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Performances and safety behaviour of rechargeable AA-size Li/Li_xMnO_2 cell®

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Abstract

An Li/Li_xMnO_2 rechargeable system was developed. The AA cell based on a lithium metal anode and lithiated manganese dioxide cathode, organic electrolyte and polypropylene separator, exhibits excellent performance and safety behaviour. The cell possesses an energy density of 125 to 140 Wh/kg and 280 to 315 Wh/l. An accumulated capacity of about 200 Ah can be achieved under cycling. The system incorporates a chemical mechanism preventing explosion, fire and venting with fire under abuse conditions such as short circuit, overcharge, deep discharge, etc.

Keywords: Rechargeable lithium cells; Manganese dioxide; Safety

1. Introduction

In the last fifteen years considerable efforts has been devoted [1,2] to the development of secondary lithium systems. Although some of the rechargeable systems using Li metal as an anode achieved remarkable electrochemical performances, in sense of capacity and cycling life, the safety issues under abuse condition remained unsatisfactory [3,4].

Various developments compromised the energy density gaining in the safety behaviour in practical implementation. Attempts to solve the safety problem were made by using an inner vent and limiting charge and discharge voltage by electrical devices for each cell in the battery [5].

Another solution to the temperature runaway under short circuit and overcharge was suggested by using a safety separator [6]. This separator is supposed to melt at temperatures lower than the critical temperatures at which deposited Li reacts exothermally with the electrolyte leading to explosion. All these solutions are space and weight consuming and not always effective.

The unsatisfactory results in the Li metal anode technology forced most of the research efforts to be directed to the so-called 'Li-ion' system [7]. This system has improved safety behaviour loosing the advantage of energy density of an Li metal anode.

In this work we developed a new version of AA-size rechargeable cell based on Li/Li_xMnO_2 system overcoming abnormal safety events. The cell possesses energy density of 125 to 140 Wh/kg and 280 to 315 Wh/l. The system incorporates a mechanism preventing explosion, fire and venting with fire under abuse conditions such as short circuit, overcharge, deep discharge, crush etc.

2. Experimental

Jelly rolled standard AA-size cells specified as TLR-7301 were assembled. The anode is Li metal and the cathode is lithiated MnO_2. The separator is a polypropylene porous film. Cathode and separator are wetted by an organic electrolyte.

Charge and discharge experiments were performed in 3.4–2.0 V window. Cycling was terminated when the capacity reached 65% of the capacity at the fifth cycle. Short-circuit experiments were carried out through 0.01 Ω where the current and the temperature were simultaneously recorded. Overcharge and overdischarge experiments were performed by using a 10 V power supplier giving a maximum constant current of 1 A.

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3. Results and discussion

3.1. Electrical performance

The electrical performance of TLR-7301 is shown in Figs. 1 to 3. Cells demonstrate a capacity of 800 to 900 mAh. The active cathode material applied has a specific capacity of 175 to 185 mAh/g in first cycle.

The accumulated capacity delivered during more than 250 cycles at 100% depth-of-discharge of the cathode (Fig. 2) reaches 170–190 Ah, and the FOM achieved is 70–80, FOM is defined as follows:

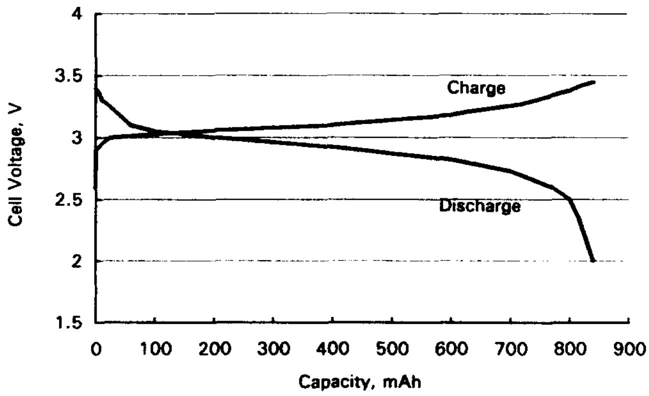

Fig. 1. Charge and discharge curves: I_c = 250 mA and I_d = 250 mA (cycle No. 5).

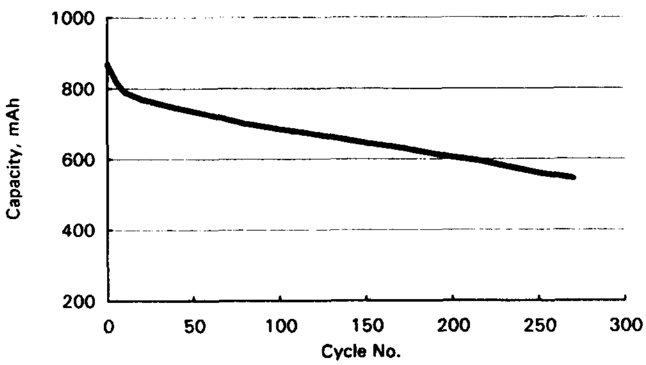

Fig. 2. Capacity vs. cycle number; I_c = 60 mA, and I_d = 250 mA (100% depth-of-discharge).

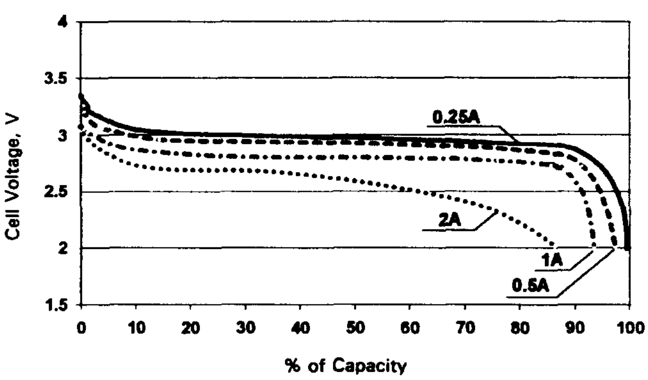

Fig. 3. Capacity vs. discharge rate.

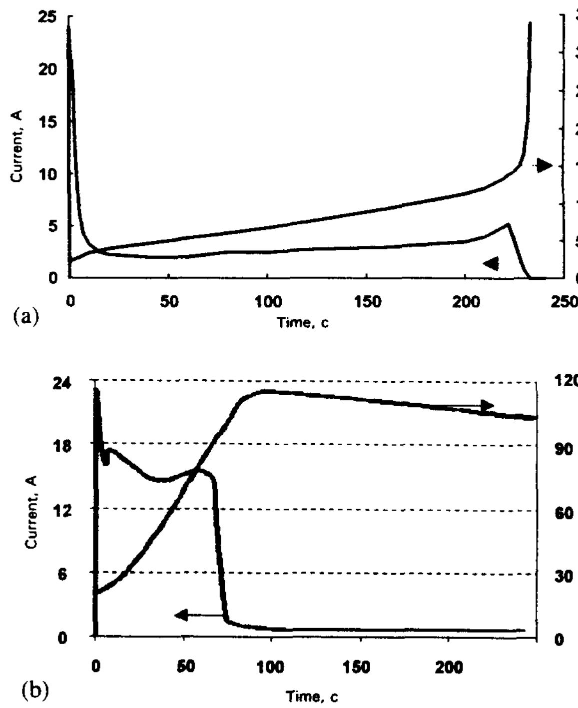

Fig. 4. (a) Short-circuit behaviour of ordinary rechargeable lithium AA-size cell after 50 cycles. (b) Short-circuit behaviour of cell TLR-7301 after 50 cycles.

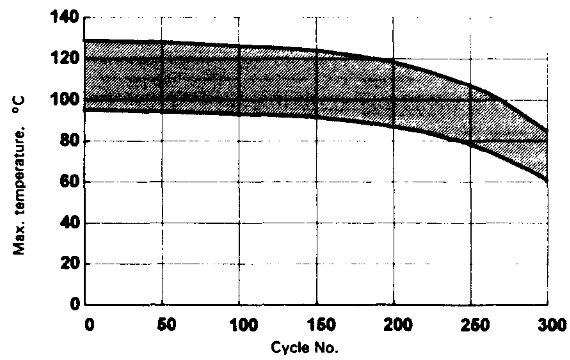

Fig. 5. Short-circuit test. Maximum temperature reached vs. cycle number; distribution of experimental results, AA-size cells.

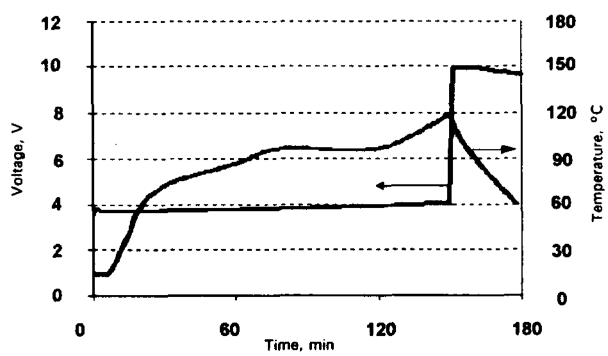

Fig. 6. Overcharge behaviour; high current: 1 A, AA-size cells after 60 cycles.

FOM = $Q_{aq}/Q_{Li} - Q_5 \times 0.65$), where Q_{aq} is the accumulated capacity during cycling, Q_{Li} is the theoretical capacity of the Li anode, and Q_5 is the capacity in the fifth cycle. The cells are able to provide currents as high as 2 A. Fig. 3 shows the discharge curve as a function of the drain rate. As it is shown more than 80% of the capacity is delivered at 2 A.

Satisfactory results were achieved also at low temperatures. Pulses as high as 1.2 A during milliseconds can be obtained at −30 °C under a drop in voltage of 100 mV maximum. The mean value of the current in this experiment was about 100 mA. The capacity of cells at this regime was 50% of the capacity achieved at room temperature at the same regime.

3.2. Safety tests

The TLR-7301 cells were tested for short circuit, overcharge, deep discharge, crush and nail penetration. Dozens of cells were exposed to each of the tests mentioned. No explosion, fire or venting with fire were observed.

In a series of papers [8,9] it was demonstrated that the probability of safety hazards for Li/Li_xMnO_2 and Li/MoS_2 accumulators increases with cycle number. Recently Laman et al. [6] presented data showing that the thermal stability of cells decreases with accumulated capacity and only by using a safety low melting separator the peak temperature at short-circuit experiment could be kept below a critical temperature at which explosion can occur.

The short-circuit test of TLR-7301 (Fig. 4) is presented in comparison to the typical behaviour of previous generation cells. The short circuit of cycled cells is usually characterized by a high peak during the several seconds on the start of shorting (25–30 A) followed by a slow current rise finally causing to temperature runaway (Fig. 4(a)). In the case of TLR-7301, short-circuit current drops abruptly continuing to decrease thanks to the inner mechanism preventing temperature rise.

The conception was that the safety problems are more critical in cells that were exposed to long cycling life. In this work, it was found that the maximum temperature the cell reaches under short circuit decreases as the number of cycles increases (Fig. 5). Inner and outer short circuits were terminated without any undesirable events. Quiet venting was observed in some of the cases, when the temperature rise caused inner pressure, overcame the limit defined by the vent construction.

Fig. 6 shows the behaviour of the cell at overcharge under a constant current of 1000 mA. The maximum temperature measured at the can was 120 °C. At this moment the voltage raised to the cutoff voltage of the charger, which in this case was 10 V. The cell was kept at this voltage about 30 min more. By that time the temperature dropped and the charger was disconnected.

No events were observed also at 300 to 500% overdischarge with a current of 1000 mA. The cells exposed to these tests were not protected by electronic devices and reached in some cases −10 V.

Crush tests to 30% of the outer diameter and nail penetration were performed and no fire, explosion or cell decomposition were observed.

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