ADDITIVE EFFECTS OF Li$^+$ ION SOLVATION COMPOUNDS ON LiClO$_4$-PROPYLENE CARBONATE ELECTROLYTIC PROPERTIES

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Summary

The additive effects of cation solvation compounds (CSC) on the Li$^+$ ionic conductivity and also on the Li charge–discharge characteristics for 1M LiClO$_4$-propylene carbonate (PC) were examined. Ethylenediamine (EDA), N,N,N′,N′-tetramethyl-EDA (TMEDA) and n-ethylene glycol dimethyl-ethers (n-glymes) were used as the CSCs. The equivalent molar conductivity (Λ) values for TMEDA and added solutions of the n-glymes were 60 - 80% higher than that in the absence of a solution addition. EDA addition, however, had no effect. The Λ enhancement on TMEDA addition was a result of not only an increase in the degree of ionic dissociation of the solute, but also of the relatively easy Li$^+$ ion migration due to the smaller practical ion radius resulting from the TMEDA–Li$^+$ complex.

The Li charge–discharge efficiency increased by about 15% on addition of TMEDA solution. This is assumed to be due to the protecting effect of TMEDA or the TMEDA–Li$^+$ complex on the electron transfer reaction between PC and the deposited Li.

1. Introduction

The additive effects of cation solvation compounds (CSCs) on electrolyte conductivity have been studied to improve the Li$^+$ ionic conductivity of high-rate Li batteries [1 - 3]. Angres *et al.* [2, 3] demonstrated the 30 - 50% equivalent molar conductivity (Λ) enhancement in LiClO$_4$-propylene carbonate (PC) by adding 12-crown-4 or 15-crown-5 ethers which improve the ionic dissociation of LiClO$_4$. Olmstead [1] reported that the additive effects of CSCs on Λ depended on the solute concentration, the combination of the CSC and the electrolyte materials, and suspected that CSC-complexed Li$^+$ ion might produce smoothly deposited lithium. Yeager [4] also reported the protection effect of 12-crown-4 ether for the Li–PC electron transfer reaction.

The CSC additive effects are of interest from various points of view. In this work, the additive effects of ethylenediamine (EDA) [7 - 9],

N,N,N′,N′-tetramethyl-EDA (TMEDA) [5, 6] and n-ethylene glycol dimethyl ethers (n-glymes) [10] on the Li$^+$ ionic conductivity and also on the dynamic Li charge–discharge characteristics were determined.

2. Experimental

2.1. Electrolytes
Lithium tetrachlorate (Kanto Chemicals Co.) was dried at 160 °C under vacuum. PC (Tokyo Kasei Co.) was distilled at about 4 Torr in a Pyrex apparatus. TMEDA and diglyme (Tokyo Kasei Co.) were distilled at normal pressure. Electrolytic solutions were prepared by mixing the appropriate amount of solute and solvents in an argon filled drybox.

2.2. Measurements
The conductivity was measured at 1 kHz using an impedance bridge (LCR digibridge model 1658, GenRad Co.). Lithium charge–discharge efficiency values were measured at a constant current density with a Rauh cell [11], using an Li counter (20 mm dia. × 0.5 mm), Li reference (Merck Co.) and Pt working (20 mm dia. × 0.5 mm; Tanaka Noble Metals Co.) electrodes. The lithium charge–discharge efficiency was calculated from the ratio of the stripping and plating charges (0.8 V cut-off vs. Li) [12]. The transport number was obtained from the concentration cell electromotive force [13, 14]. The Stokes radius was calculated using the transport number, the limiting dilution molar equivalent conductivity and the solvent(s) viscosity [14]. The solvated number was obtained from the Stokes radius, the solvent molecular volume and the Li$^+$ ion crystal radius [14].

The electrolyte preparations and all the measurements were carried out in the argon-filled drybox.

3. Results and discussion

3.1. TMEDA
3.1.1. Conductivity
Figure 1 shows the relation between Λ and the molar ratio of the TMEDA addition (R = [TMEDA]/[Li$^+$]) in 1M LiClO$_4$–PC. Λ increased approximately linearly up to $R = 1.0$ and reached a plateau at a 60% enhanced value of 8.6 ohm^{-1} cm^2 mol^{-1}, which is a little higher than that for the 12-crown-4 ether addition (7.9 ohm^{-1} cm^2 mol^{-1}) [2, 3]. This behavior suggests that the 1:1 Li$^+$–TMEDA complex formation [2, 3, 6, 15, 16] raised the degree of dissociation for these solutes [2, 3].

To evaluate the Λ enhancement mechanism and the Li$^+$ ion conductivity in TMEDA-doped solution, electrolytic parameters, such as the transport number of the Li$^+$ ion ($t_0{}^+$), were examined at infinite dilution [14]. Table 1 summarizes the results. On the addition of TMEDA, $t_0{}^+$ and the
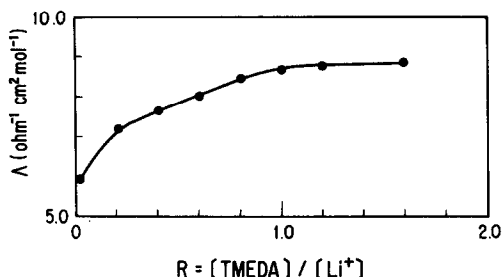
Fig. 1. Λ in 1M LiClO$_4$–PC with added TMEDA.

TABLE 1

Electrolytic parameters in LiClO$_4$–PC with added CSC*

Additive	Λ_0^+ (ohm^{-1} cm^2 mol^{-1})	t_0^+	r_{so}^+ (Å)	S_{NO}^+
TMEDA (1.3 vol%)	11.5	0.41	2.83	0.85
EDA (1.0 vol%)	8.50	0.34	4.07	2.14
Diglyme (1.1 vol%)	6.40	0.30	5.09	2.35
None	8.64	0.32	3.71	1.51

*Measurements were carried out between 0.1 and 0.001M LiClO$_4$ concentration.

limiting cationic equivalent conductivity of the Li$^+$ ion (Λ_0^+) increased from 0.32 to 0.41 and from 8.64 to 11.5 ohm^{-1} cm^2 mol^{-1}, respectively. Also, the practical solvated Li$^+$ ion radius (r_{so}^+) decreased from 3.71 to 2.83 Å. The calculated solvated number of the Li$^+$ ion (S_{NO}^+) was a little lower than 1.0. S_{NO}^+ and r_{so}^+ were calculated according to ref. 14. The difference seems to be explained by the fact that S_{NO}^+ in Table 1 was calculated assuming a spherical complex structure [14] in spite of the nearly two dimensional structure of the Li$^+$–TMEDA complex [15].

Λ enhancement in the TMEDA doped solution arises therefore not only from the increase in the degree of ionic dissociation of the solute, but also from the relatively improved Li$^+$ ion migration, which has a smaller practical ion radius based on the 1:1 Li$^+$–TMEDA complex.

3.1.2. Li charge–discharge characteristics

Figure 2 shows the relation between R and the 10th cycle average Li charge–discharge efficiency ($E_{ff,10}$) at 0.5 mA/cm^2, 0.6 C/cm^2 on the Pt working electrode in 1M LiClO$_4$–PC solution doped with TMEDA. $E_{ff,10}$ values increased up to $R = 1.0$ and showed the maximum value of 80.8% at $R = 1.0$. This value was approximately 15% higher than the original. This $E_{ff,10}$ behavior vs.R was similar to that for Λ vs.R (Fig. 1).

$E_{ff,10}$ enhancement by TMEDA addition seems to be explained as follows. The main reason for the Li cycling efficiency loss is related to the

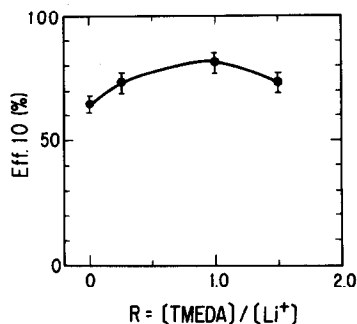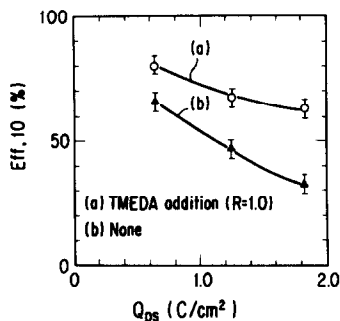Fig. 2. $E_{ff,10}$ in 1M $LiClO_4$–PC with added TMEDA, 0.5 mA/cm^2, 0.6 C/cm^2.

Fig. 3. $E_{ff,10}$ dependence on the Q_{ps} at 0.5 mA/cm^2. (a) With TMEDA addition ($R = 1.0$); (b) 1M $LiClO_4$–PC only.

PC-deposited Li electron transfer reaction [17]. TMEDA is considerably more stable to Li than PC, because TMEDA itself has electron donating characteristics and is difficult to reduce. These suggestions lead to the TMEDA or TMEDA–Li$^+$ protective effect of the PC–Li reaction.

Strictly speaking, the TMEDA protective effect is incomplete. Curves (a) and (b) in Fig. 3 show $E_{ff,10}$ dependence on the charge–discharge capacity (Q_{ps}) at 0.5 mA/cm^2 in 1M $LiClO_4$–PC with ($R = 1.0$) and without the addition of TMEDA solution, respectively. Although $E_{ff,10}$ values in the solution with added TMEDA were always higher than those in the original solution, the $E_{ff,10}$ values decreased with increased Q_{ps} values, even with TMEDA addition.

3.2. EDA

The additive effects of n-alkyl-substituted EDA were examined. This EDA is well known to have an extraordinarily high solvating effect to cations [7 - 9].

Figure 4 shows the Λ values in 1M $LiClO_4$–PC with added EDA. Λ decreased with increase in R. Table 1 shows the electrolytic parameters for EDA addition. With EDA addition, Λ_0^+ decreases and r_{so}^+ increases according to the Li$^+$–(EDA)$_2$ complexation (S_{NO}^+ is about 2.0). Although the Li$^+$–EDA complex composition is fundamentally Li$^+$–(EDA)$_2$ [8], the cluster of this complex at high EDA and $LiClO_4$ concentration is easily predicted, considering the analogous results for the interactions between Cu^{2+}–(EDA)$_2$ with excess EDA [18, 19]. Therefore, with EDA addition, the Λ decrease seems to be caused by slower Li$^+$ ion migration resulting from the larger practical Li$^+$ ion radius based on the solvation structure around the Li$^+$ ion.

Figure 5 shows the $E_{ff,10}$ results which also decrease with increasing R. This decrease is possibly due to the Li–EDA reaction, considering the similarity of the reactivity to Li between n-alkyl-substituted EDA and
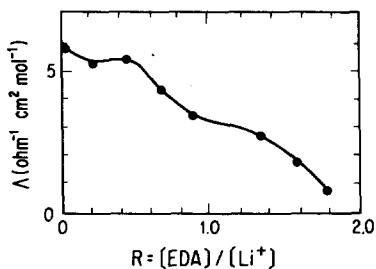
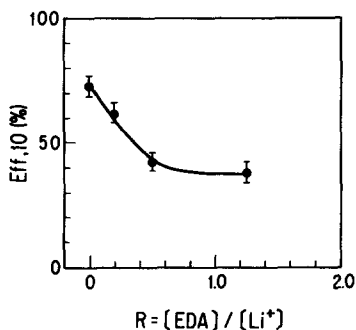Fig. 4. Λ in 1M LiClO$_4$–PC with added EDA.

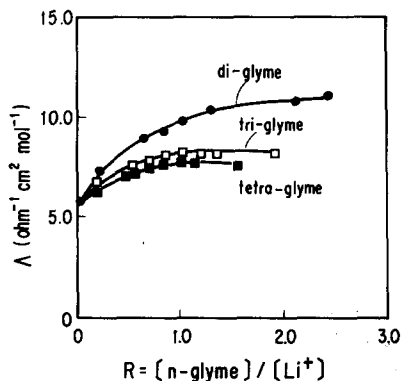Fig. 5. $E_{ff,10}$ in 1M LiClO$_4$–PC with added EDA. 5 mA/cm^2, 0.3 C/cm^2.

Fig. 6. Λ in 1M LiClO$_4$–PC with added n-glymes.

liq.NH$_3$ [20]. It may also be due to the difficulty in desolvating the Li$^+$ ion from the Li$^+$–EDA clusters [1].

3.3. n-glymes

The additive effects of n-glymes were measured. Curves (a), (b) and (c) in Fig. 6 show the Λ values in 1M LiClO$_4$–PC with added diglyme, triglyme and tetraglyme, respectively. Λ increased with increase in R up to $R \approx 1.0$ and the plateau Λ values became higher with decreasing carbon numbers; *i.e.*, the conductivity enhancement order is diglyme > triglyme > tetraglyme added solution. Table 1 shows the electrolytic parameters in diglyme doped solution. With diglyme addition, Λ_0^+ decreases and r_{so}^+ increases. This seems to be due to the (diglyme)$_n$Li$^+$ complex [10] or the partial formation of a ClO$_4^-$–diglyme complex, which is predicted by the relatively higher complexation number of the diglyme [21].

It is reported [22] that smooth Li deposition is possible by using PC doped with a small amount of tetraglyme with $LiClO_4$ and $(C_4H_9)_4N^+$, Cl^-*. In this work, Li charge–discharge efficiency values in 1M $LiClO_4$–PC with higher concentrations of n-glymes ($R = 1.0$; 10 - 20 vol%) were measured. Table 2 summarizes the $E_{ff,10}$ results. The distinct $E_{ff,10}$ changes were not obtained.

TABLE 2

$E_{ff,10}$ in 1M $LiClO_4$–PC with added n-glymes ($R = 1.0$)

Additive	$E_{ff,10}$ (%)
Diglyme	66.3*
Triglyme	60.3**
Tetraglyme	64.7*
None	67.0**, 65.0*

*0.5 mA/cm^2, 0.6 C/cm^2.
**5 mA/cm^2, 0.6 C/cm^2.

4. Conclusion

The fundamental additive effects of cation solvation compounds, using TMEDA, EDA and n-glymes, on the Li^+ ion conductivity and also the Li charge–discharge characteristics were evaluated in 1M $LiClO_4$–PC. Λ enhancements were observed with TMEDA and n-glymes added to $LiClO_4$–PC solutions. However, EDA addition was ineffective. Λ enhancement in TMEDA-doped solution resulted from not only the increase in the degree of ionic dissociation of the solute, but also from the relatively easy Li^+ ion migration with a smaller practical ion radius resulting from the TMEDA–Li^+ complex. The Li charge–discharge efficiency also increased in the TMEDA doped solution. The enhancement in Li cycling characteristics is assumed to be due to the TMEDA or TMEDA–Li^+ complex protective effect on the electron transfer reaction between PC and the deposited Li.

Acknowledgements

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*We confirmed that $E_{ff,10}$ in this solution was relatively higher (71.7%) than in one with no added dopant (65.0%).

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