CYCLING OF β-LiAl IN ORGANIC ELECTROLYTES — EFFECT OF ELECTRODE CONTAMINATIONS AND ELECTROLYTE ADDITIVES

J. O. BESENHARD, H. P. FRITZ and E. WUDY

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstr. 4, D-8046 Garching (F.R.G.)

K. DIETZ

VARTA Forschungs- und Entwicklungszentrum, Gundelhardtstr. 72, D-6233 Kelkheim (F.R.G.)

H. MEYER

Institut für Anorganische Chemie der Universität München, Meiserstr. 1, D-8000 Munich 2 (F.R.G.)

Summary

The mobility of Li in β-LiAl formed by cathodic Li incorporation is drastically reduced by small amounts of Si in the parent Al; this is shown by ^{7}Li NMR and electrochemical experiments. During long term cycling, the detrimental effect of lower Li mobility is compensated by the less spongy morphology of Si-doped electrodes. Addition of a few hundred ppm of 1,2-propanediol or methoxyethanol improves the 1st cycle Li-recovery from Si-doped β-LiAl in propylene carbonate electrolytes; paraffin oil is a non-reactive surfactant which slightly decreases the corrosion of β-LiAl.

1. Introduction

At least for low rate secondary organic electrolyte lithium batteries β-LiAl anodes seem to be one of the most promising alternatives to metallic lithium anodes, although at high rates and/or in thick electrodes, room temperature Li transport becomes problematic [1 - 4]. The discharge and cycling behaviour of β-LiAl electrodes depends strongly on (i) the purity of the Al matrix and (ii) electrolyte additives and contaminations. Impurities in the Al matrix generally decrease the Li mobility in β-LiAl [5]. On the other hand, they can improve the morphology of *in situ* formed β-LiAl. In organic electrolytes, β-LiAl (just as metallic Li) reacts with the electrolyte solution until a film of reaction product protects it from further attack [6 - 9]. Electrolyte additives can either directly influence the properties of these films or also act as scavengers which remove trace impurities from the electrode or

from the electrolyte. A search for possible routes to improve the β-LiAl/ organic electrolyte system is the aim of this paper.

2. Experimental

The experiments were performed in purified Ar atmosphere; propylene carbonate (PC) electrolytes were purified as reported earlier [5]. The water content was determined with a coulometric Karl Fischer titrator (Mitsubishi CA-02 moisture meter). Impedances were measured in the galvanostatic mode using a Solartron 1174 frequency response analyzer [10]. The super-imposed a.c. current was, in general, kept below 10 μA cm^{-2}.

Measurements of the double layer capacity on Hg were made with a dropping electrode and a phase-sensitive a.c.-polarograph (Tacussel PRG 3).

Lithium recoveries were always determined under the same standard conditions: a thick Al substrate was charged for 45 min at 1 mA cm^{-2} and discharged at the same current density to a cut-off of +2 V $vs.$ Li/Li$^+$.

3. Results

Effect of purity of Al matrix on anodic Li recoveries

The purity of the parent aluminum, from which β-LiAl is formed by cathodic incorporation of lithium, strongly influences the solid state Li mobility and, hence, the anodic Li recovery, especially at higher current densities. This effect is particularly drastic for Si contaminations (see Fig. 1).
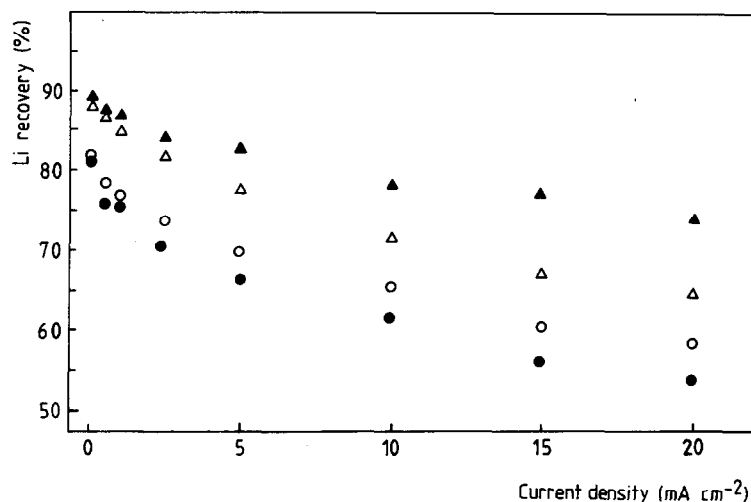

Fig. 1. First cycle Li recoveries from electroformed β-LiAl in 0.5M LiClO$_4$/PC in depen-dence of foreign metals in parent Al. $\blacktriangle$: 0.0006% Si, 0.005% Fe; $\triangle$: 0.002% Si, 0.52% Fe; $\circ$: 0.1% Si, 0.0005% Fe; $\bullet$: 0.5% Si, 0.0005% Fe; i: 1 mA cm^{-2}; charge: 2700 C cm^{-2}, discharge immediately after charge.

After some cycles, however, the Li recoveries from Si-contaminated Al even exceed those from high purity parent Al, *i.e.*, the poor Li recovery in the first few cycles is a kind of investment that pays a return in the following cycles. Si has obviously a beneficial effect on the morphology of electro-formed β-LiAl: micrographs show that reaction layers are more compact and crack propagation is much slower when Al is alloyed, for example, with 0.5% Si. Therefore, in long-term cycling experiments the per cycle losses of active material are lower for Si-containing electrodes.

The better 1st cycle Li recovery from β-LiAl based on high purity Al is not simply due to higher surface roughness. ^{7}Li NMR clearly shows that the solid state Li mobility is strongly decreased by Si contaminations (line-widths, FWHM at *ca.* 300 K: 215 Hz for samples based on Al 99.998%, 340 Hz for samples based on Al–Si-0.5). ^{7}Li NMR indicates also that the Li mobility in β-LiAl electroformed at room temperature is about the same as that in typical "battery grade", high temperature β-LiAl (*e.g.*, linewidth, FWHM 227 Hz at *ca.* 300 K for a commercial preparation — Kawecki Berylco Industries — with 48.52 at.% Li, 0.04 at.% Fe and traces of Na, K and Hg).

Figure 1 also shows that even at very low current densities, 1st cycle Li recoveries never exceed *ca.* 92% (high purity Al, extrapolation* for current density *vs.* zero).

Where has the rest of the lithium gone? In chemical analysis of dis-charged LiAl electrodes most of the missing Li does show up; in ^{7}Li-NMR it does not, *i.e.*, it is obviously not detected by methods which are sensitive to mobile Li only. Therefore we suppose that β-LiAl is not discharged to metallic Al; it is rather α-LiAl that remains, a solid solution of *ca.* 8 at.% Li in Al [11 - 14]. As the mobility of Li in α-LiAl is very low, it does not seem to be formed to a substantial degree simply by room temperature incorpora-tion of Li into Al. Baranski and Fawcett have attributed the poor Li recovery in the early discharge cycles to reduction of oxides on the Al substrate [15].

Unfortunately, the lattice constants of α-LiAl phases are so close to that of Al that they cannot be distinguished by straightforward X-ray methods (Al: $a_o = 404.95$ pm; α-LiAl with 1.93 at.% Li: $a_o = 403.81$ pm [14]; α-LiAl with 3.5 at.% Li: $a_o = 405.5$ pm [12]).

Low current density Li recovery from Al–Si-0.5-based β-LiAl is only *ca.* 80% (see Fig. 1). Again, the difference from 100% is detected by chemical analysis, but here ^{7}Li NMR shows about 10 - 15% of the original intensity, *i.e.*, of the intensity of a freshly charged electrode. However, the linewidth of the remaining Li intensity (*ca.* 410 Hz) is much higher than that observed with the original sample. Certainly, Li positions in Al–Si-0.5-based β-LiAl are non-equivalent, and Li on "slow" sites remains after discharge. Even in dis-charged β-LiAl based on high purity Al there is some ^{7}Li NMR intensity left ($<$1%); the line is also much broader (*ca.* 350 Hz) than in the original sample.

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*The recovery *vs.* current density plot can be approximately linearized by plotting recovery *vs.* square root of current density.

Lithium transport in β-LiAl occurs *via* Li vacancies [16 - 20]. Transport of either Li or Al from ordinary sites in β-LiAl can be disregarded because of their low temperature factors (B_{Li} = 1.48 Å^2, B_{Al} = 0.66 Å^2, determined at room temperature by neutron diffraction). The phase range of β-LiAl prepared at elevated temperature allows *ca.* 3% of the Li sites to be vacant [18 - 20]; these vacancies also remain at room temperature ("permanent vacancies" [21]). In view of these facts it is hard to understand why, for example, a Si contamination far below the number of Li vacancies should have so much impact on the Li mobility. One possible explanation for this effect would be a much more stoichiometric character of β-LiAl prepared by cathodic Li incorporation at room temperature.

Effect of electrolyte additives and contaminations

Surface filming is essential for the protection of β-LiAl in PC electrolytes since β-LiAl is not thermodynamically stable *vs.* PC. Nevertheless, a drastic voltage delay at the beginning of discharge is only observed after prolonged storage (Fig. 2).

It is certainly a challenging idea to improve the properties of surface films on β-LiAl by electrolyte additives. However, the effect of additives and contaminations is complex; as they are usually adsorbed or accumulated on the electrode surface, they may affect the electrode kinetics by various mechanisms.
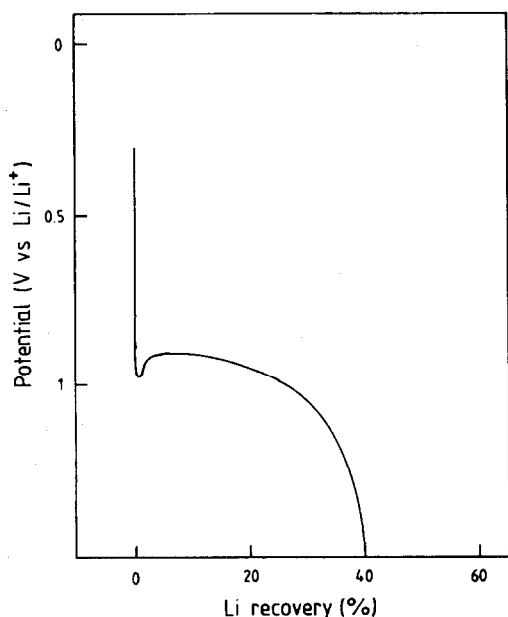

Fig. 2. Typical voltage delay of electroformed β-LiAl after storage (3500 h, room temperature) in 0.5M LiClO$_4$/PC. i = 1 mA cm^{-2}.
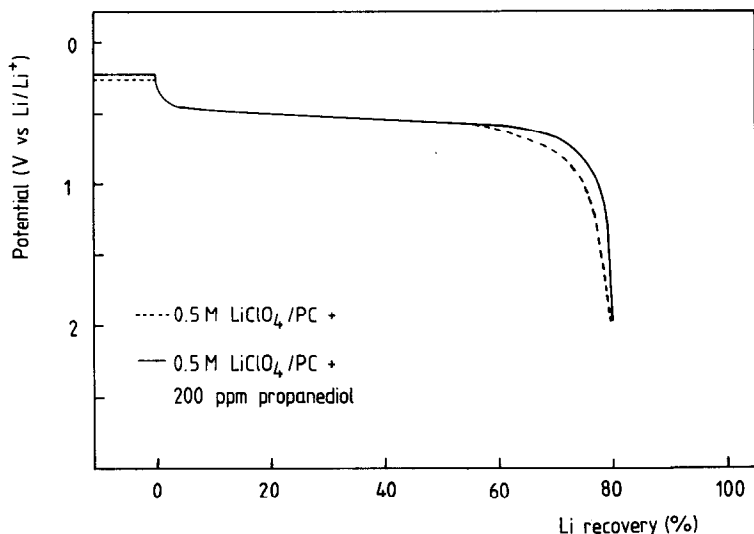
Fig. 3. Typical 1st cycle discharge characteristics of electroformed β-LiAl (basis: Al–Si-0.5) in dependence of 1,2-propanediol content. $i = 1$ mA cm^{-2}.

1,2-Propanediol, which is a common contaminant in PC electrolytes, significantly improves the 1st cycle discharge characteristic of Si-doped β-LiAl — the discharge characteristic becomes harder, although the total Li recovery is about the same (Fig. 3). From pulsed discharge experiments it can be concluded that the "rounded" end of the discharge section (see Fig. 3), which is observed in the absence of propanediol, is due to transport limitations. The discharge characteristic of high purity β-LiAl is not improved by propanediol; there is only a slightly higher overvoltage for the incorporation of Li into Al. 2-Methoxyethanol, which was recently reported to improve the cycling behaviour of metallic Li, has a similar effect to propanediol [22]. In contrast to propanediol, 2-methoxyethanol does not seem to have a detrimental effect during long term cycling.

The mechanism of the action of diols is not yet clear; they may act as "scavengers" which remove Si from surface-near regions of contaminated β-LiAl.

Some minor improvement in the cycling behaviour (slightly higher Li recovery in the 1st cycle as well as during long term cycling) of β-LiAl in PC electrolytes is observed when long-chained, saturated hydrocarbons ("paraffin oil") are added. Paraffin oil obviously acts as a surfactant: double layer capacity measurements on the dropping Hg electrode (tensametry) in PC electrolytes clearly verify a strong adsorption of paraffin oil on the Hg surface (Fig. 4). 1,2-Propanediol and polyethyleneglycols are not significantly adsorbed on Hg in LiClO$_4$/PC.

The effect of water on filming and corrosion of β-LiAl in PC electrolytes is surprisingly low: water contents in the range 20 - 500 ppm did not
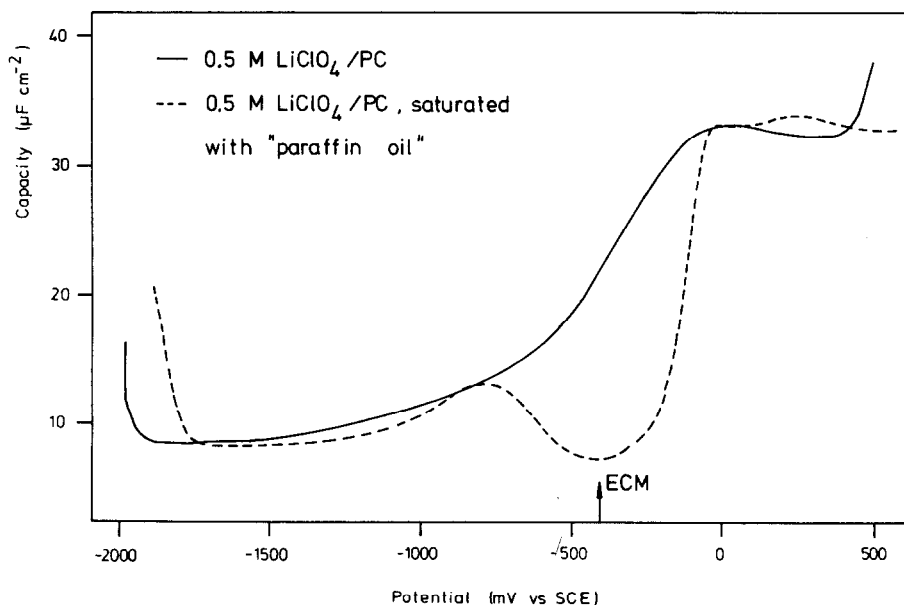
Fig. 4. Potential dependence of double layer capacity of Hg electrode in 0.5M LiClO₄/PC and LiClO₄/PC saturated with "paraffin oil"; ECM = electrocapillary maximum.

change the Li recovery significantly (determined under standard conditions after 7 day's wet stand).

The electrical properties of films on β-LiAl are quite similar to those of films on metallic Li. In a simple model they may be represented by the following equivalent circuit: a parallel combination of resistance and capacity of the film in series with the components of a film-free electrode — a parallel combination of charge transfer resistance and double layer capacity and $R_{electrolyte}$ in series [23]. The impedance spectrum of this equivalent circuit is characterized by two semicircles — as the film resistance increases drastically with time, the total impedance spectrum is soon dominated by the film properties [23]. Basically the same features are observed with β-LiAl electrodes in organic electrolytes.

Figure 5 shows an impedance spectrum of β-LiAl after storage for 6 months in 0.5M LiClO₄/PC; immediately after current flow (0.2 mA cm^{-2} cathodic) the large film resistance (of the order of 3 kΩ cm^{-2}) breaks down and the typical impedance spectrum of β-LiAl appears (a high frequency semicircle representing the charge transfer reaction and a curved Warburg branch, characteristic for diffusion limitation in pores). Impedance spectra of this type can be simulated on the basis of the equivalent circuit shown in Fig. 6.
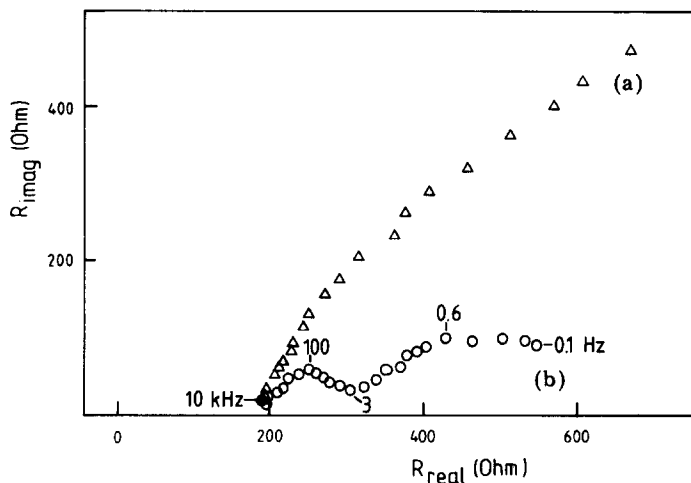
Fig. 5. Impedance of β-LiAl electrode (0.5 cm^{-2} geom) in 0.5M LiClO$_4$/PC. △: after 180 d storage; ○: immediately after beginning of discharge at 0.2 mA cm^{-2}; the upper curve is a slightly compressed semicircle (apex: *ca.* 2000 Ω at 2 Hz).
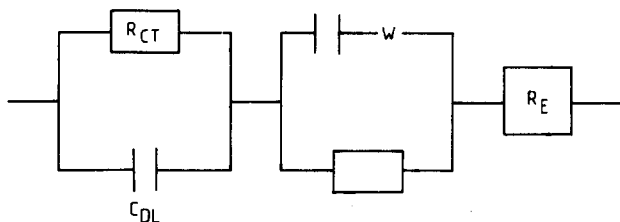

Fig. 6. Equivalent circuit allowing simulation of curve (b) in Fig. 5.

4. Conclusion

The cycling behaviour of β-LiAl in organic electrolytes can be significantly influenced by trace additives either in the parent Al substrate or in the electrolyte. A considerable stepwise improvement of this electrode by systematic work on additives seems to be a realistic perspective.

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