Lithium cycling efficiency of ternary solvent electrolytes with ethylene carbonate–dimethyl carbonate mixture

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Abstract

Lithium cycling efficiency for ternary solvent (mol ratio 1:1:1) electrolytes of different molar conductivities containing $LiPF_6$ and $LiClO_4$ with ethylene carbonate (EC)–dimethyl carbonate (DMC) binary mixture of constant mixed ratio (mol ratio 1:1) was investigated by galvanostatic experiments at 25 °C. The solvents applied to the EC–DMC mixture are 1,2-dimethoxyethane (DME), 2-methyltetrahydrofuran (2-MeTHF) and ethylmethyl carbonate (EMC). The molar conductivity of the EC–DMC–DME ternary solvent electrolytes gradually increased with the addition of DME. However, the molar conductivities of the EC–DMC–2-MeTHF and EC–DMC–EMC ternary solvent electrolytes gradually decreased with the addition of 2-MeTHF and EMC. The decrease of the molar conductivity for these solutions is attributed to a decrease of the dissociation degree for electrolytes versus a decrease of the dielectric constant rather than that of the viscosity of the EC–DMC–2-MeTHF and EC–DMC–EMC ternary solvent mixtures. The lithium cycling efficiency of every ternary electrolyte containing $LiPF_6$ was larger than those of the EC–DME, EC–EMC and EC–DMC binary electrolytes containing $LiPF_6$ at about 20 cycles. Especially, the efficiency of $LiPF_6$/EC–DMC–DME electrolyte became about 80% at 40 cycles. The nickel (working) electrode surface in binary and ternary electrolytes after dissolution by cyclic voltammetry was observed by atomic force microscopy. The formation of lithium dendrite was already observed during the first cycle in the $LiPF_6$/EC–DMC electrolyte. However, it was found that the addition of ethers such as DME and 2-MeTHF to the $LiPF_6$/EC–DMC electrolyte was helpful to suppress the formation of lithium dendrite on the nickel electrode. © 1997 Elsevier Science S.A.

Keywords: Lithium secondary batteries; Lithium cycling efficiency; Electrolytic conductivity; Organic electrolytes

1. Introduction

The electrolytic conductivity and charge/discharge characteristics of the lithium electrode are dependent on many factors, such as electrolytes, electrolyte concentration, solvent composition and the presence of impurities. Propylene carbonate (PC) or ethylene carbonate (EC)-based binary solvents with various ethers and esters have been examined mainly as the electrolytes for lithium batteries [1–9].

The application of these binary mixtures in lithium batteries is due to the relatively lower viscosity of ethers or esters, and the higher dielectric constant, chemical and electrochemical stability of PC and EC. However, we previously reported [10] that better lithium cycling efficiency and molar conductivity have been obtained in PC–diethyl carbonate (DEC)–1,3-dimethyl-2-imidazolidinone (DMI) ternary electrolytes compared with those in PC–DEC binary electro-

lytes. Other workers have already reported the advantageous conductivity and cycling behavior in ternary solvent electrolytes [11,12]. Consequently, it is interesting to study the electrolytic conductivity and charge/discharge characteristics of lithium electrode in various ternary solvent electrolytes.

The purpose of the present study is to examine the lithium cycling efficiency for ternary solvent electrolytes of different molar conductivities with EC–dimethyl carbonate (DMC) binary mixture in a constant mixed ratio.

2. Experimental

2.1. Materials

The preparation and purification of EC have been described elsewhere [13]. The solvents of DMC, EMC, DME and 2-MeTHF were used as received (battery-grade). The lithium

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salts of commercial reagent grade, $LiClO_4$ and $LiPF_6$ were dried at 120 and 60 °C in vacuum, respectively.

2.2. Apparatus and measurement

Conductivities of the electrolytes were measured using a conductometer (Toa Electronics, Model CM-60S) with a cell (Model CGT-511B). The apparatus and techniques for measurement of dielectric constant and viscosity were similar to those previously reported [14,15].

By use of a charge/discharge unit (Hokuto Denko, Model HJ-201B), the lithium cycling efficiency (charge/discharge coulombic cycling efficiency of lithium electrode) was estimated by a galvanostatic plating-stripping method which was reported by Koch and Brummer [15]. The plating (i_p) and stripping current density (i_s) were 1.3 mA cm^{-2}, and the plated charge (Q_p) was 0.13 C cm^{-2}. The lithium cycling efficiency was calculated from Eq. (1)

$$\text{Efficiency } (\%) = Q_s/Q_p \times 100 \qquad (1)$$

where Q_s is the stripped charge. The counter (0.79 cm^2) and reference electrode were prepared by pressing a thin lithium foil on the nickel net. A nickel sheet (0.79 cm^2) was used as a working electrode. The preparation of the electrolyte solutions and the assembly of the cell were carried out in an argon-filled dry box. The measurement of lithium cycling efficiency was carried out in an electric auto-dry desiccator.

In situ atomic force microscope (AFM) (Seiko Instruments, Model SPA-300) experiments were used to observe a nickel (working) electrode surface with deposition/dissolution (redox) processes by cyclic voltammetry. The platinum wire was used as the counter and reference electrodes. A fluid cell used in situ experiments was sealed from atmosphere.

3. Results and discussion

3.1. Conductivity

The variation of molar conductivities (λ) for ternary solvent electrolytes with the EC–DMC (mol ratio 1:1) binary mixture containing (a) $LiPF_6$ and (b) $LiClO_4$ at 25 °C is shown in Fig. 1. In EC–DMC–DME ternary solvent electrolytes, the molar conductivities gradually increased with the addition of DME. However, the molar conductivities of EC–DMC–2-MeTHF and EC–DMC–EMC ternary solvent electrolytes gradually decreased with the addition of 2-MeTHF and EMC. The variations of the viscosity (η) and dielectric constant (ϵ) for ternary solvent mixtures are shown in Figs. 2 and 3, respectively. In Figs. 2 and 3, both the viscosities and dielectric constants for any ternary solvent mixture decrease with increasing DME, 2-MeTHF and EMC concentration. It is difficult to elucidate the difference of conductivities between EC–DMC–DME and EC–DMC–2-MeTHF or EC–DMC–EMC ternary solvents electrolytes from the variation
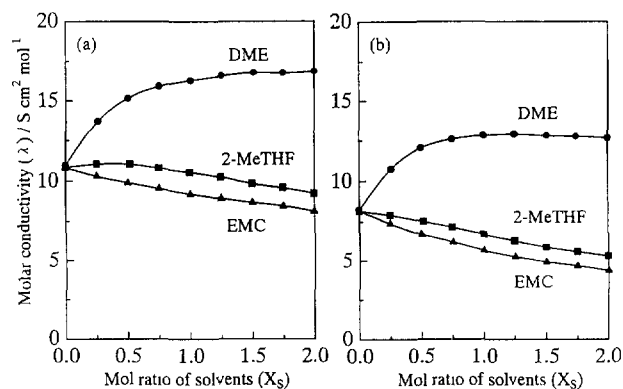

Fig. 1. Variation of molar conductivities (λ) for ternary solvent electrolytes with the EC–DMC (mol ratio 1:1) binary mixture containing (a) 1 M $LiPF_6$ and (b) $LiClO_4$ at 25 °C. X_s means the mol ratio of DME, 2-MeTHF and EMC to the EC–DMC binary mixture
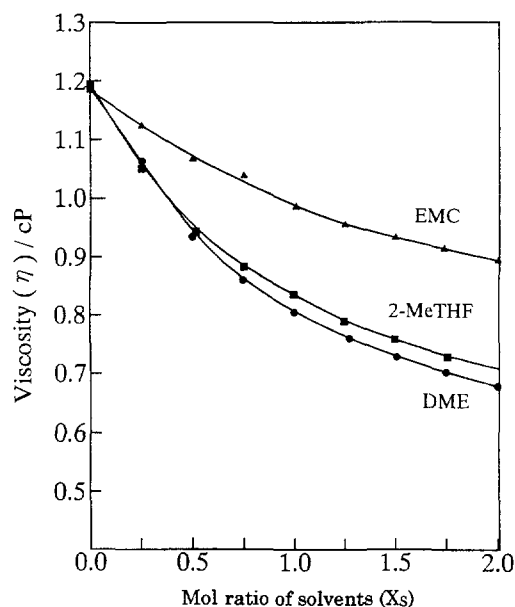

Fig. 2. Variation of viscosities (η) for ternary solvent mixture with the EC–DMC (mol ratio 1:1) binary mixture at 25 °C. X_s means the mol ratio of DME, 2-MeTHF and EMC to the EC–DMC binary mixture.

of viscosities in Fig. 2. Accordingly, the increase in molar conductivity for the EC–DMC–DME ternary electrolytes is attributed to the variation of the dielectric constant rather than that of the viscosity for EC–DMC–DME ternary solvent mixture. The further discussion is based, however, on the donor ability of the solvents. The value of the donor number (DN) and the dielectric constant are strongly related but not necessarily always in parallel. The molar conductivities of EC–DMC–DME ternary solvent electrolytes depend on the increase of the dissociation degree for $LiPF_6$ and $LiClO_4$, since the EC or DMC molecules of the solvation shell for the Li$^+$ ion are selectively substituted by the DME molecule with a higher DN than EC (DN = 16.4) or DMC molecule (it is assumed that the DN of DMC is smaller than that of DME, although that value of DMC is unknown at present). On the contrary, it is considered for the EC–DMC–2-MeTHF and EC–DMC–EMC ternary solvent electrolytes that the disso-
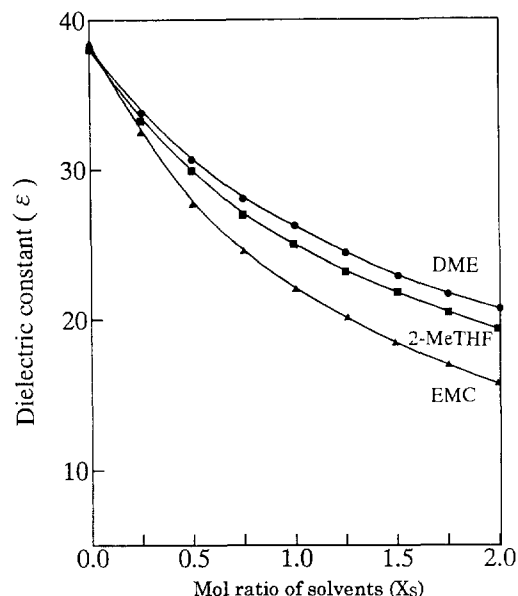
Fig. 3. Variation of dielectric constants (ε) for ternary solvent mixture with the EC–DMC (mol ratio 1:1) binary mixture at 25 °C. X_s means the mol ratio of DME, 2-MeTHF and EMC to the EC–DMC binary mixture.

ciation degree for LiPF$_6$ and LiClO$_4$ becomes small by a decrease of the dielectric constant for these ternary solvent mixtures in Fig. 3 because of the difficulty of substitution of EC or DMC for 2-MeTHF and EMC with smaller DN compared with that of DME (the DN of EMC similarly to DMC also seems to be smaller than that of DME).

3.2. Lithium cycling efficiency

The lithium cycling efficiency of binary (mol ratio 1:1) and ternary (mol ratio 1:1:1) solvent electrolytes containing LiPF$_6$ is shown in Fig. 4. In every binary solvent electrolyte, the lithium cycling efficiency decreased with increasing cycle number. Especially, the efficiency of the EC–DMC binary electrolyte decreases markedly with increasing cycle number. In contrast to binary solvent electrolytes, the decrease in lith-
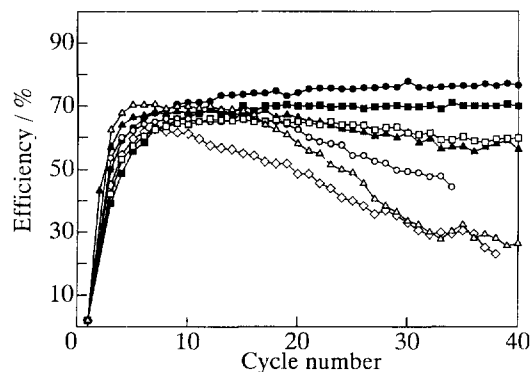

Fig. 4. Lithium cycling efficiency of the binary (mol ratio 1:1) and ternary (mol ratio 1:1:1) solvent electrolytes containing 1 M LiPF$_6$ at 25 °C. $i_p = i_s = 1.3$ mA cm^{-2}, $Q_p = 0.13$ C cm^{-2}. (●) EC–DMC–DME; (■) EC–DMC-2-MeTHF; (▲) EC–DMC–EMC; (○) EC–DME; (□) EC-2-MeTHF (△) EC–EMC, and (◇) EC–DMC
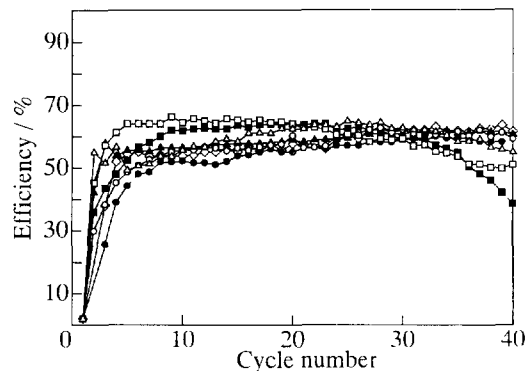

Fig. 5. Lithium cycling efficiency of the binary (mol ratio 1:1) and ternary (mol ratio 1:1:1) solvent electrolytes containing 1 M LiClO$_4$ at 25 °C. $i_p = i_s = 1.3$ mA cm^{-2}, $Q_p = 0.13$ C cm^{-2}. (●) EC–DMC–DME; (■) EC–DMC-2-MeTHF; (▲) EC–DMC–EMC; (○) EC–DME; (□) EC-2-MeTHF, (△) EC–EMC, and (◇) EC–DMC.

ium cycling efficiency for ternary solvent electrolytes excepted for EC–DMC–EMC electrolyte is hardly observed in spite of the increase in cycle number. In addition, it was found that the lithium cycling efficiency of EC–DMC–DME ternary electrolytes becomes about 80% at cycle no. 40. The lithium cycling efficiency of binary and ternary solvent electrolytes containing LiClO$_4$ is shown in Fig. 5. The difference in efficiency between binary and ternary electrolytes is small as shown in Fig. 5. This fact shows that the lithium cycling efficiency is highly influenced by the type of lithium salt. The maximum lithium cycling efficiency of ternary electrolytes containing LiClO$_4$ is lower than that of ternary electrolytes containing LiPF$_6$. Furthermore, the difference in lithium cycling efficiency with various molar conductivities of ternary electrolyte containing LiClO$_4$ is relatively small compared with that of ternary electrolytes containing LiPF$_6$ as shown in Fig. 4. The reason why the lithium cycling efficiency in these electrolytes becomes lower than 100% depends on the formation of low conducting, passivating films onto the nickel electrode, arising from the reduction of reactive impurities and the electrolytes itself [16–18]. The morphology and chemical composition of the passivating films have already described elsewhere [19–22].

3.3. In situ AFM images

In situ observation of the nickel (working) electrode surface with deposition/dissolution (redox) processes in binary and ternary solvent electrolytes by cyclic voltammetry was performed with AFM. The AFM images in EC–DMC binary electrolytes after dissolution at various cycles are shown in Fig. 6. The formation of lithium dendrite was already observed at the first cycle in LiPF$_6$/EC–DMC electrolyte (Fig. 6(a)). In this binary electrolyte, the growth of lithium dendrite proceeds with increasing cycle number, and the films on the electrode surface become considerably heterogeneous. On the contrary, the dendrite formation in the LiClO$_4$/EC–DMC electrolyte (Fig. 6(b)) was scarcely observed in spite of the increase in cycle number. The films in the LiClO$_4$/

(a) 15th cycle   (b) 15th cycle

(a) LiPF₆/EC⁻DMC   (b) LiClO₄/EC⁻DMC

Fig. 6 AFM images on the nickel electrode in binary solvent electrolytes after dissolution at various cycle numbers

(a) 15th cycle   (b) 15th cycle
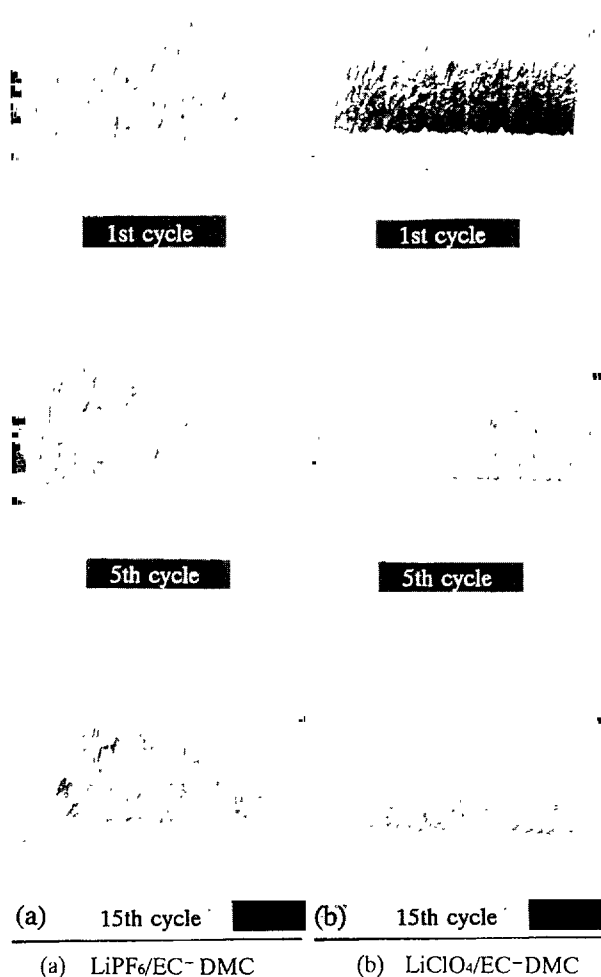
(a) LiPF₆/EC⁻DMC⁻2-MeTHF (b) LiClO₄/EC⁻DMC⁻2-MeTHF

Fig 7 AFM images on the nickel electrode in ternary solvent electrolytes after dissolution at various cycle numbers.

EC–DMC electrolyte are homogeneous compared with those in the $LiPF_6$/EC–DMC electrolyte. Accordingly, it is thought that the marked decrease in lithium cycling efficiency of the $LiPF_6$/EC–DMC electrolyte shown in Fig. 4 is dependent on the growth of lithium dendrite and the morphology of films on the electrode. The AFM images in the EC–DMC–2-MeTHF ternary electrolytes after dissolution are shown in Fig. 7. Although the formation of lithium dendrite in $LiPF_6$/EC–DMC–2-MeTHF ternary electrolyte appears to be considerably small in Fig. 7(a), the films in this ternary electrolyte is more heterogeneous than that in $LiClO_4$/EC–DMC electrolyte in Fig. 6(b). Therefore, it is assumed that the formation of films in the binary and ternary electrolytes containing $LiClO_4$ occurs homogeneously in comparison with that in the electrolytes containing $LiPF_6$. Comparing the films formed in EC–DMC binary and EC–DMC–2-MeTHF or EC–DMC–DME ternary electrolytes containing $LiPF_6$, it was found that the addition of 2-MeTHF and DME to
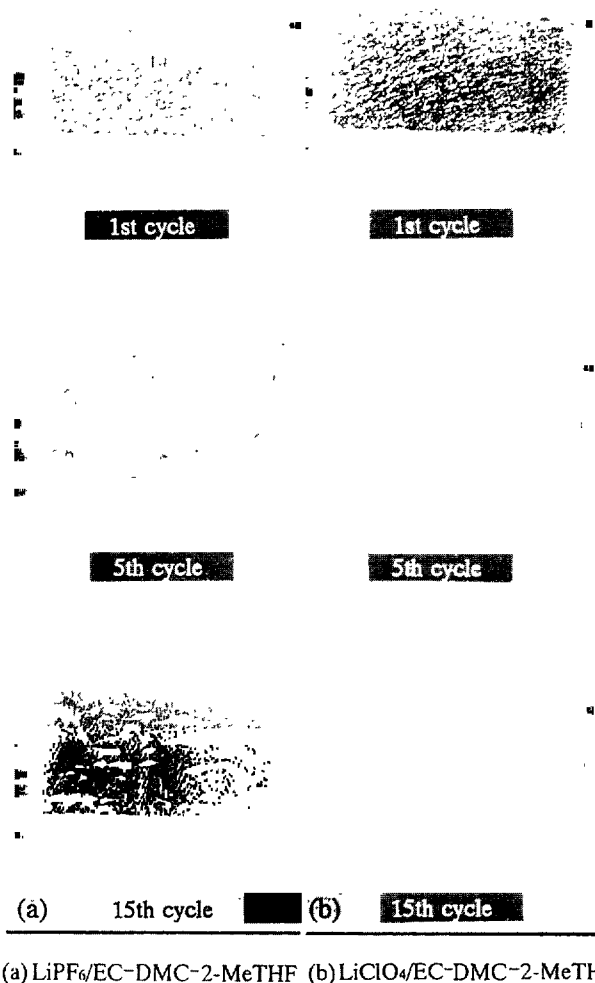
$LiPF_6$/EC–DMC binary electrolyte is helpful to suppress the formation of lithium dendrite on the nickel electrode.

4. Conclusions

The lithium cycling efficiency is highly influenced by the formation of lithium dendrite and the morphology on the surface of the nickel electrode. The addition of ethers such as DME and 2-MeTHF to $LiPF_6$/EC–DMC binary electrolyte suppresses the formation of dendritic lithium on the electrode.

Acknowledgements

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