AGEING OF RECHARGEABLE LITHIUM BATTERIES

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Summary

Ageing of secondary lithium button cells is reported for two cases: cycling and storage. In respect of cycling, 120 deep cycles have been achieved with LiAl/dioxolane − $LiClO_4$/$NiPS_3$ cells; the rate of ageing is related to both the charge cut-off potential and the nature of the cathodic material. After storage at room temperature for one year to nineteen months, fresh or cycled cells perform very well: they show only a low self-discharge (between 0 and 16%), and no noticeable ageing, so that the full capacity can be recovered in the following cycles.

Introduction

Ageing is a vague term used to describe a permanent loss of capacity occurring when cells are subjected to various treatments (cycling, storage, overcharge, overdischarge, etc. . .), different from self-discharge which is a temporary loss of capacity. Very low ageing and self-discharge after storage are paramount advantages of primary lithium cells. As far as we are aware, however, few results of ageing and self-discharge after storage are available on secondary cells, though Abraham reports a low self-discharge of Li/TiS_2 cells after 15 days at 90 °C [1]. The problem of ageing after cycling has been investigated more extensively, but conclusions are not complete. Except for the numerous cases of short-circuiting, death after cycling of cells with a cathodic intercalation material such as TiS_2 generally occurs by a slow decrease of the cathodic capacity. The major cause of declining cathode performance is ascribed to changes in electrode structure, which does not show ideal elastic behaviour due to the use of non-optimized electrode structures [1]. Further limitations appearing after optimization of the structure are not considered.

In this paper we report the effect of two causes of ageing on LiAl/$NiPS_3$ secondary cells: continuous deep cycling, and storage. Self-discharge after long-time storage has also been investigated and preliminary results are presented. Ageing of $NiPS_3$ button cells after cycling is compared with that of cells containing a new cathodic oxide material. The origin of ageing is discussed.

Experimental

The cells under investigation were flat, sealed button cells, 20 mm in diameter and 2 mm thick, and have been described elsewhere [2]. The anode was constructed by pressing lithium–aluminium alloy (50–50 at.%) powder (Lithium Corporation of America); there is an excess of negative capacity. The porosity of the electrodes and separator contained about 150 μl of the electrolyte dioxolane — 2M LiClO$_4$. The positive electrodes were constructed by Teflon bonding a mixture of active material and graphite.

Two positive intercalation materials were used: NiPS$_3$ and MO$_x$; this latter is a new variety of metallic oxide; the theoretical capacities of the positive electrodes were between 11 and 12.5 mA h per mole of lithium ions inserted. The cycling properties of NiPS$_3$ in excess electrolyte test cells have been reported previously [2].

(i) Ageing during continuous cycling

The use of LiAl alloy instead of pure lithium as a negative material avoids, in most cases, the dentritic growth of lithium during charge periods. Under optimal conditions, the cycle life of LiAl/NiPS$_3$ button cells, to a capacity fade of 50% of initial capacity, is at present 120 deep cycles. Figure 1 shows a typical example of cathode utilization in LiAl/NiPS$_3$ cells during extended cycle testing at a 1 mA cm^{-2} current density. These cells with a limited amount of electrolyte show a slow capacity decrease until death instead of short circuiting. *Post-mortem* examinations point out that death always arises from drying of the electrodes, and that cycled cathodes still have a very good mechanical resistance.

In order to determine the origin of ageing, complex plane impedance spectra of button cells have been recorded with a frequency response analyzer. The spectra depicted in Fig. 2 show two salient features:
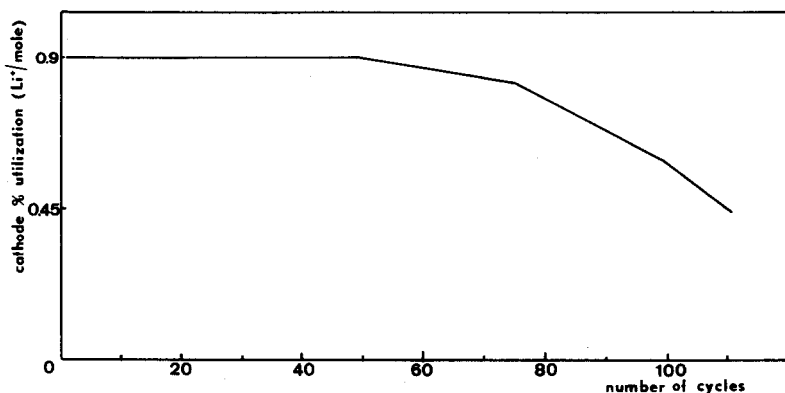

Fig. 1. Typical cycling performances of LiAl/NiPS$_3$ button cells ($i_d = i_c = 1$ mA cm^{-2}); cells cycled between voltage limits 1.0 V and 2.3 V.
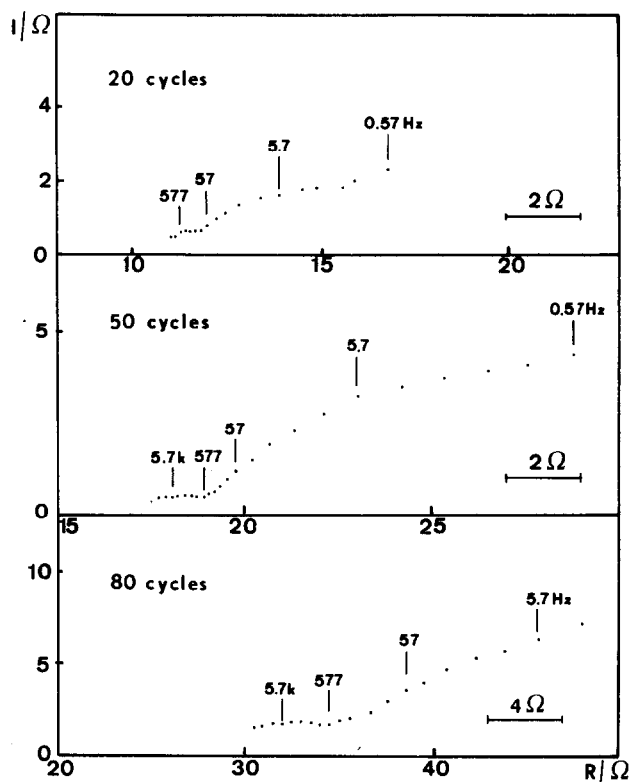
Fig. 2. Ageing of an LiAl/NiPS$_3$ button cell: increase of the complex plane impedance on cycling.

(a) a continuous increase in the electrolyte resistivity, which at 80 cycles is three times the resistivity at 20 cycles.

(b) an increase in the low frequency charge transfer resistance (ascribed to the positive limiting electrode) of the same magnitude. This increase, too, is continuous from the beginning of cycle life.

Re-use of cycled cathodes in fresh button cells provides an additional cycle life of at least fifty cycles until the next failure by drying. Therefore, the increase in the charge transfer resistance at the positive electrode/electrolyte interface does not result from ageing of the positive material itself but stems only from drying of the electrode. A possible degradation of the electrode structure is not responsible for the failure, as in the case of TiS$_2$ mentioned above [1].

As shown in Figs. 3 and 4, the ageing rate is symbatically related to the charge cut-off potential. Drying of cells is related to solvent oxidation leading to solid by-products. This degradation is not a rapid polymerization but a reaction occurring during each charge period. Although a noticeable degradation occurs with an NiPS$_3$ cathode even at 2.8 V vs. Li/Li$^+$ — degradation
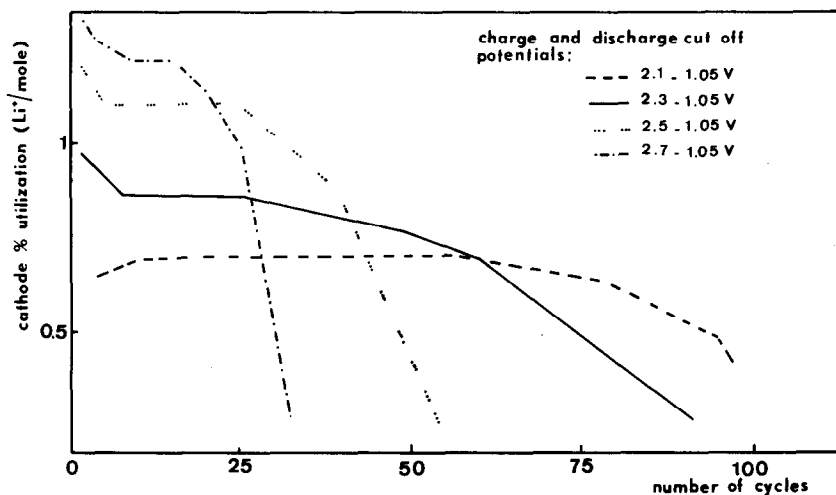
cathode % utilization (Li⁺/mole)

charge and discharge cut off
potentials:

- - - 2.1 - 1.05 V
——— 2.3 - 1.05 V
... .. 2.5 - 1.05 V
.-.-. 2.7 - 1.05 V

number of cycles

Fig. 3. Effect of charge cut-off potential on the rate of ageing of LiAl/NiPS$_3$ cells (i_d = i_c = 1 mA cm^{-2}); cells cycled down to 1.05 V; cathodic capacity 10 mA h/Li$^+$ intercalated.
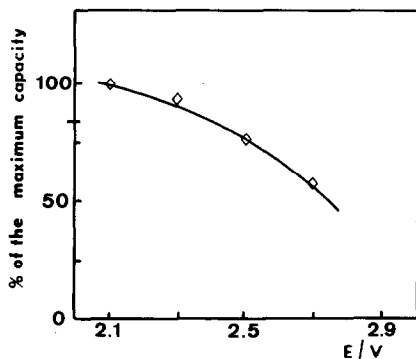
% of the maximum capacity

E / V

Fig. 4. Effect of an increase of the charge cut-off potential on the cumulative capacity delivered by LiAl/NiPS$_3$ cells. The cumulative capacity is the sum of the capacities delivered until a fade of 50%.

emphasized by the low amount of electrolyte — dioxolane has been assumed to be stable up to 3.4 V $vs.$ Li/Li$^+$ [3].

That is why we have studied the oxidation of dioxolane–LiClO$_4$ electrolyte on two different cathodic materials, NiPS$_3$ and MO$_x$. The current/potential curves of the electrolyte on these materials are reported in Figs. 5 and 6. These curves establish the part played by the positive material in the solvent oxidation. The oxidation curves on the two cathodic materials show that oxidation beyond 4 V $vs.$ Li/Li$^+$ leads to an irreversible polymer deposit covering the electrodes and prevents insertion of Li$^+$ during the following reduction step. The main difference is seen at low oxidation potentials: in the case of NiPS$_3$, oxidation is noticeable as early as 2.75 V $vs.$ Li/Li$^+$ ($i.e.$,
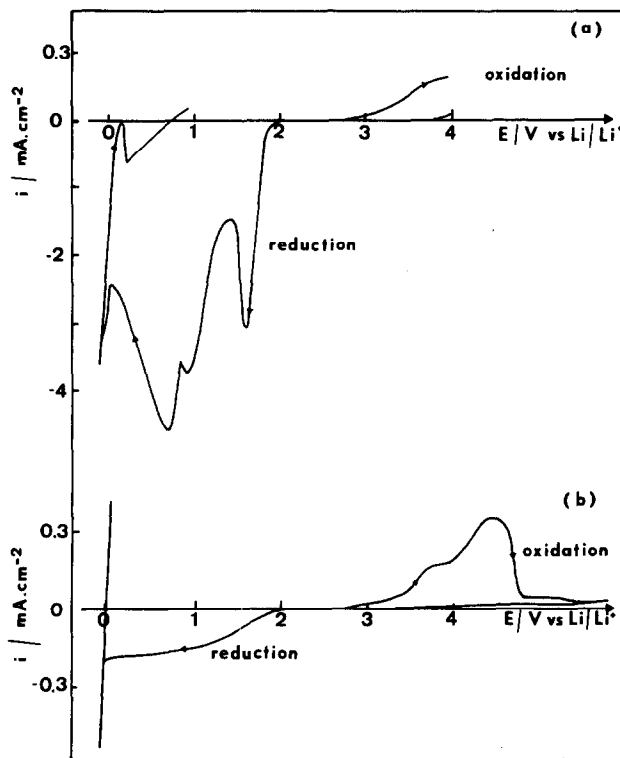
Fig. 5. Current/potential curve showing the oxidation behaviour of dioxolane–2M $LiClO_4$ electrolyte on a thin electrode of $NiPS_3$ on a nickel sinter, and subsequent reduction down to lithium deposition. First scan oxidation up to: (a) 4.0 V, (b) > 5V $vs.$ Li/Li^+ reference. Scan rate: 0.1 mV s^{-1}.

2.4 V $vs.$ $LiAl/Li^+$); in the case of MO_x, the oxidation potential is increased beyond 3 V, to about 3.1 - 3.2 V, and the beginning of oxidation is steep. This analytical result is consistent with the cycling result of MO_x cathodic material in button cells: though the reversibility of this material is not very good, 75 cycles have been carried out without degradation, with a charge cut-off potential of 3.0 V $vs.$ $LiAl/Li^+$ (Fig. 7).

Two conclusions can be drawn from these results:

— with certain cathodic materials, dioxolane can be used up to a rather high charge potential;

— there cannot be any absolute choice of electrolyte: the two components, cathodic material/solvent, must be defined together in order to obtain the best cycling results. The degree of solvent oxidation can be increased or diminished by interaction with the cathodic material. Continuing research will provide a better understanding of the principles of interaction.
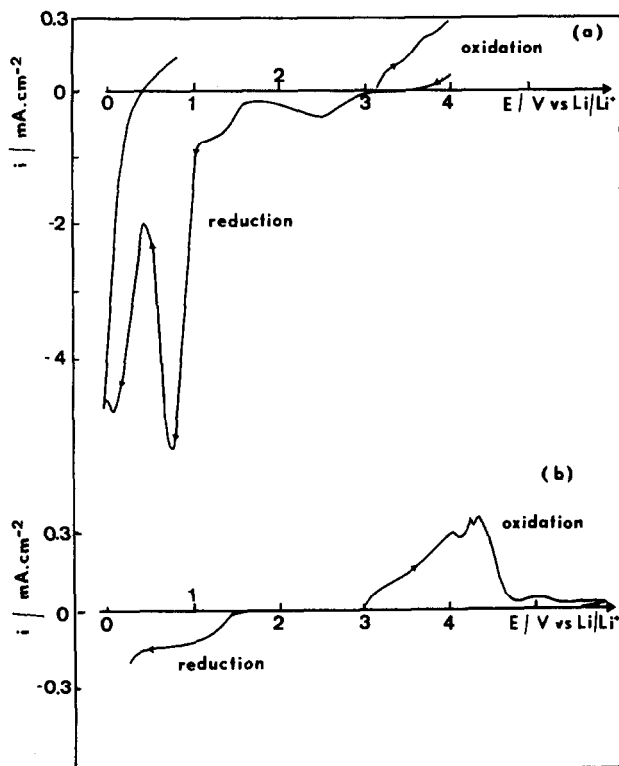
Fig. 6. Current/potential curve showing the oxidation behaviour of dioxolane–2M LiClO$_4$ electrolyte on a thin layer of MO$_x$ on a nickel sinter, and subsequent reduction down to lithium deposition. First scan oxidation up to: (a) 4.0 V, (b) > 5 V *vs*. Li/Li$^+$ reference. Scan rate: 0.1 mV s^{-1}.
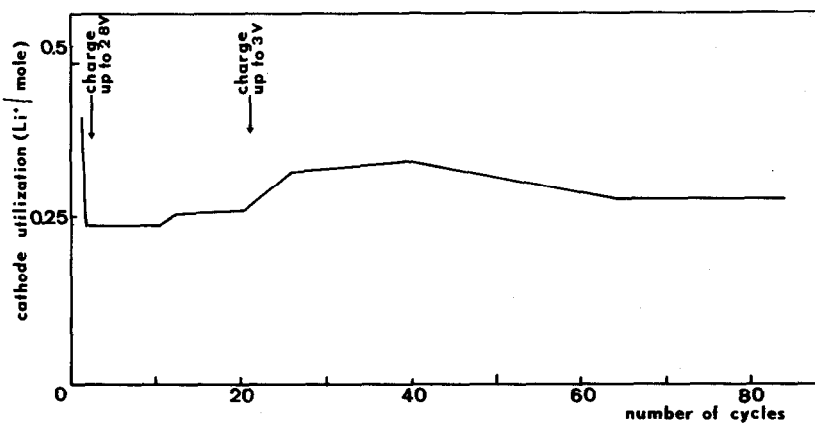

Fig. 7. Plot of cathode utilization (Li$^+$ intercalated per mole of MO$_x$) *vs*. cycle number for LiAl/MO$_x$ cell. Current density 0.5 mA cm^{-2}. Voltage limits were 1.8 V for discharge and 2.8 V and 3.0 V for charge.

TABLE 1

Ageing and self-discharge of LiAl/NiPS$_3$ button cells after storage at room temperature

Number of cells	Storage time (months)	Self-discharge (%)	Ageing (a negative value means an increase in capacity) (%)
4	19	3	0
4	17	16	−2
6	12	no measurement	−9

2. Ageing after storage

Three groups of LiAl/NiPS$_3$ button cells were stored at room temperature for one year to nineteen months, at different stages in their life, to test ageing after storage and to investigate , initially, self-discharge. The first two series, each of four button cells, were stored after, respectively, fifteen and two deep cycles. Six cells were stored in the charged state (up to 2.1 V in the first series, up to 2.3 V in the second); the two remaining cells were stored in the discharged state. The storage time of these two groups was, respectively, nineteen and seventeen months. The third series of six cells was stored in the charged state after two deep cycles and one hundred cycles of 1 mA h at low current density. The time of storage was one year.

After storage, the three groups were discharged to calculate self-discharge, and cycled for at least a few cycles to measure ageing. The results are given in Table 1. Self-discharge was low, and there is no ageing, since the majority of cells has improved their capacity.

The higher self-discharge of the second group of cells may come from the higher rest potential of those cells which were stored after charge to 2.3 V instead of 2.1 V for the first group. At present, this interpretation is only an hypothesis and requires further experiments for confirmation. By contrast, it is possible to accept that the increase of capacity in the following cycles is due to an electrode forming process: this increase did not occur in cells stored after fifteen deep cycles, and was large in the third group. In this group, measurement of ageing took place by comparison with the second cycle, and the cells were formed by the 100 shallow cycles of their cycling period.

Has the storage an effect on the cycle life? A definitive response cannot be given at present. After a few control cycles, some cells have been kept for further storage. Two others are presently being cycled to destruction. They have reached fifty cycles and are still on test.

Conclusion

With the very interesting performances obtained after storage and the low self-discharge results, many of the most critical factors have been

proved, on a laboratory scale, for these lithium secondary cells. The capacity for oxidation of the solvent, which is the actual limitation in deep cycling, does not appear as a shortcoming in storage.

Acknowledgement

References

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