

The lithium–manganese dioxide cell IV. Relationship between physicochemical properties and electrochemical characteristics of MnO_2 in nonaqueous electrolytes

N. Ilchev* and **B. Banov**

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

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Abstract

By maintaining constant chemical content and varying the physical characteristics of nonstandard samples of Faradiser M chemical manganese dioxide (CMD), a correlation was found between the electrochemical characteristics of the test samples and their specific surface area (SSA) and pore volume. The electrochemistry of different manganese dioxides in nonaqueous electrolytes is explained on the basis of their pore size distribution, SSA, and morphology. The increase of SSA of manganese dioxides of a particular crystal structure most probably enhances the electrochemical process in this cathode material.

Introduction

The electrochemical behavior of manganese dioxide in aqueous electrolytes is influenced by a number of physicochemical properties such as SSA, pore volume, pore morphology, particle morphology, 'tap' density, MnO_2 content, etc. [1–3]. In nonaqueous electrolytes the pretreatment temperature and the SSA significantly affect the utilization of different types of MnO_2 [4].

At high discharge rates chemical manganese dioxide (CMD) Faradiser M displayed the highest utilization of all materials tested in excess of electrolyte at room and low temperatures [4].

Studies performed in button cells at high current densities showed that no single MnO_2 has a universal advantage at both room and low temperatures [5]. At room temperature CMD and electrochemical manganese dioxide (EMD) offered the same characteristics. However, the low-temperature performance of CMD Faradiser M was again the best of all materials tested in identical cathode volume.

The present work was an attempt to establish a correlation between the electrochemical performance of the manganese dioxide samples studied and their physicochemical characteristics.

*Author to whom correspondence should be addressed.

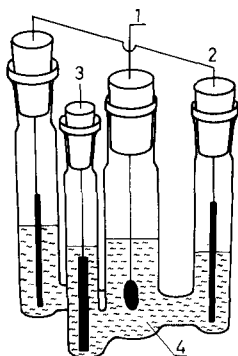


Fig. 1. Test cell diagram: 1, test cathode; 2, lithium counter electrodes; 3, lithium reference electrode; 4, electrolyte.

Experimental

Nonstandard samples of CMD Faradiser M (produced by SEDEMA, Belgium) with different surface areas (SSA) were primarily used in this investigation. In addition, the following MnO_2 products were also used: Standard Faradiser M, Faradiser WS, and EMD Tekkosha.

All of the MnO_2 samples tested were pretreated at 300 ± 2 °C for 8 h. The thermally-pretreated manganese dioxides were homogenized with carbon black (containing 35 wt.% PTFE) in a 7:3 ratio by weight. The cathodes were prepared by pressing 100 mg of the mixtures so obtained onto a nickel grid at 10 t cm^{-2} . The weight of the samples was determined to ± 0.1 mg.

The test cell contained two lithium counter electrodes (placed on each side of the cathode), and a lithium reference electrode, Fig. 1. Two discharge rates were used: 1 h and 10 h, estimated from the theoretical cathode capacity. The utilization and the corresponding capacity of the test cathodes were evaluated from the discharge curves to a 2 V cut off. All discharge temperatures were maintained with an accuracy of ± 2 °C.

For room temperature experiments a 1 M solution of LiClO_4 in PC:DME in a 1:1 ratio by volume was employed. At -40 °C the electrolyte was 0.5 M LiClO_4 in BL:DME, 2:1 by volume [5]. In all cases the water content was maintained below 50 ppm. All procedures were carried out in a dry box under an atmosphere containing less than 100 ppm H_2O .

The total pore volume of the samples was determined by low temperature nitrogen adsorption. Cumulative distribution of pore volume and pore surface was measured by Micrometrics pore-sizer 9305. For median diameter measurements a 715 E379 Cilas granulometer was used.

Results and discussion

The physicochemical characteristics of all nonstandard Faradiser M samples are listed in Table 1.

TABLE 1

Physicochemical characteristics of Faradiser M test samples

| Sample no. | SSA(BET) ($\text{m}^2 \text{g}^{-1}$) | Tap density (g cm^{-3}) | Total pore volume ($\text{cm}^3 \text{g}^{-1}$) | MnO_2 (%) | O/Mn (%) | Mn (%) | Dia. (median) (μm) |
|------------|---|------------------------------------|---|--------------------|----------|--------|---------------------------------|
| 1 | 105 | 1.87 | 0.186 | 90.3 | 1.949 | 60.1 | 38.8 |
| 2 | 104 | 1.85 | 0.178 | 89.3 | 1.945 | 58.1 | 40.5 |
| 3 | 91 | 2.04 | — | 89.9 | 1.947 | 60.0 | 36.3 |
| 4 | 89 | 2.15 | 0.129 | 90.5 | 1.957 | 59.8 | 45.1 |
| 5 | 82 | 2.29 | 0.110 | 89.9 | 1.942 | 60.4 | 36.9 |
| 6 | 41 | 2.35 | 0.061 | 90.9 | 1.958 | 59.9 | 38.1 |

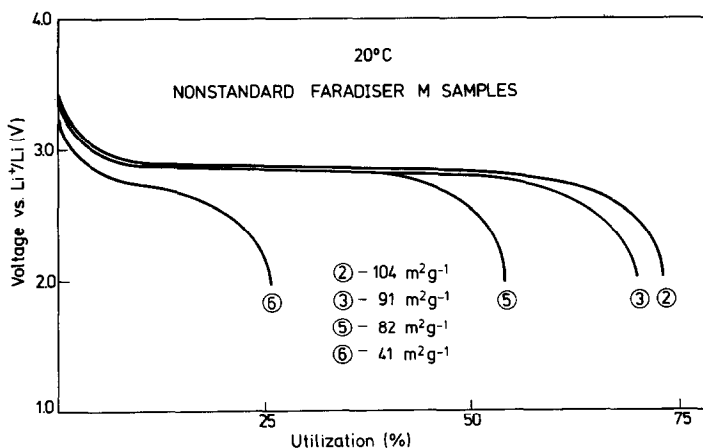


Fig. 2. Influence of specific surface area on the utilization of nonstandard samples of Faradiser M discharged at the 10 h rate at room temperature. Curve 2 is representative of samples 1 and 2; curve 3 of samples 3 and 4.

It can be seen from Table 1 that all test samples are very similar in their chemical content and median particle diameter, but they differ significantly in their physical properties.

The electrochemical behaviour of samples Nos 2, 3, 5 and 6, discharged at the 10 h rate, is shown in Fig. 2 (20 °C) and in Fig. 3 (-40 °C). The typical discharge curves presented in Fig. 2 indicate that for CMD Faradiser M with SSA higher than $80 \text{ m}^2 \text{g}^{-1}$ the utilization at room temperature increases with the SSA, without any remarkable differences in the discharge voltage. At the 10 h rate, sample 6 with SSA of $41 \text{ m}^2 \text{g}^{-1}$ does not show a flat discharge curve and the discharge voltage is comparatively lower. A comparison of samples 5 and 6 in Fig. 2 shows that halving the SSA, results in a utilization decrease of about the same order. At low temperatures, however, the SSA affects not only the utilization of the test samples, but the discharge voltage as well (Fig. 3). It is evident that at low temperature

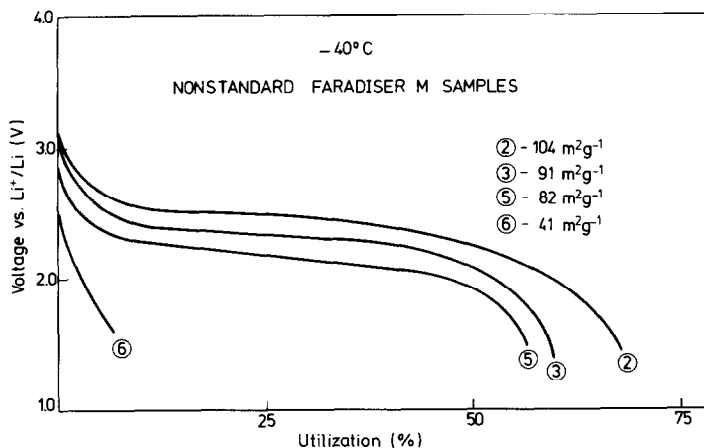


Fig. 3. Influence of specific surface area on the utilization of nonstandard samples of Faradiser M discharged at the 10 h rate at -40°C . Curve 2 is representative of samples 1 and 2; curve 3 of samples 3 and 4.

and heavy discharge rate the Faradiser M with SSA of $41\text{ m}^2\text{ g}^{-1}$ is practically unusable.

Samples Nos 1, 2 and 3, 4 have very similar discharge characteristics due to the small differences in their SSA (Table 1), and are represented in Figs. 2 and 3 by a single curve for each couple.

Figure 4 summarizes the results presented in Figs. 2 and 3. It can be seen that the specific capacity by weight (10 h rate) increases with the SSA of the test samples. Figure 4 shows that to obtain more than 50% specific capacity at the 10 h rate at room and low temperatures, the SSA must be higher than $80\text{ m}^2\text{ g}^{-1}$.

An analogous dependence is plotted in Fig. 5 which shows that the increase of the pore volume, measured by the low temperature nitrogen adsorption method, gives higher specific capacity (10 h rate) both at room and low temperatures. It is obvious from Fig. 5 that to obtain more than 50% specific capacity, the pore volume should be higher than $0.1\text{ cm}^3\text{ g}^{-1}$.

In previous papers [5, 6] we have shown that the low temperature discharge characteristics of lithium button cells designed with different MnO_2 samples deteriorate in the following way: standard product Faradiser M > Faradiser WS > Tekkosha, EMD. Figure 6 presents the cumulative distribution of pore volume (by Hg intrusion) and pore surface of these samples, depending on their diameter. One can distinguish two types of pores in Fig. 6: pores in the range $20\text{--}0.05\ \mu\text{m}$ dia. (called formally by us 'macropores'), and pores in the range $0.05\text{--}0.01\ \mu\text{m}$ ('micropores'). It is seen that the 'macropores', mostly interpreted as intervals between the particles are the dominant factor in determining the pore volume of the samples, but they have very low surface area. The 'micropores' display low volume, but they account for most of the surface area of the tested manganese dioxides. This

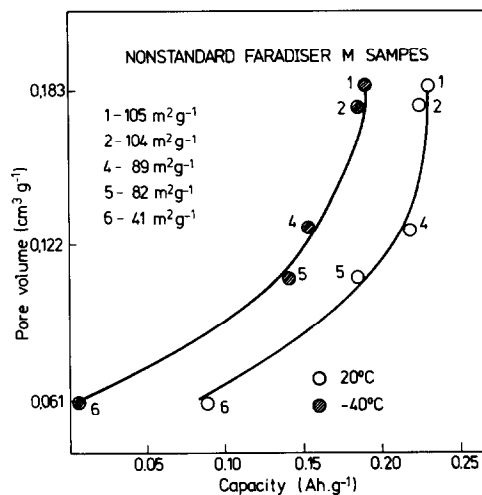
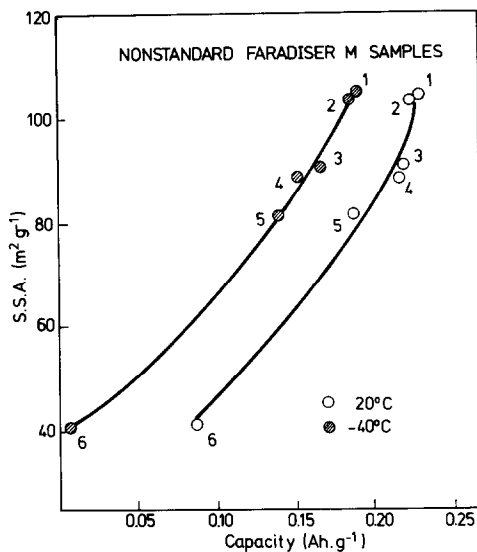


Fig. 4. Relationship between specific surface area and specific capacity by weight of different nonstandard Faradiser M samples discharged at the 10 h rate at room temperature and -40°C .

Fig. 5. Influence of specific surface area and pore volume on the specific capacity by weight of nonstandard Faradiser M samples discharged at the 10 h rate at room temperature and -40°C .

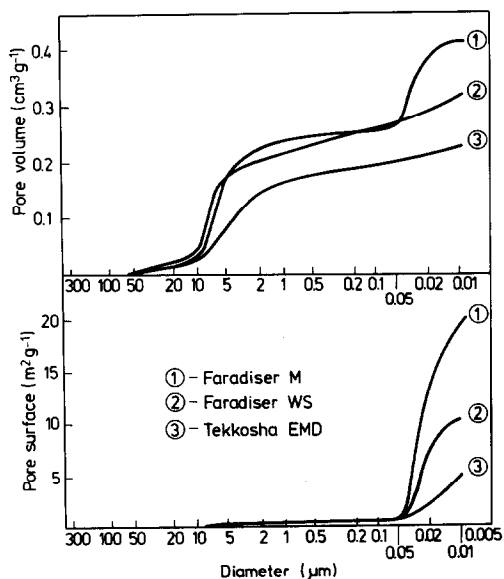


Fig. 6. Cumulative distribution of pore volume and pore surface vs. pore diameter of Faradiser M and Faradiser WS CMDs and EMD Tekkosh.

may be one possible explanation of the experimental results obtained by us [5, 6]. Presumably Faradiser M has the most favorable 'macro'-'micropores' ratio, which is very important at heavy discharge rates at low temperatures. Figures 3 and 5 show that manganese dioxides with higher pore volume, pore surface, and SSA, respectively, show higher specific electrochemical characteristics.

The porosity of standard Faradiser M (IC 12) was observed by SEM and TEM photographs (Figs. 7-9). At the highest magnification, shown in Fig. 9, it is seen that the small crystallites of Faradiser M which group together to form the spherical particles, are surrounded by pores. These

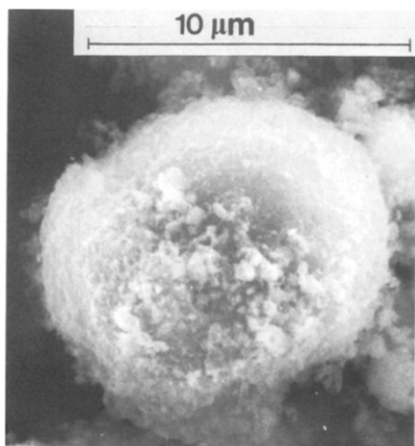


Fig. 7. Scanning electron micrograph of a Faradiser M particle ($\times 5400$).

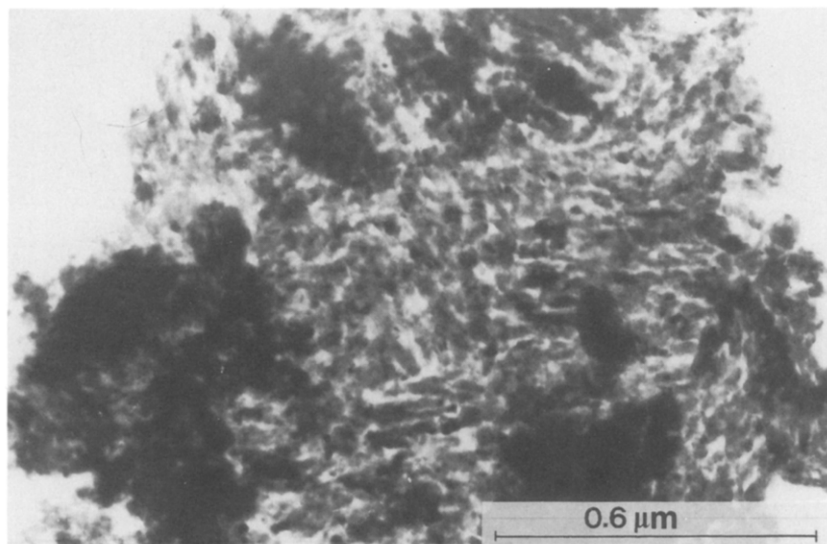


Fig. 8. Transmission electron micrograph of Faradiser M ($\times 100\,000$).

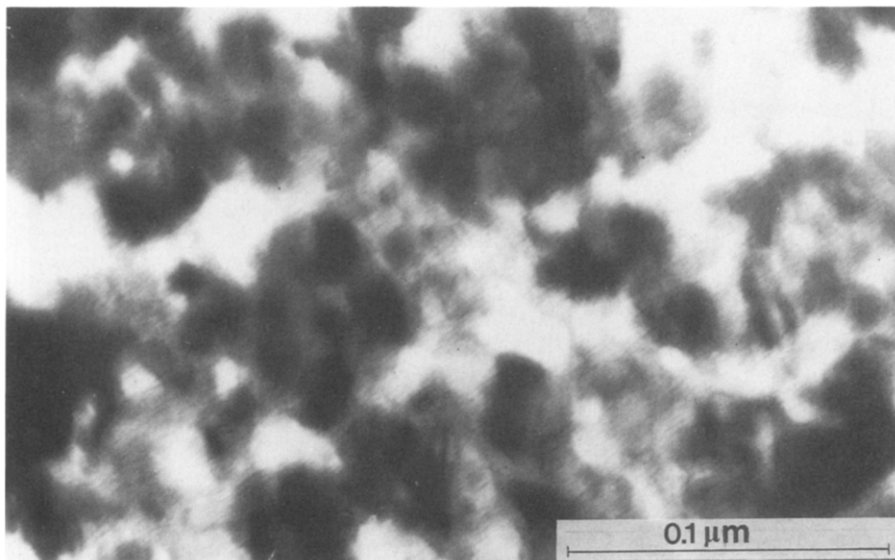


Fig. 9. TEM photograph of Faradiser M ($\times 600\,000$).

pores favour the electrochemical discharge, especially at high rates and low temperatures [4–6].

Conclusions

A correlation was found between the electrochemical performance of manganese dioxide samples in nonaqueous electrolytes and their physico-chemical characteristics. The higher the SSA and pore volume of nonstandard Faradiser M samples, the higher their specific capacity by weight. The higher porosity of standard Faradiser M most probably lowers the discharge current density, thus enhancing the electrochemical process.

Acknowledgement

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