EFFECT OF SOLVENT BLENDING ON CYCLING CHARACTERISTICS OF LITHIUM

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Summary

The suitability of electrolytes using mixed solvents has been examined for ambient temperature, rechargeable lithium batteries. Sulfolane (S) and dimethylsulfoxide (DMSO) have been used as base solvents because of their high permittivity, and ethers such as 1,2-dimethoxyethane (DME) have been blended as a low viscosity co-solvent. This blending has been found to yield electrolytes with a high conductivity, and maximum values are observed in solutions with 40 - 90 mol% ether. The cycling characteristics of lithium are also improved by blending the ethers. The coulombic efficiencies on a nickel substrate are $\geqslant 80\%$ in $S-DME/LiPF_6$ and $DMSO-DME/LiPF_6$ solutions. The lithium electrode characteristics are markedly dependent on the type of co-solvent ether, as well as on the electrolytic salt. The results of the conductance behaviour and the electrode characteristics are discussed in terms of ionic structure in the mixed solvent and the state of the electrode/electrolyte interphase.

Introduction

A large number of organic electrolyte systems have been examined for rechargeable lithium batteries. It is generally recognized that the cyclability of the negative lithium electrode is the key technology in the development of practical batteries [1]. To date, the electrolyte systems in which a high cycling efficiency for lithium has been obtained are ether-based, *e.g.*, 2-methyltetrahydrofuran (2-MeTHF)/LiAsF$_6$ and 1,3-dioxolane (DOL)/LiClO$_4$.

Sulfolane (S) and dimethylsulfoxide (DMSO) are promising solvents for such electrolytes because of their high resistance to electrochemical oxidation/reduction and their high permittivity (dielectric constant) [2, 3]. However, both S and DMSO have high melting points (m.p.) and high viscosities at ambient temperatures; both factors are inconvenient for battery electrolytes. We have attempted to blend S and DMSO with some ethers that have low m.p. and low viscosities, in order to improve the physicochemical properties of the electrolyte solutions. This work reports the electrolytic

conductivities of some lithium salts in the mixed S– or DMSO–ether systems. The blending effects on the cycling characteristics of lithium in those systems are also discussed.

Experimental

The high permittivity solvents employed in this work were S and DMSO, and the low viscosity ethers were DOL, tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME). These solvents were purified and dehydrated by the usual distillation methods (water contents in the solvents were <100 mg dm^{-3}). The electrolytic salts, LiClO$_4$ and LiBF$_4$, were dried at 80 - 150 °C under a reduced pressure, and LiPF$_6$ was used as received (Morita Chemicals).

The electrolytic conductivity of the solution was measured by an a.c. impedance bridge. The cycling characteristics of lithium electrodes were principally investigated by galvanostatic charge/discharge techniques using three electrodes in a beaker-type glass cell. A nickel or aluminium disc was used as the substrate where the cycling efficiency of lithium was measured by an accelerated method [4]. The electrochemical measurements were carried out under a dry argon atmosphere at room temperature (16 - 24 °C)
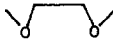
Results and discussion

Some physicochemical properties of the chosen solvents are listed in Table 1 where ϵ, η, DN and AN denote relative permittivity, viscosity, donicity and acceptor number, respectively. It can be seen that S and DMSO belong to high permittivity- and high viscosity solvents. The ethers have low viscosity as well as high donicity (DN). The latter property is a measure of the interaction between the solvent and the cation, Li$^+$ [5].

Figures 1 and 2 show the electrolytic conductivities of the lithium salts in mixed S–ether and DMSO–ether systems, respectively [6, 7]. Conductivity maxima were observed in the solutions containing 40 - 90 mol% ethers. These conductance enhancements in the mixed systems are principally due to (i) the high permittivity of S or DMSO, which allows the salt to be dissociated effectively, and (ii) the low viscosity of the ether, which causes high mobility of the dissociated ion [8]. However, the observed higher conductivity in the systems consisting of DMSO-based solvents suggests that the high donicity of DMSO is also important [9].

The highest conductivity was observed in the systems containing DME and LiPF$_6$ as the co-solvent and the salt, respectively. The maximum values of 1.5×10^{-2} S cm^{-1} in S–DME (90 mol% DME)/1 M LiPF$_6$ and 1.7×10^{-2} S cm^{-1} in DMSO–DME (40 mol% DME)/1 M LiPF$_6$ are comparable with the conductivities of LiAsF$_6$-based electrolytes [10].

TABLE 1

Selected properties of organic solvents

Solvent		ϵ_r (30 °C)	η (30 °C) $(10^{-3}$ Pa s)	DN*	AN*
S		42.5	9.87	14.8	19.0
DMSO		47.8	1.75	29.8	19.3
DME		6.92	0.40	24	—
THF		7.25	0.46	20.0	8.0
DOL		6.79	0.58	—	—

*From refs. 5 and 14.
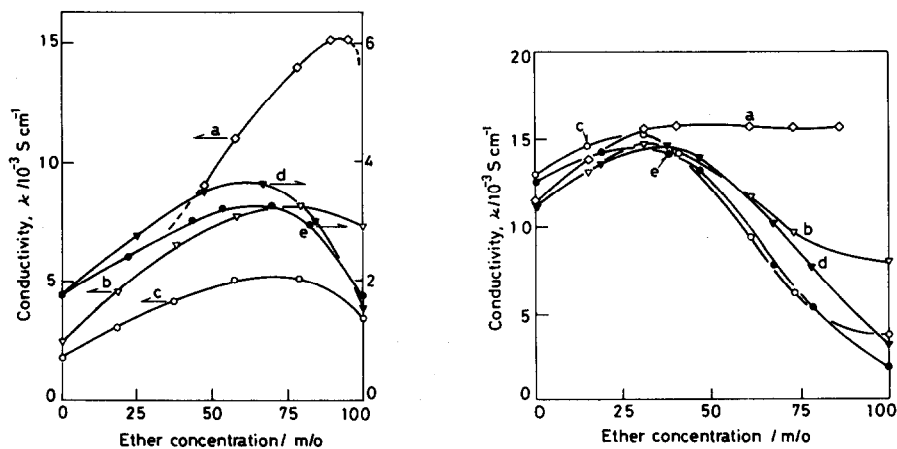
Fig. 1. Conductivities of lithium salts in S–ether systems: (a) S–DME/LiPF$_6$; (b) S–DME/LiClO$_4$; (c) S–DME/LiBF$_4$; (d) S–DOL/LiBF$_4$; (e) S–THF/LiBF$_4$ (salt concentration: 1 M in all systems).

Fig. 2. Conductivities of lithium salts in DMSO–ether systems: (a) DMSO–DME/LiPF$_6$; (b) DMSO–DME/LiClO$_4$; (c) DMSO–DME/LiBF$_4$; (d) DMSO–THF/LiClO$_4$; (e) DMSO–THF/LiBF$_4$. (Salt concentration: 1 M in all systems.)

Figure 3 shows the dependence of the lithium coulombic efficiency with cycle number when measured on a nickel substrate in S-based electrolytes [6]. The efficiency was much improved by blending S with the ethers,
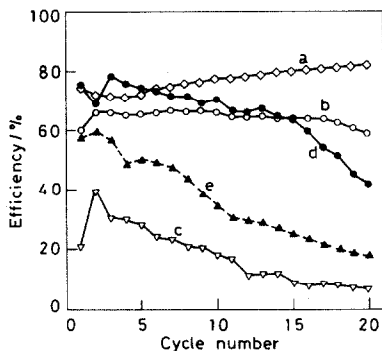
Fig. 3. Variation of efficiency of lithium on Ni substrate in S–ether (1:1 by vol.) systems: (a) S–DME/LiPF$_6$; (b) S–DME/LiBF$_4$; (c) S–DME/LiClO$_4$; (d) S–THF/LiBF$_4$; (e) S/LiBF$_4$.
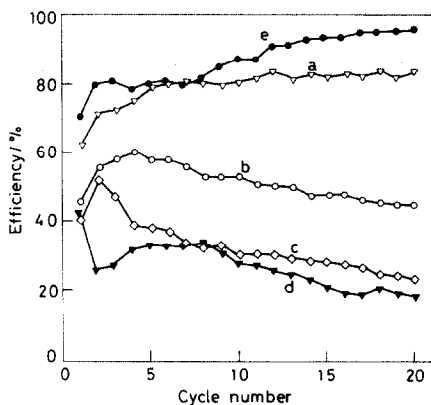
Fig. 4. Variation of efficiency of lithium on Ni (curves (a) - (d)) or Al substrate (curve (e)) in DMSO–ether (1:1 by vol.) systems: (a) DMSO–DME/LiPF$_6$; (b) and (e) DMSO–DME/LiBF$_4$; (c) DMSO–DME/LiClO$_4$; (d) DMSO/LiPF$_6$.

especially with DME and THF. Cycling in S–DME solutions showed less variation than in S–THF or S–DOL. The efficiency was also dependent on the type of lithium salt that was dissolved. The average efficiency in S–DME increased in the order LiClO$_4$ < LiBF$_4$ < LiPF$_6$.

The cycling efficiency in a solution having DMSO as the main solvent is given in Fig. 4. It can be seen that the efficiency was again dependent on the nature of both the blended ether and the electrolytic salt. With a nickel substrate, the average efficiency in DMSO–DME/1 M LiPF$_6$ was the highest in all the DMSO-based electrolytes examined. The polarization overvoltage of lithium on the nickel substrate in DMSO–DME/LiPF$_6$ was much less than that in the other electrolytes. Moreover, the potential variation of the electrode with cycle number was very small in that solution. These findings apparently account for the higher cycling efficiency in DMSO–DME/LiPF$_6$. At an aluminium substrate, however, relatively high efficiencies were obtained in DMSO–DME/LiClO$_4$ and DMSO–DME/LiBF$_4$. This substrate effect on the cycling characteristics is mainly caused by alloy formation of lithium with the substrate metal, as found when using other electrolytes [11]. That is, either production of isolated, inactive lithium [12], or the formation of a less-conductive and protective film [13] on the lithium surface, which would be one of the causes of efficiency loss, is probably prevented by the formation of an alloy between lithium and aluminium.

Figure 5 shows the dependence of the cycling efficiency on the solvent composition for the S–DME and the DMSO–DME systems. In this case, average efficiencies from cycle numbers 5 - 20 are presented. With a nickel substrate in the DMSO system (curve (b)), the efficiency in DMSO/LiPF$_6$ was about 30% at initial cycles, and it decreased with further cycles. The average efficiency reached a maximum at 50 - 70 vol% (= 40 - 60 mol%)
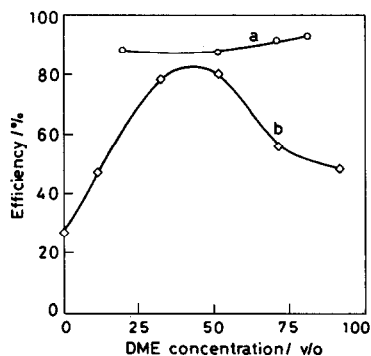
Fig. 5. Average efficiency of lithium as a function of solvent composition: (a) S–DME/ LiPF$_6$ on Al substrate; (b) DMSO–DME/LiPF$_6$ on Ni substrate.

DMSO content, where the efficiency degradation with repeating the cycle was minimum. The cause of this lithium cycling efficiency dependence on the DMSO concentration is not obvious, but the following explanation is plausible: in solutions containing high DMSO concentrations, the electrode polarization during the cycle was comparatively high. This results from a low ionic mobility in high viscosity solution. High polarization would lead to side reactions such as the decomposition of the electrolyte. In solutions of low DMSO content, Li$^+$ ions are specifically coordinated with DME molecules, which accelerates the DME decomposition through electrophilic β-elimination to form ethylene and lithium methylate [1]. Consequently, the relatively low efficiency and its subsequent degradation with cycling in solutions with DMSO concentration >90 vol% or <30 vol% will be attributable to decomposition of the electrolyte, in addition to both the inactive production of lithium and the formation of a protective film (see above).

On the other hand, cycling in S–DME using an aluminium substrate (curve (a), Fig. 5) gave a high efficiency which was virtually independent of the solvent composition. This indicates that the degradation of lithium that was deposited on the aluminium substrate was less serious than that on the nickel substrate.

Acknowledgement

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