

# Dependence of lithium metal secondary cell performance on lithium cation solvation state

Katsuya Hayashi<sup>\*</sup>, Yasue Nemoto, Shin-ichi Tobishima, Yoji Sakurai

*NTT Integrated Information and Energy Systems Laboratories, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1193, Japan*

## Abstract

We investigated the influence of the state of lithium cations in a nonaqueous electrolyte on lithium metal secondary cell performance. We used 1,2-dimethoxyethane (DME) mixed with ethylene carbonate (EC) as a mixed solvent and  $\text{LiPF}_6$  as a solute. The longest cycle life for a  $\text{Li}/\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  cell was provided by  $1.0 \text{ mol dm}^{-3}$   $\text{LiPF}_6$  EC-mixed electrolyte containing 20 vol.% of DME. This is the same point at which the state of the lithium cations in the electrolyte changes as detected by  $^7\text{Li}$ -NMR measurement. With this electrolyte composition, most of the DME selectively solvates the lithium cations. As the amount of non-solvating DME increases in the electrolyte, the cell cycle life becomes shorter. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

The electrolyte of a lithium secondary cell generally consists of a solute dissolved in a mixture of nonaqueous solvents. A lithium cation has a valence of one plus and is very small with a diameter of 0.06 nm, therefore, its electric charge density is very high. Because of this, several molecules of solvent solvate the lithium cation to reduce its electric charge density and thus achieve a stable state. The type and number of solvents which solvate the lithium cations depends on the electrolyte composition. In mixed solvent electrolytes, we can predict which solvent will have a high solvation power from its ‘donor number’ [1]. That is, a solvent with a larger donor number tends to solvate lithium cations selectively. Table 1 shows the physical properties of solvents. The donor numbers of ethylene carbonate (EC) and propylene carbonate (PC) are 16.4 and 15.1, respectively. 1,2-Dimethoxymethane (DME), an acyclic ether, exhibits the larger donor number of 20 or 24 [1]. Therefore, DME has a higher solvation power than EC or PC. Furthermore, DME provides a high oxidation potential of 4.9 V on a glassy carbon electrode.

Consequently, DME can be used as the electrolyte for 4 V class lithium secondary cells.

The charging or discharging reaction in a lithium metal cell occurs at the interface between the electrode and electrolyte. The lithium cations in the electrolyte are released from solvation and then deposited on the lithium metal anode. Therefore, we believe there is some relationship between the state of the lithium cations and the cycling efficiency of lithium electrode. The cycling efficiency cannot reach 100%. One of the reasons is that there is a side reaction in the cell, and the products are electrochemically inert compounds [2].

In this paper, we investigate the relationship between the state of lithium cations in an electrolyte and  $\text{Li}/\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  secondary cell performance.

## 2. Experimental

### 2.1. Electrolyte preparation

All the solvents we used had distilled. We mixed DME with EC or PC and then dissolved  $\text{LiPF}_6$  in the mixture. All the electrolytes we used had a water content of less than 20 ppm. The combination of EC and DME solvents with a volume ratio of 50:50, and  $\text{LiPF}_6$  solute with a

<sup>\*</sup> Corresponding author. Tel.: +81-29-287-7796; Fax: +81-29-270-4095; E-mail: hayashi@iba.iecl.ntt.co.jp

Table 1  
Physical properties of solvents

Solvent	Donor number	Molecular weight	Specific gravity ( $\text{g cm}^{-3}$ )	Concentration ( $\text{mol dm}^{-3}$ )
Propylene carbonate (PC)	15.1	102.09	1.2069	11.82
Ethylene carbonate (EC)	16.4	88.06	1.3208	15.00
1,2-Dimethoxyethane (DME)	20 (24)	90.12	0.8683	9.64

concentration of  $1.0 \text{ mol dm}^{-3}$  is denoted as 1.0 M  $\text{LiPF}_6\text{-EC/DME (50:50)}$ .

## 2.2. NMR spectra and specific conductivity

We obtained  $^7\text{Li}$ - and  $^{13}\text{C}$ -NMR spectra of electrolytes at  $20^\circ\text{C}$  using JEOL JNM GX-270. All  $^7\text{Li}$ - and  $^{13}\text{C}$ -NMR spectra were calibrated with 1.0 M  $\text{LiCl}$  aqueous solution and chloroform- $d_1$ , respectively. The specific conductivity of each electrolyte was measured at 1 kHz with an LCR bridge (GenRad, 1658 RLC Digibridge) with a cell (Yanako, C-type cell).

## 2.3. Evaluation of cycling performance of Li / $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$ cells

The  $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  we used has a high cycleability which is achieved by substituting cobalt for part of the manganese [3]. The high cycleability of this cathode makes it possible to estimate the cycling efficiency of a lithium metal anode which depends on the electrolyte used.  $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  was synthesized as described previously [3].

We fabricated Li/ $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  coin cells (23 mm in diameter, 2 mm thick). The cathode was prepared from  $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  mixed with carbon black and ethylene-propylenediene terpolymer binder in a weight ratio of 90:7:3. The cathode was coated on an aluminum substrate and the electrode surface area was  $2 \text{ cm}^2$ . All the cells were galvanostatically cycled between 3.3 and 4.3 V at  $20^\circ\text{C}$ . We evaluated the cycling performance of the Li/ $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  cells by using the figure of merit (FOM) for lithium cycling efficiency [4]. The FOM was calculated using Eq. (1). The end of cycle is the time when the capacity has fallen to 50% of its initial value.

$$\text{FOM} = \frac{\text{accumulated discharge capacity to the end of cycle (mAh)}}{\text{theoretical capacity of lithium in cathode and anode (mAh)}} \quad (1)$$

## 3. Results and discussion

### 3.1. Electrolyte composition

Fig. 1 shows the concentration of each electrolyte component in 1.0 M  $\text{LiPF}_6\text{-EC/DME (100-x:x)}$ ,  $x$ : vol.% of DME. The concentration of each electrolyte was calcu-

lated using Eq. (2) with specific gravity and molecular weight.

$$\begin{aligned} & [\text{Concentration of solvent (mol dm}^{-3}\text{)}] \\ &= \frac{[\text{Specific gravity of solvent (g dm}^{-3}\text{)}]}{[\text{Molecular weight of solvent (g mol}^{-1}\text{)}]} \quad (2) \end{aligned}$$

According to Eq. (2), the concentration of EC and DME solvent are 15.0 and 9.6  $\text{mol/dm}^3$ , respectively. We disregarded any change in the volume of solution caused by mixing the solvents and dissolving the solute.

### 3.2. State of lithium cation in the electrolyte

It has been reported that two DMEs are capable of solvating a lithium cation [5]. When the DME concentration is more than twice that of the lithium cations, all lithium cations are solvated solely by DME. When the DME concentration is less than twice of that of the lithium cations, some of the cations are solvated by DME and the others by EC. As shown in Fig. 1, the borderline is about 20 vol.% of DME electrolyte or 1.0 M  $\text{LiPF}_6\text{-EC/DME (80:20)}$ . We used the  $\text{LiPF}_6$  concentration,  $[\text{LiPF}_6]$ , not that of the lithium cations,  $[\text{Li}^+]$  in Fig. 1. The degree of  $\text{LiPF}_6$  dissociation,  $\alpha$ , is 1 or less, hence the lithium cation concentration is less than that of  $\text{LiPF}_6$  as shown by Eq. (3). In fact, it is thought that the border of solvation state is less than 20 vol.% of DME electrolyte.

$$[\text{Li}^+] = \alpha [\text{LiX}], \quad \text{LiX: lithium salt} \quad (3)$$

We measured  $^7\text{Li}$ -NMR and  $^{13}\text{C}$ -NMR spectra of 1.0 M  $\text{LiPF}_6\text{-EC/DME (100-x:x)}$ . Fig. 2 shows the relation-

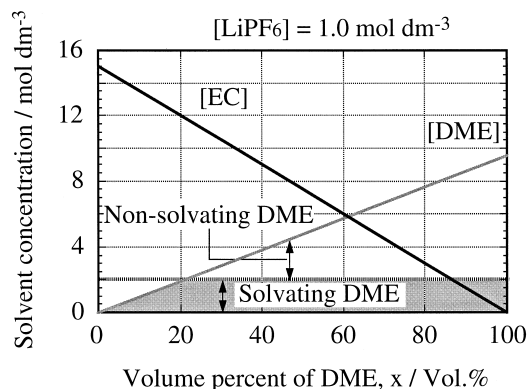


Fig. 1. Concentration of each component in 1.0 M  $\text{LiPF}_6\text{-EC/DME (100-x:x)}$ .

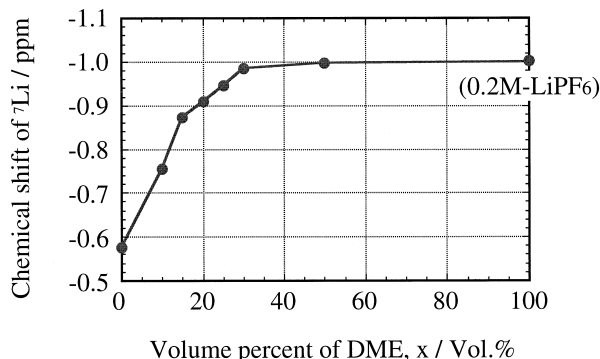


Fig. 2. Chemical shift of  $^7\text{Li}$  of 1.0 M  $\text{LiPF}_6$ -EC/DME(100- $x$ : $x$ ).

ship between the vol.% of DME and the chemical shift of  $^7\text{Li}$  in a series of 1.0 M  $\text{LiPF}_6$ -EC/DME. We used the chemical shift of  $^7\text{Li}$  with 0.2 M  $\text{LiPF}_6$ -DME as the value for 100 vol.% of DME electrolyte because of the low solubility of  $\text{LiPF}_6$  in DME. The  $^7\text{Li}$  chemical shifts for 100 to 30 vol.% of DME electrolyte have almost the same value of -1.0 ppm. From 15 to 30 vol.% of DME electrolyte, the chemical shifts change gently and then from 0 to 15 vol.%, the change is linear. Both ends exhibit straight lines and both extended lines meet at around 20 vol.% of DME. We think the state of the lithium cations is changed at this point, that is, there is a borderline between DME selective solvation and the coexistence of two solvation states.

The  $^{13}\text{C}$ -NMR spectra of each electrolyte support the above belief. Fig. 3 shows the relationship between the vol.% of DME and the chemical shift of  $^{13}\text{C}$  in a series of 1.0 M  $\text{LiPF}_6$ -EC/DME. We focused on the carbons of the DME ethane-group and on the carbon of EC carbonyl-group because both carbons are close to the site of solvation. The greatest degree of change was when the DME concentration in the electrolyte was around 20 vol.%. This means the state of the lithium cations in the electrolyte changes at this point.

### 3.3. Cycling performance of Li / $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$ cells

Fig. 4 shows cycling performance of Li/ $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  cells with a series of 1.0 M  $\text{LiPF}_6$ -EC/DME (100- $x$ : $x$ )

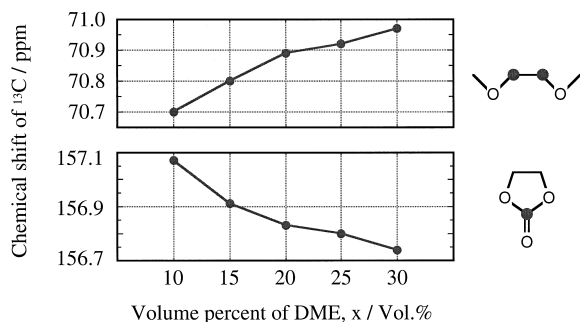


Fig. 3. Chemical shift of  $^{13}\text{C}$  of 1.0 M  $\text{LiPF}_6$ -EC/DME(100- $x$ : $x$ ).

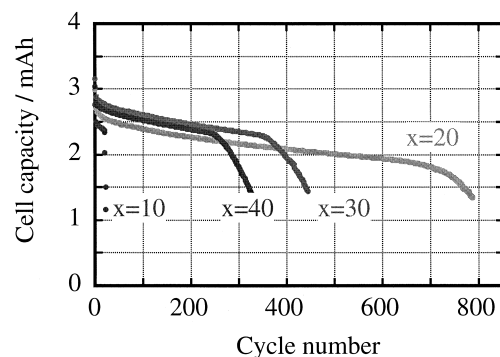


Fig. 4. Cycling performance of Li/ $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  cell with 1.0 M  $\text{LiPF}_6$ -EC/DME(100- $x$ : $x$ ).

at charge and discharge current density of  $1 \text{ mA cm}^{-2}$  and  $3 \text{ mA cm}^{-2}$ , respectively. The longest cell cycle life of 780 cycles was obtained with 1.0 M  $\text{LiPF}_6$ -EC/DME (80:20). As shown in Fig. 5, the FOM at  $x = 20$  is 40.

In the following, we focus on a solvent which does not participate in lithium cation solvation. As mentioned above, when the concentration of DME is 20 vol.%, most of the lithium cations are solvated solely by DME. This means that EC does not participate in the solvation. When  $x$  is less than 20 vol.%, EC can participate in solvation, because there are too few DME molecules to solvate all the lithium cations. When  $x$  is more than 20 vol.%, there is enough DME to solvate the lithium cations and there are also both non-solvating DME and EC in the electrolyte.

As  $x$  increases from 20, the FOM of Li/ $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  cells decreases. It is reported that an electrolyte containing EC provides suitable passivation film leading to a lithium anode with good cycling efficiency [6]. We believe that the presence of non-solvating DME has a detrimental effect on such passivation film. By contrast, as  $x$  decreases from 20, the FOM of the lithium cell also decreases. A cell with  $x = 10$  electrolyte had a greatly reduced capacity. One reason is the low specific conductivity of  $x = 10$  electrolyte. When cells are cycled at a lower current density of  $0.5 \text{ mA cm}^{-2}$ , the FOM with  $x = 10$  electrolyte is raised.

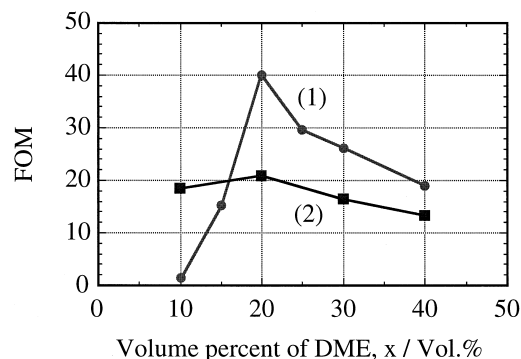


Fig. 5. FOM of Li/ $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  cell with EC/DME electrolyte at different current densities. (1) Discharge:  $3.0 \text{ mA cm}^{-2}$ , charge:  $1.0 \text{ mA cm}^{-2}$ . (2) Discharge:  $0.5 \text{ mA cm}^{-2}$ , charge:  $0.5 \text{ mA cm}^{-2}$ .

In these cycling tests,  $x = 20$  electrolyte also exhibited the maximum FOM in the series of 1.0 M  $\text{LiPF}_6\text{-EC/DME}$  (100 -  $x$ : $x$ ) (Fig. 5). We also examined a series of 1.0 M  $\text{LiPF}_6\text{-PC/DME}$  (100 -  $x$ : $x$ ). However, we could not obtain results similar to these of the above-mentioned EC/DME electrolyte. This is because there is the difference in reactivity between EC and PC in electroreduction-process [7], and PC is incapable of producing a suitable protective film on the lithium anode to provide good cycling efficiency.

#### 4. Conclusions

We have investigated the influence of the state of lithium cations in an electrolyte on lithium metal secondary cell performance with electrolytes containing DME. The longest cycle life with an  $\text{Li/LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  cell was provided with 1.0 M  $\text{LiPF}_6\text{-EC/DME}$  (80:20). In this electrolyte, most of the DME selectively solvates the lithium cations. As the amount of non-solvating DME increases, the cycle life was reduced, because these molecules damages the protective film on the lithium anode thus reducing the cycling efficiency.

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