An Application of Microwave Treatment to the Dehydration of Manganese Dioxide for Lithium Nonaqueous Cells

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Synopsis. A new dehydration technique of manganese dioxide using 2.45 GHz microwave is presented. The so-called γ and γ,β-MnO_2, each containing less than 1 wt% water, which are not attainable by heat treatment, are obtained under specified conditions by this dehydration technique.

In recent years a number of metal oxide cathodes for lithium nonaqueous cells have been investigated.[1] Among them, the manganese dioxide (MnO_2) is one of the most promising cathode materials. The battery-grade electrolytic MnO_2 commercially available, however, originally contains 5 to 10 wt% water. As such water causes serious failures in the lithium-cell system, the development of a dehydration technique has been needed. In order to remove the water, Ikeda *et al.*[2] investigated the heat treatment of electrolytic MnO_2 for lithium-cell use. The continuous heating of electrolytic MnO_2, however, concomitantly caused a structural change in MnO_2.

As has been stated above, the heat treatment of electrolytic MnO_2 is not sufficient for the dehydration of MnO_2. For this reason, we used a microwave shower in the dehydration of electrolytic MnO_2 for a lithium nonaqueous cell. The objective of this study was to determine whether or not the application of 2.45 GHz microwaves to the dehydration of electrolytic MnO_2 is effective.

Experimental

Electrolytic γ-MnO_2, obtained from the Toyo Soda Manufacturing Corporation, had a particle size of 60—100 mesh and a relatively low equi-acidic point of 2.23 on a pH scale, as determined by Tari's pH-shift method.[3]

About 100 g of electrolytic MnO_2 in a 200-ml Pyrex beaker (*ca.* 60 mmϕ × 85 mm) were treated under 2.45 GHz microwave irradiation in a Kenmore microwave oven, model 99701, which had about a 600-W magnetron output and intermittent irradiation controls. In order to determine the effects of a microwave shower on electrolytic MnO_2, the weight loss, the X-ray diffractional pattern, and the water contents of the sample before and after the microwave treatment were measured. X-Ray data were obtained by using a Shimadzu X-ray diffractometer, type VD-11, with iron K_α radiation filtered with manganese. The water contents of the MnO_2 samples were determined by the following, indirect Karl Fischer titration: about 2 g of the MnO_2 sample, which had been crushed to a fine powder, were heated on a boat in a quartz tube at an elevated temperature under a stream of dry nitrogen carrier gas. The exhaust gas was then introduced into a vessel filled with an anhydrated solvent (Mitsubishi anhydrated solvent ME). Titration was automatically achieved by using a Karl Fischer automatic titration apparatus, model MK-AS (Kyoto Electronics Manufacturing Co., Ltd.). The differential thermal analysis and thermal gravimetry were also carried out by means of a Shimadzu Thermal Analyzer, type DT-30. For the sake of magnetron safety, a commercially available microwave absorber (60 mmϕ) was always located in the oven.

Results and Discussion

In the preliminary tests for the dehydration of the electrolytic MnO_2, we selected the intermittent microwave irradiation which consists of 15 s on and 10 s off. Although the continuous irradiation was also an effective method for the dehydration of electrolytic MnO_2, hardly no dehydrated γ or γ,β-MnO_2 was thus obtained. It sometimes caused the decomposition of MnO_2 to Mn_2O_3, which depended on the irradiation time, the microwave power, and the sample weight and/or the apparent volume.

After the preliminary examinations to avoid the decomposition of MnO_2 and to achieve the dehydration, the following conditions were decided on: intermittent microwave irradiation for 5 min, followed by radiation for 25 min; this two-stage treatment was repeated several times.

In order to confirm the effect of microwave irradiation on dehydration, the water content was measured. Figure 1 shows the water distribution of MnO_2 (No. 3 in Fig. 2 and Table 1) well dehydrated by microwave treatment compared with that of the original MnO_2. The water content of the MnO_2 sample shown in Fig. 1 was determined by calculating from the released water at an elevated temperature below 700 °C, assuming that the contained water was zero at 700 °C. The original electrolytic MnO_2 contained 8.3 wt% of water. The rapid decrease in water content below 200 °C was caused by adsorbed water. Because of the decomposition of MnO_2 to Mn_2O_3 up to 500 °C (typically 550 °C), which was confirmed by thermal

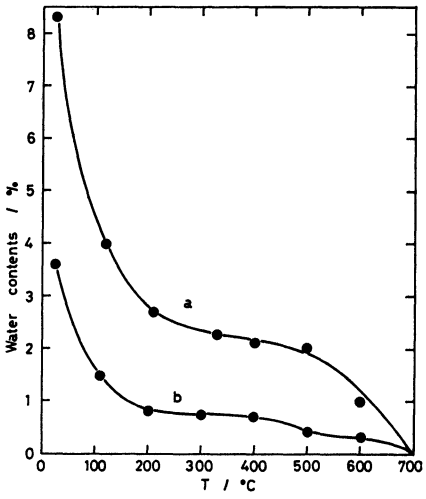

Fig. 1. Water distribution as a function of temperature. (a) Original electrolytic MnO_2, (b) microwave-treated MnO_2 (No. 3).

Table 1. Effect of microwave treatment on crystal structure and water contents

Sample No.	Microwave treatment	Classification from X-ray data	Water contents[a]/wt%
(Original)	—	γ-MnO_2	2.7±0.3
1	30 min	γ-MnO_2, trace of β-MnO_2?	1.2±0.1
2	60 min	γ-MnO_2, trace of β-MnO_2	0.9±0.1
3	90 min	γ,β-MnO_2	0.85±0.1
4	120 min	γ,β-MnO_2	0.6±0.1

a) Water removed below 200 °C was discarded.

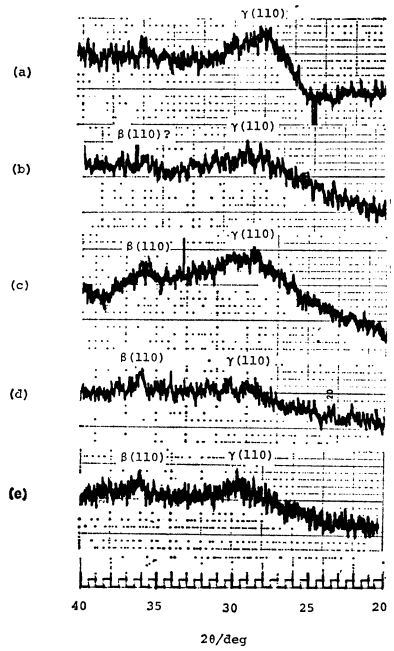

Fig. 2. Change of X-ray diffractional patterns by periodic microwave-treatment which consists of intermittent irradiation (15 s on, 10 s off) for 5 min, and the radiation for 25 min.
(a) Original MnO_2, (b) after 30 min (No. 1), (c) after 60 min (No. 2), (d) after 90 min (No. 3), (e) after 120 min (No. 4).

and X-ray analysis, a water content of less than 1.5 wt% was essentially not attainable by heat treatment.

The structural change caused by microwave treatment were also examined. The original MnO_2 showed the diffractional peaks (2θ) at about 28°, 47°, 54°, and 73°. The peaks at 47°, 54°, and 73° were not changed by microwave treatment. However, the diffused peak at about 28° was gradually decreased in its intensity, and a new peak at about 36° was observed. These delicate changes are shown in Fig. 2.

The above results are summarized in Table 1. The classification of MnO_2 was done according to the work of Fukuda.[4] The microwave treatment was concluded to be effective for the dehydration of MnO_2 from the fact that the so-called γ or γ,β-MnO_2, containing less than 1 wt% water, which could not be attained by heat treatment without the decomposition of MnO_2, was easily obtained by this treatment. Under these irradiation conditions, the water released below 200 °C was large in amount. Such adsorbed water, however, could be completely excluded by heat treatment at 200 °C, at which temperature the structural change in MnO_2 was proved not to occur.[2,3]

Further work related to lithium nonaqueous cells is now in progress in our laboratory.

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