Synthesis of EMD for Primary and Secondary Lithium Batteries

Masaki YOSHIO*, Toshiyuki MURAKAMI, Hiroshi KURIMOTO,

Hideyuki NOGUCHI and Akiya KOZAWA†

Received July 7, 1993; Accepted August 17, 1993

1. Introduction

Electrolytic manganese dioxide(EMD) has been widely used as a cathode material in primary lithium batteries for more than 15 years¹⁾. However, it has been judged unsuitable for secondary batteries because of declining capacity during cycling²⁻⁴⁾.

One of the authors(A.K.) has stressed the importance of surface area and cavities of EMD with relation to its electrochemical performance⁵⁾.

Yamaguchi has prepared high specific surface area(HSSA) EMD by anodic deposition from the sulfate bath containing phosphate ion and showed its excellent performance as a cathode of primary Li battery⁶⁾.

In this paper, we have tried to prepare the HSSA EMDs by high current density electrolysis of sulfate bath and tested as a cathode of lithium batteries. As expected, their performances in both primary and secondary lithium cells greatly depend on the SSA of EMDs.

2. Experimental

High SSA EMDs were obtained by the anodic electrodeposition on the carbon electrode from 0.4 M H₂SO₄-1 M MnSO₄ at 95 °C. The electrolysis was carried out at constant potentials at 0.750 and 1.000 V vs. Hg/Hg₂SO₄. Heat treated EMD(HEMD) were

Department of Applied Chemistry, Faculty of Science & Engineering, Saga University, (1 Honjo, Saga 840)

† Department of Applied Chemistry, Faculty of Engineering, Chubu University, (1200 Matsumoto, Kasugai, Aichi 487)

Key Words: High specific surface area, EMD, Lithium battery, BET surface area, Pore volume

prepared by heating EMDs at 300 and 400°C in air and used as the cathode of lithium batteries.

Quantachrome Autosorb-1 was used for the analysis of SSA and pore area distribution by the BET method using N₂ gas adsorption. The samples were outgassed at 200°C for 20 min in a vacuum before measurement.

The cycling character of the cathode materials was evaluated in laboratory cells as follows: Li/1 M LiPF₆ in EC:PC:benzene(4.5:4.5:1 in volume ratio)/ HEMD, where PC is propylene carbonate and EC is ethylene carbonate.

The cathode was composed of 50 mg MnO₂ mixed with conducting binder. The mixture was pressed onto a stainless screen at 800 kg/cm². Cells were cycled in the range 3.5-2.0 V with current densities of 0.1 and 4 mA/cm².

3. Results and discussion

Physicochemical properties of EMDs obtained at 0.750 and 1.000 V vs. Hg/Hg₂SO₄ are summarized with International MnO₂ common sample No. 17(IC 17) in Table 1. Applied average c.d.s were 2.3 A/dm² at 0.750 V and 3.7 A/dm² at 1.000 V, respectively.

Table 1. Physicochemical properties of EMDs obtained at 0.750(A) and 1.000 V(B) vs. Hg/Hg₂SO₄.

EMDs	Tapping Density (g/cm ³)	Weight loss at 110 °C, 2hr (wt%)	SSA* (m ² /g)
A	1.70	4.34	118
B	2.31	3.38	88
IC 17	2.26	1.53	40

*) determined by Zn absorption method⁷⁾

Apparent current efficiencies are more than 95% in both cases.

The BET-surface area of IC 17 is 40 m²/g, while those of our EMDs are higher than 80 m²/g.

Fig. 1 shows the voltage-capacity curves of the HEMD prepared from EMD obtained at constant potential of 1.000 V vs. Hg/Hg₂SO₄ and IC 17 as a cathode of primary lithium cell. Discharge voltages of our HEMD at Li_{0.25}MnO₂ are 100 (at 0.1 mA/cm²) and 400 (at 4 mA/cm²) mV higher than those of conventional HEMD obtained from IC 17. In the other word, HSSA HEMD shows extremely low polarization. HSSA EMDs obtained from sulfate bath containing phosphate has a capacity of less than 150 mAh/g at 2 mA/cm² ⁶⁾, while our EMD shows a capacity of 210 mAh/g at 2 mA/cm².

Fig. 1. Cell voltage-capacity curves of Li cells using HSSA HEMD (1 and 2) and conventional HEMD (3 and 4) at 0.1 mA/cm² (1 and 3) or 4 mA/cm² (2 and 4).

EMDs are heated at 400 °C for 5 hrs.

Fig. 2 shows the relation between BET surface area and heating time at 400 °C. The BET surface area of HSSA HEMD and conventional HEMD heated for 5 hr are 51.6 and 19.1 m²/g, respectively. BET surface area of both EMDs is remarkably decreased by heating within 1 hr. Roughly constant BET surface area is measured for the samples heated for more than 5 hr. As 1–5 hr heating of EMDs is enough to remove water, we select 5 hr as heating time at 400 °C.

Though HEMD, which has higher BET surface area and shows lower polarization in lithium cell, is obtained by the heating at 300 °C, more than 20 hrs

Fig. 2. Relation between BET surface area of HSSA EMD(○) or IC 17(●) and heating time at 400 °C.

heating is needed to remove water.

The pore volumes calculated from absorption isotherm curves with BJH method⁸⁾ are 1.1×10⁻¹ cm³/g for HSSA EMD(400 °C, 5 hr) and 5.1×10⁻² cm³/g for IC 17(400 °C, 5 hr).

It would be concluded that the reason of lower polarization and high capacity at high rate in lithium cell using HSSA HEMD as cathode is due to high surface area and pore volume of HSSA HEMD.

References

- 1) H. Ikeda, T. Saito and H. Tamura, 1st Int'l. Symp. Manganese Dioxide, Cleveland, Ohio, 1975, 384.
- 2) G. Pistoia, J. Electrochem. Soc., **129**, 1861 (1992).
- 3) S. Bach, J.P. Pereir-Ramous, N. Battier and R. Messina, Electrochim. Acta, **37**, 1301 (1992).
- 4) J. Tarascon, E. Wang, F. Shokoohi, W.R. McKinnon and S. Colson, J. Electrochem. Soc., **138**, 2859 (1991).
- 5) A. Kozawa, Handbook of Manganese Dioxide, ed. by D. Glover, B. Schumm, Jr and A. Kozawa, IBA Inc. p. 259 (1989).
- 6) M. Yamaguchi, Prog. Batt. Batt. Mat., **11**, 171 (1992).
- 7) A. Kozawa, J. Electrochem. Soc., **106**, 552 (1959).
- 8) E.P. Barrett, L.C. Joyner and P.P. Halenda, J. Am. Chem. Soc., **73**, 373 (1951).