

# High-rate lithium/manganese dioxide batteries; the double cell concept

Jürgen Drews \*, Rüdiger Wolf, Gerd Fehrmann, Roland Staub

LITRONIK Batterietechnologie GmbH and Co, Birkwitzer Strasse 79, D-01796 Pirna, Germany

Received 4 November 1996; accepted 21 November 1996

## Abstract

An implantable defibrillator battery has to provide pulse-power capabilities as well as high energy density. Low self-discharge rates are mandatory and an ability to check the state of charge is required. To accomplish these requirements, a lithium/manganese dioxide battery with a modified active cathode mass has been developed. Usage of a double cell design increases significantly the battery performance within an implantable defibrillator. The design features of a high-rate, pulse-power, manganese dioxide double cell are described.

**Keywords:** Lithium primary batteries; Applications/medical

## 1. Basic design features

The basic design is straightforward, with a rectangular-shaped prismatic case, pasted cathodes, with the battery case negative. Case and lid are made from stainless steel. The battery is hermetically sealed with the lid laser welded to the case and glass-to-metal seals for electric feedthroughs. The dimensions of the cell type LiS 2790 are  $27 \times 43 \times 9$  mm; the cell volume is 10.4 ml. Nominal capacity is 2.0 Ah. Low-rate energy density is about  $570 \text{ Wh l}^{-1}$ . The cell is cathode limited, and the organic electrolyte contains lithium perchlorate as the conducting salt. The cathode contains additives to enable a determination of the state-of-discharge when on a low-rate discharge. The current collectors are photoetched stainless steel microgrids. The cell is able to deliver a constant current pulse of 2 A for 10 s. Pulse-power performance has been tested (Fig. 1) with a pulse train regime which includes four successive pulses (each 2 A, 10 s), with a 15 s rest period between each pulse. After each pulse train, the cell remained at open circuit for 30 min. The end of discharge voltage was set at 2.1 V; all tests were performed at  $37^\circ\text{C}$ . Fig. 2 shows the results of an accelerated discharge test of the LiS 2790 under this regime.

On reaching 2.1 V during a pulse, 0.9 Ah had been discharged, which is about 45% of the low-rate capacity. The rest of the capacity available until reaching EOL (end of life) voltage of 1.5 is not usable within the pulse discharge regime. Pulse-power density of the cell with this regime is about  $420 \text{ W l}^{-1}$  from BOL (beginning of life) to MOL (middle of

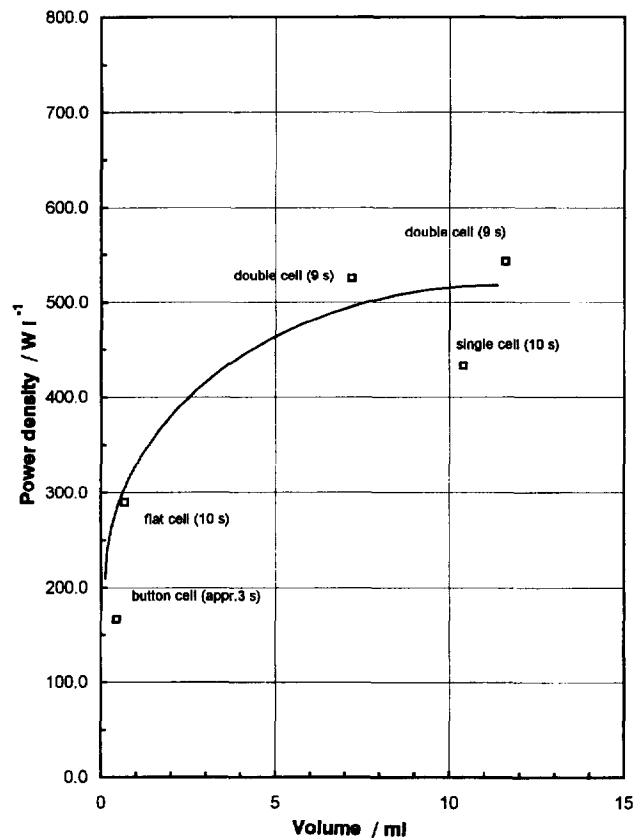


Fig. 1. Lithium/manganese dioxide cells: pulse-power density as a function of cell volume; duration of pulse in brackets.

life). The rest of the nominal capacity is available at lower discharge rates. Although a part of the capacity of the cell is

\* Corresponding author.

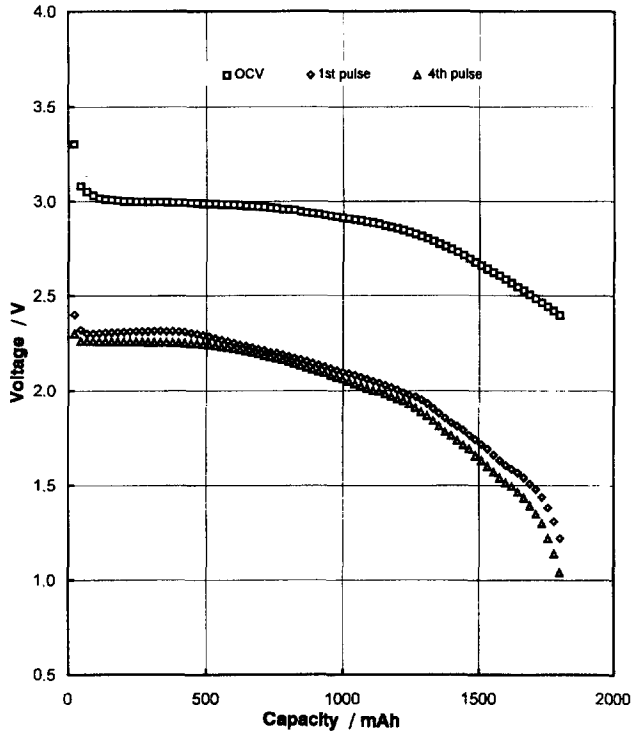


Fig. 2. Pulse discharge of single cell type LiS 2790. Four pulses of 2 A/10 s with 15 s on open-circuit between pulses and 30 min between pulse trains.

used as very low power within the defibrillator, the ratio of pulse-power and low-rate capacity had to be improved.

To provide information about the state of discharge from the battery itself is another requirement to be fulfilled by an implantable battery. Some electrochemical systems do provide such information. For example, cells using silver vanadium oxide as cathode material [1,2] show two discharge voltage levels; this feature is used for the purpose of DOD (depth of discharge) indication.

The lithium/manganese dioxide system does not provide such an inherent DOD indicator. From OCV (open circuit voltage) or discharge voltages at low rates, the DOD cannot be determined. Some workers have already tried to implement DOD indicators into manganese dioxide electrodes [3] by using different additives to the active mass. The additive should not show any deteriorative properties, nor increase the self-discharge rate or lower the cell's performance in any respect.

Our approach was based on the fact that lead compounds as well as chromoxides can be discharged as cathodes [4–6] in common organic electrolytes. The dependence of the discharge voltage on additive content is shown in Fig. 3. The LiS 2790 cells were discharged with the 2 A pulse-train regime described above.

## 2. Concept of the double cell

The discharge voltage at high rates is related directly to the current density, thus to the total active electrode surface of

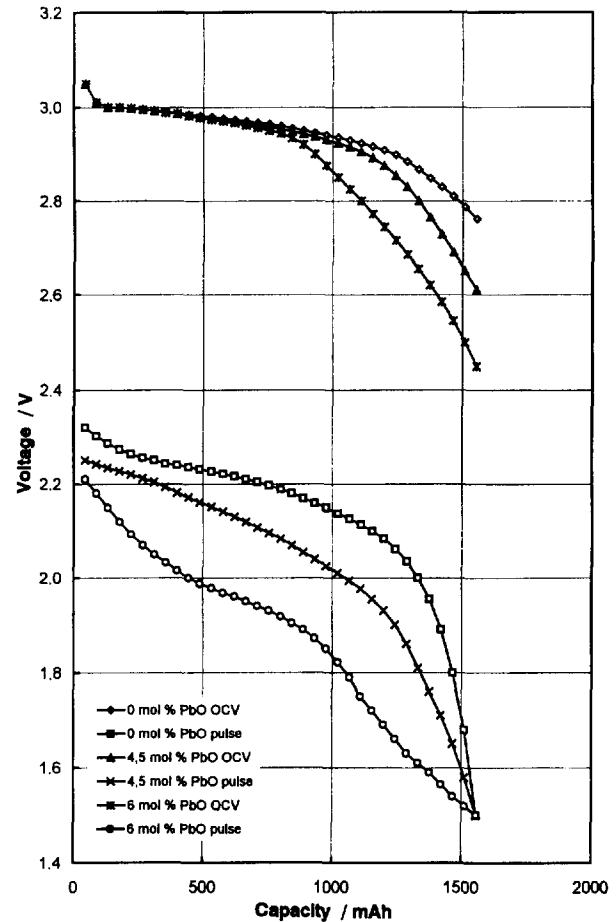


Fig. 3. Pulse discharge of single cell type LiS 2790. Four pulses of 2 A/10 s with 15 s on open-circuit between pulses and 30 min between pulse trains. Showing the effect of adding lead oxide to the cathode.

the cell. Reducing the electrode thickness, to be able to use more electrodes within one cell stack, has disadvantages and limits. The relation between passive and active components at the electrode level is shifted, causing loss in capacity. Unless the carriers are also reduced in thickness, which can lead to mechanical instability of the electrodes, this is unsuitable. Due to handling problems with thinner electrodes, the electrode thickness could not be further reduced. Two cells had to be connected in series to reduce current density during high-power discharges. With the limited space available, and to avoid external intercell connectors, a double cell with internal electrical connections was designed.

The outer dimensions of the single cell version remained nearly unchanged. The inner design of both cells is similar to the LiS 2790. The cells are cathode limited with photoetched stainless steel grids used for cathode and anode current collectors. The main feature of the concept is the usage of the battery case as the electrical connector between the two cells. With one cell the positive electrode, and with the other the negative electrode, are connected to the case. The full battery voltage of 6 V nominal is available between the two terminals, while the single-cell voltage can be obtained between the case and either cell terminal. The battery case is divided into two compartments. The separating steel sheet has a thickness

of 0.15 mm, and this amounts to a loss of available inner volume of only about 1.5%. The nominal battery capacity at a low-rate discharge into 400 kOhm is 0.8 Ah.

Pulse-power discharge capability of this, the LiS 43100, has been tested with a constant current of 1.4 A for 9 s, 15 s rest period on OC, and four pulses making one train. Between each pulse train there was a 30 min rest period on OC. End-of-discharge voltage is set at 3.0.

A typical result of such a discharge is shown in Fig. 4. Here 0.66 Ah was removed during the pulse-discharge regime, which is about 82% of the low-rate capacity. The rest of the nominal capacity is available at lower discharge rates. Pulse-power density of the cell with this regime is about  $540 \text{ W l}^{-1}$  from BOL to MOL. This is an significant increase of available pulse power in relation to the results obtained with the single-cell version, type LiS 2790 (Fig. 1.)

Performance features of both designs are summarised in Table 1.

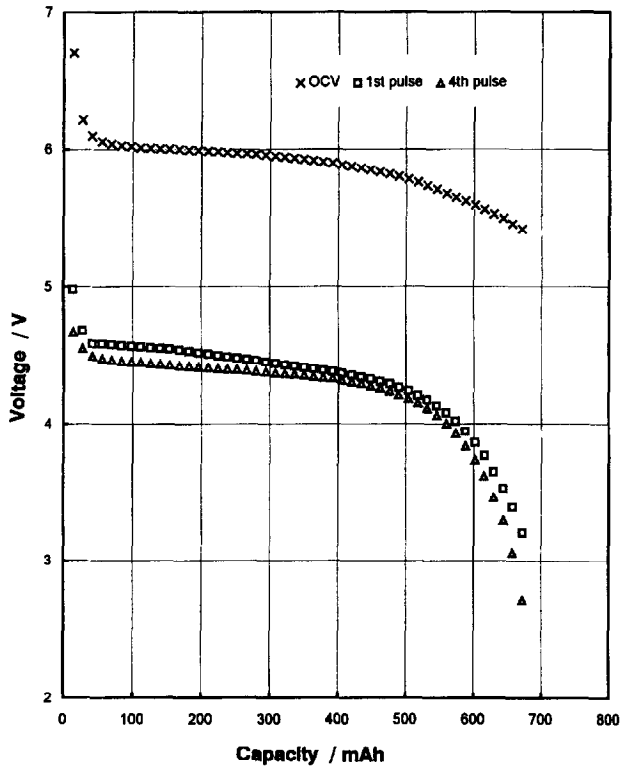


Fig. 4. Pulse discharge of the double cell type LiS 43100. Four pulses of 1.4 A/9 s with 15 s on open-circuit between pulses and 30 min between pulse trains.

Table 1  
Comparison of single cell and double cell performances

	Single cell LiS 2790	Double cell LiS 43100
Volume (ml)	10.4	11.6
Weight (g)	28	34
Nominal voltage (V)	3	6
Pulse-power density ( $\text{W l}^{-1}$ )	420	540
Usable pulse energy (Wh)	1.98	2.71

Although the double cell is about 10% larger and space utilisation has been improved, the main increase in high-rate performance is related to the reduced current density on the electrodes. Due to the partitioning into two cells, and their connection in series, the gain in pulse-power is significant.

### 3. Special performance features of a 6 V defibrillator battery

Implantable defibrillators are devices which detect and remedy fibrillation modes of the heart which can be lethal unless quick action is taken. The device has to provide electric pulses of about 15 to 40 joules [7] to the heart which is paralysed by the pulse and immediately thereafter recovers to normal operation. To charge capacitors which are able to store that amount of energy is the main task of the battery within the equipment. The desired loading time of those capacitors is between 5 and 15 s, to be as short as possible. In Fig. 5, a comparison of experimental capacitor loading times within a breadboard circuit is given. Due to requirements of the application EOD during capacitor charging is set to 2.1 V. This increases the advantageous use of the 6 V design even further. Under this condition the usable pulse capacity of the single cells is reduced to 0.9 Ah which is about 45% of the low-rate capacity compared to 82% pulse capacity with the double cell.

After optimising the amount of additive and putting the modified cathode into the double cell, a DOD indication was achieved. In Fig. 6, experimental data obtained during an

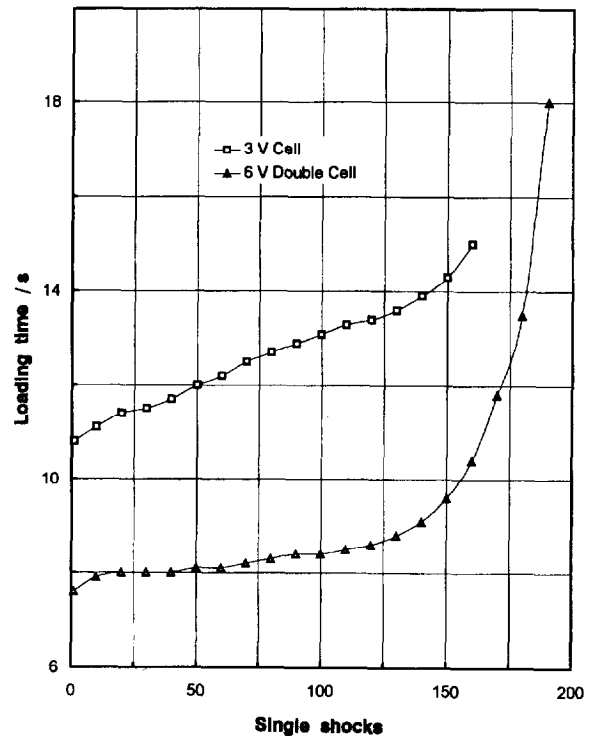


Fig. 5. Loading time of capacitor: comparison of single and double cell performance.

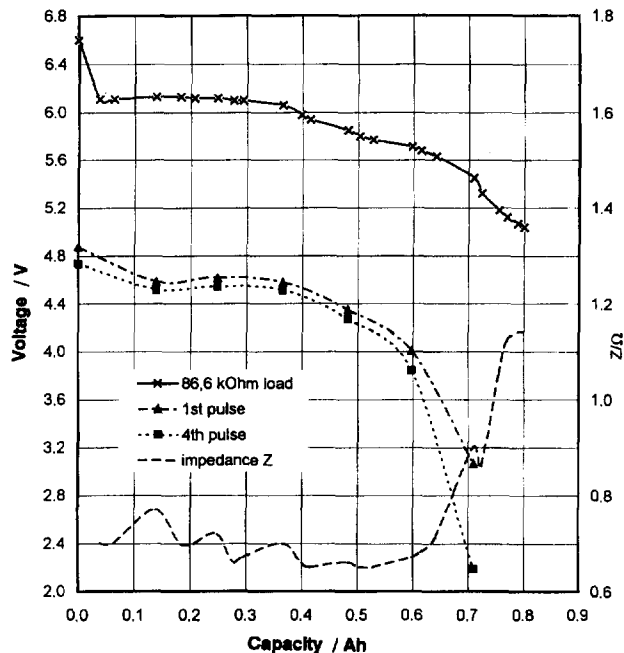


Fig. 6. One year accelerated life test of a double cell type LiS 43100. 86.6 kohm constant load, four pulses of 1.4 A/9 s with 15 s on open-circuit between pulses and a 2-month open-circuit stand between pulse trains.

accelerated one year life-test are presented. This test included a continuous discharge into 86.6 kOhm and six pulse trains per year. The voltage drop after removing 0.4 Ah is significant and can be used as an ERI (election of replacement indicator).

The long-term influence of the additives in the cathodes has been investigated for 60 months. Cells have been tested in accelerated life tests as well as life tests at 37°C. All tests showed the compatibility of the additives with the cell components.

Self-discharge has been determined using microcalorimetry. The batteries were tested after stabilising at 37°C and applying various loads. The values of  $P_L$  obtained were corrected for the reversible heat of reaction ( $TdS$ ) dissipated during discharge. The heat contributed by losses from the internal resistance of the battery was neglected. The results,  $P_{corr}$ , are given in Table 2.

The self-discharge, caused by side reactions on the lithium surface, increases with the discharge current. On open-circuit, the value is reflecting a self-discharge rate of the anode capacity of about 3% per year during the first year of life, the rate decreasing during the lifetime.

Table 2

Self-discharge of a 6 V, lithium/manganese dioxide, double cell

Load ( $10^{-6}$ A)	$P_L$ ( $10^{-6}$ W)	$TdS$ ( $10^{-6}$ W)	$P_{corr}$ ( $10^{-6}$ W)
0	15.7	0	15.7
16	18.8	-1.5	17.3
31	28.3	-3.0	25.3
60	47.8	-5.7	42.1
120	82.7	-11.5	71.2
238	150.0	-22.7	127.3

The low temperature performance of the battery is directly related to the properties of the electrolyte. The electrolyte used allows a continuous discharge of 2 mA at  $-20^\circ\text{C}$  and 0.3 mA at  $-40^\circ\text{C}$ , voltage under load being, respectively, 5.45 and 5.39. The electrolyte remains liquid without any precipitation of conducting salts down to  $-40^\circ\text{C}$ . The inherent safety of the battery is obtained by using a multilayer separator. Shorting of the battery (discharge into 1.0 mOhm, BOL) results in a current of about 9 A in the beginning, which falls to 4 A within 40 s and a temperature rise to a maximum of  $120^\circ\text{C}$  within about 3 min. Thereafter the temperature decreases within 60 min to room temperature. During the discharge the battery was placed in air at room temperature and it remained hermetically sealed.

The design features of the battery enables this power source to be used within implantable devices.

## Acknowledgements

This development work was supported by the German Ministry of Technology and Science (BMBF).

## References

- [1] C.C. Liang, M.E. Bolster and R.M. Murphy, *US Patent Nos. 4 310 609* (1982); *4 391 729* (1983).
- [2] C.F. Holmes, P. Keister and E.S. Takeuchi, *Prog. Batteries Solar Cells*, 6 (1987) 64–66.
- [3] A.N. Dey, *US Patent No. 3 658 592* (1972).
- [4] G. Pistoia and U. Mancinelli, *Electrochim. Acta*, 22 (1977) 1141.
- [5] H. Lauck and F.J. Kruger, *Ger. Patent No. DE 2 726 380* (1978).
- [6] G. Lehmann and J.P. Gabano, *Ger. Patent No. DT 2 154 092 B2* (1971).
- [7] E.S. Takeuchi, *Proc. 10th Int. Seminar Primary and Secondary. Battery Technology, Deerfield Beach, FL, 1993*.