Studies of Al–Al$_3$Ni eutectic mixtures as insertion anodes in rechargeable lithium batteries

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Abstract

This contribution will give a short overview of aluminium–nickel eutectic mixtures alloys as the anode materials in lithium secondary batteries. These compounds allow to create an alloy matrix of modified grain size with stabilizing properties toward 'mechanical stressing' during charge/discharge processes of lithium. Several electrochemical techniques have been used to investigate the electrochemical behaviour of these lithium-inserting materials. © 1997 Elsevier Science S A.

1. Introduction

The manufacturing of rechargeable lithium batteries with sufficient capacities requires a progress in the cycleability of the negative electrode. It can be improved by the use of lithium-inserting substrates. The most common materials are lithium–carbon and lithium–aluminium. Using substrate-forming alloys or intercalation compounds with lithium the reactivity against the electrolyte or the solvent can be decreased. Therefore, lithium in the host material will be 'shielded' and the formation of dendrites will be reduced or avoided if the diffusion velocity inside the host material is sufficient.

The diffusion of lithium into the alloy matrix determines the charge/discharge rate of the battery and limits the use as low- or high-rate cell. The diffusion process itself is determined by the nature of the host material and its morphology.

The main problems of lithium alloy electrodes are connected with the significant differences in volume between the pure basic material and the formed lithium alloy. Therefore, during cycling mechanical stress and cracks are induced by these volume differences (AlLi 96.8% in relation to the host lattice). Attempts have been made to avoid the problem of the volume changes by creating 'dimensionally stable' alloying electrodes in that way, that the aluminium host was prealloying by other metals which are soluble in aluminium or form intermetallic compounds with it, but do not form alloys

with lithium, such as nickel. In this way one expects to create an alloy matrix of modified grain size with stabilizing properties toward 'mechanical stressing' during charge/discharge processes of lithium.

Therefore, the suitability of different binary Al–Ni alloys as anode substrates in rechargeable lithium batteries have been tested. The changed composition by alloying of aluminium with a second metal does dramatically influence the mechanical properties and the electrochemical behaviour. On the other hand, the electrochemical properties of these substrates are also determined by the macro- and microstructure. Particularly, the eutectic mixture of Al Ni (Al/Al$_3$Ni) seems to be an interesting substrate material in rechargeable lithium batteries. The Al$_3$Ni phase is unalloyable with lithium and serves only for the improvement of the mechanical stability. The second phase of pure aluminium can receive the incorporated lithium.

2. Experimental

The preparation of the test cells was carried out as described in previous papers [1,2]. All kinds of starting metals used have been of 99.99% purity. The various metal electrodes have been prepared from small cylinders with a diameter of 5 mm (surface area: 0.196 cm^2) and have been embedded in a Teflon holder. The metal surface was mechanically polished lastly with emery paper 4000. Both the counter and the reference electrodes were lithium pellets pressed onto

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nickel nets. The electrolyte solution was prepared from propylene carbonate (PC) (Merck) distilled and stored over molecular sieves 4A, and $LiClO_4$ (Merck) gradually dried under vacuum. The content of water could be decreased to 20–30 ppm.

An EG&G Model 273A potentiostat in connection with a computer system was used for the electrochemical measurements. For the galvanostatic cycleability test we used a special equipment of the MACK–Electronic Company, Germany.

3. Results and discussion

Some different qualities of this eutectic mixture Al–Al_3Ni have been investigated. By fast quenching one gets very fine spread segregations of the Al_3Ni-phase (Fig. 1(a)). A direct heat flow (vertical Bridgeman method) leads to directionally solidified rodlike Al–Al_3Ni eutectic (Fig. 1(b) and (c)). This directionally solidified eutectic consists of an aluminium matrix of faceted Al_3Ni rods grown into it nearly parallel to each other and in the direction of heat flow.

3.1. Kinetic properties of the alloy electrode

The rate-determining step of the insertion of lithium into lithium-alloying materials is the diffusion in the host lattice which was studied by a potentiostatic transient method. The stationary diffusion process inside the solid state can be described by the Cotrell equation

$$i = zF(c_{Li}^* - c_{Li})\sqrt{\frac{D}{\pi t}} \tag{1}$$

where c_{Li}^* is the concentration of lithium in the intermetallic compound and c_{Li} represents the concentration of lithium in the starting state.

Potentiostatic measurements on aluminium and its several nickel alloys give sometimes functions of unusual response. These current–time transients can be interpreted by volume and grain boundary diffusion processes with different diffusion coefficients [2–4].

In the first step, the discharged lithium ions on top of the metal surface are dissolved in the aluminium matrix until the limiting concentration of 2.6 at.% is achieved within the α-LiAl phase in which lithium moves very slowly ($D \approx 10^{-11}$ cm^2/s). With increasing lithium content the β-LiAl phase is growing around the α-LiAl nuclei. The β-phase is a non-stoichiometric intermetallic compound with a lithium content ranging from 48 to 56 mol%. The rate of diffusion velocity inside the β-LiAl phase is higher than in the α-LiAl phase and causes a higher current density for lithium incorporation.

Fig. 2 shows the results of the chronoamperometric experiments for several substrates. Additional alloying with elements which preferably segregate at grain boundaries (i.e.
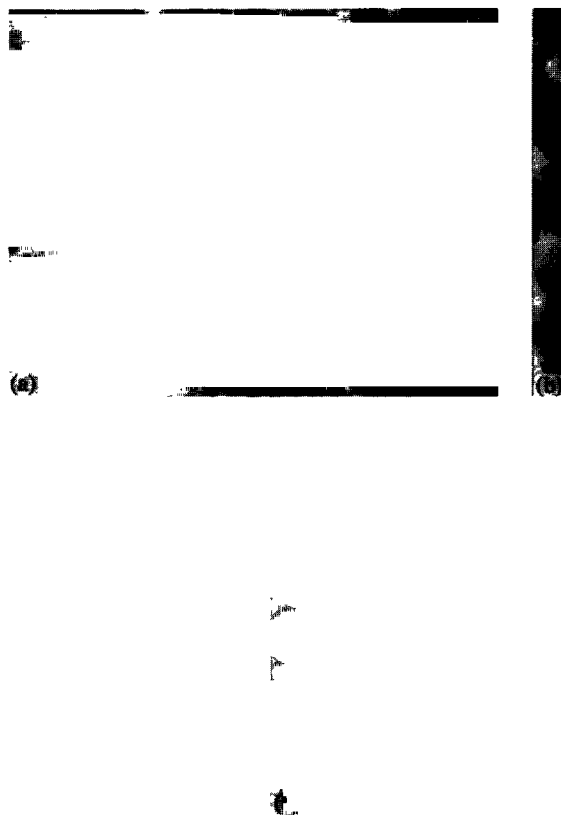

Fig. 1. SEM pictures of Al–Ni 6.3% eutectic mixtures; (a) fast quenched; (b) directionally solidified by a vertical Bridgeman method ($R = 50$ mm/h) transversally cut, and (c) directionally solidified by a vertical Bridgeman method ($R = 50$ mm/h) cut in the longitudinal section.
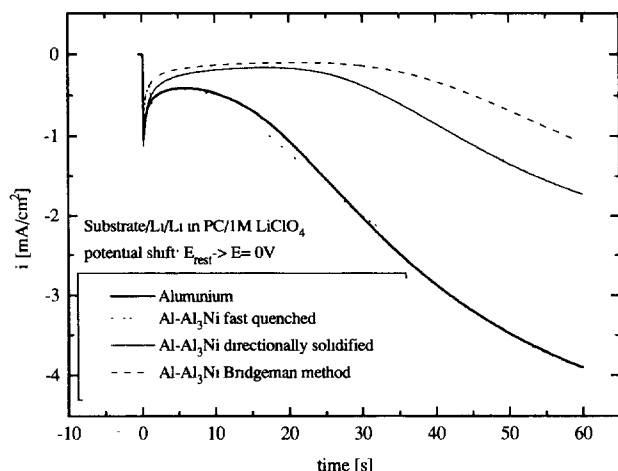
Fig. 2. Current–time behaviour of several aluminium substrates after a potentiostatic step

Fig. 3 Current efficiency of galvanostatic lithium deposition and dissolution on various host materials vs rest time after deposition (PC/1 M LiClO$_4$; |i| = 1 mA/cm^2; 0 3 C/cm^2)

nickel) influences the diffusion rate of lithium. On the other hand, their influence of the microstructure on the observed kinetics has to be considered. The diffusion process inside a polycrystalline material strongly depends on the microstructure and grain size distribution. Therefore, an accurate knowledge on the concentration of grain boundaries and their distribution as well as of the lithium concentration on the electrode surface is necessary for an exact determination of the diffusion coefficients.

The diffusion coefficients have been estimated for these substrates [4]. There values are given in Table 1.

3.2. Corrosion behaviour

The shelf life of an anode for rechargeable lithium batteries is influenced at least by two processes: (i) the normal corrosion process at the rest potential of the formed lithium alloy, and (ii) the self diffusion process inside the host material.

Both processes are running simultaneously. Fig. 3 shows the current efficiency — cathodic deposition of 0.3 C/cm^2 lithium (− 1 mA/cm^2) and anodic dissolution (+ 1 mA/cm^2) under galvanostatic conditions up to + 1 V — in dependence on the rest time between deposition and dissolution. Up to a rest time of 1 h, 80% of the deposited lithium can be dissolved during the anodic cycle. After a rest time above 5 h it gets more and more complicated to dissolve the
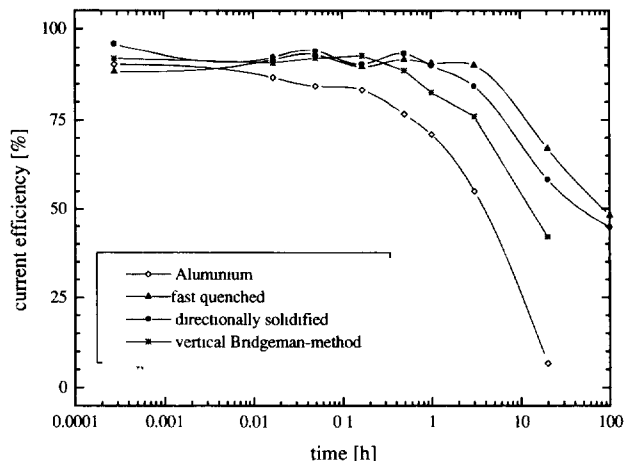
deposited lithium. The reason is mostly the self diffusion inside the aluminium matrix with a velocity of about 30 pm/ s (estimated by X-ray diffraction [1]). The normal corrosion process is much more slower then expected [4].

3.3. Cycling performance of the lithium–aluminium anodes

The usefulness of a new anode material can be examined only under real conditions. The consumer is interested in a maximum number of charge/discharge cycles with highest power density, if possible.

The cycling efficiency for pure aluminium was estimated to 88% under the used conditions (depth-of-discharge: 10%). The reversible behaviour is lost for cycle numbers much larger than 100. Comparable curves were obtained with the other substrates. With improving the orientation of the microstructure, the cycling efficiency decreases (Fig. 4). The fast quenched alloy gives the best result in the cycling tests. Inside of a fast quenched alloy one can incorporate a bigger amount of lithium at the same time.

4. Conclusions

During long time cycling the mechanical stability of an aluminium–metal alloy is improved compared with the pure

Table 1
Diffusion data for the various substrates estimated by chronoamperometry

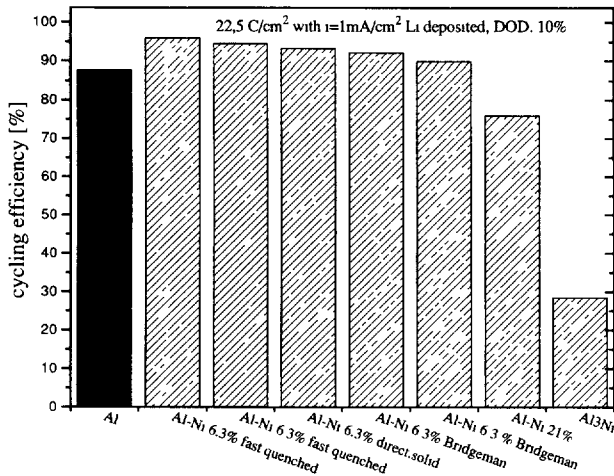| AlNi 6.3%-substrate	Intermetallic phase	$c_0 \cdot \sqrt{D}$ [mol/cm$^2 \cdot \sqrt{s}$]	D [cm^2/s]
Aluminium (pure)	α-AlLi	7.3 E-9	7.9 E-12
	β-AlLi	5 6 E-7	6 0 E-10
fast quenched	α-AlLi	3.8 E-9	2.4 E-12
	β-AlLi	6.1 E-7	8.3 E-10
directionally solidified	α-AlLi	1 1 E-8	2.1 E-11
	β-AlLi	4 5 E-7	4.6 E-10
vertical-Bridgeman	α-AlLi	6.5 E-9	7.2 E-1
	β-AlLi	4.2 E-7	3.9 E-10

Fig. 4. Average cycling efficiency of various substrates.

aluminium substrate. The insertion of lithium in the substrate will be hindered if the orientation and the growth of the Al_3Ni crystallites are increased. The reason is the great difference in velocities between the grain boundary and the volume diffusion. The transport of deposited lithium is very rapid due to the numerous grain boundaries in the case of the fast quenched eutectic mixture. Therefore, utilization of the alu-

minium substrate is more efficient. In directionally solidified materials insertion as well as re-insertion are decelerated because of the decreased lithium mobility.

It was observed that $Al–Al_3Ni$ eutectic mixtures are only suitable if using mild cycling conditions and thin layer technologies.

Acknowledgements

References

[1] I. Hauke and K. Wiesener, J. Power Sources, 43–44 (1993) 421–427
[2] S. Machill and D. Rahner, J. Power Sources, 54 (1995) 428–432.
[3] D. Rahner, S. Machill, K. Siury, M. Kloß and W. Plieth, in V.Z. Barsukov and F. Beck (eds.), New Promising Electrochemical Systems for Rechargeable Batteries, NATO ASI Ser. 3, High Technology, Vol. 6, Kluwers, Dordrecht, 1996, pp 35–61.
[4] S. Machill, Thesis, Dresden University of Technology, 1996.