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Short Communication

Development of coin-type lithium secondary batteries containing manganese dioxide/Li–Al

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Abstract

In order to develop a secondary battery with high energy density, several characteristics of coin-type cells using lithium-containing manganese dioxide as a positive material are investigated. Cells prepared from LiOH and electrolytic manganese dioxide (EMD) display higher energy density (177 Wh l^{-1}; 63 Wh kg^{-1}) than those prepared from LiOH and chemical manganese dioxide (CMD). LiOH·EMD has better cycle characteristics and storage characteristics than LiOH·CMD. Lithium-containing manganese dioxide (LiOH·EMD)/Li–Al batteries have high reliability against overcharge and overdischarge.

Keywords: Lithium-containing manganese oxide; Lithium secondary batteries; Coin-type cells; Energy density

1. Introduction

A high-energy and inexpensive lithium secondary battery is required as a memory back-up power source. In response, several kinds of coin-type, lithium secondary batteries have been developed, e.g., carbon/lithium alloy batteries [1], polyaniline/Li–Al batteries [2], V_2O_5/Li–Al batteries [3]. Unfortunately, the energy densities of these batteries are insufficient. The batteries must have high energy density in order to back-up memory during a forwarding or long-time pause.

We have reported previously [4,5] that lithium-containing manganese dioxide (heat-treated LiOH·MnO_2) exhibits much better rechargeability than γ/β-MnO_2 or spinel $LiMn_2O_4$. Since the crystal structure of lithium-containing manganese dioxide consists of Li_2MnO_3 and γ/β-MnO_2 (composite dimension), we named this material: 'composite dimensional manganese oxide' (CDMO) [6]. The optimum condition for preparing CDMO is to heat-treat LiOH and MnO_2 at about 375 °C. CDMO prepared from EMD yields a larger capacity and a smaller capacity deterioration ratio than CDMO prepared from CMD [6].

In this report, various characteristics of coin-type secondary batteries using lithium-containing manganese dioxide as a positive material are examined in order to confirm their performance as practical power sources.

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2. Experimental

Lithium-containing manganese dioxide (CDMO) was prepared by heat-treating LiOH and EMD (IBA No. 17) or CMD (I. C. No. 12) at 375 °C. A mixture of CDMO, conductive agent (carbon black), and Teflon binder was used as the positive electrode, while Li–Al–Mn alloy served as the negative electrode [7]. The electrolyte was a mixture of 1 M $LiCF_3SO_3$–ethylene carbonate (EC)/1,2-butylene carbonate (BC)/1,2-dimethoxyethane (DME) [8].

Fig. 1 shows the structure of the coin-type cell (diameter: 24.5 mm; height: 3.0 mm). The discharge characteristics, charge/discharge cycle characteristics, storage characteristics were examined using this coin-type cell.

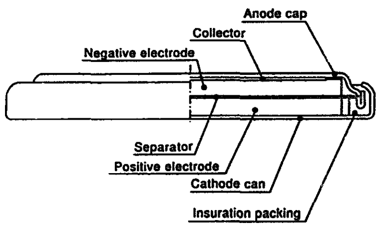

Fig. 1. Design of coin-type cell.

3. Results and discussion

Fig. 2 shows the discharge characteristics of coin-type cells with LiOH·EMD or LiOH·CMD as a positive material. The cell with LiOH·EMD has a larger discharge capacity than that with LiOH·CMD. This is because the packing density of the positive electrode with LiOH·EMD is higher than that with LiOH·CMD. The energy density of the cell using LiOH·EMD is 177 Wh l^{-1} or 63 Wh kg^{-1}. In addition, LiOH·EMD displays superior charge/discharge cycling characteristics (Fig. 3). A coin-type cell with LiOH·EMD gave 3000 cycles at a 5% depth-of-discharge (DOD) and 500 cycles at 20% DOD. Moreover, it could be used for more than 50 cycles at a deep DODs.

Fig. 4 and Fig. 5 show the storage characteristics of the cells with LiOH·EMD and LiOH·CMD, respectively. The LiOH·EMD has superior storage characteristics. The deterioration of LiOH·EMD cells during storage is thought to be smaller because the surface area of LiOH·EMD is smaller than that of LiOH·CMD and the decomposition of electrolyte on the surface of LiOH·EMD is repressed [6]. From these results, it is found that lithium-containing manganese dioxide prepared from LiOH and EMD is suitable as positive material for practical batteries.

The dependence of discharge capacity on load is presented in Fig. 6. The discharge load of 1 kΩ corresponds to a constant discharge current of about 2.5 mA. The LiOH·EMD/Li–Al cell gave a high discharge capacity of 90 mAh (159 Wh l^{-1}, 56 Wh kg^{-1}) under such a high drain. Moreover, the cell could be used over a wide range of temperature, i.e. from −20 to +60 °C (Fig. 7). The discharge capacity at −20 °C was 85% of the discharge capacity at 23 °C.

Practical batteries must have high reliability. The discharge characteristics of coin-type cells on the initial test and after 80 days of continuously applying 3.0 V at 60 °C are given in Fig. 8. The deterioration ratio is 10%. This indicates that the batteries can accommodate overcharge. The discharge characteristics on the initial test and after 20 days of discharge by short-circuiting at 60 °C are presented in Fig. 9. The deterioration ratio is only 5%. Thus, the rechargeability of lithium-containing manganese dioxide (LiOH·EMD) is maintained after an extremely deep discharge.

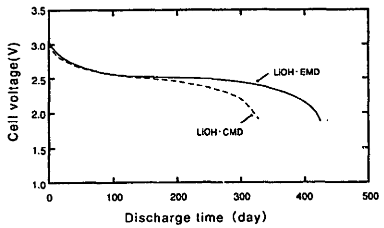

Fig. 2. Discharge curves of coin-type cells. Discharge current: 10 μA; temperature: 23 °C.

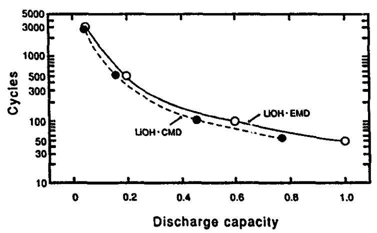

Fig. 3. Cycle characteristics of coin-type cells. Charge current: 3 mA; discharge current: 3 mA; temperature: 23 °C. A discharge capacity of 1.0 is the capacity of a coin-type cell with LiOH·EMD when discharged to 2.0 V.

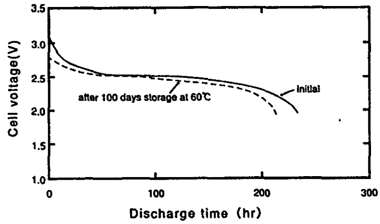

Fig. 4. Storage characteristics of coin-type cells using lithium-containing manganese oxide prepared from EMD. Storage for 100 days at 60 °C; discharge load: 5.6 kΩ (≈445 μA); temperature: 23 °C.

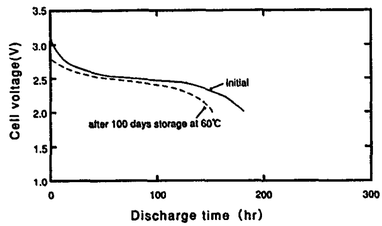

Fig. 5. Storage characteristics of coin-type cells using lithium-containing manganese oxide prepared from CMD. Storage for 100 days at 60 °C; discharge load: 5.6 kΩ (≈445 μA); temperature: 23 °C.

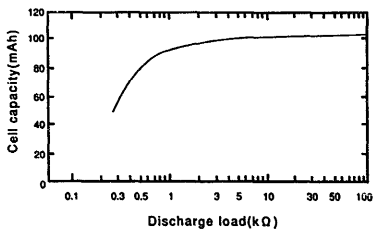

Fig. 6. Discharge load characteristics of coin-type cells. Discharge end-voltage: 2.0 V; temperature: 23 °C.

Table 1
Specifications of coin-type lithium-containing manganese dioxide/Li–Al batteries

Model	ML2430	ML2016	ML1220
Nominal voltage (V)	3	3	3
Nominal capacity (mAh)	90	25	12
Energy density ($Wh\,l^{-1}$)	159	125	122
($Wh\,kg^{-1}$)	56	35	43
Standard charge/discharge current (mA)	0.5	0.3	0.1
Maximum discharge current (continuous) (mA)	10	8	2
Maximum discharge current (pulse) (mA)	20	20	5
Charge/discharge cycle characteristics	4.5 mAh (DOD 5%) 3000 cycles 18 mAh (DOD 20%) 500 cycles	1.25 mAh (DOD 5%) 3000 cycles 5 mAh (DOD 20%) 500 cycles	0.6 mAh (DOD 5%) 3000 cycles 2.4 mAh (DOD 20%) 500 cycles
Diameter (mm)	24.5	20.0	12.5
Thickness (mm)	3.0	1.6	2.0
Weight (g)	4.0	1.8	0.7

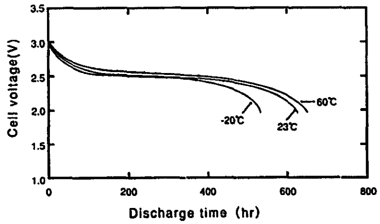

Fig. 7. Discharge curves of coin-type cells at various temperatures. Discharge load: 15 kΩ (≈165 μA).

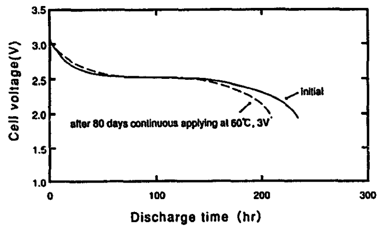

Fig. 8. Discharge curves of coin-type cells at initial and after 80 days of continuously applying 3 V at 60 °C. Discharge load: 5.6 kΩ (≈445 μA); temperature: 23 °C.

After various investigations for battery characteristics and reliability, lithium-containing manganese dioxide/Li–Al secondary batteries (ML series) have been developed. Table 1 shows the specifications of the ML series. These batteries are thought to be promising as power sources for memory back-up because of their high energy density, good cycle performance and reliability.

4. Conclusions

The characteristics of coin-type secondary batteries using lithium-containing manganese dioxide as a positive material

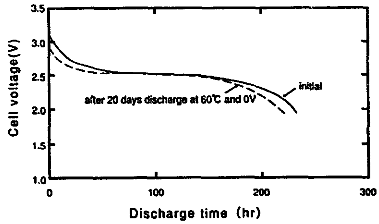

Fig. 9. Discharge curves of coin-type cells for initial test and after 20 days of discharge at 60 °C and 0 V. Discharge load: 5.6 kΩ (≈445 μA); temperature: 23 °C.

have been examined. The cells with lithium-containing manganese dioxide prepared from LiOH and EMD display higher discharge capacity, better cycle characteristics, and less deterioration during storage than those with LiOH·CMD. LiOH·EMD/Li–Al batteries display excellent battery characteristics and reliability. These batteries are considered to be promising power sources for memory back-up.

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