

More details on the new LiMnO_2 rechargeable battery technology developed at Tadiran

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Abstract

This paper describes the performance of LiMnO_2 rechargeable AA batteries developed at Tadiran. The advancement, achieved recently in this technology in terms of cycle life, capacity, energy density, low-temperature performance and high discharge currents, is presented. In spite of the use of lithium metal as the anode and liquid electrolyte solutions, these cells are considered safe due to their internal safety mechanisms based on polymerization of the solvent 1,3-dioxolane, in abuse cases © 1997 Elsevier Science S.A.

Keywords: Lithium rechargeable batteries; Cycle performances, Energy density

1. Introduction

During the past years, the major trends in the R&D of rechargeable lithium battery systems have been devoted to Li-ion 'rocking chair'-type cells and solid-state batteries containing polymeric electrolyte. It appears, however, that development and commercialization of rechargeable batteries based on Li metal anodes and liquid electrolyte solutions have lessened in importance due to the possible safety and cycle-life problems of such systems. However, Li metal batteries may have some unique advantages such as high energy and power densities, a flat discharge profile (stable operating voltage) and excellent low temperature performance.

Over the past years Tadiran has developed a rechargeable 3 V Li battery based on an Li metal anode, a Li_xMnO_2 cathode and liquid electrolyte solutions. As has already been presented [1,2], the key features of this technology are internal safety mechanisms which shut down the cell in abuse cases such as short circuit, heating above a certain temperature and overcharge. In addition, these cells have an extended cycle life of hundreds of cycles at 100% depth-of-discharge (DOD). The electrolyte solution was chosen on the basis of extensive studies on the correlation between the performance of Li anodes, their morphology and surface chemistry in a large matrix of solvents, salts and additives. This paper aims

at providing new information on the advance and performance of this technology due to recent R&D efforts.

2. Experimental

The experimental aspects of this work is described in previous publications [1,2]. In brief, standard AA cells were prepared using a Li foil anode, a polypropylene separator and an LiMn_3O_6 cathode (3 V versus Li/Li^+) prepared according to known procedures [3]. The cells were loaded with solutions of LiAsF_6 in 1,3-dioxolane stabilized with tributylamine. The initial capacity of these cells was about 800 mA/h and it stabilizes between 750 and 700 mA upon cycling.

Cycling of these cells in different regimes was performed using a computerized multichannel battery charger (Tadiran). These cells passed several safety tests including heating to 150 °C, external and internal short circuit, overcharge and crashing. Temperature, voltage and cell resistance were measured during these tests, as already reported [1,2] and shown further in this paper.

3. Results and discussion

Fig. 1 shows the typical discharge and charge profiles and the relevant major cell reaction when operating these cells in

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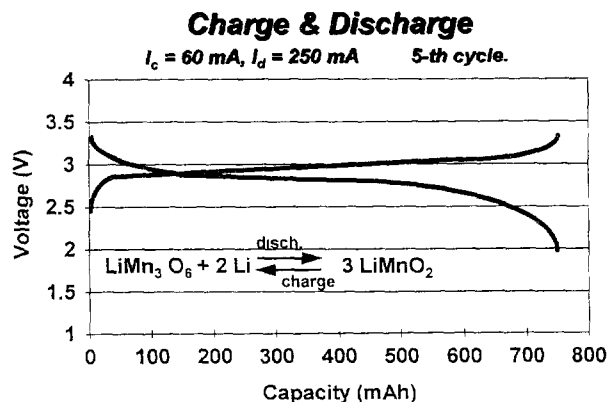


Fig. 1 Typical discharge/charge curves of the Tadiran LiMnO₂ rechargeable AA cells and the major cell reaction. $I_{\text{charge}} = 60 \text{ mA}$, and $I_{\text{discharge}} = 250 \text{ mA}$

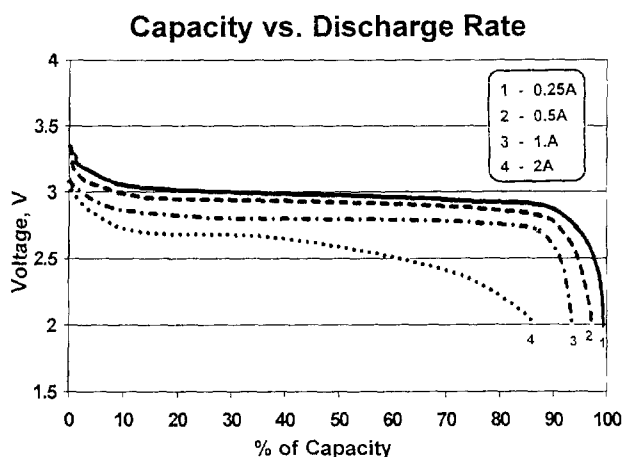


Fig. 2 Typical discharge curves vs. capacity at different currents

the 2–3.4 V voltage domain. About 750–700 mAh per AA cell could be reached as well as hundreds of 100% DOD cycles. By applying the 2–4 V domain, the capacity can increase up to 950 mAh, but cycle life deteriorates due to irreversible structural changes of the cathode.

Fig. 2 shows typical discharge curves of these cells at different currents. As demonstrated, even at high currents of about 2 A, most of the capacity is reversed. The cycle life as described later, is not detrimentally affected by applying different discharge currents up to 500 mA. Discharging these cells at higher currents may cause a deterioration in cycle life.

Fig. 3 presents a typical dependence of the discharge currents of these cells on the operation temperature. As expected, the capacity decreases at low temperatures due to an increase in the internal resistance of the battery. However, this decrease is reversible and cells operated at low temperatures return to their full capacity at room temperature.

The fact that these cells can operate at such low temperatures as -30°C is a great advantage of these batteries.

During the development of these cells further optimization was made in the electrolyte composition (the amount of the

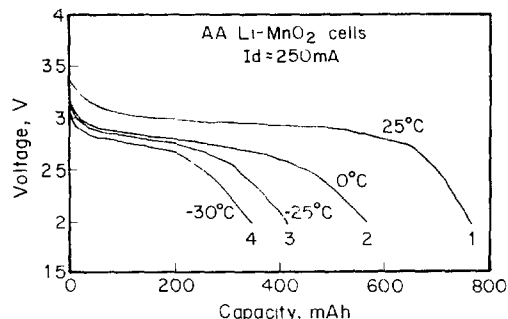


Fig. 3. Discharging curves vs. temperature.

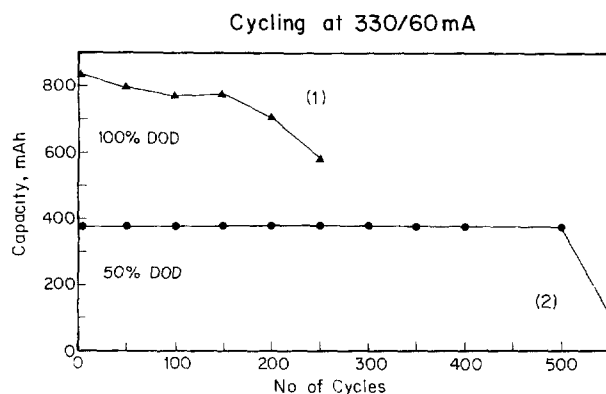


Fig. 4 Typical cycle life behavior of cells from earlier series at 100% and 50% DOD, $I_{\text{discharge}} = 330 \text{ mA}$, and $I_{\text{charge}} = 60 \text{ mA}$.

salt and the stabilizer) and the electrodes' geometry and packing within the cells.

Fig. 4 provides the typical cycling behavior of the cells of the first series. At least 250 cycles at 100% DOD could be reached before the capacity dropped to about 65% of its initial value, when the discharging current was in the range of 100–500 mA and the charging current was around 60 mA. Also, at least 500 cycles at 50% DOD could be obtained from cells of the first series developed, as shown in Fig. 4.

We opened the cells after a different number of cycles in a glove box under argon atmosphere and analyzed the various cell components.

It was found that the cathode remains very close to its initial structure and composition even after prolonged cycling.

Observing Li anodes of cells after prolonged cycling at the above regimes (relatively slow charging), they looked slightly corroded and covered with solution reduction products such as Li alkoxides, LiF and Li₃AsF₆ species [4,5]. However, a great part of the anodic material was connected together, metallic, uniform and dendrite free. This is in agreement with the very smooth morphology of Li deposition in 1,3-dioxolane solutions observed in laboratory tests [4,5]. Thus, the reason for the deterioration of the capacity upon prolonged cycling as shown in Fig. 4 is not because of a massive degradation of the electrodes but rather due to a

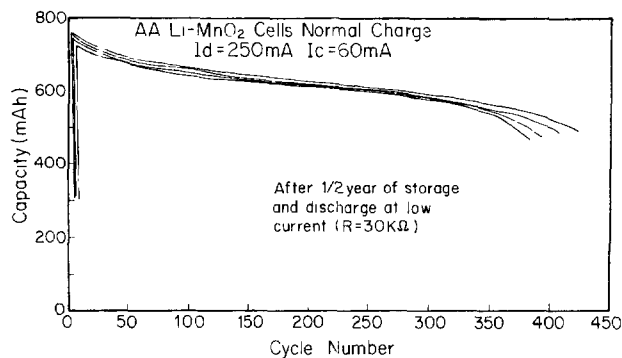


Fig. 5 A typical cycle life behavior of four different AA cells of the present series: DOD = 100%. $I_{\text{discharge}} = 250$ mA, $I_{\text{charge}} = 60$ mA. These cells were stored for six months at 25 °C while being discharged slowly via a resistor of 30 kΩ before cycling

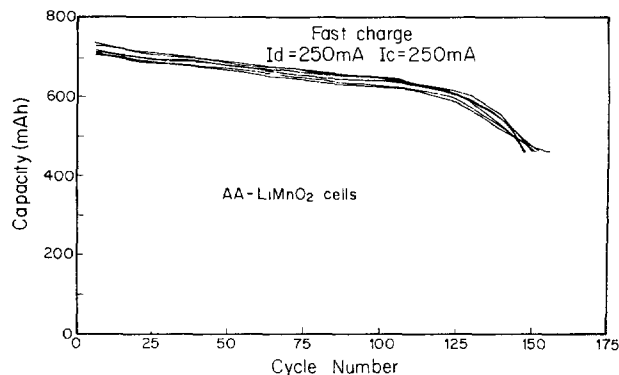


Fig. 6 Typical cycle life behavior of six different cells at fast charging; DOD = 100%. $I_{\text{discharge}} = I_{\text{charge}} = 250$ mA.

partial consumption of the solution components due to their surface reactions on the lithium.

Upon charging these batteries faster as $C/2$ – $C/3$ rate 250 mA per AA cell the cycling life decreases to about 100–150 cycles at 100% DOD. However, operating these cells at fast charging currents as 250 mA, $C/2$ – $C/3$ rate and at low DOD, many hundreds of cycles could be obtained. This may be very important because in many applications the cells are recharged before they are used to their full capacity. Thus, at these modes of operation, these cells can be discharged/charged hundreds of times in spite of the fast charging currents.

The current version of these batteries, however, may be cycled up to 400 times at 100% DOD when charged at low current (60 mA, $C/10$ – $C/12$ rate).

Fig. 5 presents typical curves of capacity versus cycle number for these batteries after being stored for half a year at room temperature while discharged slowly (shorted by a 30 kΩ resistor). The behavior of four different cells is presented in this figure.

Typical cycle life curves of cells from a recent series at fast charging (250 mA, $C/2$ – $C/3$ rate) is shown in Fig. 6 for six different batteries. As demonstrated, at least 150 cycles at about 100% DOD could be obtained before cycling was stopped when the capacity dropped to about 65% of its initial value.

The above results seem to demonstrate that the capacity, energy density and cycle life of these cells make them quite an attractive product for several applications such as mobile electronic equipment.

We attribute the high cycle life obtained in these cells to the very smooth morphology of Li deposition in 1,3-dioxolane– LiAsF_6 solutions as already reported [4,5]. The surface films formed on Li in these solutions which comprise Li alkoxides of the $\text{CH}_3\text{CH}_2\text{OCH}_2\text{OLi}$ type, Li formate, probably oligomers of dioxolane (poly DN) with OLi edge

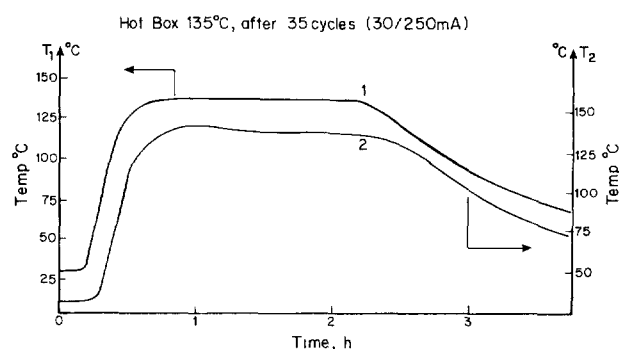


Fig. 7 The temperature measured outside the can of two batteries stored for 2 h in an oven at 135 °C after being cycled 35 times; 100% DOD. $I_{\text{discharge}} = 30$ mA, $I_{\text{charge}} = 250$ mA). (1) and (2) refer to two different batteries.

groups, LiF and Li_xAsF_y (salt reduction products) induce very smooth and uniform Li deposition. The spirally wound configuration leads to a moderate pressure of the separator on the Li anode which reduces further possible dendrite formation upon charging (Li deposition). Thereby, the corrosion of the Li anode in the cell is relatively low as well as the possibility for shorts by dendrites through the separator which also does not seem to occur.

In any event, a major consideration for Li metal–liquid electrolyte rechargeable battery obviously relates to safety. As already reported [1,2], these batteries have an internal safety mechanism which avoids their explosion upon short circuit, overcharge and heating up to 130 °C. Fig. 7 shows a typical behavior of these cells in an oven at elevated temperatures.

Two cells after 35 charge/discharge cycles were stored for about 2 h in an oven at 135 °C and their external temperature outside the can was measured. After 2 h they were taken out from the oven and were allowed to cool.

In contrast to reports on obvious thermal runaway of Li metal–liquid electrolyte secondary cells when heated above 100 °C [6], these cells do not show any thermal runaway even when heated up to 135 °C as demonstrated in Fig. 7.

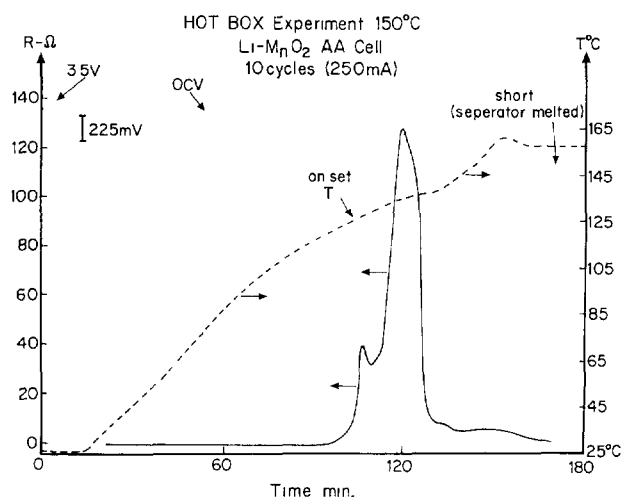


Fig. 8 Temperature, internal resistance and open-circuit voltage of a cell stored in an oven at 150 °C after being cycled 10 times at $I_{\text{charge}} = I_{\text{discharge}} = 250 \text{ mA}$

Fig. 8 presents results of a typical experiment in which a cell after cycling (10 cycles at $I = 250 \text{ mA}$) was stored in an oven at 150 °C while its external temperature, internal resistance and voltage are measured continuously.

It should be emphasized that these cells are not designed to be safe up to 150 °C although most of the cells tested at 150 °C remained stable. During these tests we recorded a few cases in which the pressure developed in cells heated to 150 °C led to an opening of their safety vent.

The highest temperature of stability of these batteries that can be guaranteed seems to be 130 °C. However, the results presented in Fig. 8 for storage at 150 °C are important and demonstrate the safety mechanism of these cells as discussed earlier [2]. In brief, the system including the solvent, salt stabilizer and electrodes is basically stable up to 120–125 °C. As was proven [2], the lithium anode is efficiently passivated up to this temperature in DN–LiAsF₆–TBA solutions.

Above this temperature, a ‘red–ox’ reaction between the solvent and the salt is initiated and produces HF which readily polymerizes the solvent. This polymerization decreases considerably the reaction of the solvent with the other cell components and increases the internal resistance of the cell. Hence, a thermal runaway of these cells due to reaction between the solvent, salt and Li anode is avoided. The temperature and internal resistance changes as shown in Fig. 8 are well explained by the above mechanism. Indeed at the onset temperature around 125 °C this internal resistance suddenly increases up to several orders of magnitude higher than its initial value (less than 0.5 Ω) due to polymerization of the solvent. These internal cell reactions indeed do not affect the temperature which rises monotonously mostly due to the heat flow from the oven.

When the oven temperature is kept below 135 °C, the internal resistance of the cell, after the solvent polymerization

took place, remains high. In these experiments where the oven temperature is 150 °C, further reorganization or reactions of the polymerized electrolyte system takes place which reduces the internal resistance to values which are about only one or two orders of magnitude higher than the initial ones.

The reactions of the polymerized electrolyte system at elevated temperature are still being investigated and thus, we still have no precise and clear explanation for the decrease in the internal resistance upon heating to 150 °C shown in Fig. 8. As proven from the open-circuit voltage measurements, continuous heating of these cells at an oven kept at 150 °C may lead to the melting of the separator which shorts the battery. However, as demonstrated in Fig. 8, a thermal runaway of the cell due to this short does not happen even at these extreme conditions because of the above changes in the composition of the electrolyte solution.

When these cells are shorted externally, no matter after how many cycles, they do not explode or open their safety vents. Their temperature rises, as well as their internal resistance, and then they cool down. It should be noted that the higher the number of cycles of the battery before an external short circuit experiment, the lower the maximal temperature measured outside the can.

This behavior is well explained based on the previous work [2] and the data related to Figs. 7 and 8. Shorting the battery causes a considerable heat dissipation due to the high current (up to 30 A) passage. The internal temperature reaches the onset value of 125 °C, then the solvent–salt red–ox reaction starts and initiates polymerization of the solvent which increases remarkably the internal resistance of the cell. This immediately decreases the current. The heat dissipation is thus stopped, the solvent is consumed by the polymerization and becomes inactive and a thermal runaway of the battery is avoided. As already reported [1,2], these batteries also have an internal overcharge protection mechanism based on the fact that the solvent polymerizes at 3.5–4 V (versus Li/Li⁺).

4. Conclusions

This paper seems to demonstrate further the breakthrough obtained in the design and production of high energy density LiMnO₂ rechargeable batteries based on Li metal and liquid electrolyte solutions. Major advantages of these batteries are high energy density, excellent low temperature performance and improved safety features, including overcharge and thermal runaway protection mechanisms. The cycle life obtainable with these batteries is also very high and comparable with that of other secondary battery systems in spite of the use of Li metal as the anode. All these battery advantages

should be attributed to the choice of the combination of 1,3-dioxolane, LiAsF₆, TBA LiMn₃O₆ and Li metal as the cell components.

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