

Investigations on rechargeable lithium alloys on the basis of Al-Ni and Al-Mn alloys

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Abstract

Different Al-Ni and Al-Mn alloying substrates have been tested by cyclic voltammetry and a.c. impedance measurements in 1 M LiClO₄/propylene carbonate (PC) at room temperature. Small portions of the second metal influence the current efficiency of lithium deposition and dissolution as well as the 'steady-state' process in the measured cyclic voltammograms. The impedance spectra of the different alloys are influenced by the metal and its concentration.

The change in volume due to changes in the morphology of Li-Al and other Li_x-M alloys (M=metal) is the central problem in the development of rechargeable negative electrodes for lithium cycling.

Attempts have been made to avoid this problem by creating 'dimension-stable' alloying electrodes in that way, that (i) small particles of the active phase of Li_xM are embedded in a stabilizing matrix [1, 2] or (ii) composite materials based on carbon are used.

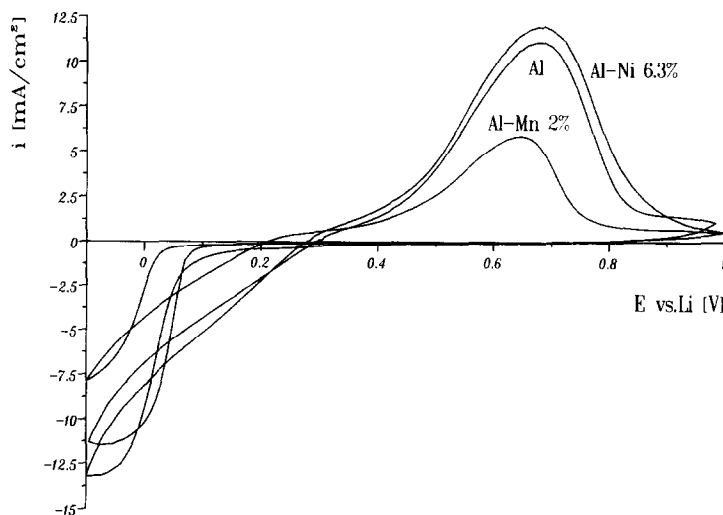


Fig. 1. Cyclic voltammogram of lithium deposition and dissolution on various alloying materials (1 M LiClO₄ in PC, sweep rate 5 mV/s).

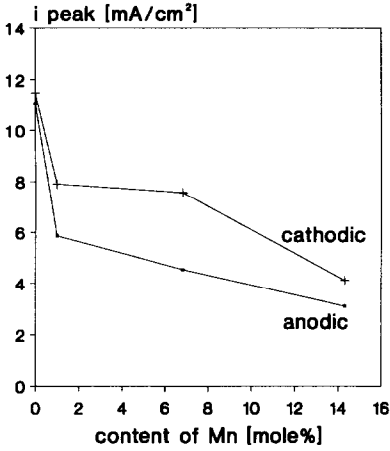


Fig. 2. Anodic and cathodic peak current densities vs. manganese content.

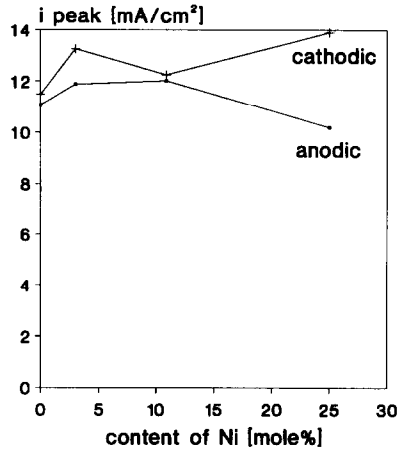


Fig. 3. Anodic and cathodic peak current densities vs. nickel content.

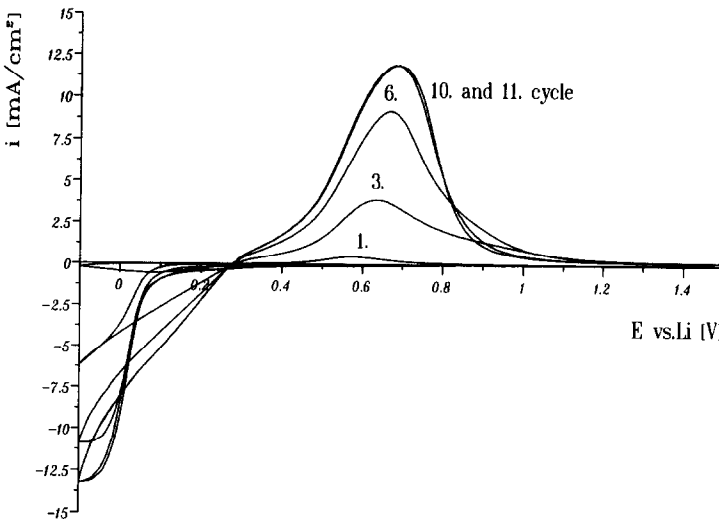


Fig. 4. Cyclic voltammogram of lithium deposition and dissolution on Al-Ni 6.3% vs. cycle number (1 M LiClO₄ in PC, sweep rate 5 mV/s).

An other way is to alloy the host material (in our case Al) with metals M', which are soluble in the base metal or form intermetallic compounds with it, but do not form alloys with Li (Ni, Mn, etc.). In this way one should be able to create an alloy of varying grain size, with stabilizing properties toward 'mechanical stressing' during the charge/discharge process of Li.

The content of metal M' in the alloy was varied in the concentration range between pure Al and 42 mass% (Mn: 2, 13, 25.3%; Ni: 6.3, 21, 42%). The experiments

TABLE 1

Efficiency of lithium cycling versus the alloy composition (sweep rate 5 mV/s, 'steady-state' cycling)

Composition	Al	Al-Mn			Al-Ni		
		2	13	25.3	6.3	21	42
Mass (%)							
Current efficiency (%)	91.5	92.4	85.0	82.4	98.3	92.4	78.8

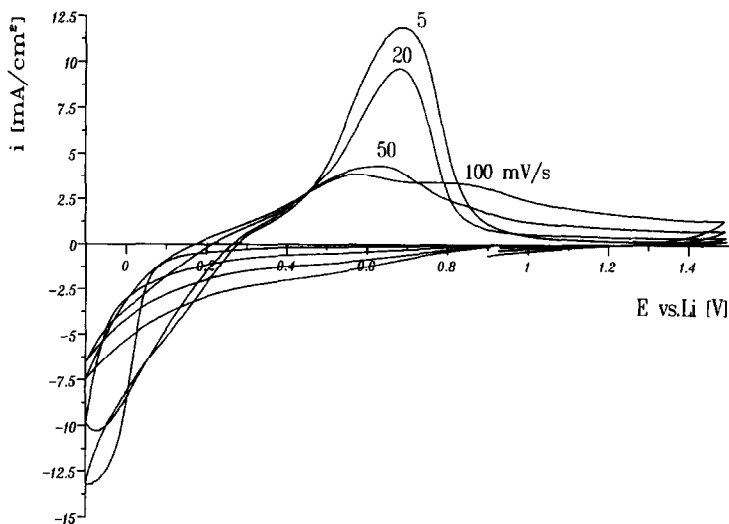


Fig. 5. Cyclic voltammogram of lithium deposition and dissolution on Al-Ni 6.3% vs. sweep rate (1 M LiClO₄ in PC).

have been carried out by a three-electrode technique in a propylene carbonate (PC) solution containing 1 M LiClO₄. An Al-M' alloy of a diameter of 5 mm (surface area: 0.196 cm²) has been used as working electrode. Two Li electrodes have been chosen as a counter and reference electrodes.

The alloying of aluminium by a metal M' does not only influence the mechanical properties but also the electrochemical behaviour. The mobility of Li in different anode materials can be studied by the method of cyclic voltammetry. The cyclic voltammograms are clearly influenced by only small portions of the alloying metal M' (Fig. 1). Manganese decreases the anodic and the cathodic peak current density independent of its content (Fig. 2). In the case of Al-Ni alloys the observed peak current densities differ only slightly from those of pure aluminium (Fig. 3).

Sufficient reproducibility is observed after a certain number of subsequent cycles. The oxide layer on the top of the surface of the alloy has to be changed during cycling and must be 'broken' into a lot of active sites. In order to reach the 'steady state' in the case of Al-Ni about 7 to 10 cycles are necessary, for Al-Mn about 15 to 18 cycles are needed (Fig. 4).

The efficiency of Li cycling expressed as ratio of anodic stripping and cathodic deposition (alloy forming) reaches 92 to 98% in the case of pure aluminium. An

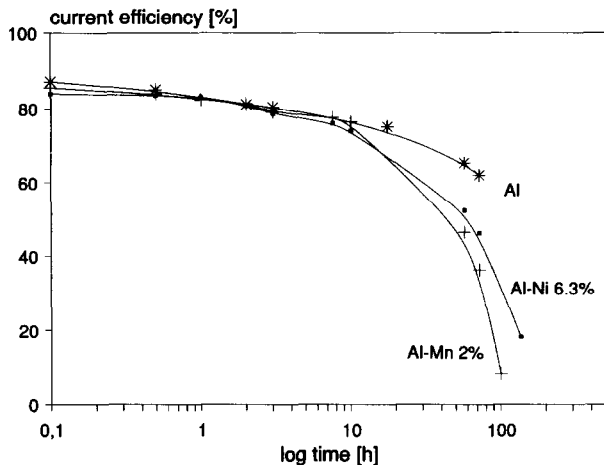


Fig. 6. Current efficiency of galvanostatic lithium deposition and dissolution on various host materials vs. rest time after deposition (1 M LiClO₄ in PC, $|i| = 1 \text{ mA/cm}^2$, 0.3 C/cm^2).

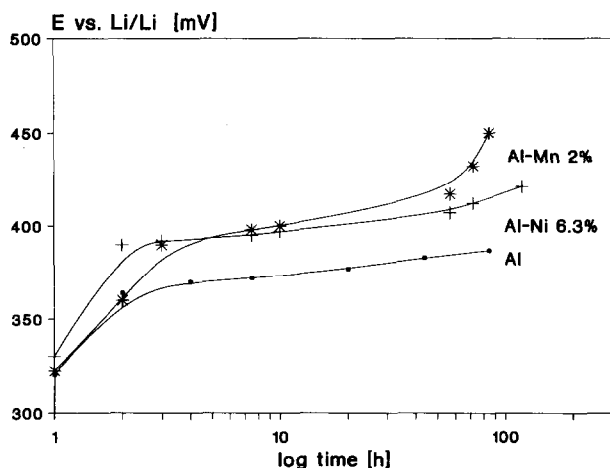


Fig. 7. Rest potential of the host material after galvanostatic lithium deposition (1 M LiClO₄ in PC, $|i| = 1 \text{ mA/cm}^2$, 0.3 C/cm^2) vs. rest time.

increase in the content of the alloying metal M' leads to a rapid decrease in the efficiency of Li cycling. An optimum of cycling and current efficiency was observed only at the composition Al-Ni of 6.3% (Table 1).

The mass transport, during the processes of Li deposition and dissolution, is influenced by the sweep rate, as shown by different peak current densities depending on the sweep rate. In the case of Al and Al-Ni the peak current densities reach a maximum value at sweep rates of about 10 mV/s (Fig. 5).

Contrary to this behaviour, Al-Mn alloys show a subsequent decrease of the peak current density when the sweep rate increases. The cycleability of Li is influenced at least by two processes: (i) the normal corrosion process at the rest potential of the formed Li alloy, and (ii) the self-diffusion process inside the host material. Both

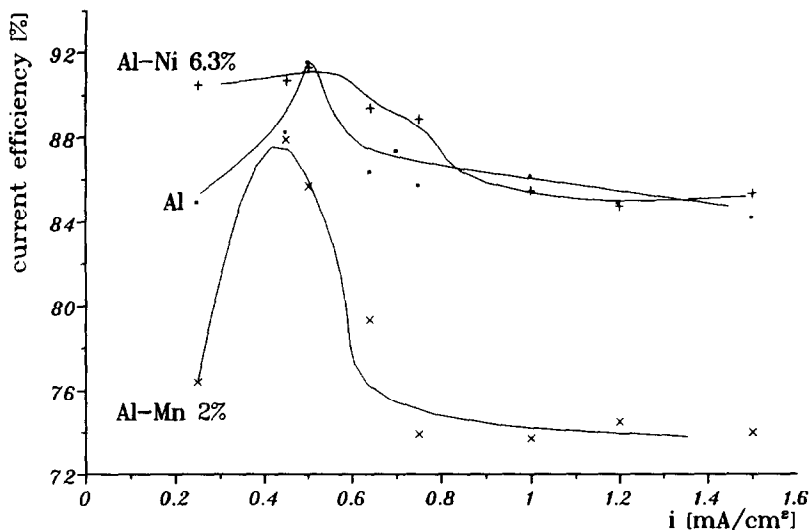


Fig. 8. Current efficiency of galvanostatic lithium deposition and dissolution on various host materials vs. plating and stripping current densities (1 M LiClO₄ in PC, 1 C/cm² lithium deposition).

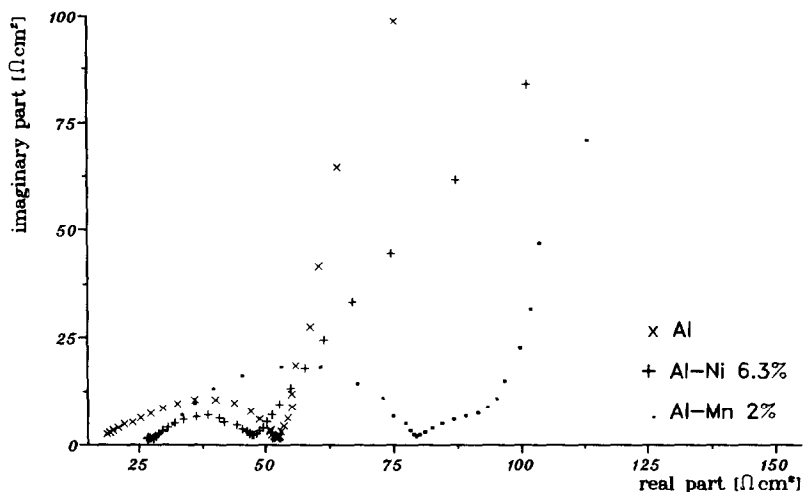


Fig. 9. Impedance spectra of Al, Al-Mn 2% and Al-Ni 6.3% after charging with lithium (0.3 C/cm²) without rest time at the rest potential.

processes are fast enough. Figure 6 shows the current efficiency (cathodic deposition of 0.3 C/cm² Li (-1 mA/cm²) and anodic dissolution (+1 mA/cm²) under galvanostatic conditions up to +1 V in dependence on the rest time between deposition and dissolution. Up to 1 h rest time, 80% of the deposited Li can be dissolved during the anodic cycle. After a rest time above 10 h, it gets more and more complicated to dissolve the deposited Li. The reasons are the normal corrosion process and the self-diffusion inside the Al matrix with a velocity of about 30 pm/s (estimated by X-ray diffraction [3]).

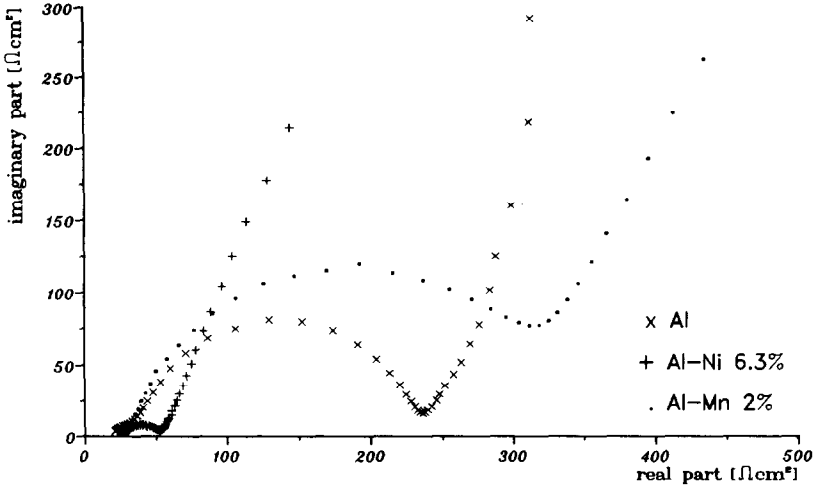


Fig. 10. Impedance spectra of Al, Al-Mn 2% and Al-Ni 6.3% after charging with lithium (0.3 C/cm^2) after a rest time of 44 h at the rest potential.

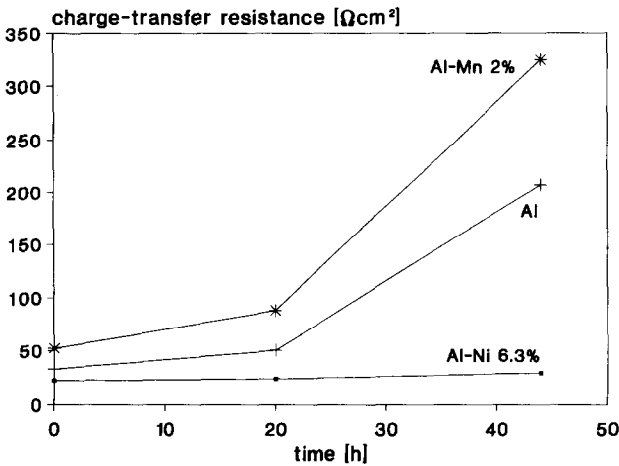


Fig. 11. Charge-transfer resistance of Al, Al-Mn 2% and Al-Ni 6.3% after charging with lithium (0.3 C/cm^2) vs. rest time at the rest potential.

The time dependence of the observed rest potential is shown in Fig. 7. Immediately after cathodic deposition, the equilibrium potential corresponds to a value of about 320 to 330 mV which is referred to as the β -phase [4]. After 2 to 5 h rest time the corrosion process and the self-diffusion process inside the host material lead to a decrease in current efficiency and an increase in the rest potential.

Therefore, during subsequent cycling the current efficiency of the deposition/dissolution process will lead to an 'optimum' cycling current density of about 0.5 mA/cm² at a current efficiency of 85 to 92% depending on the alloy composition (Fig. 8). Cycling at higher current densities lowers the current efficiency.

The relative constant rest potential during the time period (5 to 80 h) leads to the conclusion, that the chemical composition at the surface itself seems to be unchanged. According to impedance data the charge-transfer process and the diffusion process are influenced during this rest time (Figs. 9–11).

A depressed semicircle was obtained in the high frequency range corresponding to the charge-transfer process at the electrode surface. The charge-transfer resistance R_t is time dependent (Fig. 11), but the Al–Ni 6.3% system shows the lowest value. This confirms the results of the cyclic voltammogram experiments. The low frequency behaviour shows purely capacitive behaviour at the beginning of the rest period (Fig. 9). After prolonged wet standing the diffusion process is more and more apparent (Fig. 10).

References

- 1 J. O. Besenhard, M. Heß and P. Kommenda, *Solid State Ionics*, 40/41 (1990) 525.
- 2 B. A. Boukamp, G. C. Lesh and R. A. Huggins, *J. Electrochem. Soc.*, 128 (1981) 725.
- 3 U. Böttcher, *Thesis*, Dresden University of Technology, in preparation.
- 4 R. D. Armstrong, O. R. Brown, R. P. Ram and C. D. Tuck, *J. Power Sources*, 28 (1989) 259–267.