

## A study on electrolytes for manganese dioxide-lithium cells

M. Takahashi, S. Yoshimura, I. Nakane, T. Nohma, K. Nishio and T. Saito

*Functional Materials Research Center, Sanyo Electric Co., Ltd., 1-18-13 Hashiridani, Hirakata-shi, Osaka 573 (Japan)*

M. Fujimoto, S. Narukawa, M. Hara and N. Furukawa

*Soft Energy Business Headquarters, Sanyo Electric Co., Ltd., 221-1 Kaminaizen, Sumoto-shi, Hyogo 656 (Japan)*

### Abstract

The physical properties of organic electrolyte used in manganese dioxide-lithium cells play a major role in determining various cell characteristics. The influence on various cell characteristics of electrolytes has been investigated with flat cells.  $\text{LiCF}_3\text{SO}_3$  is the suitable solute in terms of low-temperature, storage and overdischarge characteristics. Mixture of ethylene carbonate (EC), 1,2-butylene carbonate (BC) and 1,2-dimethoxyethane (DME) is the suitable solvent in terms of high-rate discharge and storage characteristics.

### Introduction

The demand for manganese dioxide-lithium cells is rapidly growing, due to their many useful features, such as high voltage, high energy density, wide operating temperature range, superior storage characteristics, and economy in terms of resources.

Manganese dioxide-lithium cells were first used as low-power supplies for watches, calculators and memory backups, and recently their range of applications has been expanding considerably as they are used as high-power supplies for fully-automatic cameras.

The physical properties of the organic electrolyte used in Li cells play a major role in determining various cell characteristics.

There are a number of types of Li cells; suitable electrolyte are selected for the positive electrodes [1-3].

In this report we investigated the influence of some solutes and solvents on various cell characteristics.

### Experimental

A 0.75 M solute comprising  $\text{LiClO}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$  and  $\text{LiAsF}_6$  was examined. A mixed solvent, composed of a solvent with high dielectric constant and a solvent with low viscosity in a 30:70 mixing ratio by volume, has been used. The conductivity of the electrolyte was measured using a conductivity cell (type CG-210GL,

Toa Electronics) and the viscosity of the electrolyte was measured using a rotational rheometer (type Rheomat 30, Contravas).

Cell performance was examined with flat cells (diameter: 20 mm, thickness: 2.5 mm). The discharge tests were conducted under a constant current. A mixture of electrolytic manganese dioxide, a conductive agent (carbon), and a Teflon binder was used as the positive electrode, while Li metal was used as the negative electrode. Elemental analysis on the Li electrode surface after storage was conducted by electron-probe microanalysis (EPMA) (type X-650, Hitachi).

Decomposition products of the electrolyte were confirmed by GC-MS (type M-80B, Hitachi). The interfacial impedance was measured using Solartron 1286 ECI and Solartron 1250 FRA.

## Results and discussion

### *A study of solutes*

A mixed solvent of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) was used for this study.

Table 1 shows the conductivity, viscosity and solubility of various electrolytes. The conductivities of the electrolytes depend on the solute, while their viscosities are almost independent of the solute. The solubility at  $-20\text{ }^{\circ}\text{C}$  of the  $\text{LiCF}_3\text{SO}_3$  system is much higher than that of the others.

Figure 1 shows the initial low-rate discharge characteristics of test cells with various electrolyte. At a low-rate discharge of  $0.5\text{ mA/cm}^2$ , the discharge capacities and curves are almost independent of the type of solute.

Figure 2 shows the initial low-temperature discharge characteristics of test cells with various electrolytes. It was found that the  $\text{LiCF}_3\text{SO}_3$  system has the largest discharge capacity at  $-20\text{ }^{\circ}\text{C}$ . It is considered that the solute systems with low solubilities at  $-20\text{ }^{\circ}\text{C}$  have poor low-temperature discharge characteristics because solute is deposited on the Li electrode surface during discharge.

Discharge capacity after storage is compared with initial discharge capacity in Table 2. Initially, there is no difference. After a 40-day storage at  $60\text{ }^{\circ}\text{C}$ , equivalent to a 2-year storage at room temperature, a deterioration of discharge capacity is observed for the  $\text{LiBF}_4$  and  $\text{LiPF}_6$  systems.

Figure 3 illustrates the complex impedance plots of test cells with various electrolytes after a 40 day-storage at  $60\text{ }^{\circ}\text{C}$ . The impedance of  $\text{LiClO}_4$ ,  $\text{LiCF}_3\text{SO}_3$  and  $\text{LiAsF}_6$

TABLE 1  
Physical properties of various electrolytes

	25 $^{\circ}\text{C}$		-20 $^{\circ}\text{C}$		
	Conductivity ( $\text{mS cm}^{-1}$ )	Viscosity (cP)	Conductivity ( $\text{mS cm}^{-1}$ )	Viscosity (cP)	Solubility (M)
$\text{LiClO}_4$	12.3	1.3	7.1	3.2	1.2
$\text{LiCF}_3\text{SO}_3$	5.9	1.2	3.5	2.4	>6.0
$\text{LiBF}_4$	8.2	1.0	5.2	2.0	2.4
$\text{LiPF}_6$	17.0	1.6	7.6	3.1	1.2
$\text{LiAsF}_6$	16.3	1.3	7.3	2.7	1.0

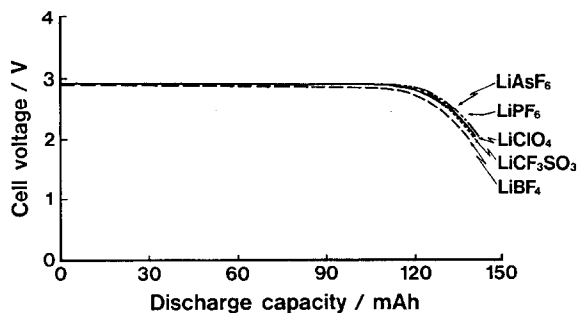


Fig. 1. Initial low-rate discharge characteristics: 25 °C, 0.5 mA cm<sup>-2</sup>.

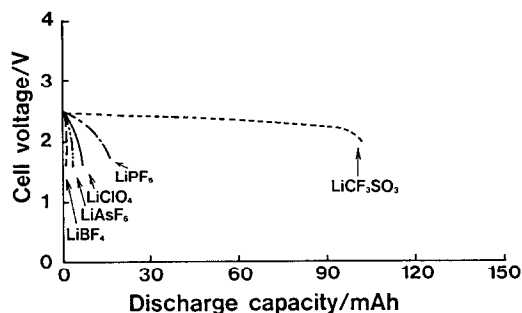


Fig. 2. Initial low-temperature discharge characteristics: -20 °C, 0.5 mA cm<sup>-2</sup>.

TABLE 2

Comparison of storage characteristics of test cells with various solutes

	Discharge capacity (mA h) <sup>a</sup>	
	Initial	After a 40-day storage at 60 °C
LiClO <sub>4</sub>	140	130
LiCF <sub>3</sub> SO <sub>3</sub>	140	130
LiBF <sub>4</sub>	140	78
LiPF <sub>6</sub>	140	115
LiAsF <sub>6</sub>	140	130

<sup>a</sup>Discharge condition: 25 °C, 0.5 mA cm<sup>-2</sup>.

systems are almost identical to their initial values, but the impedance of the LiPF<sub>6</sub> system increases by about 4 times, and that of LiBF<sub>4</sub> system increases by about 80 times. This increase in impedance may be caused by the increase in impedance of the lithium-electrolyte interface.

The results of elemental analysis of the Li electrode surface for the LiBF<sub>4</sub> system after a 40-day storage at 60 °C are given in Fig. 4. Manganese peaks appeared in the LiBF<sub>4</sub> system. This indicates a deposition of manganese ion coming from the dissolved manganese dioxide. We assume that there may be an interaction between LiBF<sub>4</sub> and manganese dioxide. The deterioration of discharge capacity during storage for the

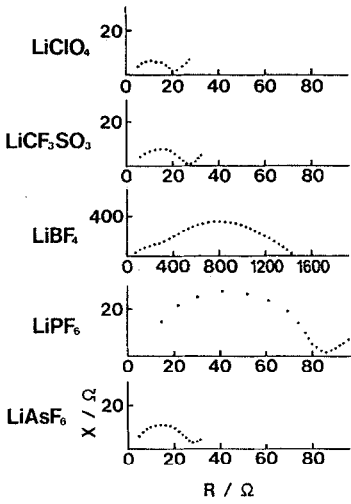


Fig. 3. Complex impedance plots of test cells with various electrolytes after a 40-day storage at 60 °C.

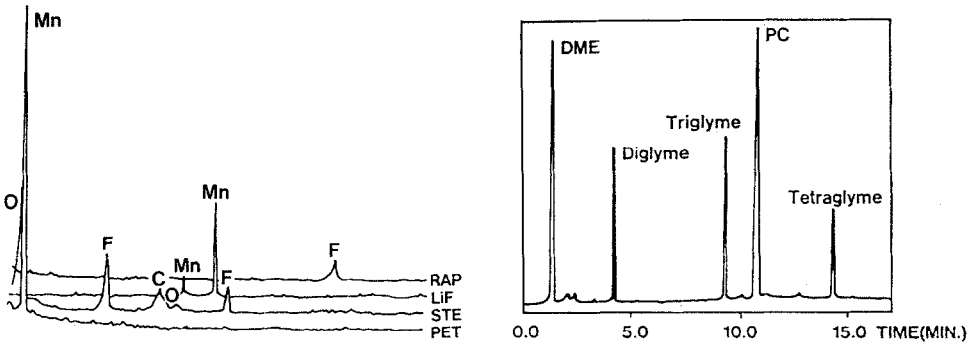


Fig. 4. Elemental analysis of the lithium electrode surface after a 40-day storage at 60 °C in the LiBF<sub>4</sub> system.

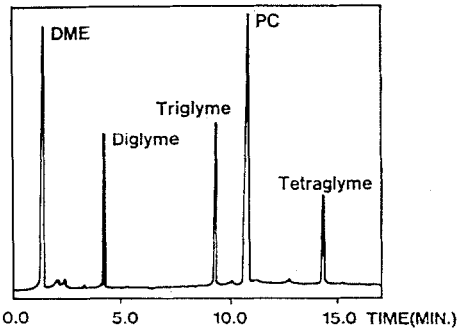
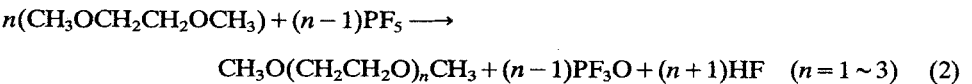
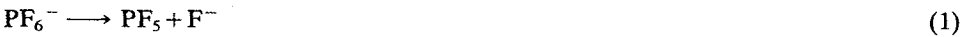


Fig. 5. Analysis of the electrolyte after a 40-day storage at 60 °C in the LiPF<sub>6</sub> system.

LiBF<sub>4</sub> system may be the result of the deposition of manganese on the Li electrode surface.

The results of electrolyte analysis for the LiPF<sub>6</sub> system after a 40-day storage at 60 °C are given in Fig. 5. Peaks of diglyme, triglyme and tetraglyme are observed in addition to PC and DME. These glymes are thought to be produced by polymerization of DME, which is caused by PF<sub>5</sub> [4]:



The deterioration of discharge capacity during storage may be the result of the reaction between decomposition products and the Li electrode.

It is important that the electrolyte used in Li cells does not decompose in the event of overdischarge. Figure 6 shows the results of the analysis of the electrolytes when  $-5$  V (versus  $\text{Li}/\text{Li}^+$ ) was applied to the  $\text{LiClO}_4$  or  $\text{LiCF}_3\text{SO}_3$  system. Whereas various decomposition products are observed for the  $\text{LiClO}_4$  system, no decomposition product is observed in the electrolyte for the  $\text{LiCF}_3\text{SO}_3$  system. This indicates that the  $\text{LiCF}_3\text{SO}_3$  system offers excellent stability during overdischarge.

#### A study on solvents

Figure 7 illustrates the discharge capacity of test cells with  $\text{LiCF}_3\text{SO}_3$  and various solvents at an initial high-rate discharge of  $5 \text{ mA cm}^{-2}$ . When PC is used as a solvent with dielectric constant, PC/DME exhibits a larger capacity than the other solvents. When DME is used as solvent with low viscosity, EC/BC/DME yields the highest capacity. It is considered that EC/BC/DME has superior high-rate discharge characteristics because of its high conductivity and low viscosity.

Table 3 shows the discharge capacities of test cells with  $\text{LiCF}_3\text{SO}_3$  and various solvents before and after storage. Mixtures of cyclic carbonic esters and DME have large discharge capacities of more than  $130 \text{ mA h}$  after a 40-day storage at  $60^\circ\text{C}$ .

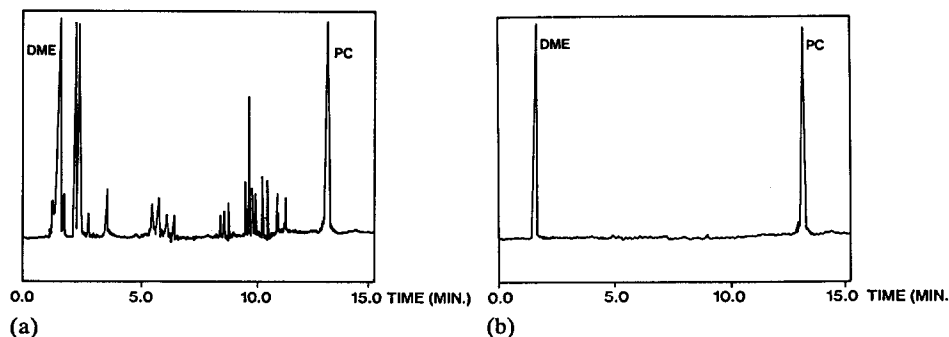


Fig. 6. Analysis of the electrolyte under the potential of  $-5$  V (vs.  $\text{Li}/\text{Li}^+$ ): (a)  $\text{LiClO}_4$ -PC/DME, and (b)  $\text{LiCF}_3\text{SO}_3$ -PC/DME.

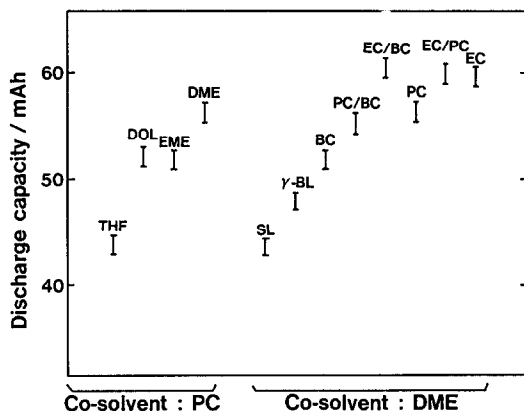


Fig. 7. Discharge capacity of tests cells with  $\text{LiCF}_3\text{SO}_3$  and various solvents at initial high-rate discharge:  $25^\circ\text{C}$ ,  $5 \text{ mA cm}^{-2}$ .

TABLE 3

Comparison of storage characteristics of test cells with  $\text{LiCF}_3\text{SO}_3$  and various solvents<sup>a</sup>

	Discharge capacity (mA h) <sup>b</sup>	
	Initial	After a 40-day storage at 60 °C
PC/DME	140	130
PC/EME	140	110
PC/DOL	140	120
PC/THF	140	115
PC/DME	140	130
EC/DME	140	135
BC/DME	140	130
EC/PC/DME	140	135
EC/BC/DME	140	135
PC/BC/DME	140	130
$\gamma$ -BL/DME	135	100
SL/DME	130	80

<sup>a</sup>EC, ethylene carbonate; PC, propylene carbonate; BC, 1,2-butylene carbonate; SL, sulfolane;  $\gamma$ -BL,  $\gamma$ -butylactone; DME, 1,2-dimethoxyethane; THF, tetrahydrofuran; DOL, 1,3-dioxolane; and EME, ethoxymethoxyethane.

<sup>b</sup>Discharge condition: 25 °C, 0.5 m A cm<sup>-2</sup>.

Moreover, EC shows superior storage characteristics. It is considered that the surface layer on Li produced by EC protects it from attacks by the electrolyte.

## Conclusions

A range of solutes and solvents for manganese dioxide–lithium cells were investigated.

$\text{LiCF}_3\text{SO}_3$  shows excellent low-temperature discharge, storage and overdischarge characteristics. The mixture of EC, BC and DME has excellent high-rate discharge and storage characteristics. Manganese dioxide–lithium cells using  $\text{LiCF}_3\text{SO}_3$ –EC/BC/DME are expected to feature excellent discharge performance and good reliability.

## References

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