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High-Rate Li-MnO_2 Cells for Aerospace Use

R. Becker-Kaiser, J. Ruch, H.-J. Harms
P. Schmöde, J. R. Welsh,
M.-J. Vollmers, H. Pack

HOPPECKE Batteries
P. O. Box 1140
D-5790 Brilon 2
Germany

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1. Introduction

HOPPECKE Li history in the search for a safe, high-rate Li technology

HOPPECKE is a company primarily concerned with the production of lead-acid and nickel-cadmium batteries which has also diversified into the field of alternative battery systems. In 1978, the R&D Department at HOPPECKE started to evaluate the advantages and disadvantages of the most common lithium systems at that time in both liquid and solid cathode technologies such as:

Lithium-
- SO_2Cl_2
- $SOCl_2$
- SO_2
- $(CF_x)_n$
- CuO
- MnO_2

A series of comparative studies were undertaken on representative cells as objectively as possible in order to appreciate the respective advantages of the different systems. After reviewing the first test results our attention was soon focussed on the following four lithium systems:

Lithium-
- $SOCl_2$
- SO_2
- $(CF_x)_n$
- MnO_2

This resulted in the decision in 1982 to adopt the Li-MnO_2 system for high-rate applications.

The reason for this was that it appeared the most promising system in its overall characteristics. With the main goal to achieve the good properties of the couple Li-MnO_2 such as high energy density, long shelf life, insignificant voltage delay and environmental safety, HOPPECKE succeeded in the development of high-rate Li-MnO_2 cells.

The development was guided by military requirements with respect to performance and by the highest safety requirements that could be achieved. The first German Military Approvals were obtained for C and D cells and several batteries in 1987/88. Further approvals were obtained in the course of time, followed by first approvals for some space applications.

Based on the considerable experience in this technology HOPPECKE was awarded a Development Contract by ESA to produce a 200 Ah high-rate cell. The cell is intended to be used in a 16 kWh battery which forms part of the electrical power system of the HERMES spaceglider.

The present paper describes the design properties and performance characteristics as well as safety aspects of our high-rate Li-MnO_2 cells which have been used for many years in several industrial and military applications. The use in some space applications is also described. As a conclusion, a brief report of the development status of our HERMES cell is given. The results, although preliminary, are very promising.

2. Design description

How did HOPPECKE LSC cells meet the high performance and safety requirements ?

Fig. 1 shows a sectional drawing of HOPPECKE LSC cells in coil type construction.

Fig. 1

- Cell case and cover:

  The cell case is a deep drawn cylindrical can of stainless steel. The cell cover contains the positive terminal feed-through insulated by a glass-to-metal seal. Both parts, cell case and cover, are hermitically sealed by plasma-arc-welding.

  The cell cover is designed as a pressure release vent which operates with very tight venting tolerances. Although the cell is not pressurized at room temperature, the internal cell pressure increases with rising temperature. At about 110°C, the vent opens and releases those components of the electrolyte with the lowest boiling point.

- Electrodes:

  The electrodes are spirally wound, and high-rate capability is achieved by the large surface area. The rigid design of the jelly roll assures that the cell resists even severe vibration and shock conditions. All connections between the cell case, terminals, tabs and current collectors are welded or riveted. No connection can be broken by chemical or mechanical degradation as the cell ages.

- Cathode:

  A mixture of MnO_2 (CMD), carbon and binder is pressed onto a metal grid. Very good electrochemical efficiencies of MnO_2 are achieved by this technique. The metal grid consists of stripes with selvaged edge on each side, hence sharp points or projections cannot occur while assembling the cathodes or even if the cell case is deformed. In particular, serious shorts by separator puncture are highly unlikely. The cathode is connected to the glass-to-metal feed-through in the cell cover.

- Anode:

  The anode consists of lithium foil rolled onto a current collector foil. The large area of the current collector makes sure that the lithium will be completely consumed at the end of discharge. The anode is connected to the cell case.

- Separator:

  Presently a double-layer separator system is used. The anode is completely enveloped by a Celgard wrap. This microporous separator is supported by a glass mat to increase the distance between anode and cathode.

- Electrolyte:

  The electrolyte consists of a mixture of different organic solvents and a lithium salt. The electrolyte is not toxic, corrosive or aggressive. The lithium salt is lithiumperchlorate ($LiClO_4$). Other alternatives were not considered because of environmental objections caused by fluorine or arsenic components. The main goal during the development phase has been to avoid environmentally doubtful liquids with halide, nitrogen or sulfur chemistry.

  Only components consisting of carbon hydrogen and oxygen were used because environmental problems are known to be minimum.

3. Performance description

What are the performance advantages of HOPPECKE LSC cells?

Fig. 2 shows the observed discharge potentials versus the capacity of D-sized HOPPECKE LSC cells. The discharges were performed over a wide temperature range on cells stored for two years with an overall constant discharge current of 2 A.

Fig. 2

Note the consistency: The capacity down to 0 V is almost the same for all discharge temperatures. The reasons for this are the precision of the limited lithium design and the ability of the anode current collector to discharge the lithium completely. Even after two years storage at ambient conditions, neither capacity losses nor serious passivation effects occur, as is shown in Fig. 3.

Fig. 3

Fig. 4 shows the capacity advantage of HOPPECKE Li-MnO_2 cells compared to standard SO_2 D cells for the temperature range of -20°C to 55°C, and with a constant discharge current of 2 A. The comparison demonstrates the excellent performance of the MnO_2 technology for high-rate applications over a wide temperature range.

Fig. 4

4. Safety aspects

What happens to LSC cells in case of abuse ?

- Overdischarge (pole reversal):

  Fig. 5 shows the behaviour of a D-sized LSC cell in the event of overdischarge.

Fig. 5

An aged cell (storage conditions 28 days at 72°C and 6 months at ambient conditions) was discharged at -30°C with a current of 5 A. The following results were obtained when a load of 200 % of the nominal capacity was passed through the cell at 5 A.

- Under the severe charge and storage conditions a voltage delay is observed, but the cell soon recovers and full capacity is available at a positive voltage.
- The temperature rises to critical values just below the venting temperature due to the increase of internal resistance at the final stage of discharge, but the separator system is not damaged.
- During the pole reversal phase no significant voltage drops or voltage instability are observed. No significant heating occurs. Hence, parallel diodes are not required, the cell is inherently safe.

These results are due to the fact that no adverse changes occur to the electrolyte, that at the end of discharge no active lithium is left on the anodes, and that the reversal current is distributed over a large electrode surface area.

Charging:

Protective diodes are recommended if inadvertent charging could occur.

Squeezing:

The safety vent opens, but no serious shorts are observed. Thus, the vented cell does not heat up. This is a result of the special grid design and the separator system.

- Overheating:

  Overheating could happen for a variety of different reasons. In all cases the safety vent will release pressure at a temperature well below the point at which the separator system would fail.

  Perhaps the simulation of an internal short by nail penetration is the most impressive example for the high safety standard of our LSC cells. The vent opens after 30 - 60 seconds due to overheating. The power of the cell is reduced because the electrolyte is ejected and further heat generation is prevented. The ejected electrolyte is not corrosive and nontoxic.

  It is most important that our cells react predictably, and that the electrochemistry is safe and well controlled, so no sudded exothermic reactions or violent explosions occur.

5. Space applications

HOPPECKE high-rate Li-MnO_2 cells for aerospace use

The high performance results and the safe electrochemical behaviour of the Li-MnO_2 couple makes this technology suitable for space applications.

Fig. 6 gives a brief overview of some applications in space missions where HOPPECKE LSC cells have been used.

Fig. 6

As a further extension of this technology, HOPPECKE is currently developing a 200 Ah high-rate Li-MnO_2 cell. This cell is a candidate to form the basis of a 16 kWh battery for a possible use in the HERMES spaceglider.

The development work was awarded by ESA to the team Telefunken System Technik (TST) / HOPPECKE in September, 1990. Within the team TST is responsible for the batterey design whereas HOPPECKE is responsible for the cell design.

A brief design and performance description, and the present status of this development is given below:

5.1 Design description (HERMES cell)

- Cell case:

  The cell case is prismatically shaped and made of stainless steel. At present, a folded cell design is used and all seams are welded by laser.

  Fig. 7 shows the complete cell.

- Cell cover:

  The cell cover contains the pole terminals, the vent and the filling tube. The terminal feed-throughs are insulated by ceramic seals. These ceramic seals have already been approved for space application.

  Fig. 8 shows the complete cell cover.

- Vent:

  The vent is a domed membrane which - in case of overpressure - is forced backwards and punctured by a star-shaped knife.

- Electrodes:

  The design of the anode and cathode is very similar to our spirally wound cells, except that they are flat. The high-rate electrical performances are achieved by the large surface area of the electrodes.

- Separator:

  The separator consists of non-woven sheets of microglassfiber with excellent mechanical properties achieved by a special binder which guarantees a maximum of safety against mechanical stress and abusive conditions.

- Cathode frames:

  The cathodes are placed in plastic frames and the whole electrode stack is mounted into the cell case. Thus, the plastic frames together with the properties of the separator gave the necessary mechanical stability so that the mechanical test requirements were fulfilled without any failures or malfunctions.

- Electrolyte:

  The electrolyte is the same mixture of organic solvents used for our commercial cell, except for a higher Li salt concentration.

5.2 Performance description (HERMES cell)

- Discharge performance:

  Fig. 9 shows the discharge performance at ambient temperature and at a constant discharge current of 40 A. The cell did not heat up significantly because the heat could be easily dissipated to the surroundings. A capacity of 208 Ah was measured to a COV of 2 V and the calculated energy densitiy was 260 Wh/kg.

Fig. 9

  Fig. 10 describes the discharge performance at nearly adiabatical test conditions (the so-called "thermal worst case" discharge mode). The test conditions simulate the situation where a very small heat transfer to the surroundings can take place. The cell was discharged with a pulsed current corresponding to a specified mission load profile for the whole battery.

Fig. 10

  Due to the higher temperatures during discharge the electrochemical efficiency of the cell was somewhat increased. The capacity measured to a COV of 2.2 V was 213 Ah, and the calculated energy density was 280 Wh/kg.

- Overdischarge (pole reversal):

  Fig. 11 shows the behaviour of a cell in the overdischarged mode. Note: No significant voltage instability and heat generation were observed. We see this aspect as one of the most important safety features. This was achieved by the safe electrochemistry and the safe design of the cell. Parallel diodes were not required.

Fig. 11

- Miscellaneous tests:

  Further tests have been performed on cells to investigate the cell behaviour in terms of low and high charging currents, rise time and response time, heat treatment and mechanical stress. The results can be summarized as follows: No hazardous or inexplainable behaviour of the cells was observed. This supports our view that Li-MnO_2 technology gives one of the safest lithium systems currently available.

6. Conclusion

- The electrochemical couple Li-MnO_2 is suitable for high rate applications
- HOPPECKE Li-MnO_2 cells have been carefully designed and developed to ensure good quality and high safety
- The combination of solid cathode electrochemistry and sealed, but safe cell design sets new standards in terms of both high performance and environmental safety
- HOPPECKE Li-MnO_2 cells and batteries meet and often considerably exceed most military requirements
- First applications of HOPPECKE Li-MnO_2 technology in space missions already have been succesful and the Li-MnO_2 system is a promising candidate for future space applications

Structure of a HOPPECKE LSC cell
in coil type construction
Schematic illustration

Fig. 1

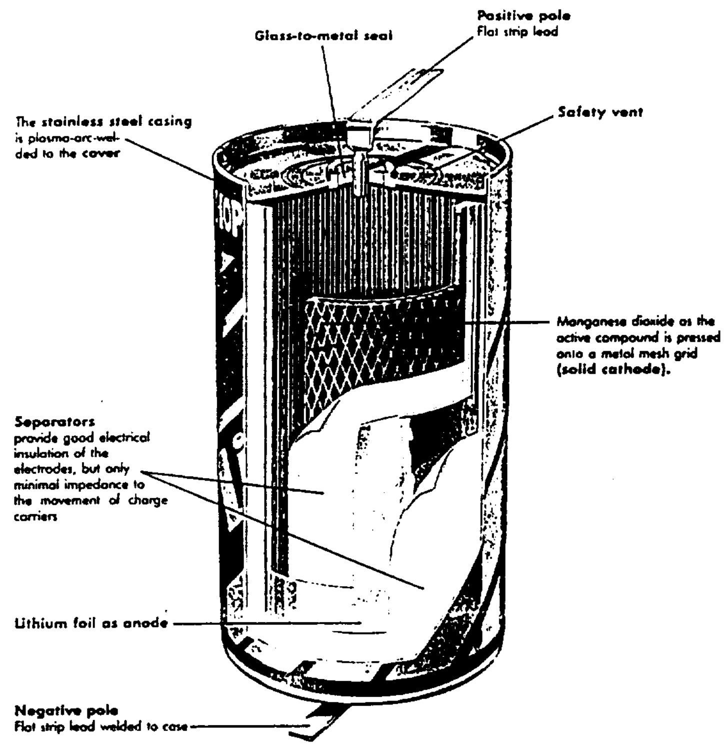

Fig. 2

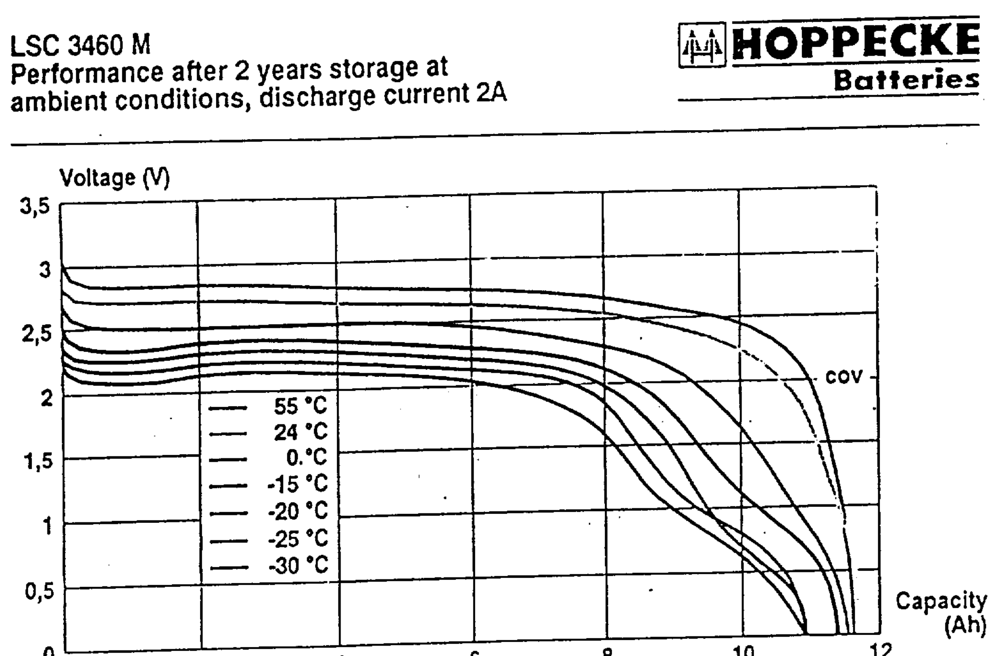

Fig. 3

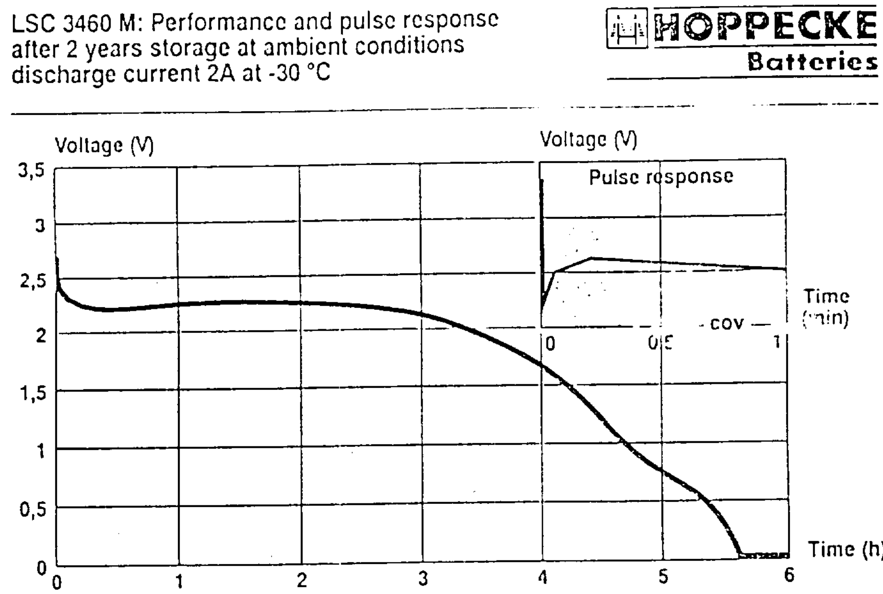
LSC 3460 M: Performance and pulse response
after 2 years storage at ambient conditions
discharge current 2A at -30 °C
HOPPECKE Batteries
Voltage (V)
3,5
3
2,5
2
1,5
1
0,5
0
Voltage (V)
Pulse response
COV
Time (min)
0
1
Time (h)
0
1
2
3
4
5
6

Fig. 4

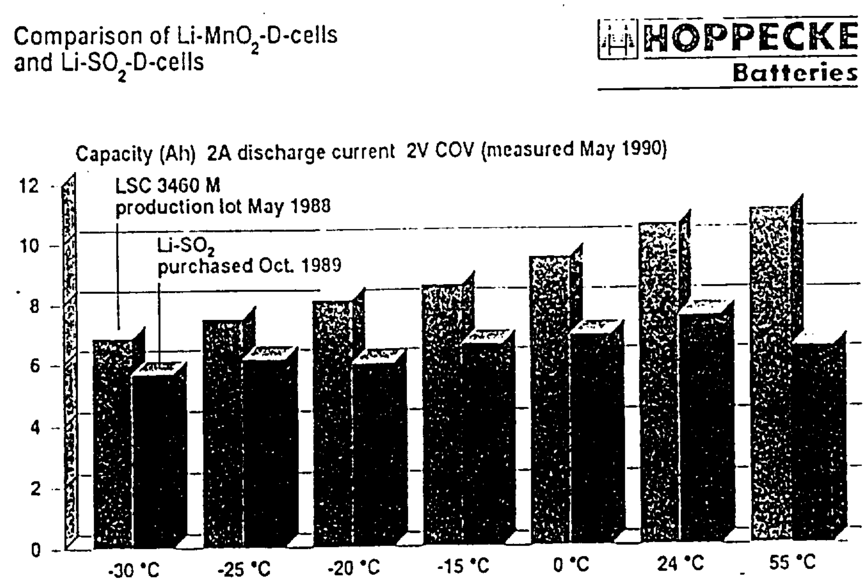
Comparison of Li-MnO2-D-cells
and Li-SO2-D-cells
HOPPECKE Batteries
Capacity (Ah) 2A discharge current 2V COV (measured May 1990)
LSC 3460 M
production lot May 1988
Li-SO2
purchased Oct. 1989
12
10
8
6
4
2
0
-30 °C
-25 °C
-20 °C
-15 °C
0 °C
24 °C
55 °C

Fig. 5

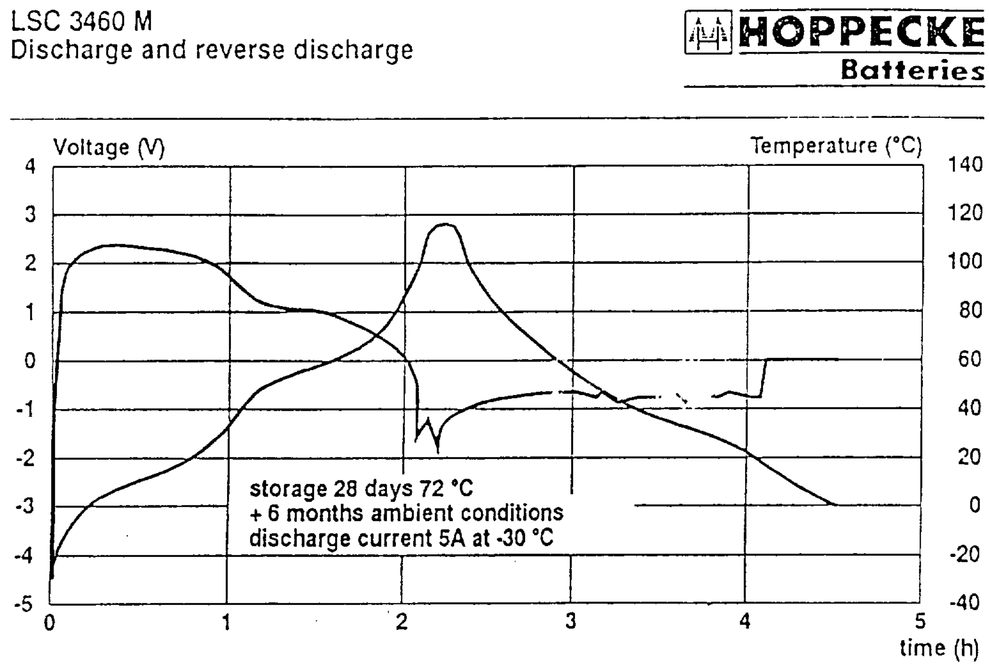

Fig. 6 HOPPECKE LSC cells in space applications

Mission	Application	Battery Systems	Approval status of Batteries
MIR 91	goggles experiment	14 V, 10 Ah and 5,6 V, 10 Ah	approved by ESA passed all mechanical tests
MIR 92	portable calculator	14 V, 4.5 Ah	concept approved by ESA delivered for mechanical testing
Cosmos 10	project biobox	28 V, 80 Ah	approval in process at ESA
Texus 23	microgravity experiment	30.8 V, 10 Ah	successful flight in Nov. 1989
MIR 92	video recorder supply	14 V, 20 Ah	delivered for prototype experiments in Feb. 1991
Cosmos 10	microgravity experiment	22.4 V, 4.5 Ah and 11.2 V, 10 Ah	will be delivered for prototype experiments in Nov. 1991

Fig. 7

200 Ah Li-MnO_2 - cell

HOPPECKE Batteries

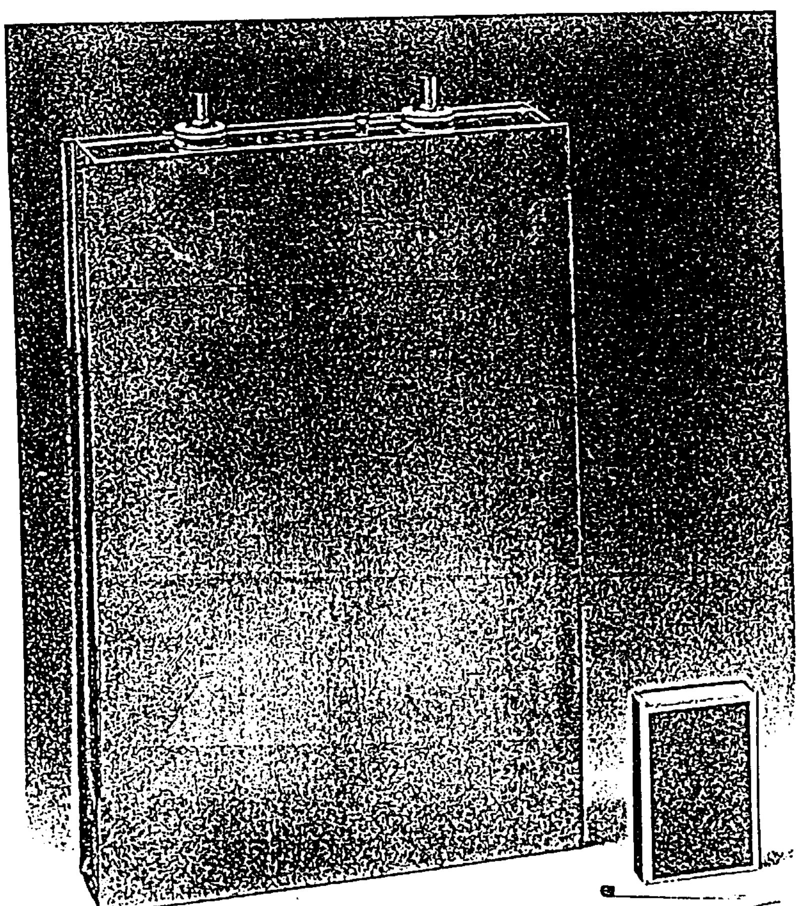

Fig. 8

200 Ah Li-MnO_2 - cell
Cell cover with vent

HOPPECKE Batteries

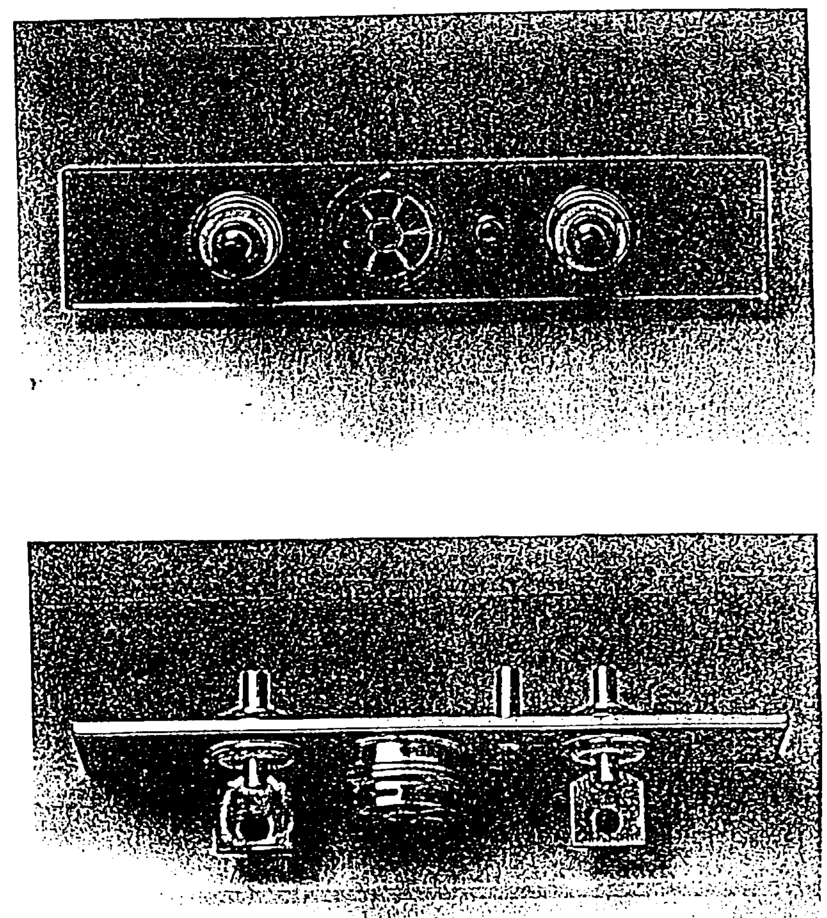

Fig. 9

200 Ah Li-MnO_2 - cell
Discharge 40 A at room temperature

HOPPECKE Batteries

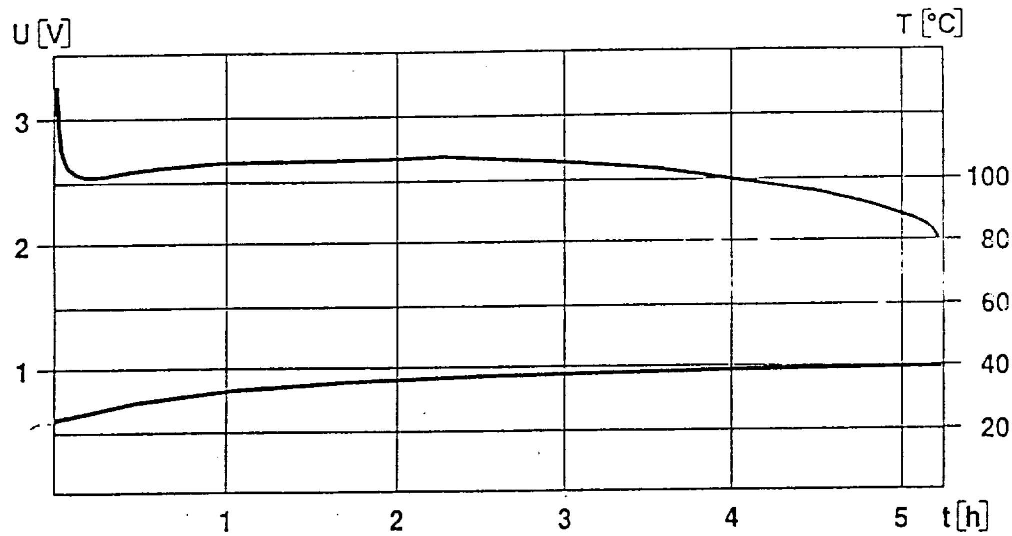

Fig. 10

200 Ah Li-MnO_2 - cell
Discharge test under thermal
worst case conditions

HOPPECKE Batteries

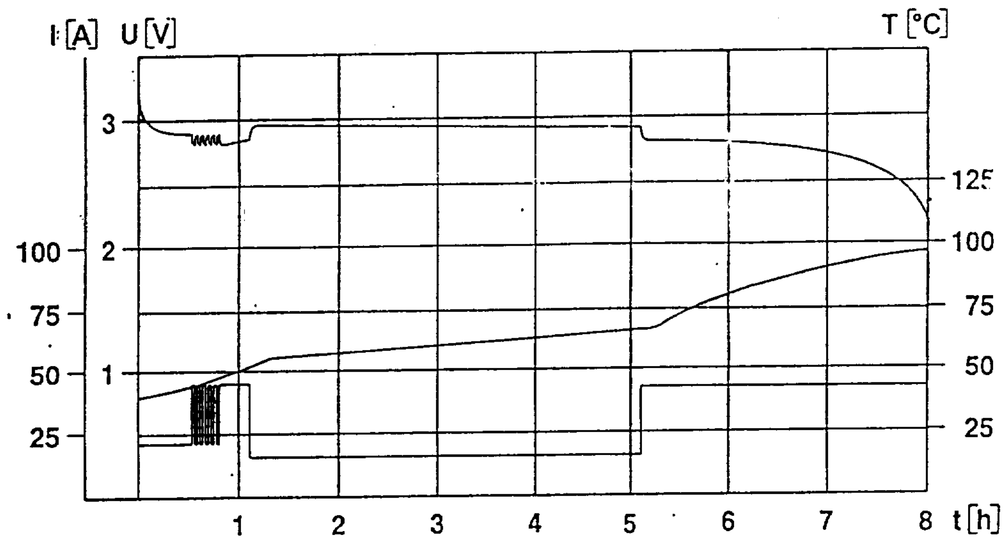

Fig. 11

200 Ah $Li-MnO_2$- cell
Overdischarge test at 40 °C
I=20 A

HOPPECKE Batteries