# DISCHARGE OF CHEMICAL AND ELECTROCHEMICAL MANGANESE DIOXIDES IN NONAQUEOUS ELECTROLYTES

Nikolai ILCHEV, Vesselin MANEV, Branimir BANOV and Anton MOMCHILOV

*Central Laboratory of Electrochemical Power Sources,*
*Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

Received April 17, 1990
Accepted June 26, 1990

*Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.*

The rate of lithium ion insertion in different types of manganese dioxide, depending on their pretreatment temperature, was investigated. To obtain maximum utilization at heavy discharge drains, the optimum thermal pretreatment temperature for different chemical and electrochemical manganese dioxides (CMD and EMD) was determined. For most types of $MnO_2$ samples this temperature is 300°C. The manganese dioxides studied display a correlation between their specific surface area and specific capacity by weight. The specific capacity by volume of different CMD and EMD samples was compared in lithium button cells. Their specific electrochemical characteristics were studied at high discharge rates in a wide temperature range. Owing to its high utilization CMD Faradiser M appears to be an excellent cathode material, especially at heavy discharge drains and low temperatures.

EMD and CMD are widely used as cathode materials in nonaqueous electrolytes. A controversy exists among investigators as to which EMD or CMD is the most suitable for primary lithium cells[1-4]. So far no correlation has been established between the physicochemical properties of the manganese dioxides and their behaviour in lithium cells[1].

The thermal pretreatment of all $MnO_2$ materials is normally carried out in the temperature range 375°–400°C (refs[1,6]). Ohzuki et al.[6] investigated equal amounts of cathode mixture from International Battery Association (IBA) $MnO_2$ samples Nos. 1–5, 8 and 10–12, pretreated at 400°C, and found that at room temperature CMD displays the highest specific capacity by weight. However, the samples tested by these authors[6] were not pretreated at the optimum temperature, which is necessary to obtain maximum utilization[7,8]. Miyzaki et al.[9] showed that at constant cathode volume EMD has a greater capacity than CMD. The $MnO_2$ types used, the pretreatment temperature and electrolyte content were not specified in this paper[9]. Similar results were obtained by Ikeda et al.[1].

The aim of the present work was to determine the specific optimum pretreatment temperature for different CMD and EMD samples, at which they show maximum utilization in excess of electrolyte. The electrochemical characteristics of EMD and

CMD were compared in button cells with constant cathode volume and optimum porosity. An attempt was made to find a correlation between the physicochemical properties of the investigated samples and their behaviour in nonaqueous electrolytes.

## EXPERIMENTAL

The International Battery Association (IBA) Samples Nos. 1—7, 9—12, 14—22, 24—27 were used. The following $MnO_2$ materials were also tested: EMD Knapsack (A. G. Hoechst); CMD (U.S.S.R.); SEDEMA CMDs Faradiser M, Faradiser WS and Faradiser TR, with different specific surface areas; EMD CEGASA (Spain); EMD Chemetals SW3 (U.S.A.); EMD (U.S.S.R.); EMD Tekkosha (Japan) and CMD X2 (Pilot run at Nikopol, Bulgaria).

The $MnO_2$ samples were treated at constant temperature for 8 h within the temperature range 250°—450°C. The test cathodes were prepared from a mixture of $MnO_2$ and Teflonized carbon black (containing 35% PTFE) in a 1 : 2 ratio by weight. The electrochemical cell contained two counter electrodes, a lithium reference electrode and the test cathode, operating in excess of electrolyte. The cathodes for CR 2530 button cells, having 0·90 ± 0·03 mm thickness and 19 mm diameter, were produced from a mixture with 20 wt. % Teflonized carbon black (containing 35% PTFE) pressed at a pressure of 1 and 5 t/cm$^2$.

The electrolytes used were 1M $LiClO_4$ in PC : DME in a 1 : 1 ratio by volume for discharges at room temperature, and 0·5M $LiClO_4$ in BL : DME 2 : 1 for low temperatures. These electrolytes contained less than 50 ppm water and all procedures were carried out in a dry box under an atmosphere with less than 100 ppm water.

The capacity and utilization of the electrodes were evaluated from the discharge curves up to 2 V cut off.

The tests in CR 2530 button cells were carried out at high constant discharge current densities: 3·55 mA/cm$^2$ at room temperature and 0·35 mA/cm$^2$ at −40°C.

In an electrochemical cell with an excess of electrolyte a high 1 h rate and a relatively light 10 h rate were used.

## RESULTS AND DISCUSSION

Figure 1 shows the utilization of different $MnO_2$ samples, depending on their pretreatment temperature. The measurements were carried out at room temperature at 1 h discharge rate in excess of electrolyte. Figure 1 indicates that the maximum utilization of most samples was reached at 300°C, while for CMD (U.S.S.R.) and IC 11 it appears at 350°C.

The dependence of the specific capacity by weight of the studied IBA samples on their specific surface area is shown in Fig. 2. A 1 h discharge rate in excess of electrolyte at room temperature was used for these measurements. It can be seen that samples with higher specific surface area have higher specific capacity, irrespective of the $MnO_2$ crystal structure and origin.

The influence of the pretreatment temperature on the specific surface area of CMD Faradiser WS is shown in Fig. 3. As can be seen, the maximum specific surface area is formed at 300°C. Since it is well known that numerous factors influence the $MnO_2$

efficiency, the behaviour of Faradiser WS cannot be attributed only to the coincidence of the two maxima of specific surface area and utilization in Fig. 3.

Figure 4 demonstrates an analogous experiment carried out with CMD Faradiser M, a laboratory product of SEDEMA. All samples were pretreated at their optimum temperature of 300°C (compare with Fig. 1). It follows from Fig. 4 that the specific capacity by weight depends strongly on the specific surface area, both at room temperature and at −40°C.

In practice, the basic criterion for button cells is their specific capacity by volume. Figure 5 presents typical discharge curves of CR 2530 Li–$MnO_2$ button cells pressed at 5 t/cm$^2$. Since the user is not concerned with small differences in the discharge voltage but mainly with the service life, it can be concluded that both Knapsack and Faradiser WS may be used successfully under the operating conditions given in Fig. 5.

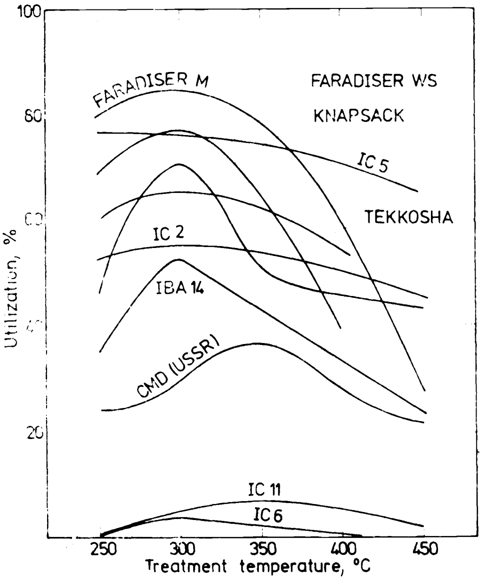

FIG. 1

Influence of the pretreatment temperature on the utilization of different $MnO_2$ samples discharged at a 1 h rate at room temperature

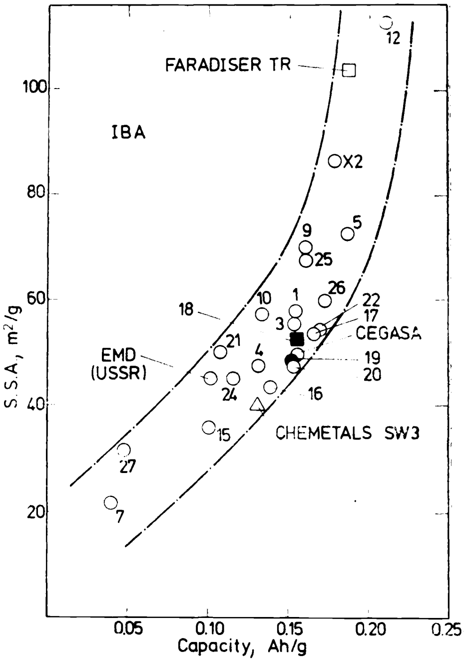

FIG. 2

Relationship between specific surface area (S.S.A.) and specific capacity by weight of different IBA samples at a 1 h discharge rate at room temperature

TABLE I

Characteristics of CR 2530 Li–$MnO_2$ cells

| $MnO_2$ | Moulding pressure t $cm^{-2}$ | Discharge temperature °C | $MnO_2$ in the cathode mix g $cm^{-3}$ | Capacity of cathode mix mAh $cm^{-3}$ |
|---|---|---|---|---|
| Knapsack | 5 | 20 | 1·75 | 306 |
| Faradiser WS | | | 1·75 | 286 |
| Knapsack | 1 | −40 | 1·57 | 8 |
| Faradiser WS | | | 1·57 | 47 |
| Faradiser M | | | 1·47 | 90 |

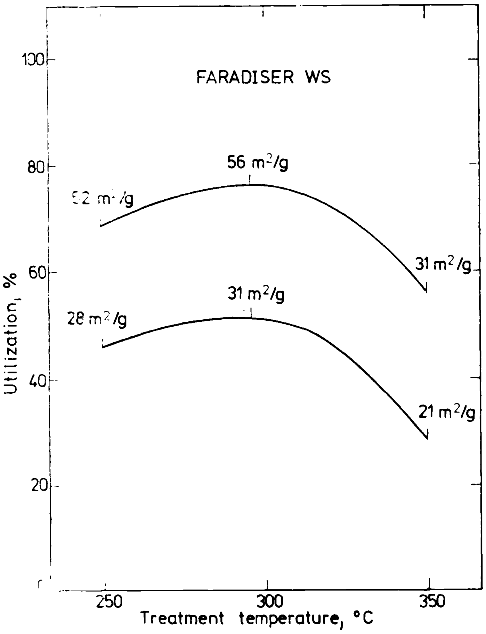

FIG. 3

Influence of the pretreatment temperature on the S.S.A. and the utilization at a 1 h discharge at room temperature

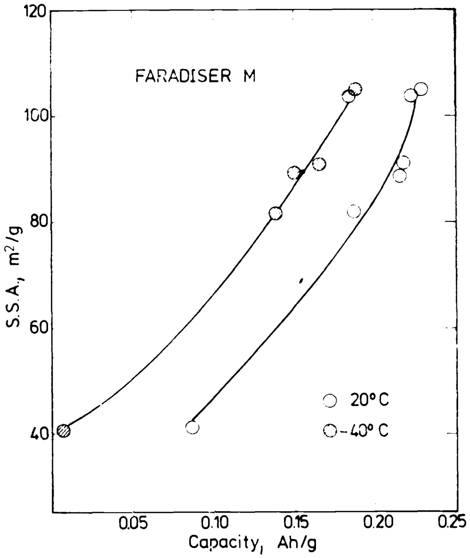

FIG. 4

Dependence of the specific capacity by weight of CMD Faradiser M on the S.S.A. at room temperature and −40°C

At low temperature analogous studies with porous cathodes pressed at 1 t/cm$^2$ were carried out. It can be seen from Fig. 6 that Faradiser M has the highest discharge voltage and specific capacity by volume. A comparison of the data presented

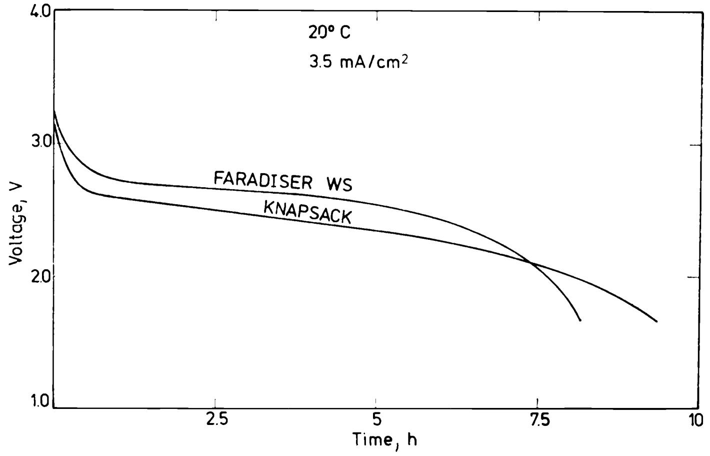

FIG. 5

Discharge curves of CR 2530 Li-MnO$_2$ button cells at 20°C and 3·5 mA/cm$^2$, 5 t/cm$^2$ cathode moulding pressure

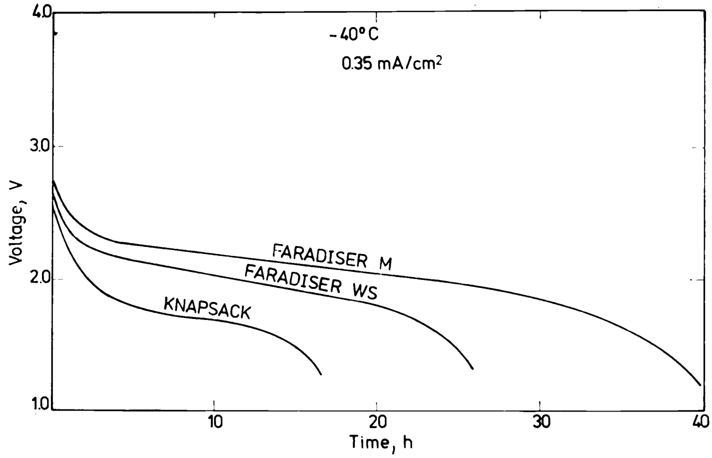

FIG. 6

Discharge curves of CR 2530 Li-MnO$_2$ button cells at −40°C and 0·35 mA/cm$^2$, 1 t/cm$^2$ cathode moulding pressure in Figs 5 and 6 is shown in Table I. It should be noted that data for Faradiser M at room temperature are not included in Table I and Fig. 5 because the cathode pellets crack at a pressure of 5 t/cm$^2$. This $MnO_2$ was used for low temperature discharges where the necessity of high cathode porosity required lower moulding pressure.

It can be concluded that different samples of $MnO_2$ have different optimum pretreatment temperatures at which they show maximum utilization. For the investigated $MnO_2$ samples the specific capacity by weight depends on their specific surface area.

In CR 2530 button cells produced at 5 t/cm$^2$ moulding pressure EMD Knapsack and CMD Faradiser WS offer the same characteristics. Owing to its high porosity and utilization at high discharge rates and low temperatures, CMD Faradiser M performs as the best of all materials tested in spite of its low apparent density.

The experimental results show that a proper selection of the $MnO_2$ type with an optimized thermal pretreatment can improve significantly the performance of the Li–$MnO_2$ system at heavy discharge drains and low temperatures down to −40°C.

## REFERENCES

1. Ikeda H., Narukawa S., Suenaga S.: *2nd Manganese Dioxide Symp., Tokyo, Japan 1980*, Vol. 2, p. 414. IC Sample Office, Cleveland, OH 1981.
2. Ikeda H. in: *Lithium Batteries* (J. P. Gabano, Ed.), p. 169. Academic Press, London 1983.
3. Hampartzumian K., Ilchev N.: J. Power Sources *8*, 35 (1982).
4. Hampartzumian K., Manev V., Ilchev N.: *New Materials and New Processes*. JEC Press, Cleveland, OH, U.S.A.
5. Ikeda H.: US. P 4,133,856 (1979).
6. Ohzuku T., Kogo Y., Hirai T. in: *Proc. 2nd Battery Material Symp.* (*3rd Manganese Dioxide Symp.*) (K. Kordesch and A. Kozawa, Eds), Vol. 2, p. 391. Graz, Austria 1985.
7. Ilchev N., Manev V., Hampartzumian K.: J. Power Sources *25*, 177 (1989).
8. Pickuet P. in: Ref.[6], p. 416.
9. Miyazaki K., Imada N. in: Ref.[6], p. 169.