

THE LITHIUM-MANGANESE DIOXIDE CELL I. OXYGEN AND WATER RELEASE DURING THE THERMAL TREATMENT OF MnO_2

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Summary

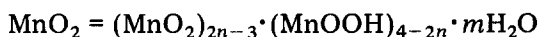
A method of selective measurement of released oxygen and water during thermal treatment of MnO_2 has been developed. It is shown that in inert medium up to 300 °C the basic weight losses are due to water release, while above 300 °C they are determined by oxygen evolution. Above 350 °C MnO_2 is thermodynamically unstable in inert atmosphere. The existence of characteristic temperatures, not exceeding 300 °C, and corresponding to the different natures of the bonded water, is confirmed. The re-absorbed water after thermal treatment of MnO_2 is of a nature similar to that contained in the untreated commercial material.

Introduction

Electrochemical power sources with lithium anodes are produced by a number of manufacturers. One of the most promising is the lithium-manganese dioxide cell, the basic properties of which have been studied by Ikeda *et al.* [1 - 4]. The same authors point out that preliminary thermal treatment of MnO_2 increases the specific capacity of the cell and provides an excellent shelf life.

The nature of bonded water in MnO_2 has been the subject of numerous early publications, a detailed bibliography of which is given in ref. 5. On the basis of precise gravimetric analysis [6] the existence of three types of bonded water is suggested. The existence of different types of bonded water was confirmed by Kanungo [7, 8].

Brenet *et al.* [9 - 12] pointed out that MnO_2 can be expressed by the general formula:



where n is the oxidation degree and m represents the neutral water molecules. This formula indicates that the trivalent manganese in the MnO_2 exists only as

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MnOOH. It is also assumed that there is molecular water in the tunnels and defects of the rather chaotic crystal structure of the MnO_2 [13].

An important step forward was made by Miyazaki [14] and Yoshimori *et al.* [15] using mass-spectroscopic and coulometric methods to analyse the products of thermal decomposition. Unfortunately, the samples were heated to between 50 °C and 100 °C, which made the determination of the characteristic temperatures difficult.

The study of evolved oxygen during thermal treatment of manganese dioxide by thermogravimetric analysis has the same shortcoming as the study of released water. Better information can be obtained by determining the value x in the formula MnO_x [1, 16 - 18]. Published data on the thermal treatment of MnO_2 in air, however, differs significantly. Ikeda *et al.* [1] showed that with increased temperature slight increases of x in MnO_x at 250 °C and 450 °C are observed. According to Giovanoli [16] x increases monotonically from 20 °C to 350 °C, while Preisler [17] and Kozawa [18] observed a peak between 200 °C and 250 °C.

In the present work a method of selective measurement of released oxygen and water during thermal treatment of MnO_2 is used. The method provides proof for the existence of characteristic temperatures and information on the kinetics of the oxygen and water release processes.

Experimental

A schematic diagram of the experimental system is shown in Fig. 1. Pure argon (<1 ppm oxygen and moisture) was passed consecutively through a chromatographic column filled with MnO_2 , an oxygen sensor [19, 20], a moisture sensor [21] and a flow meter. The chromatographic column was placed in a thermally controlled furnace whose temperature was either maintained constant (± 2 °C) or swept linearly at rates between 0.5 °C min^{-1} and 50 °C min^{-1} .

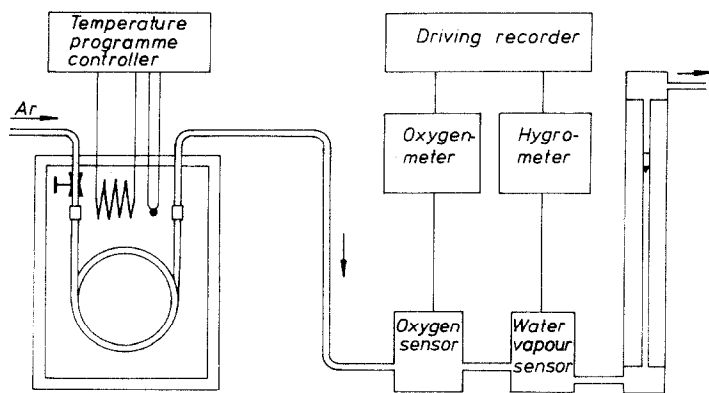


Fig. 1. Schematic diagram of the apparatus for measurement of released oxygen and water during the thermal treatment of MnO_2 .

The time response of the electrochemical oxygen sensor was 90% of the current value in less than 4 s and the accuracy was $\pm 1\%$. The time response of the electrochemical water vapour sensor was 90% of the current value in less than 1 min and the accuracy was $\pm 3\%$. The dead volumes were: 12 ml in the gas passage and chromatographic column, 3 ml in the oxygen sensor, and 18 ml in the moisture sensor.

After a series of preliminary experiments an argon flow rate of 7.3 l h^{-1} , a sample weight of 1 g, and a temperature sweep rate of $1 \text{ }^\circ\text{C min}^{-1}$ were defined as standard conditions. Under these conditions there was an additional temperature error of $0.5 \text{ }^\circ\text{C}$ for oxygen measurement and $2 \text{ }^\circ\text{C}$ for water vapour measurement due to delayed reading.

Two electrochemically produced MnO_2 (EMD) samples (Knapsack and Tekkosha) and two chemically produced MnO_2 (CMD) samples, (Faradiser M and Faradiser WS) were chosen as the subjects of this study.

The initial measurements of released water during the temperature sweep showed a very high peak at about $100 \text{ }^\circ\text{C}$, similar to that obtained by coulometric measurements [15]. The height of the peak was not reproducible and was dependent on the temperature and the relative humidity of the environment in which the sample was stored. Reproducible results were obtained by blowing dry argon through every sample for 15 h.

Results and discussion

The rate of oxygen and water released from Knapsack (EMD) as the temperature increased at a steady rate is shown in Fig. 2. It can be seen that up to $200 \text{ }^\circ\text{C}$ the main product of the thermal decomposition of the tested MnO_2 is water, above $200 \text{ }^\circ\text{C}$ the rate of oxygen evolution increases, and over $300 \text{ }^\circ\text{C}$ the weight losses due to oxygen evolution are dominant. These results refute the assumption made by a number of authors [16 - 18] that oxygen evolution is negligible up to $300 \text{ }^\circ\text{C}$ and that up to $400 \text{ }^\circ\text{C}$ the weight losses are mainly due to water release.

Naturally, the thermal stability of MnO_2 samples of different origin can differ. This is clearly shown in Fig. 3 in which the rate of oxygen evolution is plotted as a function of temperature, over a $1 \text{ }^\circ\text{C min}^{-1}$ temperature sweep, for all of the MnO_2 samples investigated. The results in Fig. 3 also suggest that it is inadvisable to give the same temperature pretreatment to all types of manganese dioxide to be used as cathode material in Li cells [4].

In practice, MnO_2 for use in Li/ MnO_2 cells is generally treated at $350 \text{ }^\circ\text{C}$ - $400 \text{ }^\circ\text{C}$ [1 - 4] for about 24 h. Therefore, it is interesting to trace the kinetics of oxygen evolution during prolonged heating at a constant temperature.

Figure 4 shows the time dependence of the oxygen evolution rate for Knapsack (EMD) at three different temperatures, $300 \text{ }^\circ\text{C}$, $350 \text{ }^\circ\text{C}$, and $400 \text{ }^\circ\text{C}$. It can be seen that only at $300 \text{ }^\circ\text{C}$, after the evolution of a certain amount of oxygen, does the rate tend to zero. It is possible that at $300 \text{ }^\circ\text{C}$ the

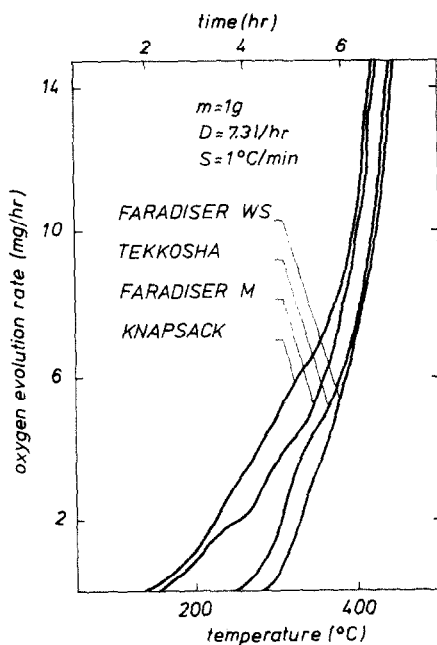
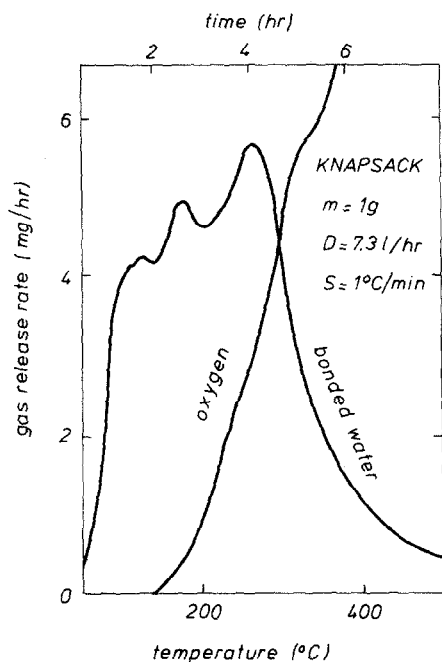


Fig. 2. Comparison of oxygen and water release rates during thermal treatment of Knapsack (EMD) at temperature sweep of $1\text{ }^{\circ}\text{C min}^{-1}$.

Fig. 3. Oxygen evolution rate for all samples during thermal treatment at temperature sweep of $1\text{ }^{\circ}\text{C min}^{-1}$.

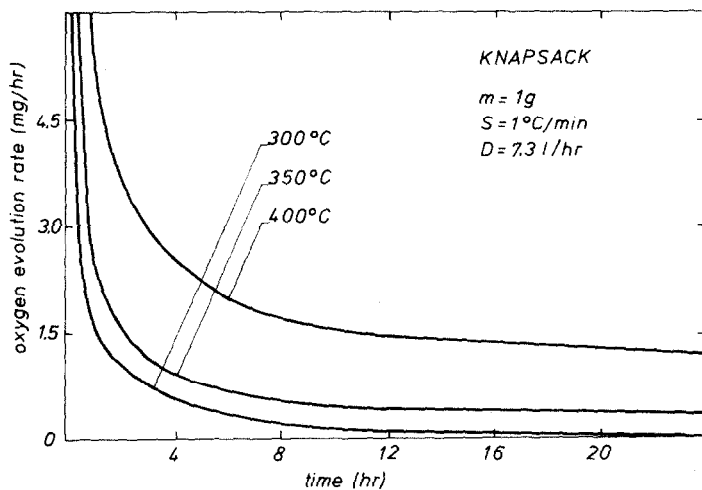


Fig. 4. Time dependence of the oxygen evolution rate at $300\text{ }^{\circ}\text{C}$, $350\text{ }^{\circ}\text{C}$, and $400\text{ }^{\circ}\text{C}$ for Knapsack (EMD).

oxygen losses are due to the surface oxygen which has a different bond energy [18] from the bulk oxygen. From the slope of the curves at $350\text{ }^{\circ}\text{C}$ and at $400\text{ }^{\circ}\text{C}$, which, after 24 h, reach a comparatively constant rate of

oxygen evolution, it is difficult to accept the assumption [18] that manganese dioxides are thermodynamically stable up to 425 °C, particularly in an inert medium.

Our research into the kinetics of oxygen evolution of the other three types of MnO_2 leads to similar conclusions. In Fig. 5, the time dependence of the oxygen evolution rate for all four types of MnO_2 investigated at 400 °C is presented. It can be seen that, for the initially more stable Faradiser WS (CMD) and Tekkosha (EMD), the oxygen evolution rate passes through a minimum. After 24 h, however, it becomes greater than that of the, initially, more unstable Faradiser M (CMD) and Knapsack (EMD). By integrating the total amount of evolved oxygen it was estimated that over 24 h at 400 °C the samples lost between 3 and 6 wt.% oxygen. This cannot be explained by the properties of the surface oxygen [18], especially considering the slope of the curves in Fig. 5.

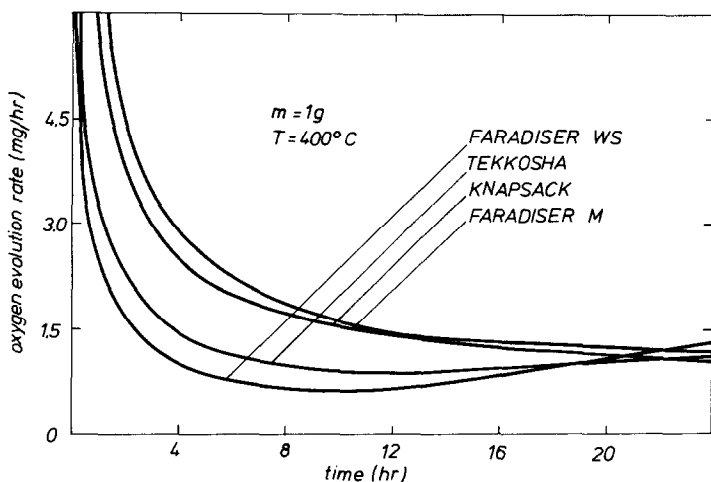


Fig. 5. Oxygen evolution rate at 400 °C as a function of time for four types of MnO_2 .

The effect which oxygen loss during prolonged heating has on the stoichiometry of MnO_2 can be seen in Fig. 6. This shows the oxygen weight losses and the respective change of x in the formula MnO_x over 48 h. It can be seen that after 48 h of heating in an inert atmosphere Faradiser M is converted into $\text{MnO}_{1.5}$. From the results shown in Figs. 5 and 6 it follows that in an inert medium (and the same may be expected for a vacuum) MnO_2 is thermodynamically unstable at 400 °C and, possibly, down to 350 °C (Fig. 4).

It is evident from Figs. 3 and 5 that the electrochemically obtained manganese dioxide is no more stable with respect to oxygen evolution than is the chemically obtained MnO_2 .

In Fig. 7 the temperature dependence of the water release rate at a continuous temperature increase of 1 °C min^{-1} for all manganese dioxide samples is presented. The results confirm the previous assumption [6] of

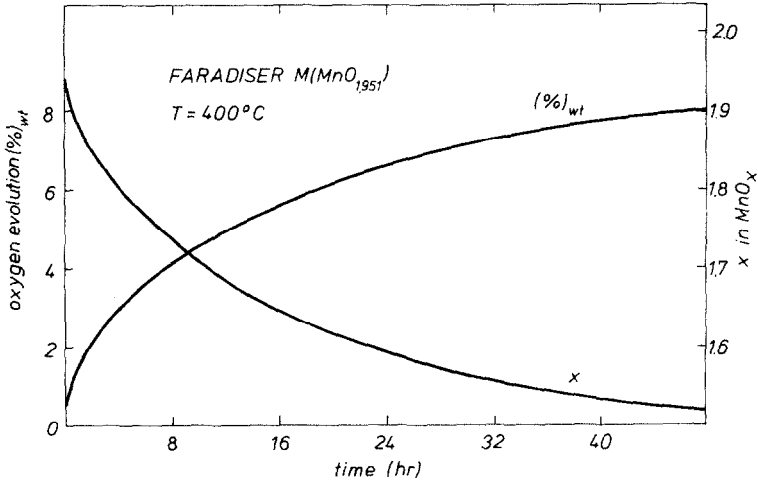


Fig. 6. Oxygen loss and change of x in the formula MnO_x as functions of time for Faradiser M (CMD) treated at $400^\circ C$.

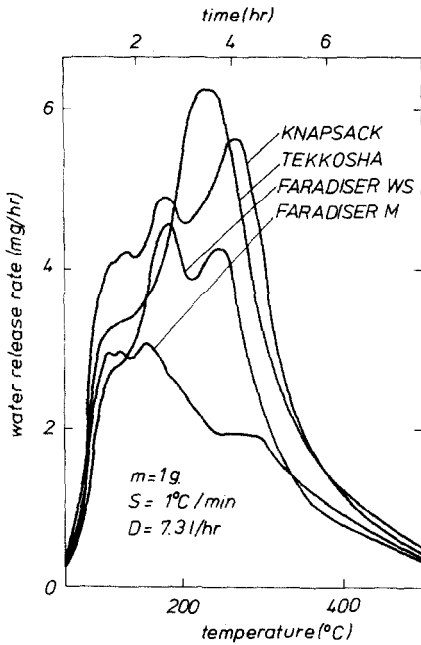


Fig. 7. Temperature dependence of the water release rate at a temperature sweep of $1^\circ C\ min^{-1}$.

characteristic peaks corresponding to the different natures of bonded water. We can classify the peaks in Fig. 7 into three basic groups:

- (i) peaks in the temperature range $100^\circ C - 130^\circ C$ are due to absorbed water;

(ii) peaks in the temperature range 150 °C - 200 °C are probably due to water in the MnO₂ micropores;

(iii) peaks in the temperature range 230 °C - 280 °C, from the results of Sato *et al.* [22], can be assumed to be due to the chemical decomposition of MnOOH to Mn₂O₃ with water release.

These results raise one question. Is the water released above 300 °C (Fig. 7) more tightly bound than that corresponding to the peaks in the range 230 °C - 280 °C or is its release kinetically limited? To answer this a series of curves was obtained under conditions similar to those in Fig. 7, but in this case the samples were pretreated at 300 °C for 6, 12, 24, 48, and 96 h. The curves for Knapsack (EMD) are shown in Fig. 8 in comparison with that of an untreated sample. It can be seen that during prolonged heating at 300 °C the amount of bonded water in the MnO₂ decreases significantly, including that part of the bonded water which, in an untreated sample undergoing a 1 °C min⁻¹ temperature sweep, is removed at 500 °C. The results in Fig. 8 clearly demonstrate that a temperature of 300 °C is sufficient to remove all bonded water but there are substantial kinetic barriers to the diffusion of water from the inner crystal structure to the gas medium. These kinetic barriers probably decrease with increased temperature, giving the false impression that the necessary temperature to release this water should be considerably higher [1, 2].

In practice, cathodes for Li/MnO₂ cells undergo two thermal treatments. The first one is to remove bonded water from the commercial MnO₂

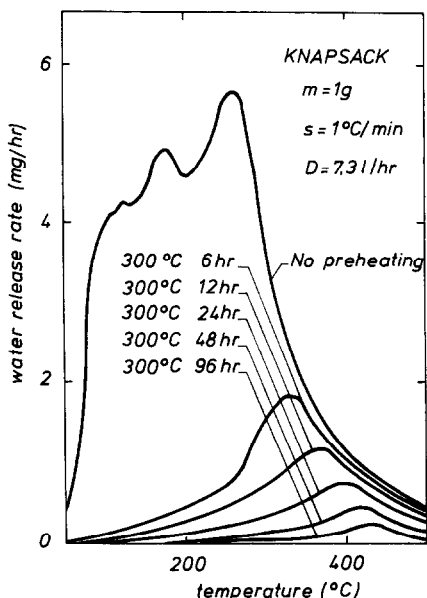


Fig. 8. Released water for Knapsack (EMD), pretreated at 300 °C for 6, 12, 24, 48, and 96 h, compared with released water for untreated sample.

and the second one is to remove water re-absorbed during the manufacture of the cathode. To determine the temperature at which the re-absorbed water can be removed, we compared a Knapsack sample pretreated at 300 °C for 48 h with a second sample, initially treated under the same conditions and then stored for 48 h at 25 °C in an 80% relative humidity. The results are shown in Fig. 9 where it can be seen that most of the re-absorbed water is on the surface (~100 °C). At the same time, the removal of a substantial amount of re-absorbed water needs considerably higher temperatures, similar to those of thermally untreated MnO₂. Consequently, the most suitable temperature for secondary thermal treatment of MnO₂ in the cathode should be the optimum temperature for its initial treatment, provided that it does not degrade the binder in the cathode.

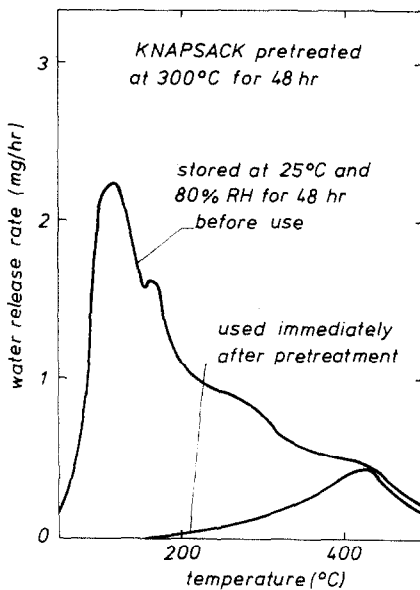


Fig. 9. Comparison of released water for Knapsack (EMD), pretreated at 300 °C for 48 h and for the same sample additionally stored for 48 h at 25 °C and 80% relative humidity.

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