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SCIENCE DIRECT®
Journal of Power Sources 129 (2004) 34–37
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

PoLiFlex™, the innovative lithium-polymer battery

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Abstract

The new Varta PoLiFlex™ polymer technology exhibits beside a high rate performance and a very low swelling behaviour under high-temperature storage an excellent safety performance due to the combination of a shut down separator, electrolyte additive and a proprietary treated cathode material.

Keywords: PoLiFlex™; Swelling; Abuse overcharge

1. Introduction

Major improvements and developments with respect to safety of lithium ion batteries and packs such as one-shot fuses, IC+ MOSFET, PTC, shutdown separators [1,2], chemical shuttles [3,4] and modified cathode materials [1,5] have been achieved for use of these cells in portable applications. However, still safety concerns with these batteries under abuse conditions especially the potentially violent reaction of the lithium ion cells at very high temperatures or under extreme overcharge conditions remain as primary challenges of battery manufactures and their customers.

Lithium ion polymer batteries using plasticized electrolytes where a liquid electrolyte is embedded into a porous polymer matrix have been proven to achieve considerable gain in safety comparatively to standard lithium ion batteries. Using this technique Varta microbattery has developed a new generation of thin polymer batteries, PoLiFlex™, superior in performance and safety to lithium ion batteries. The following report highlights some details of this new type of battery.

2. Experimental

PoLiFlex™ batteries are fabricated by use of a polymer electrolyte based on a PVDF-copolymer binder matrix, a graphitized carbon negative electrode material, a high density Lithium cobalt oxide positive electrode material. The cells are packed into a plastic coated aluminium soft pack. Negative and positive electrode fabrication are prepared using proprietary formulations [6]. The charge–discharge regime is between 4.2 and 3.0 V. Cells have been constructed according to Table 1.

3. Results and discussion

3.1. Performance

Fig. 1 shows the discharge curves of the PoLiFlex™ batteries at various discharge rates between 0.2 and 3 C while in Fig. 2 the temperature behaviour under GSM conditions is depicted. PoLiFlex™ batteries offer superior low temperature performance and a good ambient temperature cycle life. The soft pack may be expanded by gas evolution of fully charged cells in case elapsed periods of time at high temperature. Charging to 4.2 V, the PLF 423566 type has been stored at 80 °C for 48 h. However, swelling of the cells during storage has come out to be very low as summarized in Table 2. We assume this excellent low swelling behaviour may be strongly attributed to the use of a particular polymer electrolyte composition which shows improved electrochemical stability towards delithiated lithium cobalt oxide in combination with a proprietary coating of the positive electrode aluminium current collector.

3.2. Safety

One of the most important safety criteria of modern rechargeable lithium cells is the open voltage overcharge behaviour such as 12 V at one or two C-rate in case of failure of the protection circuit module. Fig. 3 shows the thermal

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doi:10.1016/j.powsour.2003.11.009

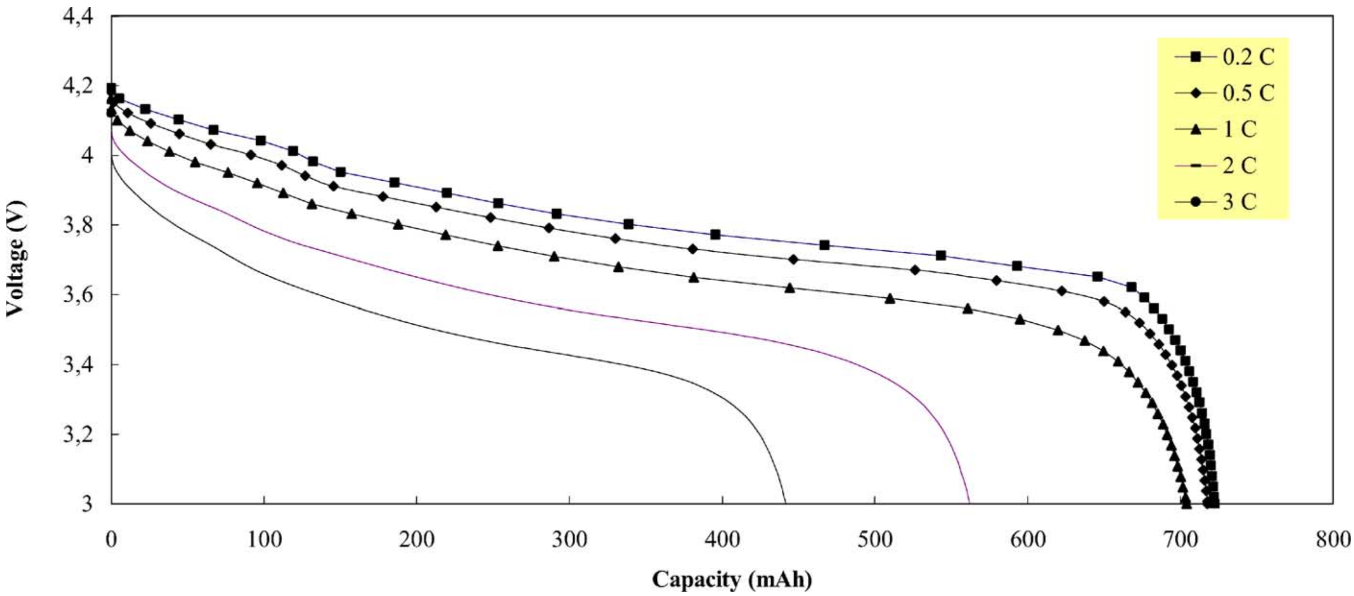

Fig. 1. Rate performance of PLF 383562 PoLiFlex^{TM}.

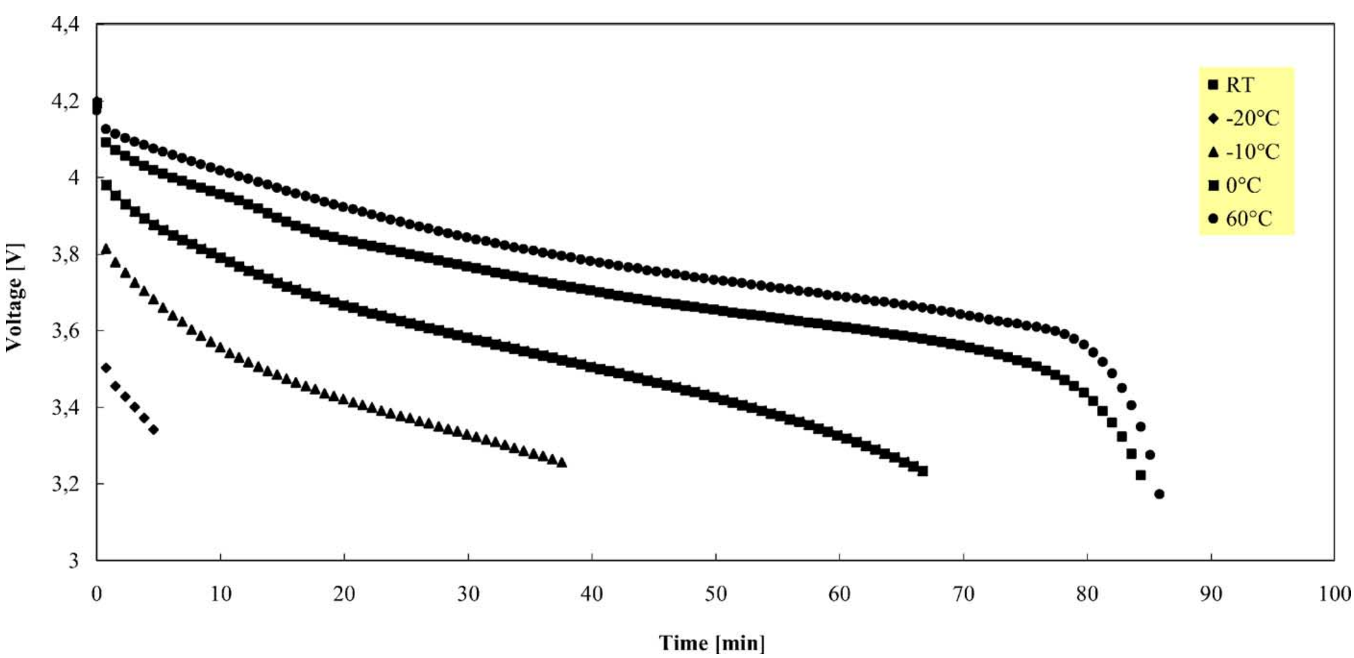

Fig. 2. Temperature dependence of PLF 383562 PoLiFlex^{TM} under GSM profile (2 A at 600 μs–0.25 A at 4 ms).

runaway which is commonly observed in the lithium ion cell under abuse overcharge conditions. The abrupt temperature decrease is due to burn out of the temperature sensing device mounted onto the top of the cell.

For both Li-ion and lithium polymer cells high safety levels can be achieved by changing inherent cell chemistry while preserving other benefits, which will may even led to so called PCM-less cells in the future.

Figs. 4 and 5 show examples of a favourable overcharge cell behaviour. The cell temperature increases as a function

Table 1

Type	Dimension (mm)	Thickness (mm)	Typical capacity at 0.2 C (mAh)
383562	3.8 × 35 × 62	3.8	750
423566	4.2 × 35 × 66	4.2	900

Table 2

PLF 423566	Thickness (mm)
Before test at RT	4.22
After at 24 h (80 °C hot)	4.25
After at 24 h (80 °C cold)	4.23
After at 48 h (80 °C hot)	4.27
After at 48 h (80 °C cold)	4.24

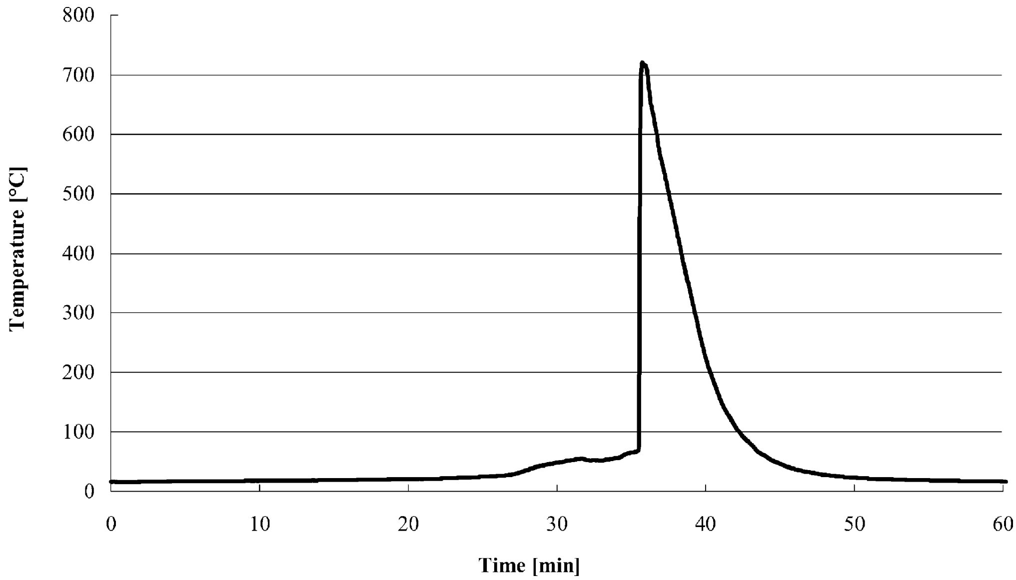

Fig. 3. External skin temperature for 900 mA lithium ion cell overcharged at 900 mA with a 12 V power supply.

of progressing overcharge but when the cell reached about 100 °C in the case of a polyethylene microporous containing shut down separator and in the presence of an overcharge protecting additive in the electrolyte, the current is interrupted and the cell begins to cool down. It has been carried out that the reproducible achievement of this favourable behaviour is quite complex and may be affected by several factors. Generally, the electrolyte additives mostly in use are fluorinated aromatic rings such as trifluorobenzene or difluoroanisole. The idea is that the fluorinated ring is not cracked within the voltage operating regime of the cell but in case of severe overcharge. The pieces of cracked fluorinated rings behave extremely aggressive and are by this suitable to passivate the cathode surface to make the cell highly resistive and by this way to stop the ongoing overcharge current. However, also the choice of the separator material may influence this desirable behaviour. Polyolefine microporous films are generally used as separators in secondary lithium cells. The film is required to have, in addition to such general characteristics of micro-porous films as good mechanical strength and permeability, the so-called fuse effect or shutdown which means when the inside of the battery is overheated the separator is molten to form a continuous film which covers the electrode and breaks the electric current and thus makes the cell safe. The separator must have a high heat resistance, too, because, when the temperature rises very rapidly the inside battery temperature may continue to rise even after the fuse effect has been initiated with the re-

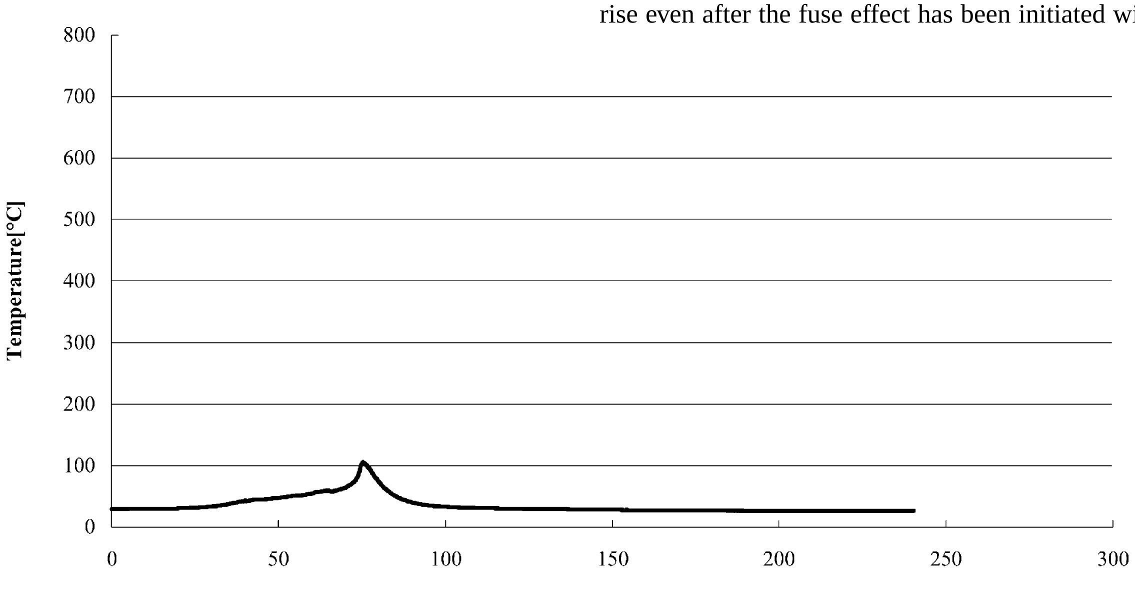

Fig. 4. External skin temperature for PLF 423566 overcharged at 1 C rate with a 12 V power supply with a shut down separator and an additive A.

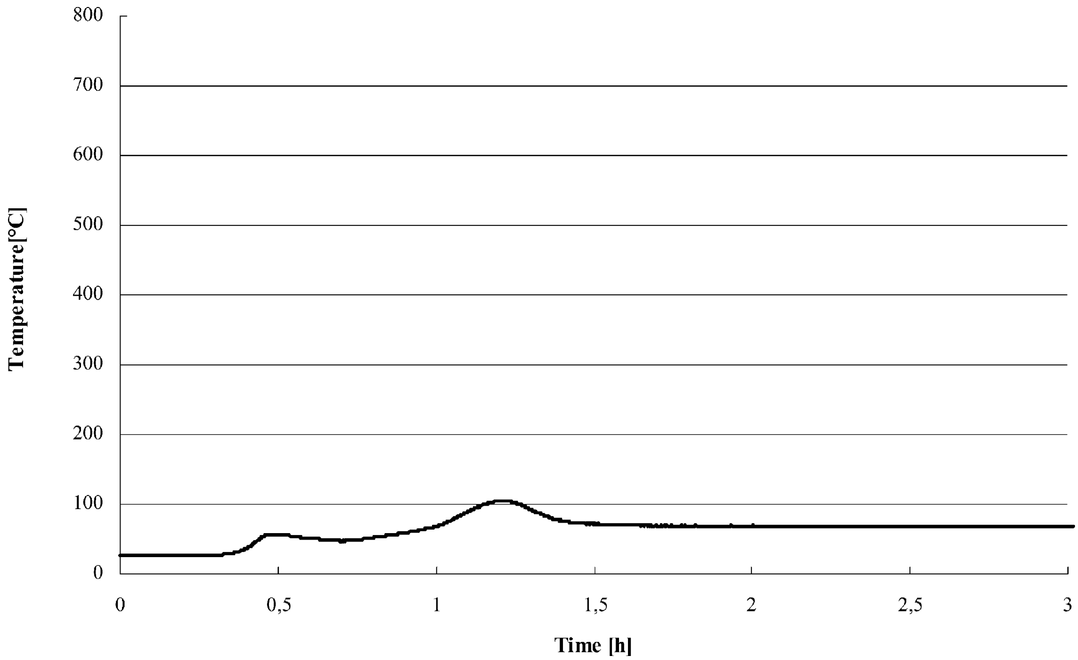

Fig. 5. External skin temperature for PLF 423566 overcharged at 1 C with shut down separator and in the presence of protecting additive B.

sult that sometimes the separator film nevertheless breaks down to cause the return of electric current resulting in internal short-circuit. Another important requirement for the separator is a fast increase of the impedance at the moment of the shutdown in order to cut rapidly the electric current.

High molecular weight polyethylene (PE) blended with a specific amount of super-high molecular weight PP-separators seem to be better than polypropylene (PP) or trilayer sequence PP/PE/PP based ones. The effect is not yet fully understood. Maybe also the unique shutdown property of the PE is in addition necessary or the additives can even accelerate shut down on PE but not on PP. Also improved cathode materials may help to shift the critical voltage for thermal runaway of the overcharged cell that the additive can trip completely. This may help to choose additives with higher trip voltages in the regime of 4.8 V instead of 4.4 or 4.6 V to ensure that the cycling of the cell with 4.2 V cut-off voltage is not negatively influenced by slow decomposition of the additive.

4. Conclusions

PoLiFlex^{TM} is a new concept based rechargeable lithium cell. All time ongoing improvements in capacity, good cyclability, very low high temperature swelling and very good deep temperature characteristics are combined with a complex and innovative safety concept.

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