

## Investigation of an electrolyte for lithium secondary batteries with lithium-containing manganese dioxide as the positive material

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### Abstract

We have already developed lithium-containing manganese dioxide (CDMO, composite dimensional manganese oxide) with excellent rechargeability and high discharge capacity for use as a positive electrode material in lithium secondary batteries. We also have improved the cycle performance of lithium-aluminum alloy for use as a negative electrode material by adding manganese to aluminum. The effect of an electrolyte on battery performance such as cycle life, discharge characteristics at low temperature and storage characteristics, were investigated for CDMO/Li-Al flat cells.  $\text{LiCF}_3\text{SO}_3$  showed excellent discharge characteristics both at room temperature and  $-20^\circ\text{C}$ . In addition, the charge/discharge cycle at room temperature was best when using  $\text{LiCF}_3\text{SO}_3$ -ethylene carbonate (EC)/1,2-butylene carbonate (BC)/1,2-dimethoxyethane (DME), as electrolyte.

### Introduction

The demand for a secondary battery with high energy density is increasing with the advancement of electronic devices. As a result, the research and development of lithium secondary batteries have been intensified. In this project, a high-voltage, inexpensive Li secondary battery using Li-containing manganese dioxide as the positive electrode material [1, 2] and Li-Al alloy as the negative electrode material has been investigated [3].

The importance of the electrolyte in Li secondary batteries has been pointed out by many workers because of its large effect on battery cycling performance [4-8]. Furthermore, the operating temperature and storage characteristics of the batteries depend mainly on the properties of the electrolyte [9-12].

We have investigated the relationship between CDMO/Li-Al secondary battery performance and the electrolyte. In this report, we describe the optimum composition of electrolytes containing both Li salts and organic solvents for use in CDMO/Li-Al secondary batteries.

### Experimental

CDMO was prepared by heat treating LiOH and electrolytic manganese dioxide (IBA no. 17). A mixture of CDMO, conductive agent (acetylene black), and Teflon binder was used as the positive electrode, while a lithium-aluminum alloy containing

a small amount of manganese [3] served as the negative electrode with capacity larger than the positive electrode.

The electrolyte was prepared using several Li salts and organic solvents. The following Li salts were used:  $\text{LiCF}_3\text{SO}_3$  (Mitsubishi Petrochemical Co., Ltd.),  $\text{LiClO}_4$  (Kishida Chemical Co., Ltd.),  $\text{LiPF}_6$  and  $\text{LiBF}_4$  (Hashimoto Chemical Co., Ltd.). A mixture of solvents with high dielectric constant: ethylene carbonate (EC), propylene carbonate (PC) and 1,2-butylene carbonate (BC), and solvents with low viscosity: 1,2-dimethoxyethane (DME), 2-methyltetrahydrofuran (2MeTHF) and 4-methyl-1,3-dioxolane (4MeDOL) was used as the organic solvent. All solvents were obtained from Mitsubishi Petrochemical Co., Ltd., and used as received.

Charge/discharge cycle characteristics were examined using flat cells (diameter: 24 mm, thickness: 3 mm) at 25 °C. Both charge and discharge current densities were 1.1 mA/cm<sup>2</sup> and depth-of-discharge was 17%. The discharge characteristics at -20 °C were examined at 0.4 mA/cm<sup>2</sup>; a.c. impedance was measured with electrochemical interface (Solartron model 1186) and frequency response analyzer (Solartron model 1170).

## Results and discussion

### Effects of lithium salts

Figure 1 shows the charge/discharge cycle characteristics of CDMO/Li-Al flat type cells at 25 °C using  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiCF}_3\text{SO}_3$  and  $\text{LiBF}_4$  as the Li salt. Each Li salt was dissolved in PC/DME (volume ratio 50:50) to a concentration of 1 M. In the case of  $\text{LiBF}_4$ , deterioration of the cycle characteristics was observed after 30 cycles and the cell voltage was lower than that of cells with other Li salts. The cells with other salts, however, showed good cycle characteristics for more than 300 cycles.

Figure 2 shows the effect of salt concentration on discharge characteristics of cells using  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiClO}_4$  and  $\text{LiPF}_6$  at -20 °C. It was found that the dependence of discharge capacity on salt concentration was much larger for  $\text{LiClO}_4$  than for  $\text{LiCF}_3\text{SO}_3$  and  $\text{LiPF}_6$ . From these results, it is believed that  $\text{LiCF}_3\text{SO}_3$  shows good discharge characteristics at -20 °C because of its high solubility [13]. Since  $\text{LiClO}_4$

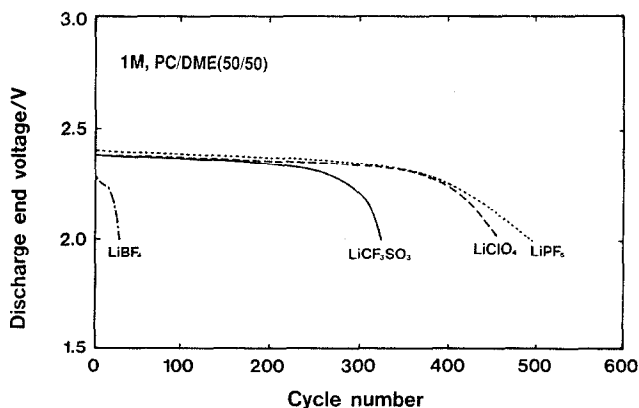


Fig. 1. Charge/discharge characteristics of CDMO/Li-Al flat type cells with various lithium salts at 25 °C; current density: 1.1 mA/cm<sup>2</sup>; depth-of-discharge: 17%, and maximum charge voltage: 3.25 V.

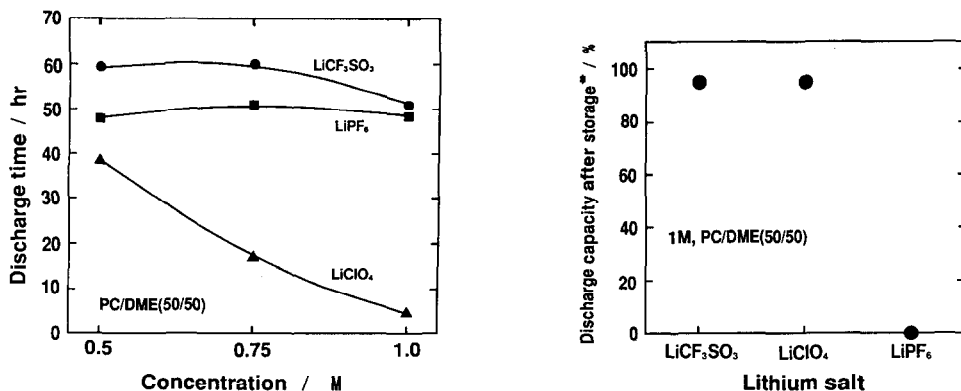


Fig. 2. Dependence of concentration of various lithium salts on discharge characteristics of CDMO/Li-Al flat type cells at  $-20^{\circ}\text{C}$ ; current density:  $0.4\text{ mA/cm}^2$ .

Fig. 3. Discharge capacities of CDMO/Li-Al flat type cells before and after storage with  $\text{LiClO}_4$ ,  $\text{LiCF}_3\text{SO}_3$  and  $\text{LiPF}_6$ ; 20 days storage at  $60^{\circ}\text{C}$ , current density:  $0.4\text{ mA/cm}^2$ ; \*relative value to initial capacity.

has a low solubility at  $-20^{\circ}\text{C}$ , it is thought that the excess of  $\text{Li}^+$  ions dissolved from the Li-Al electrode during cell discharge caused the precipitation of salt on the electrode, which was the reason for the decrease in capacity. The small decrease in capacity obtained with  $\text{LiPF}_6$ , despite a similar solubility to  $\text{LiClO}_4$ , might be due to a slower rate of salt precipitation.

Figure 3 shows the discharge capacity of cells with  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiClO}_4$  and  $\text{LiPF}_6$ , before and after 20 days storage at  $60^{\circ}\text{C}$ . Cells after storage were discharged under the same conditions as those before storage. In the case of both  $\text{LiCF}_3\text{SO}_3$  and  $\text{LiClO}_4$ , deterioration was very low, while those cells with  $\text{LiPF}_6$  showed serious deterioration because corrosion of the positive can (stainless steel SUS 430) had occurred.

Such evaluation of the Li salts indicates that  $\text{LiCF}_3\text{SO}_3$  has many excellent features for use in CDMO/Li-Al secondary batteries. Therefore, we investigated the optimum solvent for electrolytes containing  $\text{LiCF}_3\text{SO}_3$ .

### Effect of organic solvents

Figure 4 shows the cycle characteristics of CDMO/Li-Al flat type cells at  $25^{\circ}\text{C}$  using several mixed solvents. Solvents with high dielectric constant — EC, PC, BC — were mixed with DME. EC was used as a cosolvent for the low-viscosity solvents — DME, 2MeTHF, 4MeDOL. The best cycle life was obtained with EC/DME. It has been reported that EC-based electrolytes showed good Li cycling efficiency because EC has lower reactivity with Li than PC [6, 7]. Therefore, it is thought that EC/DME is more stable for Li-Al than other mixed solvents.

However, the discharge characteristics of EC/DME (volume ratio 50:50) at  $-20^{\circ}\text{C}$  were inferior because EC has higher melting point than PC and BC; the results are shown in Fig. 5. In this experiment,  $0.75\text{ M LiCF}_3\text{SO}_3$  was used from the results shown in Fig. 4. In order to improve the discharge characteristics of EC/DME at  $-20^{\circ}\text{C}$ , we investigated a three-component solvent in which we added PC or BC to EC/DME. The discharge characteristics of cells at  $-20^{\circ}\text{C}$  with the three-ingredient

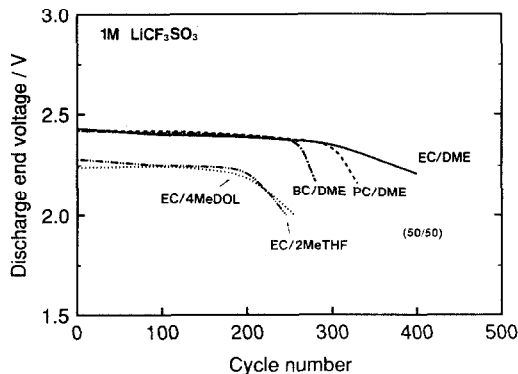


Fig. 4. Charge/discharge characteristics of CDMO/Li-Al flat type cells with several mixed solvents; current density:  $1.1 \text{ mA/cm}^2$ ; depth-of-discharge: 17%, and maximum charge voltage: 3.25 V.

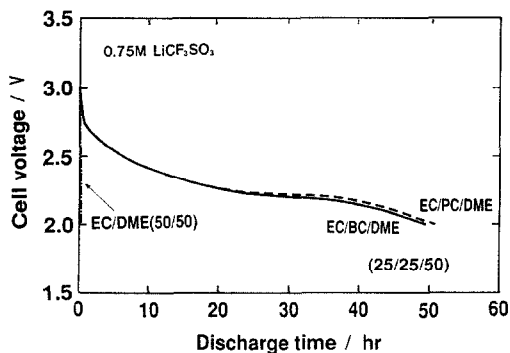


Fig. 5. Discharge characteristics of CDMO/Li-Al flat type cells at  $-20 \text{ }^\circ\text{C}$  with EC/DME, EC/PC/DME and EC/BC/DME; current density:  $0.4 \text{ mA/cm}^2$ .

solvents, EC/BC/DME and EC/PC/DME (volume ratio 25:25:50), were better than those of EC/DME; the results are shown in Fig. 5.

In addition, cycle characteristics of cells with the three-component solvents, especially EC/BC/DME, were improved compared with those of EC/DME as shown in Fig. 6. The relationship between cycle performance and a.c. impedance for the cells with several mixed solvents are summarized in Fig. 7. It was found that solvent showing a low impedance, ( $\theta$ , obtained from Cole-Cole plots for the CDMO/Li-Al cells), showed excellent cycle performance. We believe that the properties of the surface films on the Li-Al electrode were improved for charge/discharge cycling when using the three-ingredient solvents.

## Conclusions

We have investigated electrolytes for CDMO/Li-Al cells, and found that  $\text{LiCF}_3\text{SO}_3$  gives excellent discharge characteristics at low temperatures, and storage characteristics. In addition,  $\text{LiCF}_3\text{SO}_3$  showed a long cycle life when used with EC/DME solvent. We succeeded in improving the discharge characteristics of EC/DME at  $-20 \text{ }^\circ\text{C}$  by adding

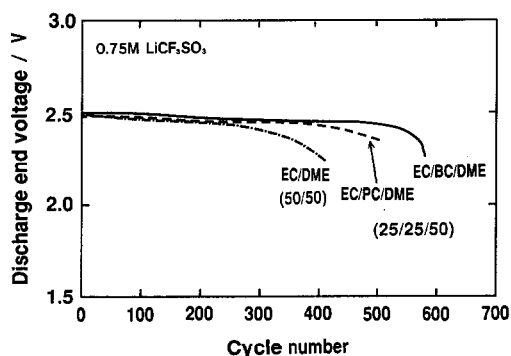


Fig. 6. Charge/discharge characteristics of CDMO/Li-Al flat type cells with EC/DME, EC/PC/DME and EC/BC/DME; current density: 1.1 mA/cm<sup>2</sup>; depth-of-discharge: 17%, and maximum charge voltage: 3.25 V.

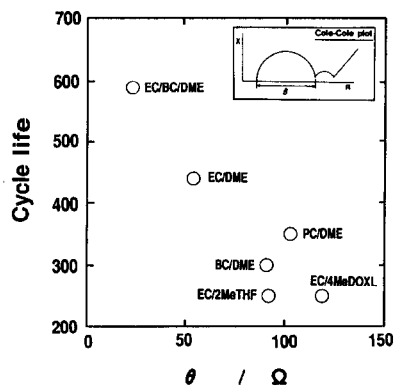


Fig. 7. Relationship between cycle life and a.c. impedance of CDMO/Li-Al flat type cells with LiCF<sub>3</sub>SO<sub>3</sub> and several mixed solvents; current density: 1.1 mA/cm<sup>2</sup>.

PC or BC. The three-component solvent systems, especially EC/BC/DME, showed better cycle performance than did EC/DME.

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