

Synthesis of γ - MnO_2 from LiMn_2O_4 for Li/ MnO_2 Battery Applications

M. M. THACKERAY AND A. DE KOCK

*National Institute for Materials Research, CSIR, P.O. Box 395,
Pretoria 0001, South Africa*

Received November 16, 1987

Introduction

γ -Manganese dioxide (γ - MnO_2) is used widely as an electrode material in zinc cells, for example, in Leclanché and alkaline cells, and in lithium cells (1, 2). It can be synthesized as a high purity product either electrolytically (EMD) or by various chemical methods (CMD); the preferred material for most battery applications is EMD. The structure of γ - MnO_2 may be regarded as an intergrowth of a rutile- and a ramsdellite-type phase. EMD contains, typically, 4-5 w/o H_2O which is present as surface and occluded water. The water component of EMD is essential for the effective operation of aqueous zinc cells; however, in nonaqueous Li/ MnO_2 cells the water must be removed to ensure a long shelf-life and a high discharge capacity. In practice it is difficult to remove the water entirely from EMD. Heat treatment of EMD to 350-420°C, which causes a transformation of the γ - MnO_2 to an electrochemically active γ/β - MnO_2 phase, leaves 1-2 w/o H_2O bound to the crystal lattice (3). If heated above 450°C, the γ/β - MnO_2 phase loses oxygen and the remaining water to

form Mn_2O_3 , which has inferior electrochemical properties.

This paper reports a novel method for synthesizing an almost anhydrous γ - MnO_2 product by acid digestion of the spinel LiMn_2O_4 . The γ - MnO_2 product can be completely dehydrated at 300°C and yields a predominantly β -type phase which shows good electrochemical activity in lithium cells. Manganese dioxide phases prepared by this method are compared with those obtained from the acid digestion of another spinel, Mn_3O_4 .

Experimental

LiMn_2O_4 was prepared by the solid-state reaction of Mn_2O_3 or Mn_3O_4 with Li_2CO_3 (Koch Light, 99%) in air, initially at 600°C to decompose the Li_2CO_3 and finally at 900°C for 16 hr. Mn_2O_3 and Mn_3O_4 samples were prepared by heating EMD (obtained from Delta (EMD) (Pty) Ltd, Nelspruit, South Africa) in air to 600 and 1000°C, respectively, for 22 hr. Various types of MnO_2 were prepared by the digestion of Li Mn_2O_4 and Mn_3O_4 in 0.5 M H_2SO_4 at various temperatures. The products were heated for 22 hr, in air, at temperatures be-

TABLE I
REACTION CONDITIONS USED FOR THE PREPARATION OF VARIOUS MnO_2 SAMPLES FROM LiMn_2O_4 AND Mn_3O_4 IN 0.5 M H_2SO_4 AND THEIR $[\text{H}^+]$ CONCENTRATION

Sample no.	Starting material	Reaction temp (°C)	Reaction time (days)	Heat treatment (°C)	End product	$[\text{H}^+]$ (w/o)
1	LiMn_2O_4	25	4	75	λ - MnO_2	0.03
2	LiMn_2O_4	30	14	75	λ/γ - MnO_2	0.15
3	LiMn_2O_4	40	13	75	γ - MnO_2	0.13
4	LiMn_2O_4	40	13	120	γ - MnO_2	0.11
5	LiMn_2O_4	40	13	200	γ - MnO_2	0.09
6	LiMn_2O_4	40	13	300	β - MnO_2	0.02
7	LiMn_2O_4	40	13	350	β - MnO_2	0.01
8	LiMn_2O_4	60	3	75	γ - MnO_2	0.21
9	LiMn_2O_4	80	1	75	γ - MnO_2	0.25
10	LiMn_2O_4	90	7	75	γ - MnO_2	0.35
11	Mn_3O_4	30	7	75	γ - MnO_2	0.49
12	Mn_3O_4	60	1	75	γ - MnO_2	0.51
13	Mn_3O_4	60	4	75	γ - MnO_2	0.32
14	Mn_3O_4	60	4	200	γ - MnO_2	0.26
15	Mn_3O_4	60	4	300	γ - MnO_2	0.17
16	Mn_3O_4	60	4	350	γ/β - MnO_2	0.12
17	Mn_3O_4	95	0.25	75	γ - MnO_2	0.41
18	EMD (IC.1)	—	—	75	γ - MnO_2	0.50
19	EMD (Delta)	—	—	75	γ - MnO_2	0.50
20	EMD (Delta)	—	—	350	γ/β - MnO_2	0.10
21	EMD (Delta)	—	—	420	γ/β - MnO_2	0.09

tween 75 and 350°C to remove surface and occluded water.

The water content of each MnO_2 sample was assessed in terms of the $[\text{H}^+]$ -ion concentration which was determined by gravimetric methods. Particle-size analyses were undertaken on a Malvern particle-size analyzer. Powder X-ray diffraction patterns were obtained on an automated Rigaku diffractometer with $\text{CuK}\alpha$ radiation, monochromated by a graphite single crystal.

Results and Discussion

The reaction conditions used for the synthesis of MnO_2 samples from LiMn_2O_4 and Mn_3O_4 are summarized in Table I. The $[\text{H}^+]$ concentration in each sample and in EMD standard samples is also tabulated; an $[\text{H}^+]$ concentration of 0.11 w/o is equivalent to 1 w/o H_2O . The powder X-ray diffraction pat-

terns of LiMn_2O_4 and some selected MnO_2 samples, between 15 and $70^\circ 2\theta$, are compared in Fig. 1.

The $[\text{H}^+]$ concentration in two unheated EMD standard samples is 0.5 w/o. By contrast, the $[\text{H}^+]$ concentration in MnO_2 samples prepared from LiMn_2O_4 varies widely and is highly dependent on the reaction temperature and time. At 25°C, lithium is extracted from LiMn_2O_4 and yields an anhydrous, highly crystalline, λ - MnO_2 phase which retains the Mn_2O_4 spinel framework structure (Sample 1) (4); this phase has been well characterized, both structurally and electrochemically (5–7). As lithium is only a light scatterer of X-rays, the powder X-ray diffraction pattern of λ - MnO_2 closely resembles that of LiMn_2O_4 (Figs. 1a and 1b).

If the reaction temperature is raised to 40°C and the reaction time extended, a sin-

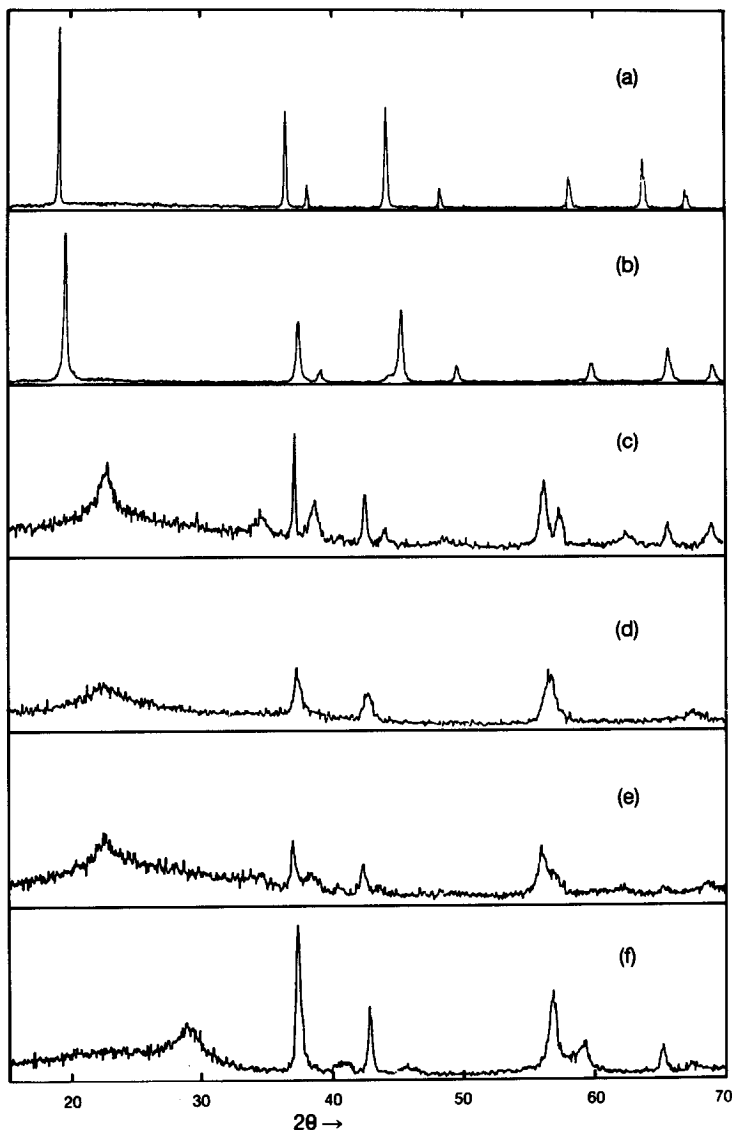


FIG. 1. Powder X-ray diffraction patterns of (a) LiMn_2O_4 , (b) $\lambda\text{-MnO}_2$, (c) $\gamma\text{-MnO}_2$ from LiMn_2O_4 at 40°C , (d) EMD standard, (e) $\gamma\text{-MnO}_2$ from LiMn_2O_4 at 90°C , and (f) $\beta\text{-MnO}_2$ from $\gamma\text{-MnO}_2$ (Sample 3) heated at 300°C . $\text{CuK}\alpha$ radiation.

glc-phase $\gamma\text{-MnO}_2$ product is obtained (Sample 3, Fig. 1c); this product is significantly more crystalline than EMD (Sample 19, Fig. 1d) and contains only about one-quarter of the water content of EMD ($[\text{H}^+] = 0.13$). The X-ray pattern of Sample 3 is similar to a CMD product (8, 9). A more

rapid conversion from LiMn_2O_4 to $\gamma\text{-MnO}_2$ can be achieved by raising the reaction temperature above 40°C (Samples 8–10), but these products contain a higher water content than Sample 3, as reflected in their $[\text{H}^+]$ content of 0.21, 0.25, and 0.35 w/o, respectively.

Samples with a relatively high water content were generally less crystalline than Sample 3 and adopted greater EMD-like character, for example, Sample 10 (Fig. 1e).

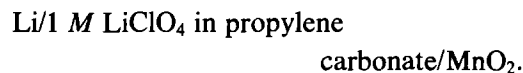
It is well-known that acid digestion of Mn_3O_4 results in the formation of γ - MnO_2 (10). The water content of these samples, however, is significantly higher than those prepared from $LiMn_2O_4$ at the same temperature. For example, a γ - MnO_2 phase produced from Mn_3O_4 at 30°C after 7 days (Sample 11) has an $[H^+]$ concentration of 0.49% and an EMD-like diffraction pattern, whereas the product synthesized from $LiMn_2O_4$ at 30°C after 14 days (Sample 2) has an $[H^+]$ content of only 0.15% and an X-ray pattern characteristic of a two-phase λ/γ - MnO_2 product. The absence of the λ - MnO_2 phase in the X-ray patterns of Mn_3O_4 samples that had been treated with acid, particularly at room temperature, suggests that the conversion of Mn_3O_4 to γ - MnO_2 does not occur via an intermediate λ - MnO_2 phase, despite the fact that Mn_3O_4 contains the Mn_2O_4 spinel framework. Therefore, it would appear that the anhydrous λ - MnO_2 phase is a critical component in the manufacture of γ - MnO_2 phases with anomalously low water content.

The powder X-ray diffraction spectrum of the γ - MnO_2 sample prepared from $LiMn_2O_4$ at 40°C (Fig. 1c) contains certain broad, diffuse lines and other sharp lines; this phenomenon has been accounted for by de Wolff (11) in terms of a structure consisting of a random intergrowth of the rutile (β)- and ramsdellite-type structures. Heat treatment of this phase to 300°C removes the water almost entirely ($H^+ = 0.02$ w/o H_2O). The X-ray diffraction pattern of this heat-treated sample shows a product with β - MnO_2 characteristics (Fig. 1f) and contains both broad and sharp peaks, indicative of a significant degree of strain within the small crystals. A higher degree of crystallinity in the β - MnO_2 phases, as reflected

by a sharpening of the broad peaks, could be achieved by heat treatment to 350°C.

The production of γ - MnO_2 from $LiMn_2O_4$, which is accompanied by some dissolution of manganese in the acidic solution, results in a substantial reduction in particle size. The average particle size in typical $LiMn_2O_4$, λ - MnO_2 , and γ - MnO_2 samples was determined to be 20, 11, and 7.5 μm , respectively.

Preliminary electrochemical tests on the MnO_2 phases derived from $LiMn_2O_4$ have been conducted in Li/MnO_2 cells of the type:



The data indicates that the β - MnO_2 phase (Sample 6) exhibits a slightly superior capacity to heat-treated EMD when discharged at low current rates (30 $\mu A/cm^2$). The good electrochemical activity which allows the particles to break up when lithiated can be attributed to the strain in the MnO_2 crystallites and their small particle size; the lithiated product " Li_xMnO_2 ," which forms during discharge, is virtually amorphous. Detailed electrochemical data on these manganese dioxide phases will be published elsewhere.

References

1. R. HUBER, K. V. KORDESCH, A. KOZAWA, AND D. B. WOOD, in "Batteries," Vol. 1, "Manganese Dioxide" (K. V. Kordesch, Ed.), Dekker, New York (1974).
2. G. PISTOIA, *J. Electrochem. Soc.* **129**, 1861 (1982).
3. H. IKEDA, U.S. Patent 4,133,856.
4. J. C. HUNTER, *J. Solid State Chem.* **39**, 142 (1981).
5. A. MOSBAH, A. VERBAERE, AND M. TOURNOUX, *Mater. Res. Bull.* **18**, 1375 (1983).
6. J. C. HUNTER AND F. B. TUDRON, *Proc. Electrochem. Soc.* **85**(4), 441 (1985).

7. W. I. F. DAVID, M. M. THACKERAY, L. A. DE PICCIOTTO, AND J. B. GOODENOUGH, *J. Solid State Chem.* **67**, 316 (1987).
8. W. K. ZWICKER, W. O. J. GROENEVELD MEIJER, AND H. W. JAFFE, *Amer. Mineral.* **47**, 246 (1962).
9. JCPDS Powder X-ray diffraction file: 14-644.
10. T. OHZUKU, H. HIGASHIMURA, AND T. HIRAI, *Electrochim. Acta* **29**, 779 (1984).
11. P. M. DE WOLFF, *Acta Crystallogr.* **12**, 341 (1959).