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SOME CRITICAL CONSIDERATIONS IN THE DESIGN OF MULTICELL LITHIUM–MANGANESE DIOXIDE BATTERIES

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Summary

A Li–MnO_2 counterpart of the standard 6F22 Leclanché battery was designed in 3 different versions — paper lined, spiral wound, and layer stacked. The performance of all 3 types was tested according to the IEC discharge conditions, and the results were juxtaposed with Leclanché and zinc–air batteries of identical size and voltage. The merits and shortcomings in terms of capacity, polarization, ability to withstand continuous discharge, and technological back up are discussed. Although all 3 designs displayed superior characteristics as compared with the Leclanché batteries, optimum performance can be achieved by observing several critical requirements concerning the design, materials, and technology.

Introduction

Progress in the advancement of Li–MnO_2 batteries for consumer use has been slower than expected for several reasons: the basic advantage — high voltage — has, in turn, become an obstacle for the acceptance by a market adapted to 1.5 V cells, even when the size is within the IEC standards [1]. Commercialized Li–MnO_2 cells are in peculiar sizes [2] and tailored mainly to replace AgO–Zn batteries, or are a forced choice for the owner of a 3 V single-cell-operated calculator, watch, etc. Electronic engineers on the other hand are reluctant to design new equipment based on a power source with an unpredictable future, and prefer the worldwide available Leclanché system. Economic considerations further accentuate this impasse.

A break-through in this vicious circle was attempted by designing and testing a Li–MnO_2 counterpart of the standard 6F22 (006P) Leclanché transistor battery in 3 versions, all identical in size and voltage (9 V) but with superior capacity and shelf-life. The discharge characteristics of all 3 versions were determined according to the IEC standard methods under 900 ohm load, and intermittent or continuous conditions. The curves were juxtaposed with the equivalent in size 6F22 Leclanché battery, and its zinc–air analogue, the KRONA VC battery, which with its high capacity, but restricted shelf and active life [3] inherent to the system, has completely replaced the Leclanché system (in the USSR).

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Experimental

Version "A" of the 3 LOM 500 Li–MnO_2 battery

The design is quite similar to a paper-lined system, and consists of a thermosetting plastic moulded container, Fig. 1(3), an extruded Li anode (2), an injected cathode black mix (1), and a carbon rod collector (4). This battery is based on inexpensive materials, and offers the possibility of mass-production with a slightly modified, compact, paper-lined Leclanché battery machine (*e.g.*, ACME) which can be easily housed in a dry room or chamber. The construction is quite simple, but needs soldering or spot welding of the intercell connections. The capacity is typically twice that of a 6F22 battery, it is suitable only for intermittent discharge (4 h daily, 5 day week), and the polarization is higher than that of the other 2 systems, mainly due to the carbon rod–black mix interface. as shown in Fig. 2.

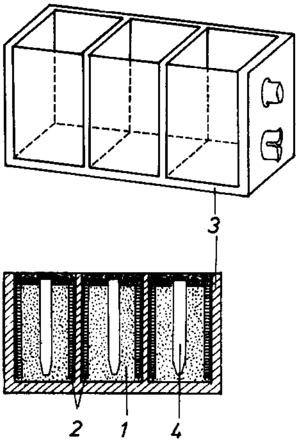


Fig. 1. 3 LOM 500 — version "A".

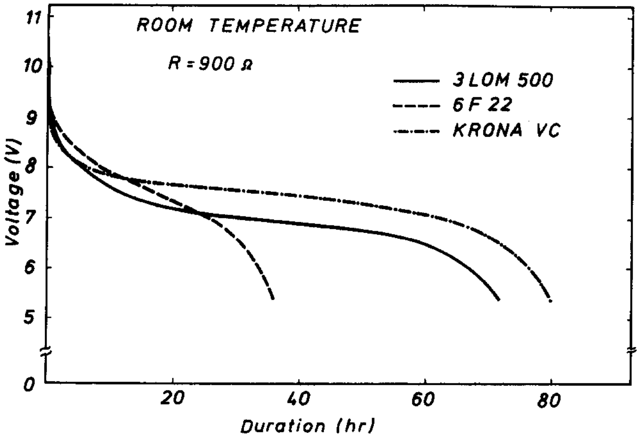


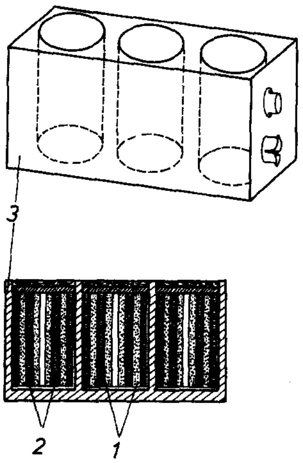
Fig. 2. Discharge curves of 3 LOM 500 "A", 6F22, and KRONA VC. All discharges intermittent, 4 h daily, 5 day week.

Version "B" of the 3 LOM 500 Li–MnO_2 battery

This design is a combination of 3 typical spiral wound cells in a common moulded plastic container (phenolic, DAP, etc.) — Fig. 3. The MnO_2 cathode (1) is pressed on an expanded metal grid, the Li anode (2) is unsupported foil, and the container (3) is hermetically sealed after assembly. The gains in capacity as compared with the Leclanché 6F22 are not spectacular, but this Li–MnO_2 version is suitable for discharge under continuous conditions, while the 6F22 and KRONA VC are only suitable for intermittent discharge, since both cannot support other regimes without substantial capacity loss, Fig. 4.

Version "C" of the 3 LOM 500 Li–MnO_2 battery

This is a construction very similar to the layer stack Leclanché or KRONA VC approach, and offers the possibility of production in a 2 or 4



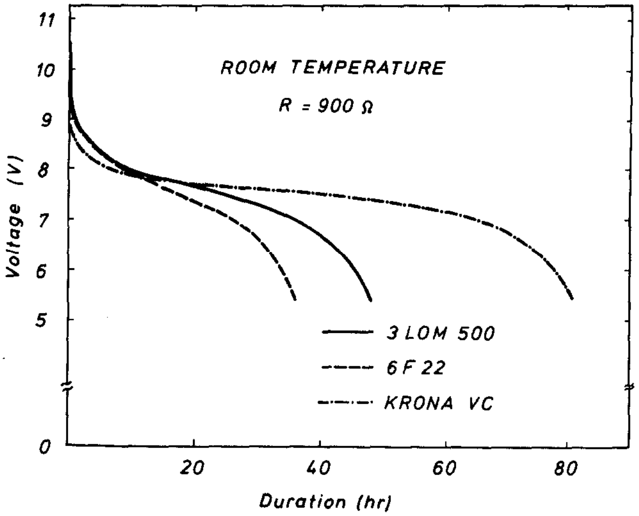
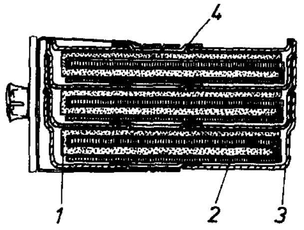


Fig. 3. 3 LOM 500 — version "B".

Fig. 4. Discharge curves of 3 LOM 500 "B" (continuous), 6F22 and KRONA VC (intermittent).



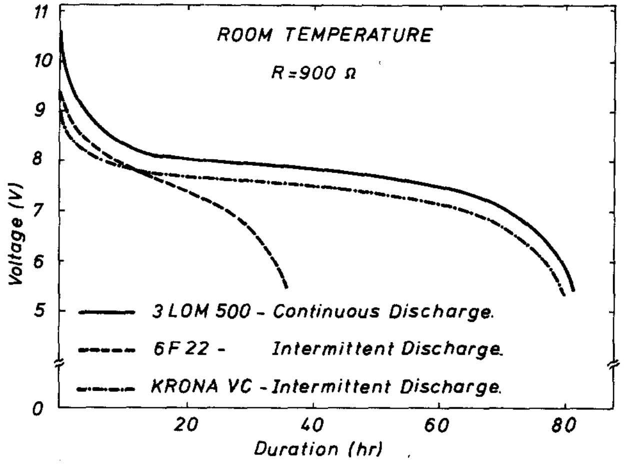


Fig. 5. 3 LOM 500 — version "C".

Fig. 6. Discharge curves of 3 LOM 500 "C" (continuous), 6F22 and KRONA VC (intermittent).

electrode system, convenient for mass production, and requires no soldering or spot welding of the intercell connections. Figure 5 shows the cross-section of a 4 electrode system, where the Li anode (1) and the pressed tablet of MnO_2 (2) are mounted in a plastic cup (3) with a conductive intercell contact foil (4), and the entire structure is pressed and sealed. The discharge curves in Fig. 6 show that, even under continuous discharge, compared with the intermittent discharge of 6F22 and KRONA VC batteries, this version of the Li–MnO_2 battery is superior both in capacity and polarization, and is a real challenge in every respect to all existing systems.

Discussion

The analysis of all these performances suggests that multicell Li–MnO_2 designs are very promising structures, provided some critical considerations are observed:

(a) The plastic materials used in multicell designs must be carefully selected, mainly from the thermosetting types resistant to organic media.

(b) The dimensional changes of an Li–MnO_2 cell due to the dissolution of the Li anode are not always compensated for by the expansion of the MnO_2 cathode, and this effect can become crucial in a multicell stacked system, where negative dimensional changes may occur and lead to a deterioration of the anode–cathode interface. Therefore, a continuous pressure must be ensured along the short axis of the prism (version "C") by a properly designed metal jacket. This pressure must be applied during the entire active life of the battery.

(c) Intercell contact is no problem with the soldered or welded designs "A" and "B", but it becomes a decisive factor in version "C", requiring also adequate pressure in the same direction.

(d) A very reliable air-tight seal is the most severe requirement, since the leakage of electrolyte, together with moisture pick-up and the high intercell voltage (3 V), may ruin the battery much more rapidly than Leclanché layer stack cells, due to enhanced self-discharge.

(e) Wound designs offer no advantage in a rectangular battery.

(f) To increase the electrode surface beyond a certain extent is not the best way to reduce polarization. Instead, more active cathode formulations must be sought [4, 5] which may improve the discharge characteristics. Each type of MnO_2 requires specific thermal treatment conditions (temperature, dwell time, scanning rate, etc.) and a universal regime cannot be applied to all types of electrolytic manganese dioxide or chemical manganese dioxide if we want to obtain optimum performance.

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