

LITHIUM ELECTRODES BASED UPON ALUMINIUM AND ALLOY SUBSTRATES

I. IMPEDANCE MEASUREMENTS ON ALUMINIUM

R. D. ARMSTRONG, O. R. BROWN* and R. P. RAM

Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU (U.K.)

C. D. TUCK

Alcan International Research Laboratories, Banbury (U.K.)

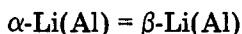
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Summary

Impedance measurements have been used to confirm that, for the LiAl electrode based upon a pure aluminium substrate in propylene carbonate/LiClO₄ (1.0 mol dm⁻³) at room temperature, the rate-limiting process at the equilibrium potential in the overall exchange reaction



is the phase change



At potentials sufficiently far from equilibrium the rates are limited partly by the phase change and partly by the interfacial charge transfer process. In addition, in the case of electrodes carrying thick layers of $\beta\text{-Li(Al)}$, diffusion of lithium through the alloy phase makes a further contribution to rate control.

Introduction

In 1971 Dey [1] showed that alloys of lithium with various metals, including aluminium, could be formed by cathodic polarisation of the substrate metals in LiClO₄/propylene carbonate electrolyte at room temperature. In 1977 Rao *et al.* [2] examined the possibility of using Li-Al alloy as an alternative to lithium for the negative electrode of rechargeable lithium cells with organic electrolytes in order to avoid problems associated with the formation of dendrites. In the past decade several groups of workers have pursued this idea [3 - 5]; in particular, Epelboin *et al.* [3] showed that

* Author to whom correspondence should be addressed.

dendrite formation did not occur provided that excessive charge densities and current densities were avoided, and that an electrode charged to 50 - 100 C cm⁻² could be put through several hundred cycles. Those authors concluded that the performance of the electrode was limited mainly by the diffusion of lithium through the alloy.

Several alloys of lithium and aluminium exist [6]; in particular the α -phase is a dilute (<7 at.%) solution of lithium in aluminium, whereas the β -phase is the intermetallic compound LiAl with a Zintl structure [7]. In the metallurgy literature the β -alloy is sometimes referred to as the δ -alloy [8]. In α -LiAl the aluminium fcc lattice is retained with its unit cell size virtually unchanged. In that alloy both metals are relatively immobile; D_{Li} (cm² s⁻¹) is reported [9] as 10⁻¹⁶ at 140 °C and has been estimated as 10⁻²² at 25 °C [9]. By contrast, in β -LiAl the diffusivity of lithium has been reported to be remarkably high ($D_{\text{Li}} = 10^{-8}$ cm² s⁻¹) at 25 °C [11]. This unusual feature has been ascribed to the very high number of lattice vacancies in β -LiAl which allow quite wide variations from the simple stoichiometry; the lithium content can range between 45 and 56 at.%. Mobile vacancies in the lithium sub-lattice are especially important, and the diffusion coefficient of lithium in β -LiAl is highest when the lithium content is lowest [7].

This property of fast lithium transport is essential for the application of LiAl alloy as a battery electrode; rapid charging relies upon facile formation of the β -phase, and rapid discharge requires avoidance of the formation of a coherent layer of the α -phase near the alloy-electrolyte boundary [10]. Contrasting with the conclusions of Ebelboin *et al.* [3], other workers [6, 10, 12] have found no evidence during the charging process for rate control by the diffusion of lithium through β -LiAl; instead the rate was limited by the solid reaction at the boundary between β -LiAl and Al (or α -LiAl).

Polarisation curves obtained for a charged LiAl electrode in an organic electrolyte containing a lithium salt, instead of indicating a well-defined equilibrium potential, display a "dead" region of some 40 mV where no steady current is recorded [13]. However, potential step amperometry within that potential range showed transient currents limited by diffusion of lithium in the alloy ($D_{\text{Li}} = 7.7 \times 10^{-6}$ cm² s⁻¹ at 25 °C).

Owen *et al.* [14] reported much larger values for the diffusion coefficient of lithium in the α -phase than those previously published; their electrochemical measurements indicated values in the range 10⁻¹² - 10⁻¹³ for D_{Li} (cm² s⁻¹). These workers found no evidence for significant diffusion over-voltage during charge or recharge of the LiAl electrode; growth of the β -phase was rate-determining.

Apparent disagreement over the contribution made by the diffusion of lithium to control of the rate of charging of the LiAl electrode prompted further investigation. Certainly, it is expected that the transport process must eventually become rate-limiting as the intermetallic layer thickens. Indeed, potentiostatic charging transients do not simply rise to a limiting

level indicating overlap of the growing centres but, instead, the currents pass through a maximum and fall at long times towards a steady value. Alekseeva *et al.* [15] have interpreted the fall as a change in the geometry of the Al/LiAl interface following coalescence of the centres.

In this series of papers we attempt to identify the conditions under which diffusion or the kinetics of the α - β phase change, or the surface processes are rate limiting. Our study begins with the use of impedance measurements at, or near to, the equilibrium potential.

Experimental

All experiments and preparations of all solutions were carried out in a large dry box (Lintott Engineering) filled with argon and recirculating through drying columns containing molecular sieves which were regenerated regularly and automatically. The solvent, propylene carbonate, supplied by BDH Chemicals, was dried over 4A molecular sieves for one month and was then distilled under vacuum (1 Torr and 79 °C) using a modified Widmer column with a reflux ratio 10:1. The first 25% and final 25% of the distillate were discarded. The purified solvent was transferred to the dry box without exposure to air. The electrolyte, LiClO₄, supplied by BDH, was dried in a furnace at 200 °C by passing dry nitrogen for 48 h and was then transferred via a desiccator to the dry box. Aluminium working electrodes were polished with diamond pastes (14 μm , 3 μm , 1 μm and 0.25 μm), etched in 4 M aqueous KOH solution (30 s), rinsed with pure water, and dried for 24 h in an oven. These electrodes were of two kinds, each used with its own type of cell. Most measurements were made with two-sided foil electrodes, 0.15 mm in thickness and 1 cm square, mounted by a method similar to that used by Baranski *et al.* [13]. These were arranged in a glass cell with lithium counter electrodes parallel to, and at either side of, the foil. These counter electrodes were constructed by packing lithium metal (Aldrich 99.9%) into glass cups containing nickel current collectors. The other type of aluminium working electrode was single-sided: a circular coupon of thickness 0.5 mm and exposed area 0.8 cm². This was used in a PTFE cell with a lithium counter electrode in a parallel plane. For both cells the reference electrodes were lithium microelectrodes in the form of narrow, Luggin-like capillaries packed with the metal.

Impedance measurements were made over the frequency range 5 mHz - 1 kHz using an Apple II Plus microcomputer with suitable interfacing circuits [16]. Electrodes were given a controlled charge and then rested at open-circuit for two or more hours before the impedance spectrum was recorded at a potential near to the open-circuit value. All experiments were performed at room temperature (22 \pm 2 °C) in 1.0 M LiClO₄ solution.

Results

Impedance spectra were taken of foil specimens containing various charges (0.05 - 130 C cm⁻²). A semicircle was obtained at the higher

frequencies corresponding to the charge-transfer process at the electrode surface in parallel with the interfacial capacitance, C_{dl} . With increasing charge, C_{dl} increased from $5 \mu\text{F cm}^{-2}$ at 0.1 C cm^{-2} to $40 \mu\text{F cm}^{-2}$ at 3.0 C cm^{-2} , with no further increase at higher charges. This dependence of C_{dl} upon charge suggests that the capacitance is confined to the growing active centres of the alloy, the remainder of the electrode surface being still covered with the air-formed oxide.

The low frequency behaviour depended upon the experimental conditions: overvoltage and electrode charge. Electrodes charged with only small amounts of lithium ($\leq 10 \text{ C cm}^{-2}$) showed purely capacitive behaviour towards zero frequency at the equilibrium potential (Fig. 1). Values of this low-frequency capacitance, C_p , were plotted as a function of the amount of charge in the electrode (Fig. 2) and it is seen that the dependence is linear (0.1 V^{-1}). When values of charge exceeding 100 C cm^{-2} were used, then the low-frequency value of capacitance was so large that it could not be detected as an imaginary impedance within the range of frequencies available. Under those circumstances the low frequency impedance was of a Warburg type (Fig. 3). With less-charged electrodes, Warburg behaviour was also seen to be sandwiched between the high-frequency charge-transfer semicircle and the low-frequency C_p (Fig. 4).

Away from the equilibrium potential, C_p gave way to another semicircle whose radius fell rapidly as the numerical overvoltage increased (Figs. 4 and 5).

Discussion

Two groups of authors have previously reported impedance measurements for this system. In one study [13] the lowest frequency examined was

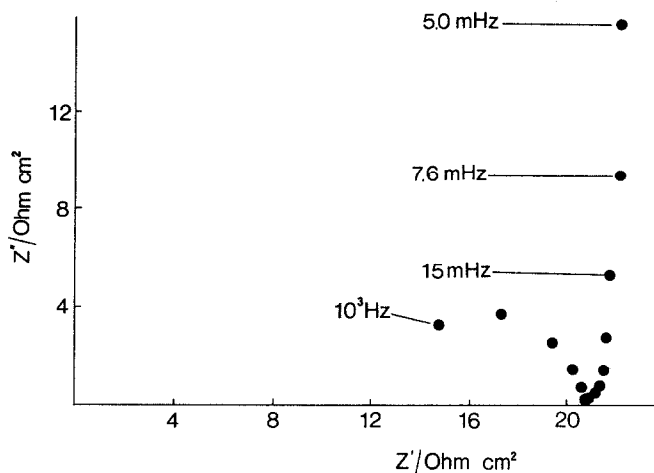


Fig. 1. Impedance spectrum of aluminium, previously charged with 10 C cm^{-2} of lithium, taken at the equilibrium potential, 0.36 V .

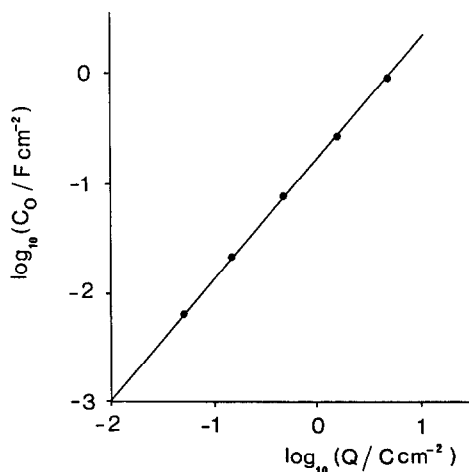


Fig. 2. Dependence of the limiting low-frequency capacitance (taken at 5 mHz and at the equilibrium potential) upon the lithium charge.

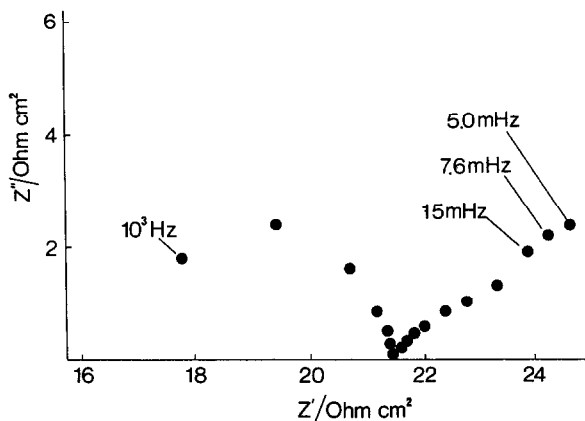


Fig. 3. Impedance spectrum of aluminium, previously charged with 127 C cm^{-2} of lithium, taken at the equilibrium potential, 0.36 V.

5 Hz and so only high-frequency features were observed. In the other [3], most data were obtained under conditions of quite large direct current densities (*i.e.*, far from equilibrium), and so comparison with the present work is precluded except for one set of results which relates to zero direct current. However, even in that case it seems probable that the thickness of the β -layer was large ($50 - 100 \text{ C cm}^{-2}$) in relation to the lowest frequency used (10^{-2} Hz), so that a limiting low-frequency capacitance was not seen.

In essence, the results of the present work correspond to those reported by Baranski and Fawcett [13] who used potential steps of amplitude 55 mV.

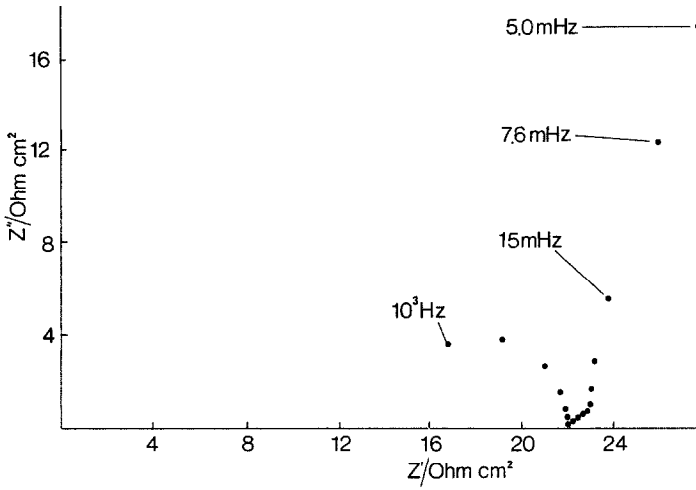


Fig. 4. Impedance spectrum of aluminium, charged with 10 C cm^{-2} lithium, taken at an overvoltage of 20 mV.

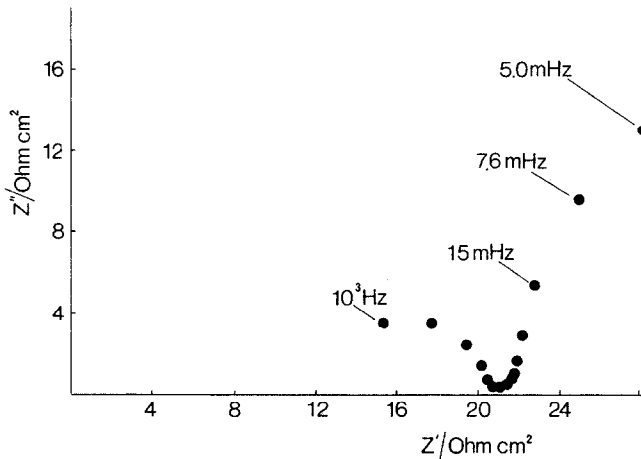


Fig. 5. Impedance spectrum of aluminium, charged with 10 C cm^{-2} lithium, taken at an overvoltage of -20 mV .

Both sets of measurements show that near to the equilibrium potential the α - β phase change does not take place; variations in potential simply promote changes in the activity of lithium in the β -layer whose thickness remains fixed. The amount of charge which passes to, and from, the layer at low frequencies is proportional to the thickness of the layer, *i.e.*, to the amount of lithium within it.

If β -LiAl behaved as an ideal solution of the two elements then the capacitance should be simply related to the state of charge. Differentiation of the Nernst equation gives

$$dE = (RT/F) d \ln c \quad (2)$$

But the lithium concentration, c , is related to the charge density, Q , by

$$Q = Fcx$$

where x is the thickness of the β -layer. So

$$d \ln c = d \ln Q = dQ/Q$$

So the capacitance, C , can be expressed

$$C = dQ/dE = QF/RT$$

The observed linear variation of capacitance with state of charge is predicted, but the observed proportionality constant (0.1 V^{-1}) is some 40 times lower than the predicted value, indicating that the alloy does not behave as an ideal solution. Considering non-ideality, eqn. (2) becomes

$$dE = (RT/F) d \ln c + (RT/F) d \ln f \quad (3)$$

Supposing $d \ln f/d \ln c \gg 1$, then eqn. (3) becomes

$$dE = (RT/F) d \ln f$$

and so we obtain

$$C = (QF/RT) d \ln c/d \ln f$$

This equation expresses the observed dependence of C upon Q . The large value (40) of $d \ln f/d \ln c$ is a consequence of the particular stability of a particular alloy composition. This might be expected to be 50 at.% lithium, but it has been suggested elsewhere [10, 13] that it is 48 at.% lithium. The rapid variation of lithium activity with concentration in β -LiAl has been reported previously [17].

These results provide further evidence for the substantial cathodic overvoltage associated with the growth of the β -LiAl phase, discussed previously by Owen *et al.* [14].

The large value found for $d \ln f/d \ln c$ throws doubt upon the values reported (*e.g.*, ref. 13) for D_{Li} in β -LiAl because calculation of such values assumes the applicability of Fick's law. Garreau and Thevenin [18] have reminded us that, in general, Fick's law should read

$$\text{flux} = -D \text{grad } c(1 + d \ln f/d \ln c)$$

and so the apparently large values calculated for D might, in part, result from the non-ideality term.

If the layer of β -Li(Al) was sufficiently thick in the present study, then at moderate frequencies, diffusion of lithium through the layer became rate-determining and a Warburg impedance was seen, from which the diffusion coefficient of lithium was calculated to be $5 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ assuming ideality (or 1.25×10^{-12} allowing for non-ideality). This result is two orders of magnitude lower than the previously reported value.

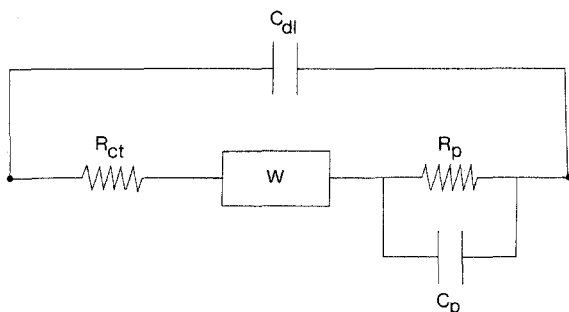


Fig. 6. Equivalent circuit for an aluminium electrode charged with lithium.

At positive overvoltages exceeding 20 mV, the concentration of lithium in the β -phase falls to a sufficiently low level for material near the boundary with the α -phase to disproportionate to α -Li(Al) and enriched β -Li(Al). This occurrence of the phase change is represented by a resistance, R_p , shunting the low-frequency capacitance, C_p (Fig. 6). Similarly, at sufficiently negative overvoltages the lithium concentration in the β -phase rises high enough to make the reverse process possible.

The system can be represented accurately by the equivalent circuit shown in Fig. 6. The charge-transfer resistance, R_{ct} , was highest at the equilibrium potential and for small electrode charges where the growing centres of β -Li(Al) had not overlapped and so the active area was lower than the geometric area of the electrode.

Conclusions

At, and near to, the equilibrium potential, interconversion of the α - and β -phases of LiAl does not proceed at a significant rate and can therefore be regarded as the rate-limiting process. This process alone is responsible for the overvoltages, especially the cathodic overvoltage, which persist at very low current densities. Earlier work [3] which identified diffusion as rate-limiting under these conditions did not include measurements at frequencies sufficiently low to probe the kinetics of the phase change. The proposed equivalent circuit (Fig. 6) adequately describes the behaviours observed under various conditions and allows the work of previous investigators to be reconciled.

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