THIN FOIL LITHIUM-ALUMINIUM ELECTRODE. THE EFFECT OF THERMAL TREATMENT ON ITS ELECTROCHEMICAL BEHAVIOUR IN NONAQUEOUS MEDIA

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Summary

The effect of the microstructure of aluminium foil electrodes on the electrochemical behaviour of the Li–Al alloy at ambient temperature has been studied by X-ray diffraction, texture goniometric and scanning electron microscopic (SEM) techniques.

It was found that thermal annealing of aluminium electrodes close to the theoretical recrystallization temperature of Al reduces the overvoltage of Li alloying and increases the cycling efficiency.

It is suggested that the observed uniform, fine-grain microstructure of the β-Li–Al electrode on the annealed substrate reduces the effective current density during cycling.

Introduction

Lithium–aluminium alloys were studied in detail by Epelboin *et al.* [1] and Gareau *et al.* [2, 3] as an alternative anode material in lithium secondary cells operating at ambient temperatures. These authors demonstrated that the Li–Al phase can be cycled continuously with high efficiency provided that the electrochemically-deposited initial alloy layer is in the range 50 - 100 C cm^{-2}. The alloy electrodes were characterized by the efficiency E at equal anodic and cathodic charges, $Q_a = Q_c$.

In our previous papers [4 - 6] it was shown that the β-Li–Al phase deposited on a 0.5 mm thick aluminium foil can be cycled 400 times at $Q_c = 2$ C cm^{-2} and a charge density of 3 mA cm^{-2}. The increase of Q_c leads to a strong reduction in E, most probably as a result of its deterioration of the mechanical bond between the alloy and the substrate.

Recently Maskell and Owen [7] revealed the possibility of utilizing a thin aluminium substrate as a secondary Li–Al electrode. The good adhesion

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between the alloy and the foil is considered by the authors to be a suitable condition for maintaining the integrity of the electrode during continuous cycling. The experimentally determined 6% per cycle capacity decay makes its use in a secondary Li cell doubtful.

The aim of this work was to study the effect of the microstructure of the aluminium foil on the electrochemical behaviour of the Li–Al alloy at ambient temperature.

Experimental

The material for the substrate was 100 μm Al foil (99.99% Al) made in Japan. The electrodes were prepared by rolling nickel exmet (3×0.2 mm) onto the aluminium foil using well cleaned steel rollers. The thickness of the electrodes was about 100 μm and their area 1 cm^2. A nickel wire was welded to serve as a current lead. The electrodes were etched in 5% KOH for 5 - 6 min, washed and dried in acetone, then polished with emery paper, 6/0, in a glove dry box flushed with argon.

The cell, which was assembled in the same dry box, consisted of an hermetically-sealed, cylindrical glass vessel housing the test, the counter, and the reference electrodes.

Both the counter and the reference electrodes were 0.5 mm thick Li foil pressed onto a Ni net. The counter electrode (2 cm^2) was parallel to the test electrode.

The electrolyte solution was 1 M LiClO$_4$ (Merck) in propylene carbonate (PC) (Merck) which was dried over 4 Å molecular sieves. The total moisture content was always below 50 ppm. The X-ray diffraction measurements were carried out in a high temperature X-ray chamber. For the SEM studies the Li–Al electrode samples were placed in evacuated cuvettes in a dry box atmosphere and subsequently coated with a 100 Å gold film.

Results and discussion

The cold-rolled aluminium foil has a highly stressed structure. The insertion of lithium during the formation of the β-Li–Al phase creates additional stresses in the substrate due to the almost doubling of the molar volume of the alloy.

The microstructure of the aluminium foil used in this study is shown in Fig. 1. Spherulites of various shapes and sizes, probably resulting from cold rolling, are visible in this Figure.

The preliminary electrochemical investigation of electrodes prepared from this foil revealed, as shown by curve 1 in Fig. 2, a high overvoltage of lithium insertion at 2 mA cm^{-2}. The irregular microstructure of the aluminium substrate is maintained in the Li–Al alloy, as illustrated in Fig. 3, for charges $Q_c = 2$ C cm^{-2} for the same electrode. The Li insertion proceeds on
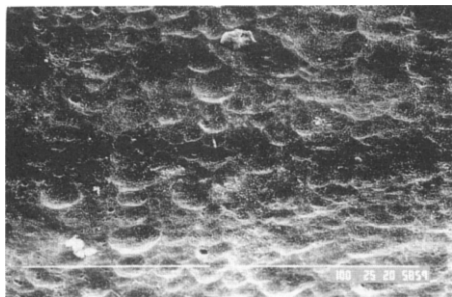
Fig. 1. SEM pictures of as-delivered aluminium foil, 100 μm thick (×250).
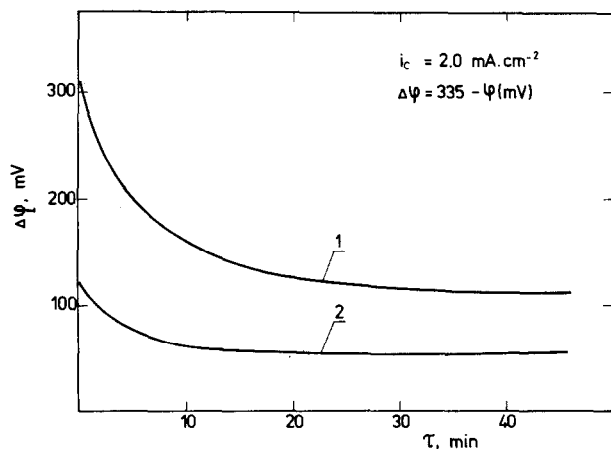

i_c = 2.0 mA·cm^{-2}

$\Delta\psi$ = 335 − ψ(mV)

Fig. 2. Effect of annealing of aluminium foil on the insertion overvoltage of Li, $\Delta\varphi$ at 2 mA cm^{-2}: 1, unannealed Al foil; 2, annealed Al foil.
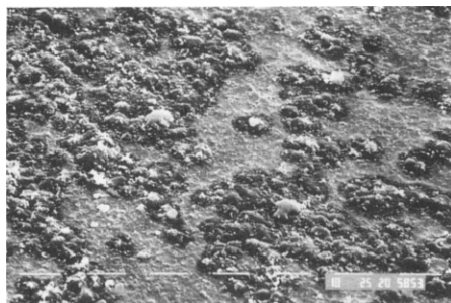

Fig. 3. SEM pictures of β-Li–Al alloy of unannealed Al foil (×500), Q_c = 2 C cm^{-2}.

selected sites, and this is the most likely cause of the relatively high overvoltage.

Preliminary experiments with thermally-annealed electrodes at temperatures close to the theoretical temperature of aluminium recrystallization [8] revealed a considerable reduction in the overvoltage of lithium deposition (curve 2, Fig. 2).

This leads us to believe that the microstructure of the aluminium foil has an effect on the electrochemical behaviour of the Li–Al electrode.

In order to elucidate this effect, a series of X-ray and microscopic investigations was performed.

Samples of the aluminium foil were heated at a rate of 50 °C min^{-1} in the X-ray high-temperature chamber. Diffraction patterns and microstructures of the samples were recorded at specific temperature intervals.

Figure 4 illustrates the diffraction patterns of aluminium samples heated to 20, 300, 320, 350, and 550 °C, while Fig. 5 shows the SEM pictures taken at 350, 400, and 550 °C. It can be seen from Fig. 4 that up to 300 °C the aluminium samples are amorphous for the X-ray diffraction. At 320 °C a texture formation process begins, indicated by the disappearance of the (111) peak ($d = 2.33$ Å) and a considerable increase in the (200) peak. The character of the X-ray pattern does not change upon raising the temperature to 550 °C.

The texture goniometer measurements revealed that a (100) texture is formed upon heating the aluminium sample within the range 320 - 550 °C. The SEM pictures in Fig. 5 demonstrate that the microstructure of aluminium changes substantially over the same temperature range as a result of recrystallization, leading to the formation of new crystallites and, subsequently, to their overlapping (*cf.* Fig. 5(a) and (c)).

In order to obtain a more uniform structure across the thickness of the foil we studied slower rates of heating. It was found experimentally that a
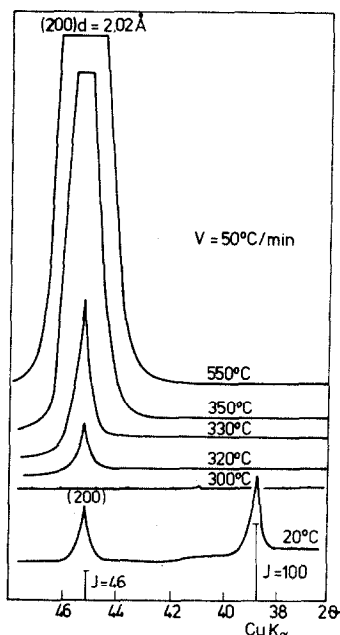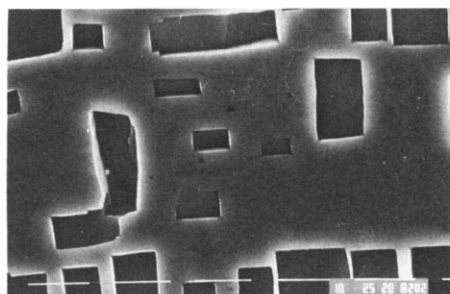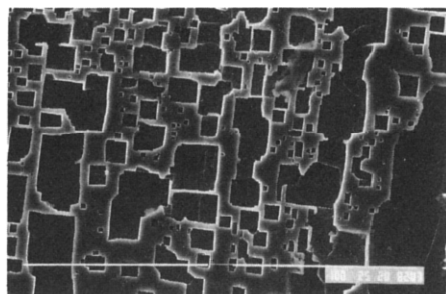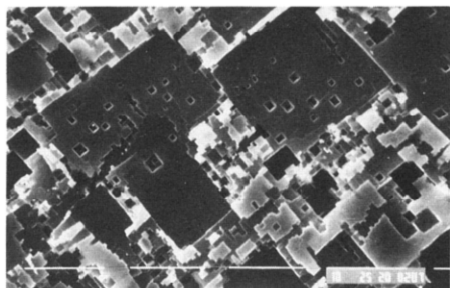

Fig. 4. X-ray diffraction patterns of Al foil annealed at different temperatures. Heating rate 50 °C min^{-1}.

(a)

(b)

(c)

Fig. 5. SEM pictures of Al foil at different temperatures (a) ×750, (b) ×250, (c) ×1000). (a) 350 °C; (b) 400 °C; (c) 550 °C. Heating rate 50 °C min^{-1}.

considerable improvement in the electrochemical behaviour of the Li–Al foil electrode is achieved by heating to 450 - 550 °C at a rate of 200 - 300 °C h^{-1}, followed by holding at that temperature for 4 - 7 h, and then cooling at 20 - 50 °C h^{-1}.

The microstructure of the aluminium foil after this form of heat treatment is shown in Fig. 6. One can see uniformly large Al crystals, of about 100 μm in size, formed from the small, uniform spherulites shown in Fig. 7. The X-ray analysis again confirmed the preferred (100) orientation.
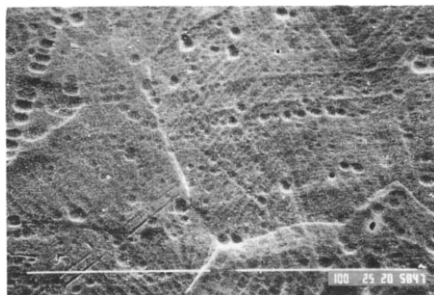

Fig. 6. SEM picture of annealed aluminium foil (×250). Conditions: heated to 450 - 550 °C at 200 - 300 °C h^{-1}, held at temperature for 4 - 7 h, cooled at 20 - 50 °C h^{-1}.
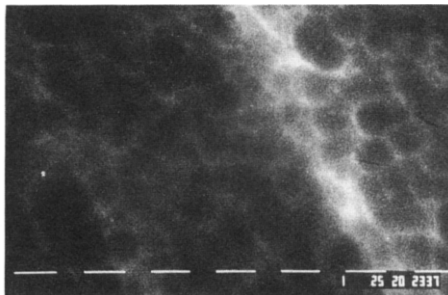
Fig. 7. SEM picture of annealed Al foil (×5000).
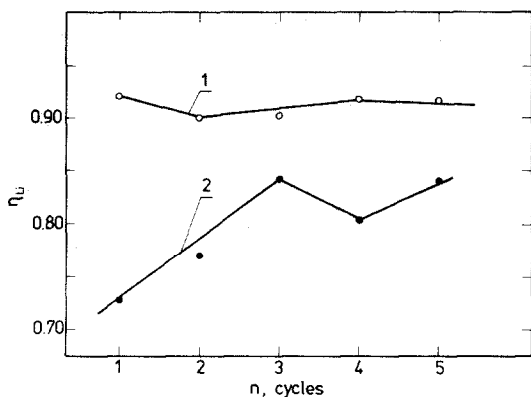
Fig. 8. Effect of cycling on the coulombic efficiency, η_{Li}, of β-Li–Al, $Q_c = 2$ C cm^{-2}, $i_a = i_c = 2$ mA cm^{-2}. 1, annealed Al foil; 2, as-rolled Al foil.

The electrochemical behaviour of Li–Al electrodes was assessed by determining the coulombic efficiency

$$\eta_{Li} = Q_a / Q_c$$

where Q_c is the charge during cathodic deposition and Q_a the charge during anodic dissolution, using the method described in ref. 4.

Figure 8 shows the experimental data of η_{Li} in the first few cycles for thermally annealed (curve 1) and for as-rolled Al foil (curve 2). The increase in the coulombic efficiency from 0.80 to 0.93 is most likely associated with changes in the structure of the starting aluminium foil.

The SEM pictures of Li–Al electrodes deposited on annealed aluminium foil confirm the uniform insertion of lithium over the entire electrode surface (Fig. 9). It is seen that the formation of the Li–Al alloy does not proceed along the phase boundaries of the large 100 μm crystals, as supposed by some authors [9], but rather on the small (about 1 μm) crystallites which form on the larger ones. In this way the substructure of the large aluminium crystals is inherited. The uniform fine-grain microstructure of the β-Li–Al electrodes on the annealed substrate is the most likely cause of the faster Li diffusion in the substrate. It may be supposed that this structure reduces
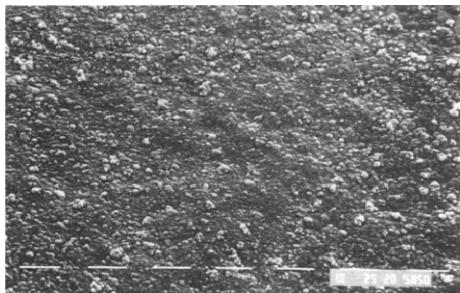

Fig. 9. SEM picture of β-Li–Al alloy on annealed Al foil ($\times$500), Q_c, 2 C cm^{-2}.

the effective current density during cycling, thus reducing the overvoltage of Li insertion. The long cycling experiments presented below were therefore undertaken with annealed aluminium foil electrodes only.

In order to prepare electrodes having a longer cycle life it is necessary, initially, to deposit a larger excess of Li. The amount of Q_o was determined experimentally by assessing the maximum number of useful cycles, n, of the reversible electrode. These were defined as the number of balanced cycles with equal charge during deposition and dissolution, $Q_c = Q_a$, and in which the overvoltage at the end of the discharge (dissolution) did not exceed by 100 mV the overvoltage at the end of the second discharge.
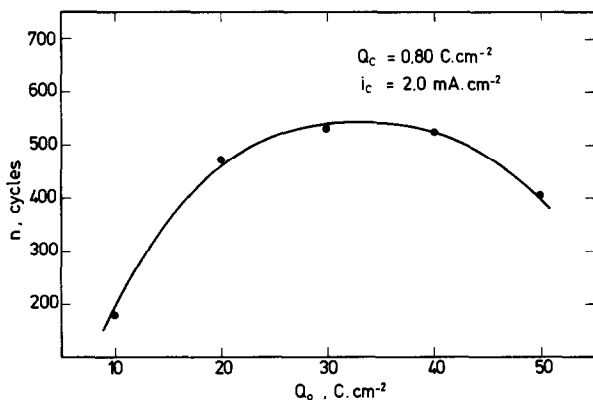

Fig. 10. The effect of the initially deposited Li (Q_o) on the cycling capability (n) of Li–Al electrodes at $i_c = 2.0$ mA cm^{-2} and $Q_c = 0.80$ C cm^{-2}.

The dependence of n on Q_o at $Q_c = Q_a = 0.8$ C cm^{-2} and $i = 2$ mA cm^{-2} is presented in Fig. 10, which shows that the maximum number of cycles is at $Q_o = 30$ C cm^{-2}. This value is about 60% of the theoretical charge necessary to convert the electrode entirely into the β-Li–Al phase, and is of the same order of magnitude as that reported by Maskell and Owen [7] for 50 μm aluminium foil electrodes. Figure 11 reveals that for charges, Q_o, larger than 30 C cm^{-2}, the value of n drops significantly, most likely because of mechanical degradation of the electrodes.

The effect of Q_c on the cycling efficiency (E) at $Q_o = 30$ C cm^{-2} is presented in Fig. 11, revealing that the increase in Q_c leads to a decay in E. A similar result was reported earlier by us for the case of thicker (0.5 mm) aluminium foil electrodes [4].

For practical purposes it is important to know the coefficient of aluminium utilization. It can be calculated in a way similar to that for the estimation of the cycling efficiency on lithium substrates [10]

$$\eta_{Al} = 1 - Q/nQ_c$$

where Q is the charge necessary to convert all the aluminium into the Li–Al alloy, Q_c is the cycled charge and n the number of cycles.
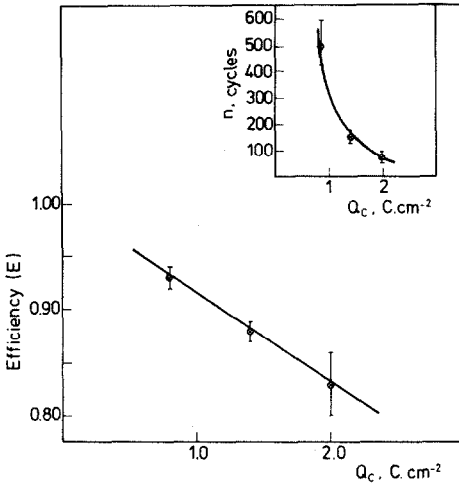
Fig. 11. The effect of the charge density (Q_c) on the efficiency (E) of the cycling capability (n) of Li–Al electrodes at a constant current density $i = 2$ mA cm^{-2} and constant $Q_o = 30$ C cm^{-2}.
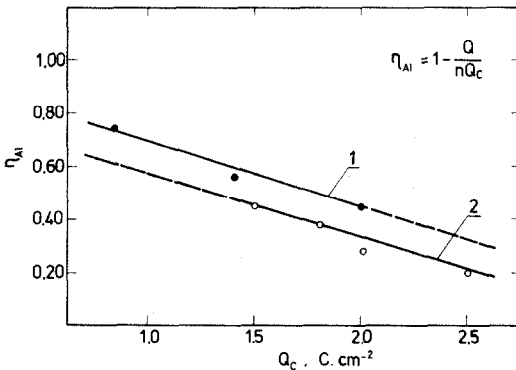

Fig. 12. Effect of charge density, Q_c, on the coefficient of Al utilization, η_{Al}, for electrodes prepared from Al foil: 1, 100 μm thick; 2, 500 μm thick.

Figure 12 presents the value of η_{Al} as a function of Q_c for 100 μm aluminium foil electrodes. The dependence for the case of 0.5 mm aluminium foil electrodes, based on our previous investigations [4], is also shown. The decrease in the foil thickness, the use of the Ni exmet collector, as well as the annealing procedure, bring about a considerable improvement in the aluminium utilization.

Conclusions

It is shown that the thermal annealing of aluminium foil leads to a reduction in the overvoltage of lithium alloying as well as to an increase in cycling efficiency.

X-ray analyses and SEM observations provide evidence that the uniform fine-grained, microstructure of a β-Li–Al electrode on the annealed substrate is the most likely cause of these beneficial effects.

List of symbols

Q_o	Charge used to preform a layer of β-Li–Al alloy (C cm^{-2}).
Q_a	Charge used for Li dissolution (C cm^{-2}).
Q_c	Charge used for Li deposition (C cm^{-2}).
i_c	Cathodic current density (mA cm^{-2}).
i_a	Anodic current density (mA cm^{-2}).
n	Electrode cyclability (cycles).
$\Delta\varphi$	Overvoltage of Li deposition (mV).
η_{Li}	(Q_a/Q_c) Coulombic efficiency of Li.
E	$\dfrac{nQ_c}{nQ_c + Q_o}$ cycling efficiency.
η_{Al}	($1 - Q/nQ_c$) coefficient of Al utilization.

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