

Short Communication

Discharge characteristics of manganese dioxide/lithium cells in various electrolyte solutions

Koji Nishio, Seiji Yoshimura, Toshihiko Saito

New Materials Research Centre, Sanyo Electric Co., Ltd., 1-18-13 Hashiridani, Hirakata, Osaka 573, Japan

Received 10 October 1994; accepted 18 November 1994

Abstract

The discharge characteristics of manganese dioxide/lithium cells are studied in various electrolyte solutions that consist of a mixture of propylene carbonate and various non-cyclic di-ethers as a solvent. The high-rate discharge characteristics are found to be greatly influenced by the conductivity of the electrolyte solution. An electrolyte solution of propylene carbonate and 1,2-dimethoxyethane exhibits the largest discharge capacity. On the other hand, the capacity at low temperature (–20 °C) discharge is the highest in a cell that employs a mixture of propylene carbonate and ethoxymethoxyethane as a solvent.

Keywords: Lithium cells; Manganese dioxide; Discharge characteristics

1. Introduction

Manganese dioxide/lithium (MnO_2/Li) cells have many advantages, such as a high operating voltage, a high energy density, a low self-discharge rate, and a wide range operating temperature [1,2]. Consequently, there have been recent calls for MnO_2/Li cells to be used in high-power and low-temperature applications.

It has been pointed out that the choice of both solutes and solvents for electrolyte solutions is very important to improve the discharge characteristics of lithium cells [3–5].

This paper reports the effects of various electrolyte solutions containing propylene carbonate (PC) and non-cyclic di-ethers on the discharge characteristics of MnO_2/Li cells.

2. Experimental

2.1. Preparation of electrolyte solutions

A mixture of PC and a non-cyclic di-ether containing 1 M LiClO_4 was used as an electrolyte solution. The

Table 1
Various di-ethers used as solvent

Abbreviation	Name	Structure	Number of carbon atoms in one molecule
DMM	Dimethoxymethane	$\text{CH}_3\text{OCH}_2\text{OCH}_3$	3
1,1-DME	1,1-Dimethoxyethane	$\text{CH}_3\text{OCH}(\text{CH}_3)\text{OCH}_3$	4
1,2-DME	1,2-Dimethoxyethane	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$	4
DEM	Diethoxymethane	$\text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5$	5
1,1-DMP	1,1-Dimethoxypropane	$\text{CH}_3\text{OCH}(\text{C}_2\text{H}_5)\text{OCH}_3$	5
2,2-DMP	2,2-Dimethoxypropane	$\text{CH}_3\text{OC}(\text{CH}_3)_2\text{OCH}_3$	5
EME	Ethoxymethoxyethane	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5$	5
1,1-DEE	1,1-Diethoxyethane	$\text{C}_2\text{H}_5\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$	6
1,2-DEE	1,2-Diethoxyethane	$\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5$	6
1,1-DEP	1,1-Diethoxypropane	$\text{C}_2\text{H}_5\text{OCH}(\text{C}_2\text{H}_5)\text{OC}_2\text{H}_5$	7
1,2-DnBE	1,2-Di- <i>n</i> -butoxyethane	$\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{OC}_4\text{H}_9$	10

PC and non-cyclic di-ethers were mixed in a 1:1 volume ratio. The non-cyclic di-ethers used in the study are listed in Table 1.

2.2. Physical properties of electrolyte solutions

The physical properties of the electrolyte solutions were measured at 25 °C. Conductivity, viscosity and density were determined with a conductivity cell (Toa Electronics, Model CG 210GL), a rotational rheometer (Contravas, Model Rheomat 30) and an automatic densimeter (Kyoto Electronics Manufacturing, Model DA 101B), respectively.

2.3. Discharge tests

Experimental, flat-type MnO_2/Li cells with an outer diameter of 20.0 mm and a height of 2.5 mm were made in order to study the effect of electrolyte. In these cells, a mixture of MnO_2 , graphite and a binder was employed as the cathode. Stainless steel was used for both the cathode can and the anode cap, and polypropylene resin was used for the insulation packing.

Table 2
Physical properties of electrolyte solutions (25 °C) ^{a,b}

Solvent	Conductivity ($10^{-3} \text{ S cm}^{-1}$)	Viscosity (cP)	Density (g cm^{-3})
PC/DMM	8.1	1.9	1.12
PC/1,1-DME	6.0	2.4	1.12
PC/DME	13.3	2.3	1.12
PC/DEM	4.6	2.4	1.06
PC/EME	9.9	2.7	1.11
PC/1,2-DEE	8.3		1.11

^a Mixing ratio: PC/di-ether = 1/1 (volume ratio).

^b Solute: 1 M LiClO_4 .

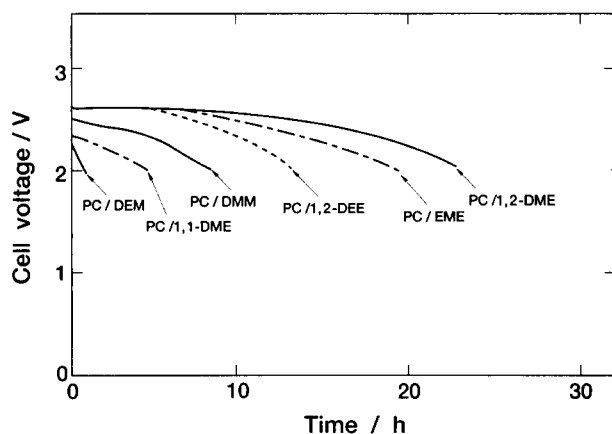


Fig. 1. High-rate discharge characteristics of MnO_2/Li cells using various electrolyte solutions. Solvent: mixture of di-ether and propylene carbonate (1:1 volume ratio); solute: 1 M LiClO_4 . Discharge conditions: temperature = 25 °C, and load = 550 Ω .

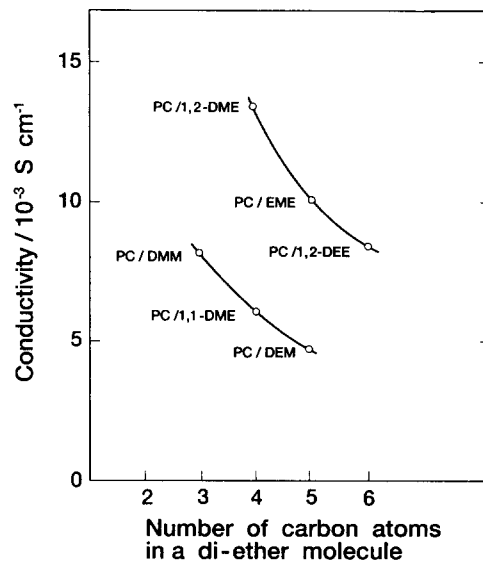


Fig. 2. Conductivity of electrolyte solution vs. number of carbon atoms in a di-ether molecule. Solvent: mixture of di-ether and propylene carbonate (1:1 volume ratio); solute: 1 M LiClO_4 .

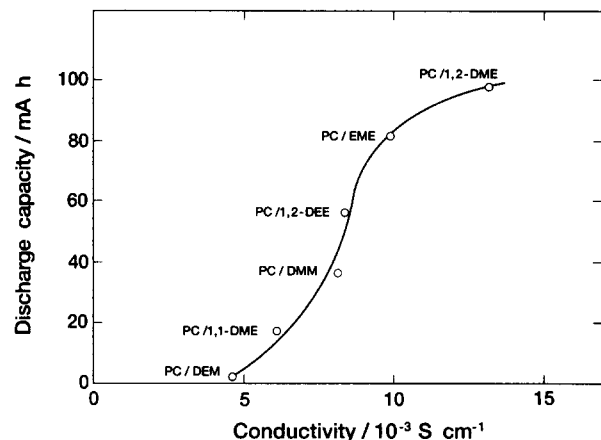


Fig. 3. High-rate discharge capacity vs. conductivity of electrolyte solution. Solvent: mixture of di-ether and propylene carbonate (1:1 volume ratio); solute: 1 M LiClO_4 . Discharge conditions: temperature = 25 °C, and load = 560 Ω .

The discharge tests were conducted with a constant resistance of 560 or 3.6 k Ω .

3. Results and discussion

Table 2 gives the physical properties of the electrolyte solutions containing a mixed solvent of PC and various non-cyclic di-ethers. 1,1-DMP, 2,2-DMP, 1,1-DEE, 1,1-DEP and 1,2-DnBE were unable to be used as co-solvents, because these ethers were not homogeneously miscible with PC.

Fig. 1 shows the high-rate discharge characteristics for the flat-type test cells with various electrolyte solutions. The discharge capacity of the cell using PC/1,2-DME, 95 mAh, was the highest, and that using PC/

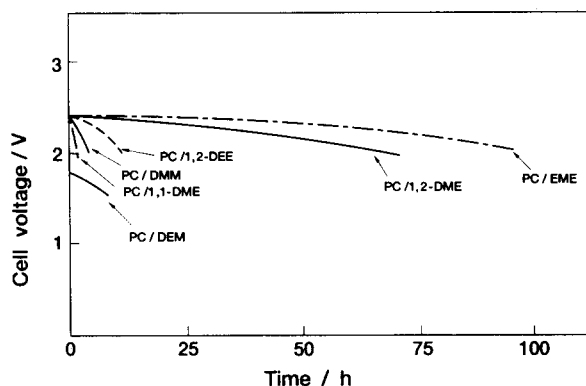


Fig. 4. Low-temperature discharge characteristics of MnO_2/Li cells using various electrolyte solutions. Solvent: mixture of di-ether and propylene carbonate (1:1 volume ratio); solute: 1 M LiClO_4 . Discharge conditions: temperature = -20°C , and load = $3.6\text{ k}\Omega$.

EME, 80 mAh, was the second highest. The discharge capacities for the electrolytes followed the order of PC/1,2-DME > PC/EME > PC/1,2-DEE > PC/DMM > PC/1,1-DME > PC/DEM.

The relationship between the conductivity of the electrolyte solution and the number of carbon atoms in the di-ether (dialkoxyethane) molecule is presented in Fig. 2. For both 1,2-dialkoxyethanes and 1,1-dialkoxyethanes, the conductivity decreased with increasing number of the carbon atoms. The conductivity of the electrolyte solution containing a 1,2-dialkoxyethane was higher than that containing a 1,1-dialkoxyethane, when both had the same number of carbon atoms in a molecule. The structure of specifically solvated lithium ions with two 1,2-dialkoxyethanes has been reported to be very compact [6], and this is considered to be the reason for high conductivity.

The relationship between the high-rate discharge capacity and the conductivity of the electrolyte solution is shown in Fig. 3. The discharge capacities of the test

cells followed the order of the conductivities of the electrolyte solutions.

Fig. 4 shows low-temperature discharge characteristics at -20°C . The discharge capacities for the solvents were: PC/EME > PC/1,2-DME > PC/1,2-DEE > PC/DMM > PC/1,1-DME > PC/DEM. Under this discharge condition, the discharge capacity for PC/EME, viz., 55 mAh, was higher than that for PC/DME, viz., 35 mAh. This is considered to result from the low solubility of LiClO_4 in PC/DME at low temperature.

4. Conclusions

Studies of the discharge characteristics of MnO_2/Li cells with various electrolyte solutions containing PC and non-cyclic di-ether have shown that a PC/1,2-DME solution is suitable for high-rate discharge. On the other hand, an electrolyte solution containing PC/EME is appropriate for low-temperature discharge.

The conductivity of the electrolyte is influenced by the structure of the solvent. PC/1,2-dialkoxyethane exhibits greater conductivity than PC/1,1-dialkoxyethane. The order of the high-rate discharge capacities corresponds to the order of the electrolyte solution conductivities.

References

- [1] H. Ikeda, T. Saito and H. Tamura, *Denki Kagaku*, 45 (1977) 314.
- [2] H. Ikeda, in J.P. Gabano (ed.), *Lithium Batteries*, Academic Press, New York, 1983, Ch. 8.
- [3] M. Takahashi, S. Yoshimura, I. Nakane, T. Nohma, K. Nishio, T. Saito, M. Fujimoto, S. Narukawa, M. Hara and N. Furukawa, *J. Power Sources*, 43/44 (1993) 253.
- [4] R. Janinski, *Electrochem. Technol.*, 6 (1968) 28.
- [5] Y. Matsuda, *Denki Kagaku*, 48 (1980) 665.
- [6] Y. Matsuda, H. Nakashima, M. Morita and Y. Takasu, *J. Electrochem. Soc.*, 128 (1981) 2552.