

ETHYLENE CARBONATE-BASED ELECTROLYTES FOR RECHARGEABLE LITHIUM BATTERIES

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Summary

The properties of new ethylene carbonate (EC)-based electrolytes have been examined in an effort to obtain an electrolyte solution of higher conductivity than EC/2-methyltetrahydrofuran(2-MeTHF) without suppressing the lithium (Li) cycling efficiency more than necessary. Three, linear-structured solvents (LSs) and four, ring-structured solvents (RSs) have been used as co-solvents of EC. LiAsF_6 is used as the electrolyte. Although modifying 2-MeTHF improves conductivity, no electrolyte system has a higher Li cycling efficiency than EC/2-MeTHF. Of the organic electrolytes examined in this work, the EC/2-MeTHF/THF ternary mixed solvent system shows approximately 50% higher conductivity and the highest Li cycling efficiency, with a value 1.2% lower than EC/2-MeTHF. Since our results were only obtained from lithium half-cell tests, future applications and cathode compatibilities must be thoroughly examined.

Introduction

Recently, extensive research has been directed towards various solute-solvent systems used as organic electrolytes in nonaqueous lithium (Li) batteries. Since current Li battery applications vary widely, organic electrolyte systems must be optimized for each purpose. Our group previously clarified the effectiveness of ethylene carbonate (EC) in Li cycling efficiency improvement and proposed an LiAsF_6 -EC/2-methyltetrahydrofuran(2-MeTHF) mixed solvent system [1]. This electrolyte shows high Li cycling efficiency and relatively high conductivity. It is suitable for Li secondary batteries having very long cycle lives used at moderate work rates and at mainly ambient temperature. However, if a higher work rate at ambient temperature, or if a relatively higher rate at temperatures lower than 0 °C, is required, the conductivity must be improved.

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Our purpose was to propose a new EC-based electrolyte having a higher conductivity than EC/2-MeTHF, with Li cycling efficiency suppressed as little as possible. As EC co-solvents, three, linear-structured solvents (LSs) and four, ring-structured solvents (RSs) were used. LiAsF₆ was used as the electrolyte.

Experimental

Lithium cycling tests were galvanostatically conducted on an Li substrate (Li-on-Li cycling (0.5 mA cm⁻²)) [1]. The average efficiency per cycle, E_a , was calculated from

$$E_a = [Q_{ps} - Q_{ex}/n]/Q_{ps} \times 100 (\%)$$

where n is the cycle number of apparent "100%" cycles, Q_{ps} is the stripped charge (0.6 C cm⁻²), and Q_{ex} is the excess Li charge (1.8 C cm⁻²) at the start of the experiment. Hereafter, 1 M LiAsF₆-EC/2-MeTHF(1/1) represents the electrolyte solution of mixed solvents of EC and 2-MeTHF (mixing volume ratio = 1/1) dissolved in 1 M LiAsF₆.

The association constant (K_A) was calculated by the Bjerrum equation [1, 2] because there is no complete understanding of complex solvent-solute interactions at high solute concentrations such as 1 M [3]. Although this equation does not consider the formation of triple ions and gives a smaller than actual value [3], it can be used to compare K_A values on a relative basis.

Results and discussion

The physical properties and abbreviations for the solvents are shown in Table 1 [1, 5, 6]. The viscosity order is EC >> RS > LS. EC has an extraordinarily high dielectric constant. RS and LS have relatively lower dielectric constants but AN is an exception. The LS molecular volume (V_s) tends to be lower than that of RS. The donor number (D_N) value order is RS > EC ≈ LS. The D_N value is a parameter measuring the solvent to cation solvation power.

Figure 1 shows the conductivities of EC-based electrolytes. The conductivity order is EC/LS > EC/RS > EC/PC in the range -10 to 25 °C. For example, the conductivity EC/AN is approximately three times greater than that of EC/2-MeTHF at 25 °C. The conductivity order for EC/LS is EC/AN > EC/MF > EC/MA.

Of the EC/RS mixed systems, EC/2-MeTHF/THF ternary, and EC/THF binary, mixed solvents show 50 - 65% higher conductivities than EC/2-MeTHF. EC/2-MeDOL has a conductivity comparable with that of EC/2-MeTHF. EC/diMeTHF has a lower conductivity than EC/2-MeTHF because diMeTHF has a high molecular volume and a relatively higher viscosity.

TABLE 1
Physical properties of solvents

Solvent		η (25 °C, cP)	ϵ (25 °C)	D_N	V_s (Å ³)
Linear-	Methylformate (MF)	0.328	8.5	16.5	131.7
Structured	Acetonitrile (AN)	0.339	35.95	14.1	87.2
Solvent (LS)	Methyl acetate (MA)	0.364	6.7	16.8	102.4
Ring-	Tetrahydrofuran (THF)	0.456	7.6	20	134.8
Structured	2-methyl THF (2-MeTHF)	0.460	6.2	18	169.6
Solvent (RS)	4-methyl-1,3-dioxolane (4-MeDOL)	0.54 ^a	4.4 ^a	—	142.6
	2,5-dimethyl THF (diMeTHF)	0.72	—	—	192.7
	Ethylene carbonate (EC)	2.53 ^b	95.3	16.4	110.4

ϵ : dielectric constant; η : viscosity; D_N : donor number; V_s : molecular volume.

^a30 °C.

^bEC/PC(1/1).

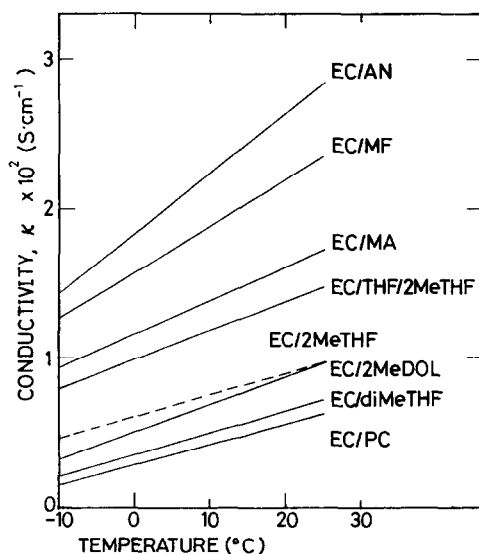


Fig. 1. Conductivities of EC-based electrolytes.

Figures 2 and 3 show the relationship between the conductivities at 25 °C and the solvent viscosity on the one side and the association constant (K_A) for LiAsF_6 on the other. It has been proposed that viscosity is in reverse proportion to the diffusion constant [7]. As shown in Figs. 2 and 3 the conductivities of both EC/LS and EC/RS tend to increase with decrease in viscosity, though there is not always a relationship between K_A and conductivity. These results agree with reports [8, 9] that enhancement of

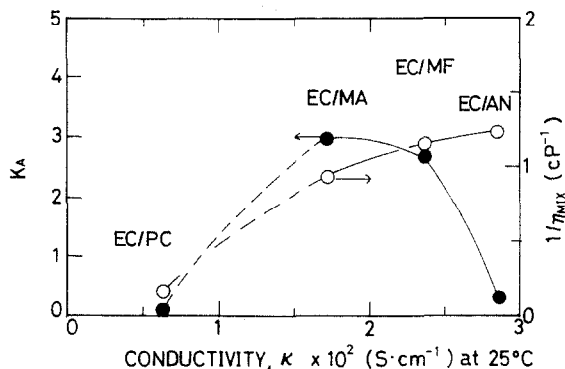


Fig. 2. Relationship between the conductivities at 25 °C, the solvent viscosity, and the association constant for several EC-based electrolytes.

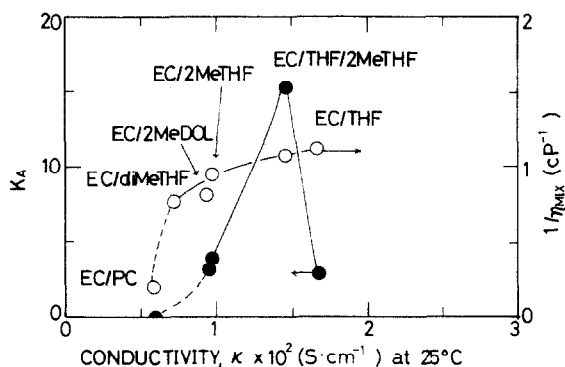


Fig. 3. Relationship between the conductivities at 25 °C, the solvent viscosity, and the association constant for several EC-based electrolytes.

the ion migration rate, based on a decrease in viscosity, is effective for the conductivity of high dielectric esters or high dielectric solvent/low viscosity solvent mixed systems incorporating lithium salts such as LiAsF_6 , due to a sufficiently high degree of ionic dissociation. EC/LS showed a higher conductivity than EC/RS. The main reason for this is considered to be that LS has a somewhat lower viscosity and a lower molecular volume than RS. LS is often used as the electrolyte solvent of a reserve cell working at extremely low temperatures (<40 °C) [10] for this very reason. The additional effect on the conductivity of AN's high dielectric constant must also be considered for EC/AN.

Table 2 shows Li cycling efficiencies for EC-based electrolytes compared with those for single solvent electrolytes. Both EC/RS and EC/LS show higher Li cycling efficiencies than RS or LS single solvents; this confirms the effect of EC on Li cycling efficiency. The Li cycling efficiencies of EC/RS tend to be higher than those of EC/LS, while the conductivities for EC/LS are higher than for EC/RS. Of the mixed solvents having a higher

TABLE 2

Li cycling efficiency (E_a) for 1.5 M LiAsF₆-EC/LS or EC/RS(1/1)

Solvents		E_a (%)*
EC/LS	EC/AN	95.2(85.4)
	EC/MA	94.0(89.8)
	EC/MF	91.3(84.6)
EC/RS	EC/2-MeTHF	97.2(93.8)
	EC/2-MeDOL	92.6(88.9)
	EC/diMeTHF	95.9(91.9)
	EC/THF/2-MeTHF(1/1/1)	96.0

*Values in parentheses are for 1.5 M LiAsF₆-RS or -LS single solvent electrolytes.

conductivity than EC/2-MeTHF, EC/THF/2-MeTHF shows the highest Li cycling efficiency. Its value is 1.2% lower than EC/2-MeTHF.

Since the Li cycling efficiency decrease is primarily caused by reaction between solvent and deposited Li [10], the solvent atmosphere around the deposited Li is important. This atmosphere is closely related to the solvation state of the Li⁺ ions, *i.e.*, the solvation power of the solvent with Li⁺ ions. ¹³C-NMR spectra were measured to obtain information on the solvation state of the Li⁺ ions in the mixed solvents examined in this work.

Table 3 provides examples of the NMR measurements results. In all the LiAsF₆-EC mixed solvent systems shown in Table 3, chemical shifts for both EC and the co-solvents show a downfield shift as compared with the solvent alone. This result means that all the solvents interact with Li⁺ ions. The chemical shift values of both EC and MA in LiAsF₆-EC/MA show a stronger downfield shift than LiAsF₆-EC or -MA. Also, the chemical shift value of EC in LiAsF₆-EC/AN shows a downfield shift against LiAsF₆-EC, although the chemical shift value of AN in LiAsF₆-EC/AN shows an upfield

TABLE 3

¹³C-NMR spectra data for LiAsF₆-EC/AN and EC/MA

Sample	$\Delta\delta$ vs. TMS		
	EC C=O	AN C≡N	MA C=O
1.5 M LiAsF ₆ -AN	—	1.5	
1.5 M LiAsF ₆ -EC	1.5	—	
1.5 M LiAsF ₆ -EC/AN(1/1)	1.7	1.3	
1.5 M LiAsF ₆ -MA	—	—	2.4
1.5 M LiAsF ₆ -EC/MA(1/1)	2.3	—	3.0

 $\Delta\delta$: difference in chemical shift values between electrolyte solution and solvent(s) alone.

shift against $\text{LiAsF}_6\text{-AN}$. This is because MA has a higher D_N and AN has a lower D_N than EC. These results indicate that in the mixed solvents used here, there is no complete selective solvation of Li^+ by any one solvent component because the difference in D_N values (ΔD_N) is less than 4 [10] (the ΔD_N between EC and THF having the highest D_N , is 3.6). That is, there is a mixture of solvents around the deposited Li where the concentration of the solvent with the higher D_N may be somewhat greater than the solvent of lower D_N . The main reason for the higher efficiency of EC/RS over EC/LS is considered to be due to RS having a lower reactivity than LS (LS is well known to cause Li instability [2]), and RSs examined here seem to have a higher reactivity than 2-MeTHF.

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