LOW TEMPERATURE DISCHARGE CHARACTERISTICS OF LITHIUM–MANGANESE DIOXIDE CELLS*

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Summary

Lithium–manganese dioxide cells have not only excellent specific energy and shelf life characteristics, but they are also capable of very promising performance at temperatures as low as −40 °C (−40 °F). The polarization and discharge curves of cylindrical and button cells at −40 °C are compared in an effort to evaluate the useful low temperature operation range. The cathode design, and type of MnO_2 strongly affect the low temperature behaviour. Although the excellent low temperature performance of the Li/SO_2 system can probably never be equalled, due to some diffusion shortcomings inherent in the Li/MnO_2 cells, for low and moderate current drains covering many meteorological, military, and consumer applications, Li/MnO_2 batteries are very competitive in terms of simple technology, increased safety, and price, offering satisfactory operation within the range −40 to +71 °C (−40 °F to +160 °F).

Introduction

Regardless of the spectacular progress in the design and technology of conventional aqueous electrolyte cells, the low temperature performance of almost all known systems continues to remain poor below −18 °C (0 °F) [1]. Some exceptions, such as sintered Ni–Cd accumulators, or specially designed AgO–Zn and AgO–Cd power sources, which are capable of excellent performance at heavy drains and very low temperatures, achieve their superior characteristics either at the expense of a sophisticated technology (Ni–Cd) or very active anode mass [2, 3], in the two latter cases, but prohibitively high prices restrict their areas of application.

The use of aqueous electrolytes always decreases the power and energy output at low temperatures due to a substantial increase in the specific

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resistance, and diffusion or activation limitations, as well as freezing hazards, cause the discharge behaviour to be even worse.

Lithium–sulphur dioxide cells display unique low temperature discharge characteristics, and their exceptional properties have been proved in LO 14 and LO 20 cylindrical, spirally wound cells [4]. But the Li/SO_2 cell is basically an expensive power source characterized by a sophisticated manufacturing technology, hazards inherent in pressurized systems and dangerously high short-circuit currents. Consequently, the prospects of a wide consumer field of application, regardless of some opinions to the contrary [1], are very questionable. The Li/SO_2 cell design covers basically cylindrical cells, with specific weight and volume parameters becoming less attractive for small sizes when the can/active component ratio becomes increasingly unfavourable. Sealing and venting difficulties further interfere with the construction of small button cells, and potential SO_2 leakage hazards discourage the design engineer.

The recently developed Li/MnO_2 button and cylindrical cells LOM 225, LOM 14, and LOM 20, although having lower specific energy and power characteristics compared with the Li/SO_2 counterparts, along with some advantages such as high voltage, long shelf life and simple manufacturing technology, have displayed very good low temperature characteristics, especially at low and moderate drains. Obviously, the exceptional performance inherent in a liquid depolarizer system such as Li/SO_2 can probably never be matched, but for many practical applications needing a low cost battery for low temperature operation the Li/MnO_2 cell is an excellent alternative.

Experimental

Parallel batches of Li/MnO_2 cells were prepared by identical routine production methods with two different types of manganese dioxide: electrolytic MnO_2 manufactured by Tekkosha, Japan, and chemical MnO_2, Faradizer WS, with very low water content [5], produced by Sedema S.A., Belgium. Two types of Li/MnO_2 cells were tested: pressed powder, flat button cells 22 × 7.5 mm, electrode area 3 cm^2, LOM 225, and cylindrical, spirally wound LOM 14 cells in steel or zinc cans, equivalent in size to the IEC R 14 Leclanché cell ("C"-size). In all cases discharge was carried out continuously on a 7 day week basis, the cells being wrapped in plastic foil containing water absorbent molecular sieve to avoid frosting. The current–voltage curves were traced manually, with 5 minutes observation for each point, to a cut off voltage of approximately 2 V.

Figure 1 compares the polarization characteristics of LOM 225 button cells manufactured with the two types of MnO_2, at different temperatures. A good retention of room temperature values is observed at −40 °C, and the cell is still usable even at −60 °C at low drains or intermittent discharge, especially if Faradizer WS is used in the cathode formulation.

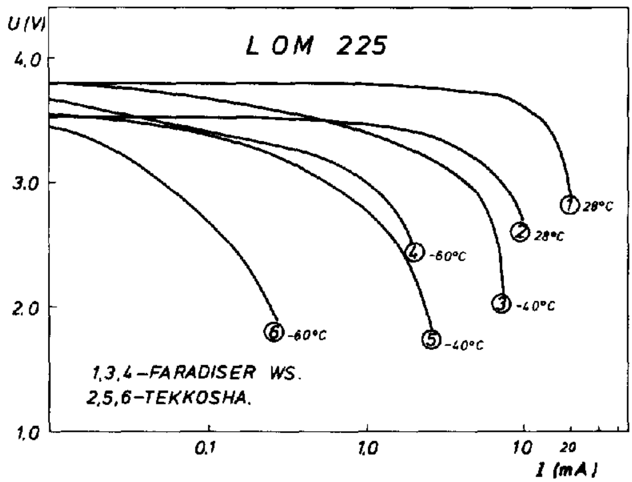

Fig. 1. Polarization characteristics at various temperatures of LOM 225 cells with different types of MnO_2.

The low temperature performance can be further improved by the use of a tetrahydrofuran–propylene carbonate solvent instead of the conventional dimethoxyethane–propylene carbonate electrolyte. Figure 2 juxtaposes the low temperature performance of LOM 225 cells with different solvent formulation.

The discharges curves of the LOM 225 cells are quite similar to those of the equivalent Sanyo cells [6].

Figure 3 juxtaposes the discharge curves, of cells manufactured with each type of MnO_2, at −40 °C. Figure 4 provides the same comparison at a 10-fold higher current at room temperature.

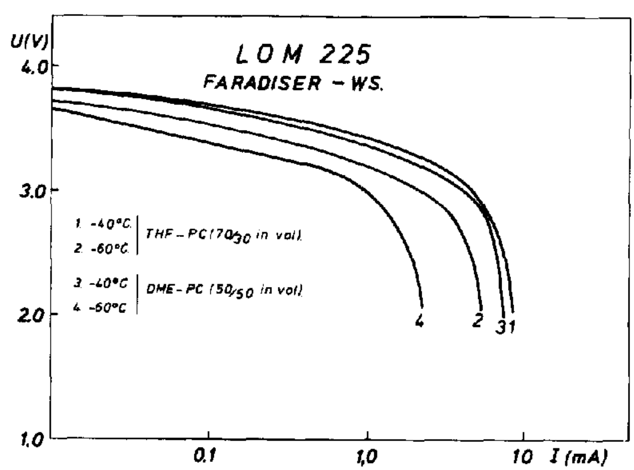

Fig. 2. Low temperature polarization curves of LOM 225 cells with different solvents.

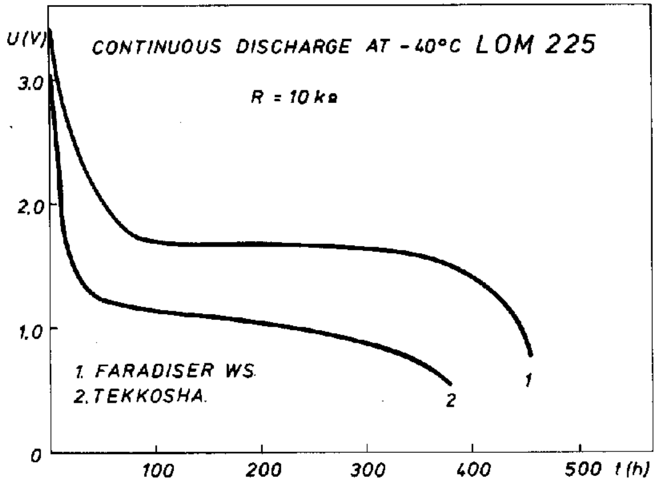

Fig. 3. Discharge curves at −40 °C of LOM 225 cells with different types of MnO_2.

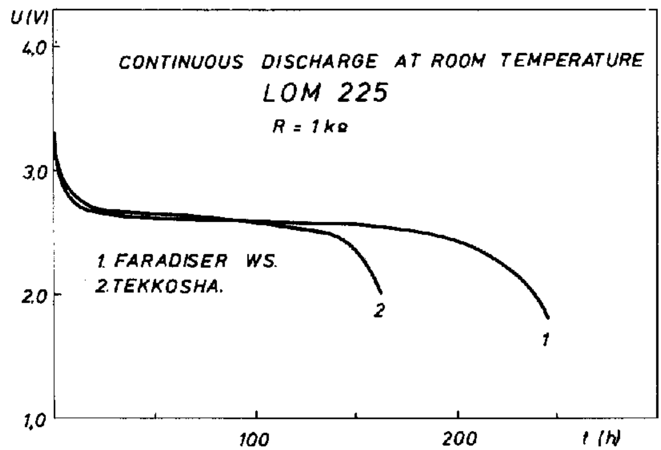

Fig. 4. Discharge curves at room temperature of LOM 225 cells with different types of MnO_2.

The current–voltage curves for the cylindrical LOM 14 cell at different temperatures are compared in Fig. 5. Since the cell is spirally wound, no substantial difference is observed up to 100 mA. On the other hand, energy loss in the discharge behaviour is quite substantial, as shown in Fig. 6.

Discussion

The discharge characteristics of Li/MnO_2 cells depend strongly on the type of MnO_2 [7], and this effect becomes more pronounced at low temperatures and on continuous discharge. However, a substantial difference exists

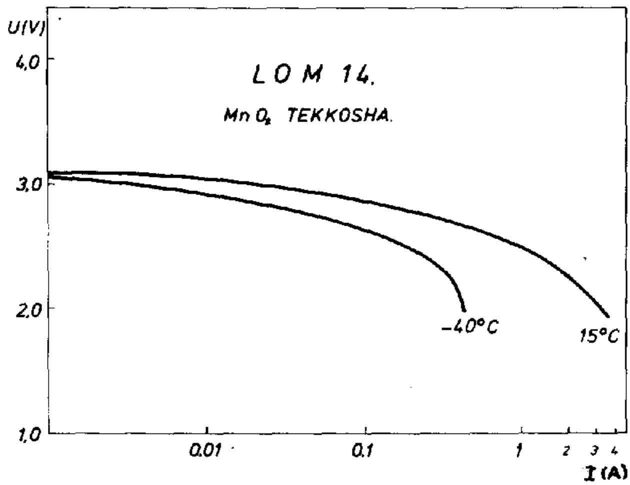

Fig. 5. Polarization curves at 15 and —40 °C of LOM 14 cylindrical cell.

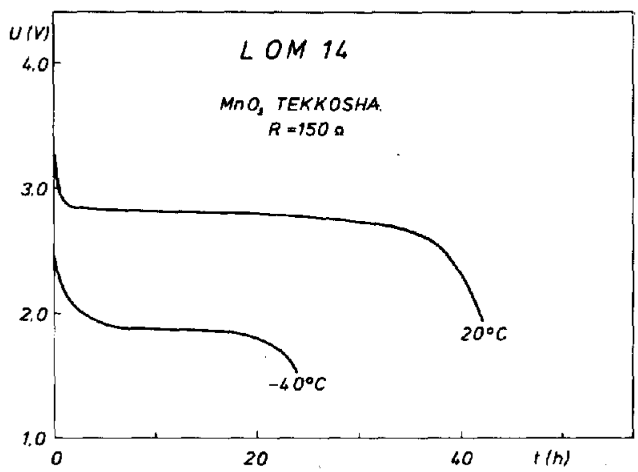

Fig. 6. Discharge curves at 20 and —40 °C of LOM 14 cylindrical cell.

between the room temperature and the low temperature behaviour: at room temperature the type of MnO_2 only affects the duration of discharge, *i.e.*, the A h capacity, as seen in Fig. 4, while at low temperatures the average discharge voltage is also drastically reduced, decreasing the overall watt hour output of the cell. In the case of LOM 225 button cells the type of MnO_2 appears to be crucial for the low temperature performance. The parameter most affected is the low temperature plateau which is approximately 1.8 V with pressed Faradizer WS cathodes, and 1 V only with Tekkosha. On the other hand, the cylindrical LOM 14 cell with Tekkosha MnO_2, as seen in Fig. 6, retains about 35% of its watt hour output at —40 °C since the voltage drop for similar current densities is not so drastic as compared with the button cells. Obviously, the thin, spiral wound cathodes of LOM 14 cells are less affected by diffusion limitations than are the thick, pressed, button cell cathodes.

The low temperature behaviour of a button type Li/MnO_2 cell reflects basically the properties of the MnO_2 in the cathode formulations, hence, it can be used as a precise criterion for the suitability of the product for lithium cells. The different types of MnO_2 available on the market are mainly tailored to ensure good performance in Leclanché cells, and an unambiguous correlation between their merits as cathodes in Leclanché and lithium cells has yet to be established [7].

Conclusions

The experimental results show that Li/MnO_2 cells can be substituted successfully for the superior, but in some respects disadvantageous, Li/SO_2 system in low drain, low temperature applications. Their low temperature performance depends heavily on the type of MnO_2 used, and the discharge voltage plateau can be improved by both cathode design and proper selection of the MnO_2 type.

All experiments were carried out with standard design Li/MnO_2 cells. A careful modification of the spiral cathode, or multi-electrode button cell design, together with optimized thermal treatment [8] and proper choice of MnO_2, can further improve the low temperature performance of the Li/MnO_2 system.

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