# ORGANIC ELECTROLYTE SOLUTIONS FOR RECHARGEABLE LITHIUM BATTERIES

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## Summary

Several combinations of organic solvents and lithium salts have been examined as electrolytes for ambient-temperature, rechargeable lithium batteries. Ethers (1,2-dimethoxyethane, tetrahydrofuran, 1,3-dioxolane, etc.) have been used as the base solvents, as they are electrochemically stable and have a low reactivity towards lithium metal. In the main, mixed-solvent systems have been adopted to improve the solubility of electrolytes and, hence, the electrolytic conductivity of the solution. The charge/discharge characteristics of the lithium negative electrode have been examined in these electrolytes. The cycling characteristics of $Li/TiS_2$ cells with the electrolytes containing crown ethers have also been investigated. The electrochemical properties of the electrodes and the charge/discharge characteristics of these cells are markedly influenced by the composition of the electrolyte.

The electrode reaction mechanisms are briefly discussed for these systems.

## Introduction

During the development of ambient-temperature, rechargeable lithium batteries, it has been noted that the choice of the electrolyte system is of special importance in determining the cell performance [1]. Some ethers, such as tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME), have been used as a cosolvent of the electrolyte for primary lithium batteries. The ethers have strong affinity for $Li^+$ ions. Thus, it might be expected that the solvent composition of the ether-based electrolyte will influence the cycling characteristics of not only the lithium negative electrode but also the lithium-insertion positive. However, there have been only a few studies of the effects of the solvent composition on the cycling behaviour of the electrodes [2].

This work is concerned with electrolyte solutions consisting of ether solvents for rechargeable lithium batteries. The conductivity of the electrolyte and the cycling characteristics of lithium have been investigated in mixed-ether systems. Also, the addition of cyclic polyethers (crown ethers)

to the electrolyte system has been examined. The effects of the $Li^+$–ether interactions on the electrode characteristics are discussed.

## Experimental

The solvents comprised mixtures of DME and THF, DME and 1,3-dioxolane (DOL), and THF and DOL. Propylene carbonate (PC) containing crown ethers (12-crown-4 = 12C4 and 15-crown-5 = 15C5) was also used as the solvent. The solvents were purified and dehydrated by usual distillation methods. The electrolytic salts were anhydrous $LiClO_4$, $LiBF_4$ and $LiPF_6$. The conductivity of the solution was measured by an impedance bridge method (10 kHz a.c.). The electrochemical behaviour of the lithium negative electrode was studied in a beaker-type glass cell (100 cm$^3$). The cycling efficiency of the lithium electrode was determined by a galvanostatic charge/discharge method using a nickel substrate [3]. A cylindrical Teflon-cell was employed in the measurements of the charge/discharge performance of the $Li/TiS_2$ cell [4]. The composition of the positive electrode after cycling was examined by both chemical and X-ray diffraction (XRD) analyses. The electrochemical experiments were carried out in dry argon atmosphere at room temperature (16 - 24 °C).
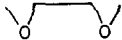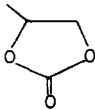
## Results and discussion

### Mixed-ether electrolytes [4 - 7]

Selected properties of the ethers are listed in Table 1. The ethers generally have low permittivities, but exhibit relatively high donicities. The latter property is associated with the strong affinity of the ether towards $Li^+$ ions [8], and also with the solubility of the lithium salt. Table 2 shows the electrolytic conductivity in the blended ether systems. The conductivity of $LiBF_4$ was improved by blending the ethers: the maximum value was observed for a blending ratio of about 50:50. The effect of solvent blending on the conductance of the lithium salts can be explained in part by the specific solvation of the $Li^+$ ion. In the DME-DOL system, for instance, the $Li^+$ ion is preferentially coordinated with DME molecules because DME has a higher donicity than DOL [5]. The interaction between $Li^+$ ions and DME leads to a smaller ionic radius of the solvated species, and therefore the mobility is higher than that of loosely solvated $Li^+$ ions [9].

Regarding the salt, the order of conductivity was $LiPF_6 > LiClO_4 > LiBF_4$ for the same solvent composition. The conductivity of 1 M $LiPF_6/$DME–THF, namely, $1.5 \times 10^{-2}$ S cm$^{-1}$, is comparable with, or higher than, those of $LiAsF_6/THF$ and $LiClO_4/DOL$ [10]. The salt dependence of the conductivity is probably related to the size of anion, which mainly determines the type of ion-pair formation. Whereas $LiClO_4$ tends to form contact ion pairs in such low permittivity solvents as the blended ether, $LiPF_6$,

TABLE 1

Selected properties of organic solvents

| Solvent | | $\epsilon_r(30\,°C)$ | $\eta(30\,°C)$ $(10^{-3}\,Pa\,s)$ | DN* |
|---|---|---|---|---|
| DME | | 6.92 | 0.40 | 24 |
| THF | | 7.25 | 0.46 | 20.0 |
| DOL | | 6.79 | 0.58 | — |
| PC | | 66.8 | 2.25 | 15.1 |

*From refs. 8 and 14.

TABLE 2

Electrolytic conductivity ($\kappa$) of mixed ether solutions at 30 °C

| Solute (1 M) | Solvent | $\kappa$ $(10^{-3}\,S\,cm^{-1})$ |
|---|---|---|
| LiClO$_4$ | DME | 7.18 |
| | THF | 3.82 |
| | DOL | 3.52 |
| | DME–DOL (1:1) | 9.00 |
| | THF–DOL (1:1) | 4.78 |
| LiBF$_4$ | DME | 3.73 |
| | THF | 1.80 |
| | DOL | 1.54 |
| | DME–DOL (1:1) | 3.95 |
| | THF–DOL (1:1) | 2.33 |
| LiPF$_6$ | DME–DOL (1:1)* | 16.8 |
| | DME–THF (1:1) | 15.4 |

*Triphenylphosphine (4 g dm$^{-3}$) addition.

whose anion size is largest of the three, is mainly present as a conductive, solvent-separated ion pair in those systems [22].

Figure 1 shows the variation in the charge/discharge efficiency of lithium with cycle number for the ether–ether mixed systems (mixing ratio =
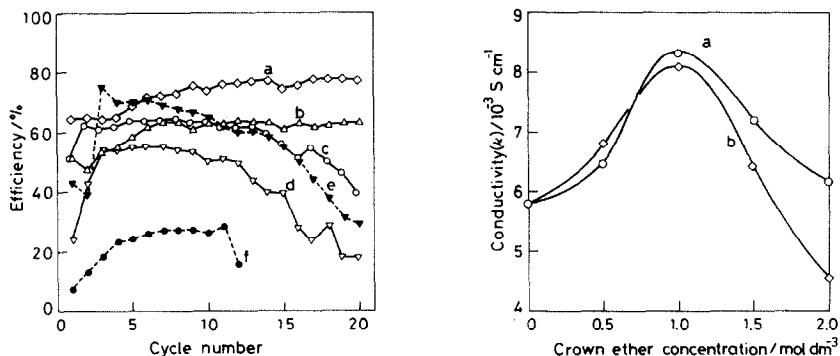
Fig. 1. Charge/discharge efficiency of lithium on a nickel substrate with cycle number. (a) $LiPF_6$/DME–THF; (b) $LiBF_4$/THF–DOL; (c) $LiBF_4$/DME–DOL; (d) $LiBF_4$/DME–THF; (e) $LiBF_4$/THF; and (f) $LiBF_4$/DOL. $i_p = i_s$ = 2 mA cm$^{-2}$, $Q_p$ = 0.2 C cm$^{-2}$.

Fig. 2. Conductivity of 1 M $LiClO_4$ in mixture of PC and crown ether; (a) PC–12C4, (b) PC–15C5.

50:50 by volume). The efficiency was highest in $LiPF_6$/DME–THF and scarcely varied with cycle number. In this system, the polarization of the lithium electrode during the charge/discharge cycle was relatively small. Among the solutions of $LiBF_4$, the efficiency in DME–DOL (or THF–DOL) was higher than that in DME–THF. Thus, a higher efficiency might be expected in $LiPF_6$/DME–DOL (or THF–DOL) than in $LiPF_6$/DME–THF. However, DOL-based systems containing $LiPF_6$ form gels because of the DOL polymerization. Chemical modification of the solvent and/or the use of some additive can prevent the polymerization of DOL [12].

*Electrolytes containing crown ethers [13]*

Figure 2 shows the conductivity of 1 M $LiClO_4$ in the crown ether-added PC. For both 12C4 and 15C5, the addition of 1 mol dm$^{-3}$ provided the greatest improvement in the conductance. The crown ethers coordinate with the Li$^+$ ions to form 1:1 complexes, which assists dissociation of the electrolyte and leads to a reduction in the radius of the solvated Li$^+$ ion. However, the addition of more than 1 mol dm$^{-3}$ of crown ether increases the solution viscosity, and thereby decreases the conductivity.

The charge/discharge behaviour of an $Li/TiS_2$ cell with a PC–crown ether electrolyte is shown in Fig. 3. From separate experiments, it was confirmed that the voltage variation of the cell with time was virtually determined by the potential of the positive $TiS_2$ electrode. The addition of 12C4 to the electrolyte improved both the utilization and the rechargeability of the $TiS_2$ electrode. The cathodic discharge of layered compounds such as $TiS_2$ is based on the electrochemical intercalation of Li$^+$ ions into the crystal lattice. In the PC-based solutions, the Li-intercalation appears to be accompanied by solvent co-intercalation [13]. As crown ethers coordinate more strongly with Li$^+$ ions than PC, the contribution of the ether molecules to
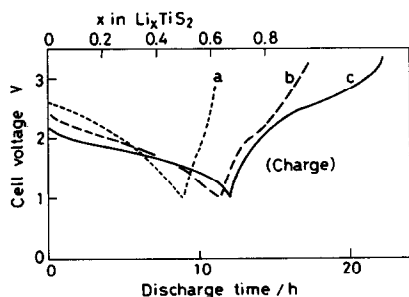
Fig. 3. Discharge/charge curves of Li/TiS$_2$ cells. (a) PC; (b) 1 M 15C5–PC; (c) 1 M 12C4–PC.
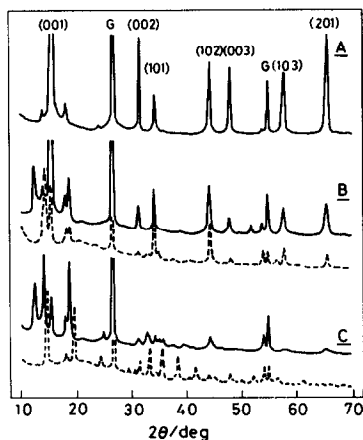
Fig. 4. XRD patterns (Cu K$\alpha$ radiation) of TiS$_2$ positive electrode. (A) before discharge; (B) after discharge (Li$_{0.11}$TiS$_2$); (C) after discharge (Li$_{0.28}$TiS$_2$). Solid curves in 1 M 12C4–PC, and broken curves in PC. Parentheses denote the index planes of TiS$_2$, and "G" is caused by graphite blended into the positive material as a conductive reagent.

the discharge process is also considered feasible in the crown ether-containing electrolytes.

Figure 4 shows XRD patterns of the positive electrode before, and after, discharging the cell. The differences in the diffraction patterns of pure PC and 12C4-containing PC may be attributable to differences in the species to be intercalated. The lithium content incorporated in the positive electrode after the discharge was determined by chemical analysis using atomic absorption spectroscopy. The results were almost consistent with the calculated values based on Faraday's law, irrespective of whether the electrolyte contained the crown ether or not. Therefore, the characteristics of the diffraction pattern must be based on the degree of solvation of the Li$^+$ ions. That is the observation of the larger interlayer spacing of TiS$_2$ after discharge from the crown-ether containing electrolyte suggests that the crown-ether complexed Li$^+$ ion was intercalated from the PC-12C4 electrolyte, whereas unsolvated Li$^+$ ions, or partially solvated Li$^+$ ions, were intercalated from the pure PC electrolyte. However, the intercalation of the crown-ether solvated Li$^+$ ions may contribute to the improvement in the discharge utilization (Fig. 3). The open-circuit potential of the partially discharged TiS$_2$ electrode (Li$_x$TiS$_2$) was dependent on the solvent used (PC > PC–15C5 > PC–12C4). This also suggests that the intercalation of lithium is accompanied by (at least partly) the co-intercalation of the solvated organic molecules.

On the other hand, the addition of the crown ethers to the PC-based electrolytes did not show any significant effects on the charge/discharge efficiency of the lithium negative electrode, except for a relatively low polarization in the crown ether-containing solutions. Further investigations

are being conducted on the addition or blending effects of organic compounds that have strong interaction with $Li^+$ ions or metallic lithium on the charge/discharge cycling behaviour of electrodes in lithium cells.

## Acknowledgement

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