

THE LITHIUM-MANGANESE DIOXIDE CELL II. BEHAVIOUR OF MANGANESE DIOXIDE IN NONAQUEOUS ELECTROLYTE

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Summary

The rate of lithium ion insertion in different types of manganese dioxide, depending on their pretreatment temperature, has been studied. At high discharge rates different manganese dioxides have specific optimum temperatures of thermal treatment at which they show maximum utilization. For most types of manganese dioxide that temperature is 300 °C. The manganese dioxides which we have studied display a correlation between the specific surface area and specific capacity by weight. Under the experimental conditions in the test electrodes high discharge rates are obtained even at low temperatures.

Introduction

A controversy exists as to which manganese dioxide is the most suitable for lithium cells. From the discharge curves of button cells, Ikeda *et al.* [1] showed that at low discharge rates (0.1 mA cm^{-2}) the International Common MnO₂ Sample No. 11 (IC 11 CMD — Kerr McGee Corp., USA) was the most suitable, while cells with the International Common MnO₂ Sample No. 12 (IC 12 CMD — SEDEMA, Belgium) showed the lowest capacity. Moreover, Ikeda *et al.* [1] did not find any correlation between the physicochemical properties of the investigated manganese dioxides and their behaviour in lithium cells. At higher discharge rates (1 mA cm^{-2}) Pistoia [2] found a reverse relationship, with IC 11 not showing satisfactory utilization, while IC 12 displayed a utilization better than 70%.

The thermal treatment of MnO₂ before being made into lithium cell cathodes is carried out in the temperature range 375 °C - 400 °C [1, 3]. According to different authors the duration of treatment varies between several minutes and 24 h [4 - 6].

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In the present work, using test electrodes, the utilization of different manganese dioxides and their thermal treatment have been determined at high discharge current densities. In these test electrodes the manganese dioxide was uniformly distributed in a highly conductive and highly porous matrix. Due to the large surplus of conducting agent the ohmic losses in the electrode were eliminated. In addition, the high porosity ensured a surplus of electrolyte in the bulk of the electrode which was one order of magnitude greater than the MnO_2 volume. It should be noted that in the test electrode technological problems associated with the cathode, and those related to the construction and material balance of the cells, were disregarded. Under the test conditions the rate determining stage in the discharge process was the insertion of lithium ions in the crystal structure of MnO_2 .

Experimental

The International Common MnO_2 Samples Nos. 2, 5, 6, 11, 12 and 14 were used in the present work. The following MnO_2 products were also tested: CMD Faradiser WS (S.S.A. 52 and $28 \text{ m}^2 \text{ g}^{-1}$) produced by SEDEMA, Belgium; EMD Knapsack (A.G. Hoechst, FRG); CMD (USSR); λ -CMD obtained by the authors and prepared according to Hunter [7, 8]; β -CMD (S.S.A. $56 \text{ m}^2 \text{ g}^{-1}$) prepared by oxidation of MnCO_3 [9] and obtained from the Technical University of Dresden, GDR.

The manganese dioxides investigated were treated at constant temperatures for 8 h within the range 250°C - 450°C . The tests were performed at $25 \pm 2^\circ\text{C}$ intervals. The MnO_2 samples treated at each temperature were homogenized with carbon black (containing 35% PTFE) in a 1:2 ratio by weight. The test cathodes were prepared by pasting 50 mg of the obtained mixtures onto a nickel grid, the weight of the samples being determined to ± 0.1 mg. The cell contained two lithium counter electrodes placed on each side of the test electrode, and a lithium reference electrode. The cathode preparation and cell assembly were carried out in a dry box with less than 20 p.p.m. H_2O . A 1 M solution of lithium perchlorate in PC:DME in a 1:1 ratio by volume, with water content below 50 p.p.m. was used. The capacity and utilization of the electrodes were evaluated from the discharge curves to a 2 V cut off. Two discharge rates were used: a high discharge rate (1 h rate) and a relatively light discharge (10 h rate), estimated from the theoretical cathode capacity.

Results and discussion

Different manganese dioxides showed maximum utilization at different heat treatment temperatures. The maximum utilization of most types of manganese dioxide investigated was reached by treatment at 300°C (Fig. 1). For IC 2 and IC 5 the utilization was not very dependent on the thermal

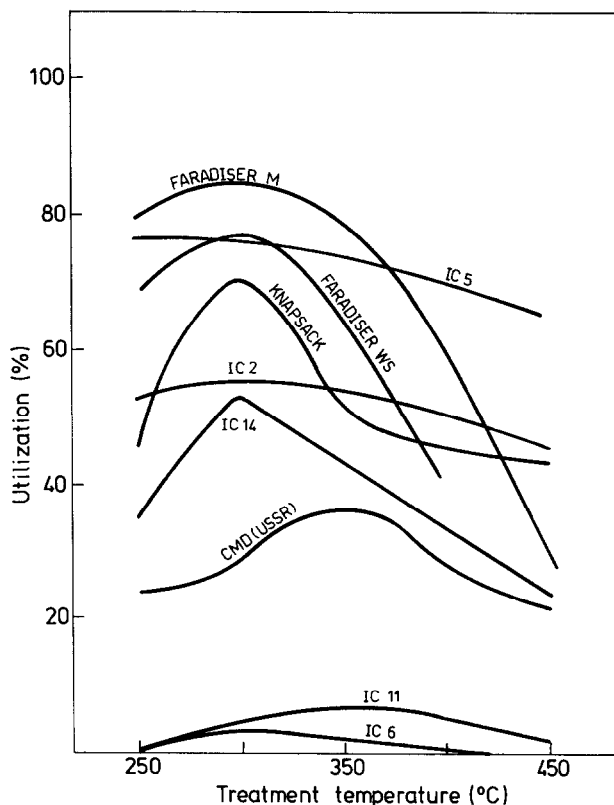


Fig. 1. Influence of the treatment temperature on the utilization of different MnO_2 samples discharged at the 1 h rate at room temperature.

treatment temperature, while for Faradiser M, Faradiser WS (S.S.A. $52 \text{ m}^2 \text{ g}^{-1}$), and Knapsack it decreased more sharply at temperatures above the maximum. Figure 1 shows that at high discharge rates Faradiser M, Faradiser WS and IC 5 displayed the highest utilization. Figure 1 also demonstrates that a universal thermal treatment of manganese dioxides of different origin at identical temperatures is incorrect.

In the case of Faradiser M and Faradiser WS a combined thermal treatment regime was also tested — 8 h at 300°C and 0.5 h at 400°C . For both samples, under these conditions utilization decreases considerably from the maximum utilization at 300°C (68% for Faradiser M and 54% for Faradiser WS), see Table 1. By maintaining a constant optimum temperature of 300°C , we tested the influence of the duration of thermal treatment on the utilization of Faradiser M and Faradiser WS. It can be seen from Table 1 that treatment for longer than 8 h decreases the utilization. These differences in utilization became very large when the MnO_2 was treated at temperatures higher than the optimum, e.g., 400°C . Table 1 shows that 30 h at 300°C is less detrimental to performance than 8 h at 400°C . This is in good agreement with the results presented in Part 1 of this paper [10].

TABLE 1

Influence of the duration of thermal pretreatment on utilization (in percentage) at the 1 h discharge rate at room temperature

CMD	300 °C			400 °C
	8 h	20 h	30 h	8 h
Faradiser M	85	75	72	60
Faradiser WS (52 m ² g ⁻¹)	77	72	67	42

TABLE 2

Influence of the discharge conditions on utilization (in percentage) for different MnO₂ samples treated thermally at 300 °C for 8 h

Discharge rate	1 h	10 h
Faradiser M	85	92
Faradiser WS	77	85
Knapsack	70	80
IC 2	56	80

Table 2 compares the utilizations of different MnO₂ samples discharged at 1 h and at 10 h rates. It can be seen that at the lower discharge rates the utilization was always higher.

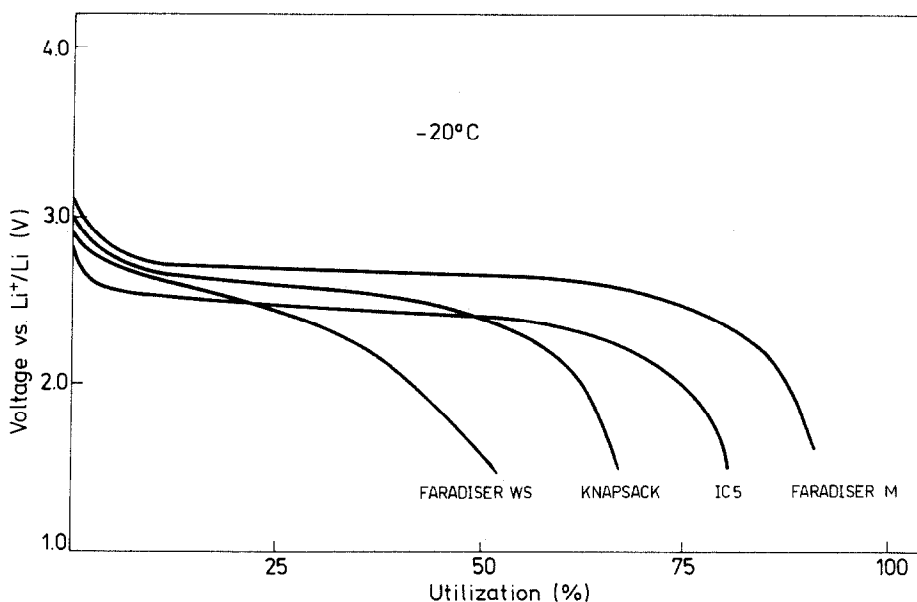


Fig. 2. Discharge curves obtained at the 10 h rate.

Analogous studies at the 10 h rates were also carried out at -20°C . The discharge curves of Fig. 2 show that under these conditions, after pretreatment at their optimum temperature, Faradiser M and IC 5 have the highest utilization, while Faradiser M and Knapsack have the highest discharge voltage. It was also evident that, unlike at room temperature, Knapsack showed a higher utilization than did the Faradiser WS.

We checked whether the optimum temperature for maximum utilization of Faradiser M at room temperature differed from that at -40°C and found, as shown in Fig. 3, that there was no change.

In the case of Fig. 4, the manganese dioxides were again pretreated at their optimum temperatures: it shows that at -40°C Faradiser M and IC 5 display the highest utilization to 1.5 V cut off.

Figure 5 shows the influence of the specific surface area on the utilization of two samples of $\beta\text{-MnO}_2$. The maximum utilization of both β -manganese dioxides follows a pretreatment temperature of 300°C , as was the case with most of those in Fig. 1.

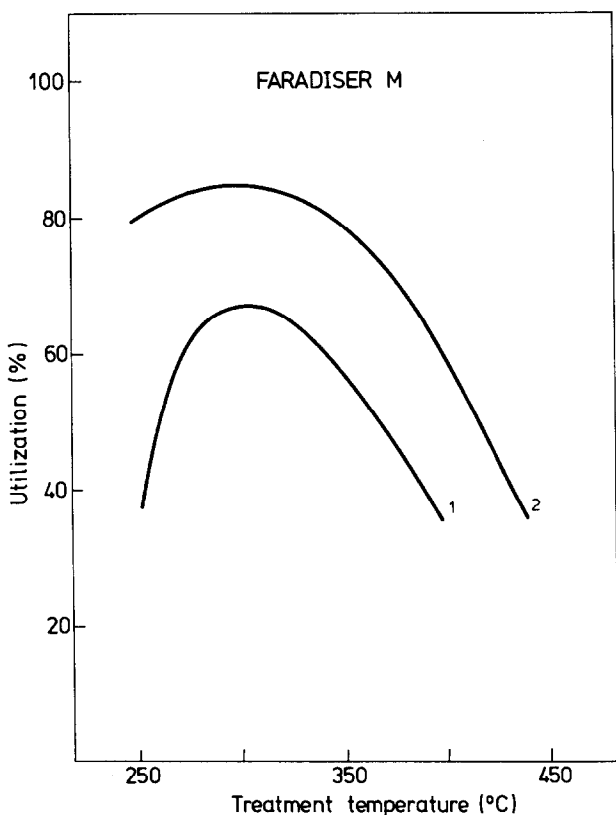


Fig. 3. Influence of the treatment temperature on the utilization of Faradiser M discharged at the 1 h rate at room temperature (Curve 1), and at the 10 h rate at -40°C (Curve 2).

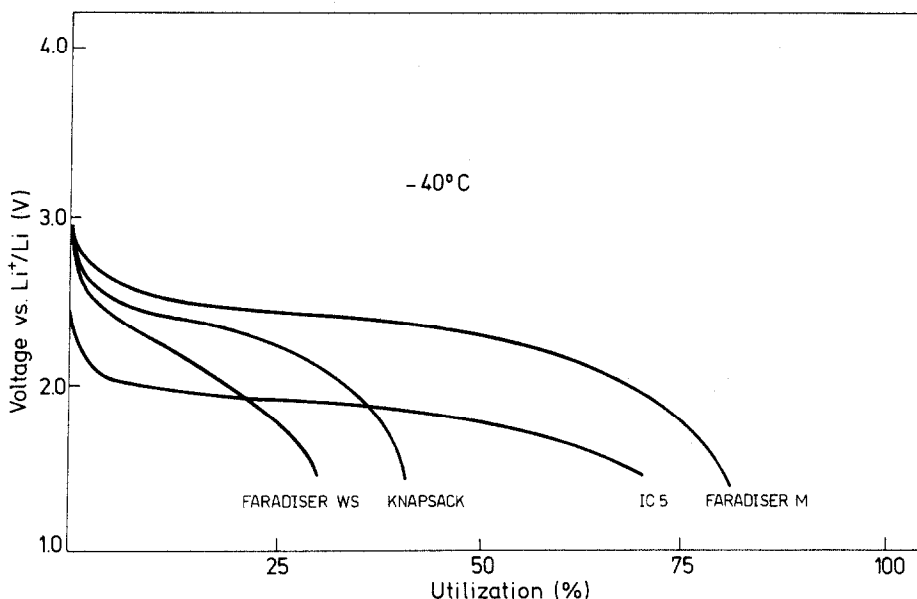


Fig. 4. Discharge curves at the 10 h rate.

The influence which the pretreatment temperature has on the specific surface area of Faradiser WS is presented in Fig. 6. It can be seen that maximum specific surface area is formed at 300 °C. The results are similar to those obtained by Kozawa [11] who found a maximum at 250 °C for other manganese dioxides. There are numerous factors influencing the utilization of MnO_2 ; therefore the behaviour of this material in nonaqueous electrolytes cannot be explained solely by the coincidence of the maxima of specific surface area and utilization in Fig. 6.

Figure 7 shows the dependence of the specific capacity by weight of the studied manganese dioxides on their specific surface area. All were pretreated at their optimum temperature and a correlation can be observed. The manganese dioxides with higher specific capacity by weight have higher specific surface area, irrespective of their crystal structure and origin. These results are in agreement with the investigations made by Smith *et al.* [12], who found that the most active dioxides in aqueous electrolytes have the highest areas.

Among the types of MnO_2 investigated by us, Faradiser M has the maximum specific surface area. Figure 8 shows the utilization of this unique manganese dioxide as a function of discharge temperature after applying optimum thermal pretreatment conditions. Despite the decreasing temperature, Faradiser M discharges with minimum loss of utilization.

Conclusion

At high discharge rates, different types of manganese dioxide used as cathode materials in nonaqueous electrolytes have specific optimum pre-

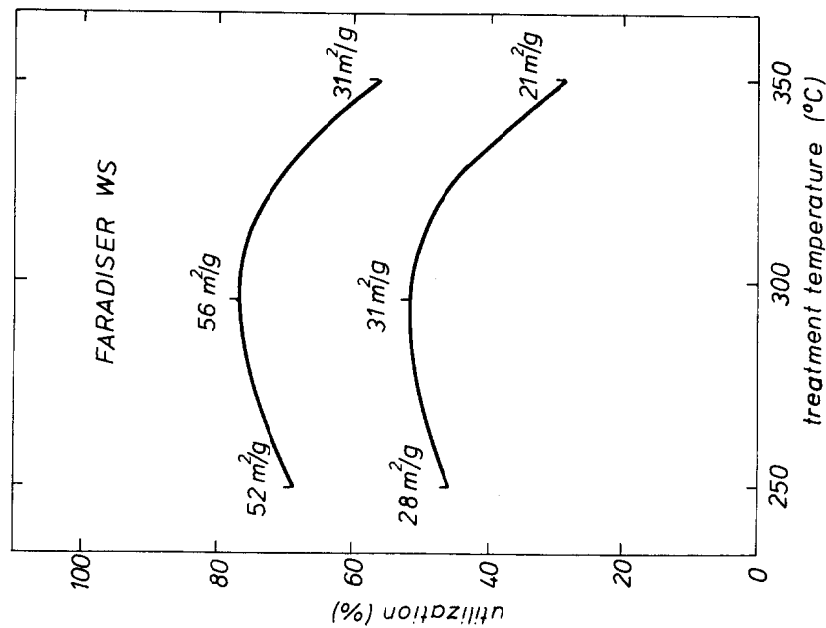
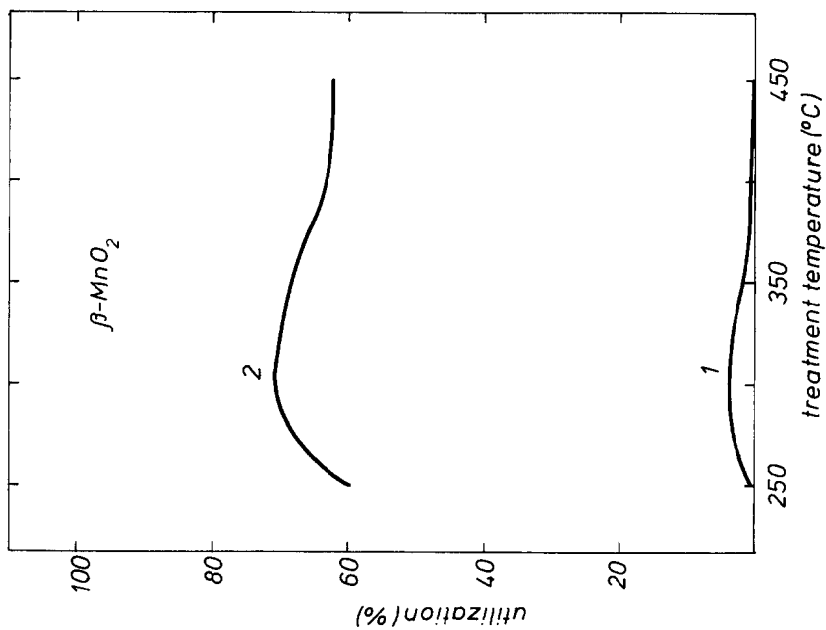


Fig. 5. Influence of the S.S.A. on the utilization of $\beta\text{-MnO}_2$ discharged at the 1 h rate at room temperature: Curve 1, IC 6 ($1 \text{ m}^2 \text{ g}^{-1}$); Curve 2, CMD ($56 \text{ m}^2 \text{ g}^{-1}$), prepared according to ref. 9.

Fig. 6. Influence of the thermal treatment on the S.S.A. and the utilization at the 1 h discharge rate at room temperature.

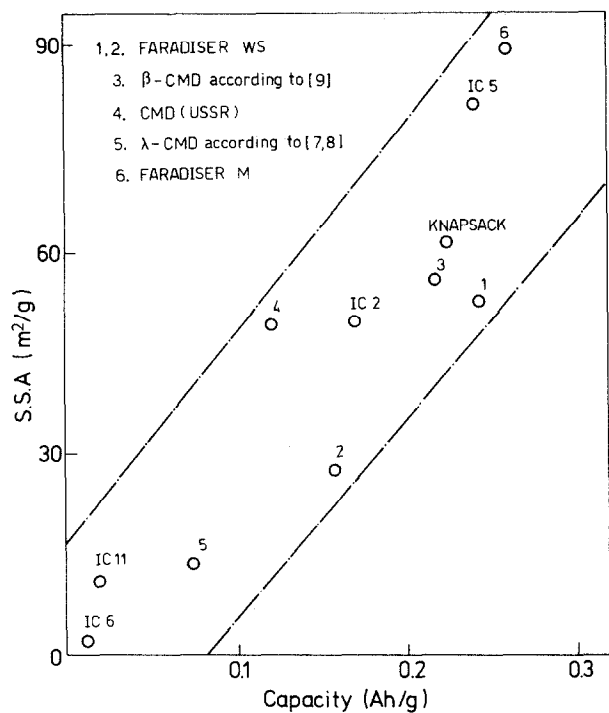


Fig. 7. Relationship between S.S.A. and specific capacity by weight of different MnO_2 samples at a 1 h discharge rate at room temperature.

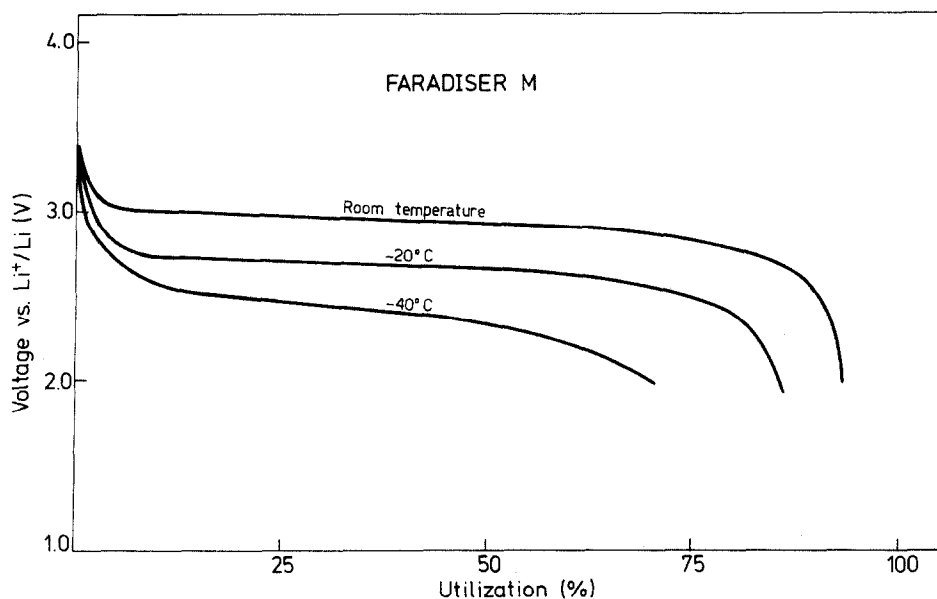


Fig. 8. Discharge behaviour of Faradiser M at a 10 h rate.

treatment temperatures, with which they achieve maximum utilization. For most types this is 300 °C but if it is sustained for more than 8 h the utilization is degraded.

It was found that at high discharge rates CMD, Faradiser M and IC 5 displayed the highest utilization in nonaqueous electrolyte at room temperature, while at low temperatures Faradiser M had the best performance.

For the investigated manganese dioxides a correlation exists between specific surface area and specific capacity by weight.

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