

THE LITHIUM-MANGANESE DIOXIDE CELL III. A COMPARISON OF ELECTROLYTIC AND CHEMICAL MnO_2 IN LITHIUM BUTTON CELLS AT HIGH DISCHARGE RATES

NIKOLAI ILCHEV

Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences,
Sofia 1040 (Bulgaria)

(Received December 2, 1988; in revised form May 18, 1989)

Summary

Electrolytic and chemical manganese dioxides have been investigated by using the same cathode volume in lithium button cells. Their specific electrochemical characteristics are compared at room and at low temperatures. Due to its high utilization and discharge voltage the chemical manganese dioxide shows excellent performance as a cathode material, especially at both high discharge rates and low temperatures.

Introduction

Electrolytic and chemical manganese dioxides (EMD and CMD) are widely used as cathode materials in primary lithium cells [1, 2].

Our previous investigations [3] using test electrodes in cells with an excess of electrolyte, showed that at high discharge rates CMD Faradiser M (Sedema product) has the highest discharge voltage and maximises utilization at room and low temperatures.

Ohzuku *et al.* [4] investigated equal amounts of cathode mixture produced from 9 different IC MnO_2 samples pretreated at 400 °C. In electrochemical cells with a limited amount of electrolyte these authors found that at room temperature and with a low discharge rate (0.1 and 0.5 mA cm^{-2}) CMD IC 8 and IC 12 display the highest discharge voltage and specific capacity by weight. In this case [4], however, the MnO_2 samples were not pretreated at their optimum temperature, which is necessary for maximum utilization [3, 5].

Comparing equal weights of EMD and CMD cathode mixture in test cells with a limited amount of electrolyte, Miyazaki *et al.* [6] also found that, at room temperature and with a current density of 1.2 mA cm^{-2} , CMD develops a higher discharge voltage and has a greater capacity. By maintaining a constant cathode volume, however, these authors showed that the EMD

capacity is greater than that of CMD. The MnO_2 types used, the pretreatment temperature, and electrolyte content were not specified in this paper [6].

Similar results were obtained by Ikeda *et al.* [1] when discharging CR 2025 button cells at room temperature and at 0 °C with low discharge current densities when using 5.6 and 12 k Ω resistance loads.

The aim of the present work was to compare the electrochemical characteristics of EMD and CMD in cathodically-limited button cells with identical cathode volumes and optimum porosities by using high discharge rates at room and low temperatures.

Experimental

In a previous work [3] we showed that of all the MnO_2 samples investigated at high discharge rates the Sedema CMDs Faradiser M and Faradiser WS, the International Common Sample No. 5, and EMD Knapsack have maximum utilization. The utilization of IC 5 at room temperature is similar to that of Faradiser WS, while at low temperatures its operating voltage drops below 2 V [3]. For this reason, Faradiser M, Faradiser WS and Knapsack were chosen as test MnO_2 samples for this present work based on previous studies [3]. Additionally, a comparative trial using Tekkosha EMD and the latest Sedema CMD, Faradiser TR was also carried out.

All the MnO_2 samples were pretreated at their optimum temperature (300 °C for 8 h) [3] which gives maximum utilization. These samples were then mixed with 20 wt.% Teflonized carbon black (containing 35% PTFE). Cathodes of 0.90 ± 0.03 mm thickness and 19 mm dia. were produced at a moulding pressure of 1 and 5 t cm^{-2} . When using PTFE powder at a moulding pressure of 1 t cm^{-2} , however, it was necessary to treble the amount of binder, *i.e.*, 20 wt.%, in order to obtain a sufficiently solid cathode. Cathodically limited Li- MnO_2 button cells containing these cathodes were produced with a nonwoven polypropylene separator.

A 1 M solution of LiClO_4 in PC:DME at 1:1 ratio by volume was used as cell electrolyte for the discharge at room temperature, while for low temperatures the solution was 0.5 M LiClO_4 in BL:DME, PC:DME, and BL:THF at 2:1 ratio.

The electrolytes used contained less than 50 ppm water and all procedures were carried out in a dry box under an atmosphere containing less than 100 ppm H_2O .

High constant discharge current densities were applied: 3.55 mA cm^{-2} for room temperature and 0.35 mA cm^{-2} and 1 mA cm^{-2} for low temperatures. The utilization and specific capacity of the MnO_2 cathodes were calculated from the discharge duration (determined to 2 V cut off).

All discharges were carried out with fresh cells and all temperatures were maintained with an accuracy of ± 2 °C.

Results and discussion

Figure 1 presents typical discharge curves of Li-MnO₂ formed with a moulding pressure of 5 t cm⁻² and assembled in button cells. They were obtained at a high discharge current density of 3.5 mA cm⁻² and at 20 °C. It is evident from Fig. 1 that the Faradiser WS and Knapsack samples display practically the same specific capacity although the operating voltage of CMD Faradiser WS was higher. The results shown in Fig. 1 are included in Table 1 along with those from other evaluations reported later in the text.

A basic criterion for button cells is their specific capacity by volume. Since the user is not concerned with small differences in the discharge voltage but mainly with the operation time, both Faradiser WS and Knapsack can be used successfully under the operating conditions given in Fig. 1.

Unfortunately, no investigations could be carried out with Faradiser M under these conditions since the cathode pellets cracked at a pressure of 5 t cm⁻². Miyazaki *et al.* [6] observed a similar phenomenon during the formation of the cathode mixture for alkaline MnO₂ cells [7].

This fact, together with the requirement for a higher cathode porosity in cells designed for operation at low temperature [8], necessitated the use of a lower moulding pressure. Figure 2 shows typical, 20 °C, 3.5 mA cm⁻² discharge current density discharge curves of button cells containing Faradiser WS, Faradiser M, and EMD Knapsack samples moulded at the optimum pressure of 1 t cm⁻² [9]. It can be seen from Fig. 2 and Table 1 that Faradiser WS is the most suitable MnO₂ at room temperature when using a low moulding pressure of 1 t cm⁻². It is also evident that, due to the higher apparent density of the Knapsack and Faradiser WS samples, the amount of active mass in the cathode in these is greater than that in Faradiser M. De-

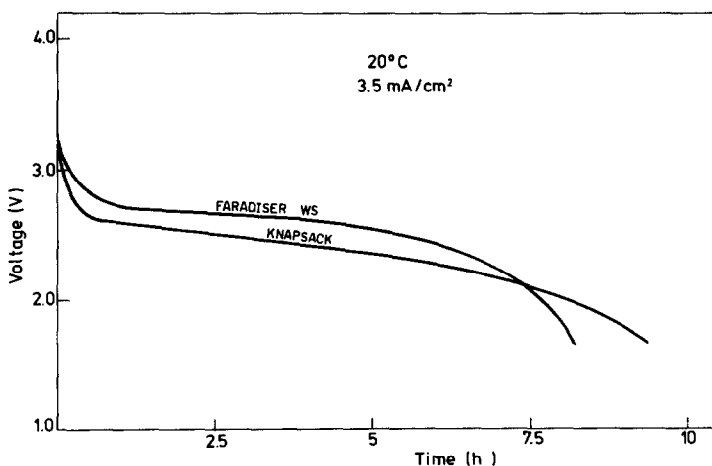


Fig. 1. Discharge curves of Li-MnO₂ button cells at 20 °C and 3.5 mA cm⁻², 5 t cm⁻² cathode moulding pressure.

TABLE 1
Lithium-manganese dioxide button cell characteristics

MnO ₂	Fig.	Moulding pressure (t cm ⁻²)	Discharge temperature (°C)	Discharge current (mA cm ⁻²)	MnO ₂ in the cathode mix (g cm ⁻³)	MnO ₂ utilization (%)	Capacity of cathode mix (mA h cm ⁻³)
Knapsack	1	5	20	3.50	1.75	59	306
Faradiser WS					1.75	56	286
Knapsack	2	1	20	3.50	1.57	54	255
Faradiser WS					1.57	80	376
Faradiser M					1.47	68	310
Knapsack	4	1	-20	0.35	1.57	46	216
Faradiser WS					1.57	53	255
Faradiser M					1.47	61	278
Knapsack	5	1	-20	1.00	1.57	12	59
Faradiser WS					1.57	15	71
Faradiser M					1.47	41	188
Knapsack	6	1	-40	0.35	1.57	2	8
Faradiser WS					1.57	10	47
Faradiser M					1.47	20	90
Faradiser TR		1	-20	0.35	1.52	54	192
Tekkasha					1.57	40	196

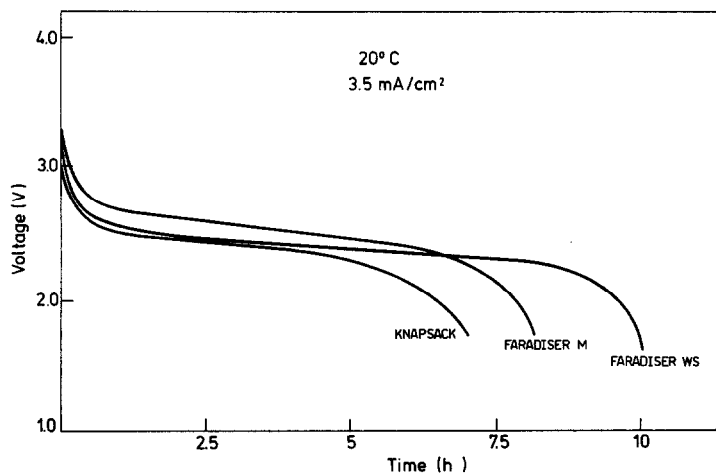


Fig. 2. Discharge curves obtained with different MnO₂ samples at 20 °C and 3.5 mA cm⁻², 1 t cm⁻² cathode moulding pressure.

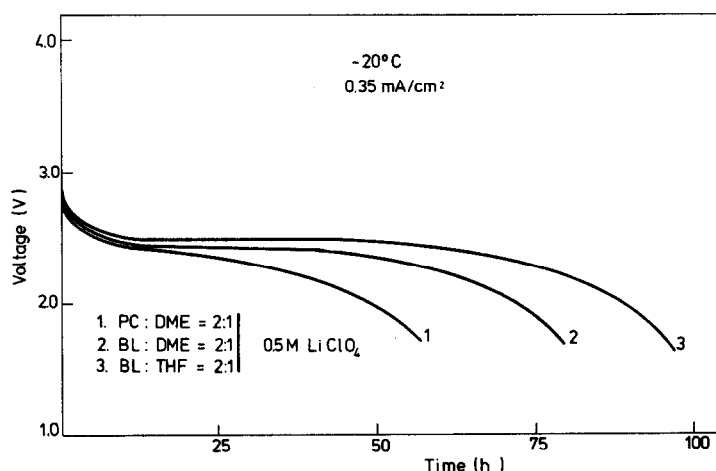


Fig. 3. Discharge curves obtained with Faradiser M and different electrolyte types.

spite this, however, Faradiser M shows a higher specific capacity by volume owing to its good utilization at high discharge rates.

A comparison of the results of Figs. 1, 2, and Table 1 shows that for discharge at room temperature, the decreased cathode mixture moulding pressure increases the utilization by weight of CMD Faradiser WS due to the increased porosity. This effect compensates for, and surpasses, the decreased MnO₂ content in the active cathode mass caused by the lower pressure. The specific capacity by volume increases as a result.

The low temperature discharge curves of the Li-MnO₂ button cells are strongly dependent on the type and ratio of the solvents used, the composition of the cathode mixture, the moulding pressure, the type of MnO₂ etc.

[10 - 13]. Figure 3 shows the discharge curves of Li-MnO₂ button cells at -20 °C and with a 0.35 mA cm⁻² discharge current density. The Faradiser M sample was used with electrolytes consisting of a 0.5 M solution of lithium perchlorate in the following solvents: PC:DME at a 2:1 ratio by volume, BL:THF 2:1 and BL:DME 2:1. The cathodes were moulded at a pressure of 1 t cm⁻². It can be seen from Fig. 3 that the highest capacity at low temperature was obtained using the BL:THF solvents. Since it is well known that THF reacts with lithium during prolonged storage [14], all subsequent evaluations at low temperature were carried out with the BL:DME mixture.

Figure 4 presents the discharge curves of Li-MnO₂ button cells at -20 °C and a discharge current density of 0.35 mA cm⁻². It can be seen that CMD Faradiser M has the highest discharge voltage.

Comparison of the three MnO₂ samples in Fig. 4 and Table 1 shows that because of its high utilization under these discharge conditions, Faradiser M displays the highest specific capacity by volume.

Figure 5 again gives the discharge curves obtained at -20 °C, but at a higher discharge current density - 1 mA cm⁻². In Fig. 5 Faradiser M displays the highest discharge voltage and capacity, while the difference between Knapsack and Faradiser WS is negligible. It can be seen from Table 1 that, despite its lower apparent density, Faradiser M shows higher utilization and specific capacity by volume when compared with the other two samples under the conditions of Fig. 5.

At the lower temperature of -40 °C and a discharge current density of 0.35 mA cm⁻² we observed a considerable difference in the discharge curves of EMD Knapsack and CMD Faradiser WS. It can be seen from Fig. 6 that the Knapsack discharge curve decreases below 2 V and this manganese dioxide is practically unusable under the discharge conditions stated there. A

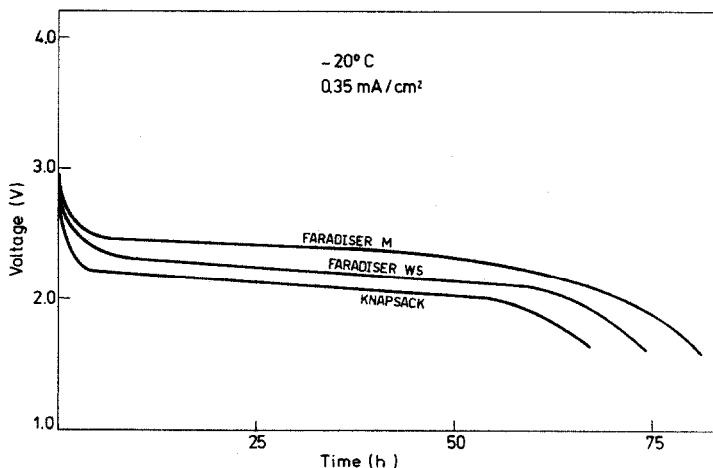


Fig. 4. Discharge curves obtained with different MnO₂ samples at -20 °C, 0.35 mA cm⁻², and a 1 t cm⁻² cathode mix moulding pressure.

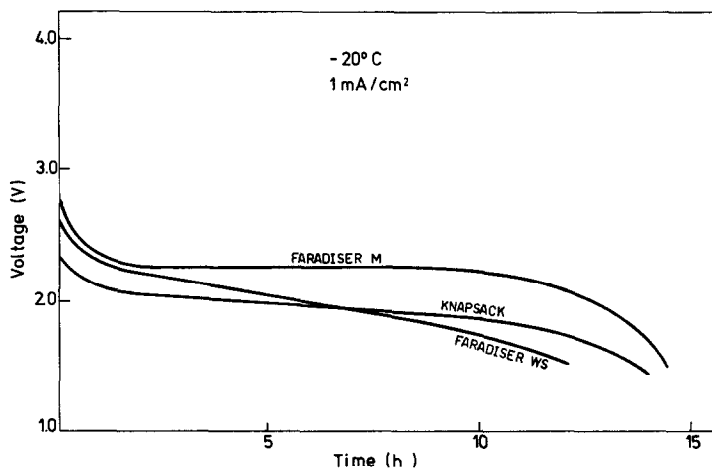


Fig. 5. Discharge curves obtained at -20°C , 1 mA cm^{-2} , and a 1 t cm^{-2} cathode mix moulding pressure.

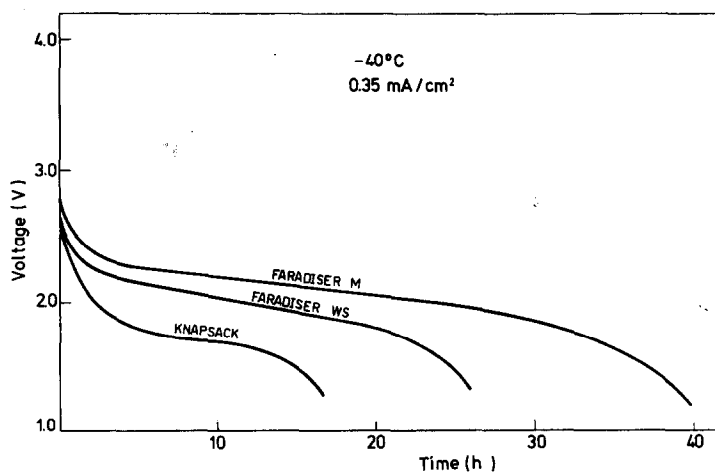


Fig. 6. Discharge curves at -40°C , 0.35 mA cm^{-2} , and a 1 t cm^{-2} cathode moulding pressure.

comparison of the data presented in Fig. 6 and Table 1 shows that Faradiser M again has the highest operating voltage and specific capacity by volume.

Analogous studies carried out at -20°C with EMD Tekkosha (Japan) and CMD Faradiser TR are shown in Table 1. The results obtained do not differ significantly from the Knapsack and Faradiser WS data for the same temperature.

We also checked whether the cathode pellet technology affected the low temperature characteristics of Li-MnO₂ button cells. Figure 7 (curve 2) shows the discharge curve of a cathode with 20 wt.% PTFE powder using a

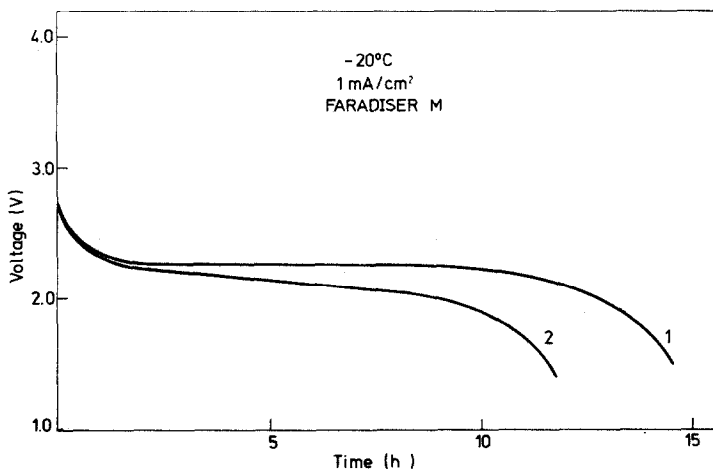


Fig. 7. Discharge curves obtained with Faradiser M at -20°C and 1 mA cm^{-2} current density. Curve 1, with binder content 20 wt.% Teflonized carbon black (7 wt.% PTFE); curve 2, with binder content 20 wt.% PTFE powder.

moulding pressure of 1 t cm^{-2} and a discharge current density of 1 mA cm^{-2} at -20°C . Curve 1, which was presented in Fig. 5, is included here for comparison.

Curves 1 and 2 in Fig. 7 were obtained with cathodes containing equal weights of MnO_2 . When using Teflonized carbon black the difference in the discharge times was 30% higher. A similar result was also obtained with these at -40°C .

Conclusions

The studies performed at high discharge rates showed that no single manganese dioxide has a universal advantage at both room and low temperatures. In cells designed for operation at room temperature, with conventional cathode moulding pressure, EMD Knapsack and CMD Faradiser WS appear to offer more or less the same characteristics. Using a lower cathode moulding pressure (higher porosity cathode), however, the room temperature performance of CMD Faradiser WS surpasses the highest performance of Knapsack EMD obtained under any conditions.

At low temperatures, with porous cathodes, Faradiser M is the best of all materials tested.

The high porosity of Faradiser M [15, 16] is an advantage at high discharge rates and low temperatures [8]. In this case, due to its high utilization and high discharge voltage, CMD Faradiser M compensates its low apparent density. In cathodically limited Li- MnO_2 button cells this manganese dioxide shows a specific capacity by volume several orders higher than that of EMD.

References

- 1 H. Ikeda, S. Narukawa and S. Suenaga, *2nd Manganese Dioxide Symp., Tokyo, Japan, 1980*, Vol. 2, IC Sample Office, Cleveland, OH, 1981, p. 414.
- 2 H. Ikeda, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, London, 1983, p. 169.
- 3 N. Ilchev, V. Manev, K. Hampartzumian, *J. Power Sources*, 25 (1989) 177.
- 4 T. Ohzuku, Y. Kogo and T. Hirai, in K. Kordesch and A. Kozawa (eds.), *2nd Battery Material Symp. (3rd MnO₂ Symp.)*, Graz, Austria, 1985, Vol. 2, IBA (Int. Battery Material Association), IC MnO₂ Sample Office and JEC Press, p. 391.
- 5 P. Picquet, in K. Kordesch and A. Kozawa (eds.), *2nd Battery Material Symp. (3rd MnO₂ Symp.)*, Graz, Austria, 1985, Vol. 2, IBA (Int. Battery Material Association), IC MnO₂ Sample Office and JEC Press, p. 416.
- 6 K. Miyazaki and N. Imada, in K. Kordesch and A. Kozawa (eds.), *2nd Battery Material Symp. (3rd MnO₂ Symp.)*, Graz, Austria, 1985, Vol. 2, IBA (Int. Battery Material Association), IP MnO₂ Sample Office and JEC Press, p. 169.
- 7 J. Brenet, P. Picquet and J. Welsh, *2nd Manganese Dioxide Symp., Tokyo, Japan, 1980*, Vol. 2, IC Sample Office, Cleveland, OH, 1981, p. 214.
- 8 E. E. Casey, *J. Power Sources*, 8 (1982) 83.
- 9 N. Ilchev, K. Hampartzumian, *Ext. Abstr., 15th Conf. Higher Inst. Chem. Technol., Sofia, 1984*, Vol. 2, p. 350.
- 10 J. Watanabe, R. Okazaku, M. Nakai and Y. Toyoguchi, *Prog. Batteries Sol. Cells*, 3 (1980) 70.
- 11 K. Hampartzumian and N. Ilchev, *J. Power Sources*, 8 (1982) 35.
- 12 A. Kozawa, *Ext. Abstr., 3rd Int. Meeting Lithium Batteries, Kyoto, Japan, May 1986*, p. 36.
- 13 N. Furukawa, M. Hara and S. Yoshimura, *Ext. Abstr., 3rd Int. Meeting Lithium Batteries, Kyoto, Japan, May 1986*, p. 83.
- 14 V. Koch, *J. Power Sources*, 9 (1983) 247.
- 15 P. Picquet and J. Welsh, *New Mater. New Processes*, 2 (1983) 12.
- 16 J. Welsh and P. Picquet, *Prog. Batteries Sol. Cells*, 2 (1979) 119.