
L_2	Kinetic factor when dynamics of the interaction is the r.d.s.
$K_1 = \frac{\partial Q}{\partial t^{1/2}}$	Rate constant when the diffusion in the solid state is the r.d.s. ($A\text{ s}^{1/2}\text{ cm}^{-2}$)
$K_2 = \frac{\partial Q}{\partial t}$	Rate constant when dynamics of the interaction is the r.d.s. ($A\text{ cm}^{-2}$)
$K = \frac{\partial l}{\partial t}$	Rate constant of the formation of a Li-Al layer (cm s^{-1})
C_M	Concentration of the atoms M of the incorporating metal
a_M^{n+}	Activity of the metal ions in the solution
μ	Chemical potential of the incorporating metal
T	Abs. temperature ($^{\circ}\text{K}$)
E	Electrode potential (V) vs. Li/Li ⁺ reference electrode
t	Time for the lithium incorporation into Al (s)
S	Electrode area (cm^2)
V_m	Molar volume ($\text{cm}^3\text{ mole}^{-1}$)
ρ	Density of the Li-Al alloy (g cm^{-3})
M	Molecular weight (g mol^{-1})
F	The Faraday (C mol^{-1})
v	Scanning rate (V s^{-1})
D	Diffusion coefficient of Li into Al ($\text{cm}^2\text{ s}^{-1}$)
K_3	Rate constant of the electrocrystallization process of the β -phase of Li-Al
i_0	Exchange current density (A cm^{-2})
ΔH_0	Apparent activation energy of the Li incorporation into the Li-Al alloy (kcal mole^{-1})

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