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Solvation states and properties of binary mixtures of halogenated cyclic carbonates and a linear carbonate

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Abstract

The solvation states and properties of organic solvent electrolytes were investigated by ^{13}C NMR measurements. The electrolytes were binary mixtures composed of halogenated cyclic carbonates such as chloroethylene carbonate (Cl-EC) or trifluoropropylene carbonate (TFPC) and a linear carbonate. Comparisons were made with the non-halogenated propylene carbonate (PC)/dimethyl carbonate (DMC) system. The solution structures of Cl-EC/DMC and TFPC/DMC systems, differing from those of PC/DMC system, have both cyclic and linear carbonates solvating to lithium ions. A study was also carried out on the performances of the model cells using organic electrolytes containing Cl-EC and TFPC as solvent, carbon anode, and lithium foil counter electrode. The current density dependence of the system using the pure TFPC as a solvent was much different from that of other systems. This is mainly due to the properties of interface between electrolyte and electrode of the cell. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The solvation states of organic solvent electrolytes were measured by using ^{13}C NMR, and cell performances of lithium ion batteries using these solvent electrolytes were investigated. Previously, we investigated the ethylene carbonate (EC) and dimethyl carbonate (DMC) mixed system and found that lithium ions are mainly solvated by EC and the solvation is highest when the molar ratio of EC:DMC is about 1:4 [1].

The aim of this study was to find a novel electrolyte for lithium secondary batteries, so solvation states of electrolytes and the cell performances for halogenated carbonate systems were investigated. In this study, chloroethylene carbonate (Cl-EC) and trifluoropropylene carbonate (TFPC), which can be utilized for the electrolyte of lithium ion secondary batteries [2,3], were used. The solvation states of electrolytes were investigated by the spectral shift of the carbonyl carbon using ^{13}C NMR. The cell performances were investigated by using amorphous carbon as an anode and lithium foil as a counter electrode.

2. Experimental

Propylene carbonate (PC), dimethyl carbonate, chloroethylene carbonate, and trifluoropropylene carbonate were used as solvents. Their molecular structures are shown in Fig. 1. Lithium hexafluorophosphate (LiPF$_6$) was used as supporting electrolyte.

The mixed solvents were prepared by mixing cyclic carbonate (PC, Cl-EC and TFPC) with DMC at levels of 25, 50, and 75 vol.%. The electrolytes were prepared by dissolving LiPF$_6$ at a 1 mol/l concentration in the mixed solvents.

The ^{13}C NMR spectra were measured using a JEOL JNM-GX 400 FT NMR measurement system. The solvation shifts of each mixture fraction were calculated through Eq. (1), which uses the difference between the chemical shift for the carbonyl carbon in mixed solvent and the chemical shift for the carbonyl carbon in the electrolyte.

$$\Delta\delta = \delta_s - \delta_o \tag{1}$$

where $\Delta\delta$ represents solvation shift, δ_s the chemical shift of carbonyl carbon in electrolyte and δ_o chemical shift of carbonyl carbon in mixed solvent.

Molecular orbital calculations were done with the Gaussian version 94 program. A 1:1 (Li$^+$: solvent) solvation structure model binding with carbonyl oxygen was optimized with and without the COSMO (conductor-like
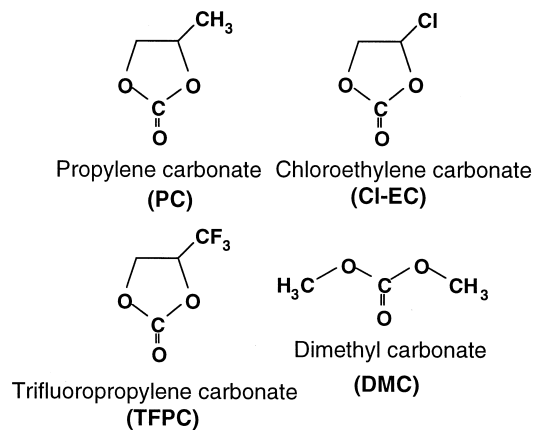
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Fig. 1. Molecular structures of the solvents.

Fig. 2. Relationship between solvation shift and mixing ratio.

screening model) method [4]. Change of net charges on the solvent molecule was estimated by comparing the calculation results for a solvent molecule in the neutral state and the solvation state. The solvation enthalpy ΔH was calculated by Eq. (2).

$$\Delta H = H_s - (H_0 + H_{Li}^+)\qquad(2)$$

where H_s signifies heat of formation for the solvation state, H_0 heat of formation for the neutral state, and H_{Li}^+ heat of formation for the lithium cation.

Conductivities of the electrolytes were measured in an argon atmosphere using a TOA CM-30V conductivity meter.

The cell performances were measured by using model cells, which were composed of amorphous carbon as the anode, lithium foil as the counter electrolyte, a polyethylene separator, and the electrolytes. The anode was made of amorphous carbon and poly(vinylidene fluoride) (PVDF) was used as binder polymer. The content of PVDF was ca. 10 wt.%. The cell was run between 0.01 and 1.0 V at a constant current. The current density dependence was measured at 0.5 mA/cm^2 charge current and discharge current was varied between 0.5 mA/cm^2 and 1.5 mA/cm^2. The impedance spectra were measured using a Hokuto Denko, HZ-1 potentio/galvanostat measurement system, in the frequency range of 30 kHz to 0.03 Hz.

3. Results and discussion

Fig. 2 shows the relationships between the solvation shifts ($\Delta\delta$) for the carbonyl carbon and the volume fraction of the cyclic carbonates. In the PC/DMC mixed system, the $\Delta\delta$ for PC decreases with an increase in the PC fraction, and $\Delta\delta$ for DMC is almost constant for all the fractions. This result indicates that the lithium ions are mainly solvated by PC molecules. The reciprocally proportional relationship between $\Delta\delta$ of PC and volume fraction of PC is because with ^{13}C NMR, $\Delta\delta$ is measured as a mean throughout the entire solvent. With any mixing ratio,
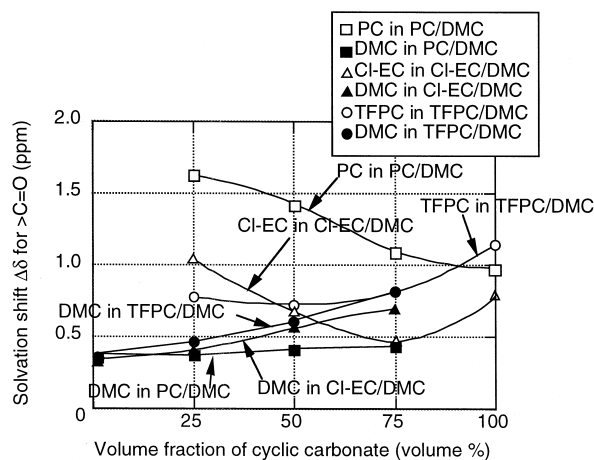
the number of PC molecules solvating to lithium ions is constant and below 25% of whole solvents. With a high PC ratio, the ratio of free molecules not solvating to lithium ions is high, causing $\Delta\delta$ in the light of the total solvent measured to be small.

With the Cl-EC/DMC system, as the Cl-EC content increased, $\Delta\delta$ of DMC increased. These results indicate that lithium ions were solvated not only to Cl-EC molecules but also to DMC molecules. Because of electron attracting chlorine group, the electron density of oxygen atom in the carbonyl group which affects the solvation to the lithium ions, for Cl-EC is smaller than that for PC molecule. Table 1 shows the solvation enthalpies of carbonates calculated by the molecular-orbital (MO) method. The value for PC is very much larger than that for DMC. The value for Cl-EC is smaller than that for PC and close to that for DMC. The results of calculation by MO method also bear out that with the Cl-EC/DMC system, both Cl-EC and DMC are solvate to lithium ions, which agree with the results of ^{13}C NMR measurement. The $\Delta\delta$ of Cl-EC has its minimum value at 75 vol.% of Cl-EC. In the Cl-EC/DMC system, DMC molecules also solvate to lithium ions. Thus, the number of Cl-EC molecules solvating to lithium ions decreases if DMC is added to the system. Therefore, $\Delta\delta$ of Cl-EC at 75% is lower than that at 100%. If more DMC is added, the number of free Cl-EC molecules not solvating to lithium ions decreases, like in the PC/DMC system. Thus, in the Cl-EC/DMC system, the $\Delta\delta$ of Cl-EC has its minimum at 75 vol.% of Cl-EC.

For the TFPC/DMC mixed system, the curves in Fig. 2 are similar to that of the Cl-EC/DMC system. TFPC

Table 1
Solvation enthalpies of the solvents for lithium ion

	PC	Cl-EC	TFPC	DMC
Solvation enthalpy (kcal/mol)	−55.6	−49.2	−49.6	−46.8
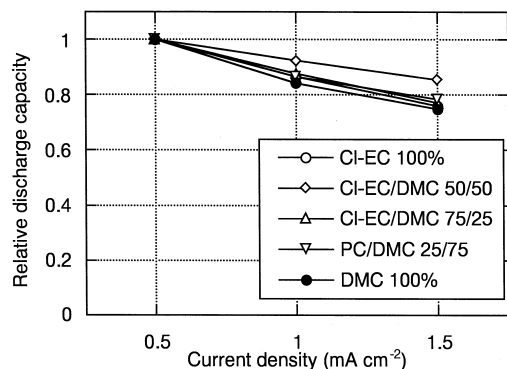
Fig. 3. Discharge capacity vs. current density for Cl-EC/DMC systems.

Fig. 5. Conductivity vs. relative capacity (capacity at 1.0 mA cm^{-2}/at 0.5 mA cm^{-2}).

molecule also has an electron attracting trifluoromethyl group, and the lithium ion is solvated by both DMC and TFPC molecules. In this case, the $\Delta\delta$ of TFPC has its minimum value at 50 vol.% of TFPC, and its maximum value at 100 vol.% of TFPC. From the results of Fig. 2, the solvation to lithium ion of TFPC molecule is weaker than that of Cl-EC molecule, therefore the $\Delta\delta$ of DMC in the TFPC/DMC system is the highest compared with the other PC/DMC and Cl-EC/EMC systems. As shown in Table 1, the solvation enthalpy of TFPC molecule is lower than PC molecule. The results suggest that lithium ions are solvated by both TFPC and DMC molecules the same as in the Cl-EC/DMC mixed system.

Fig. 3 shows the current density dependence of model cells for Cl-EC 100%; Cl-EC/DMC mixed at 75%/25% and 50%/50%; PC/DMC mixed at 25%/75%; and DMC 100% electrolyte systems. The vertical axis represents the relative discharge capacity normalized by discharge capacity at current density of 0.5 mA/cm^2. This is done because the discharge capacities differ among the systems. The current density dependence is almost the same for all systems. These results show that the current density dependences of pure Cl-EC system and Cl-EC/DMC mixed systems are the same as that of PC/DMC system in the
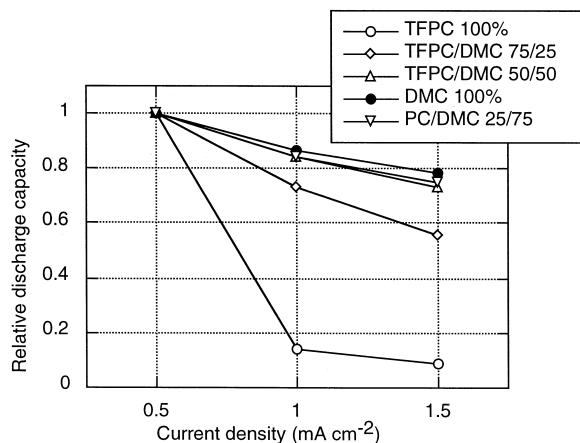
range of 0.5 to 1.5 mA/cm^2. Furthermore the conductivity of pure Cl-EC system is six times smaller than that of PC/DMC 25%/75% mixed system.

Fig. 4 shows the current density dependence of model cells for pure TFPC and TFPC/DMC mixed systems. For the pure TFPC system, the discharge capacity at 1.0 mA/cm^2 is almost seven times smaller than that at 0.5 mA/cm^2. For the TFPC/DMC 75%/25% system, the current density dependence is better than that of the pure TFPC system, and for TFPC/DMC 50%/50% system, the current density dependence is almost equal to that of PC/DMC 25%/75% mixed system. The current density dependence of the cell was recognized as being related to conductivity of the electrolyte. However, the pure Cl-EC system and the pure DMC system give almost equal conductivities as the pure TFPC system, almost 2 mS/cm. Therefore, conductivity has little effect on the current density dependence of pure TFPC system. To clarify the relationship between the current density and the conductivity, a plot of the relative discharge capacity of cells vs. conductivity of electrolytes is shown in Fig. 5. The data show that there is no relationship between relative discharge capacity and conductivity of electrolyte. From the results of Fig. 5, the current density dependence of the cells can not be explained by the bulk properties of the electrolyte. The reason why the TFPC system has a low

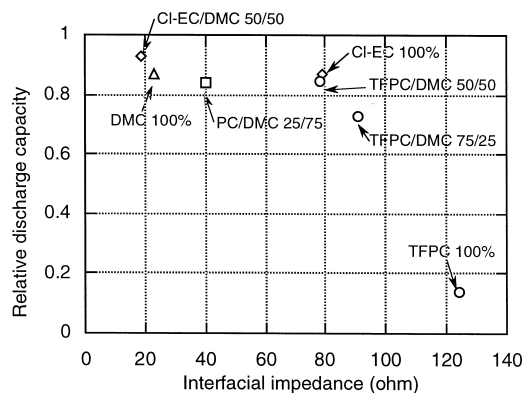Fig. 4. Discharge capacity vs. current density for lithium/amorphous carbon.

Fig. 6. Relative discharge capacity (capacity at 1.0 mA cm^{-2}/at 0.5 mA cm^{-2}) vs. interfacial impedance.

Table 2
Interfacial impedances at charged states of model cells derived from AC impedance measurements

	PC	PC/DMC 50/50	Cl-EC	Cl-EC/DMC 50/50
Interfacial impedance (Ω)	28	40	79	19
	TFPC	TFPC/DMC 75/25	TFPC/DMC 50/50	DMC
Interfacial impedance (Ω)	124	91	78	23

discharge capacity at higher than 1 mA/cm^2 is probably due to the effect of impedance of the interface between the electrode surface and electrolyte. Table 2 lists the interfacial impedances of model cells for charged states. The interfacial impedance of TFPC system is the highest, therefore current density dependence seems to be influenced by the interfacial impedance. Fig. 6 shows the relative discharge capacity vs. interfacial impedance of the cells. There is a region at which the relative discharge capacity changes significantly, i.e., at about 100 Ω of interfacial impedance. On the surface of the anode, an organic film is formed from decomposition of the electrolyte [4,5], therefore the interfacial impedance is affected by the property of the surface film. Lithium alkyl carbonates are known as the components of the surface films when the carbonates are used as the electrolyte solvents. For pure Cl-EC, pure TFPC, and pure DMC as the electrolyte solvent, the surface films formed are decomposition of the respective solvents, so their compositions differ among the systems. In particularly for the TFPC system, the surface film probably has the trifluoromethyl ($-CF_3$) group which changes the surface energy, so the property of surface film formed from the pure TFPC system is very different from that of the films of other systems. In the case of EC/DMC and PC/DMC mixed systems, lithium ions are mainly solvated by cyclic carbonates, EC or PC, therefore the surface films are probably made of the cyclic carbonates. However, as mentioned above, the lithium ions were solvated by DMC as well as by TFPC for the TFPC/DMC mixed system. Therefore, the surface films of these systems are likely to be a mixture of decomposition products of TFPC and DMC. As shown in Table 2, the interfacial impedance is extremely high when pure TFPC is used as solvent, and the interfacial impedance of DMC system is equivalently low like the other hydrocarbon systems; i.e., pure PC and PC/DMC systems. Then for the TFPC/DMC mixed system, the interfacial impedance is smaller than that of pure TFPC system. The decrease of interfacial impedance by mixing with DMC is also found for the Cl-EC system. However, since the interfacial impedance of pure Cl-EC system is smaller than the pure TFPC system, the influence of the impedance is not significant for the Cl-EC system.

The maximum current density measured at this study is 1.5 mA/cm^2. This value corresponds to about 2 C of the rate to the charge capacity. From the results of this study, the system for which the conductivity of electrolyte is about 2 mS/cm, gives an identical rate property as for the system with conductivity higher than 10 mS/cm, at the proper interfacial impedance. This result suggests that a cell which has a good rate property can be made by using the electrolyte having 10^{-3} S/cm order conductivity, when the cell has decreased interfacial impedance.

4. Conclusion

The structures of Cl-EC/DMC and TFPC/DMC mixed systems are different from the structure of a hydrocarbon system such as PC/DMC. The solvation to lithium ions by Cl-EC and TFPC was weaker than that by PC due to the effect of substituted electron attracting halogenated groups; then lithium ions were solvated by both cyclic carbonate and linear carbonate in the Cl-EC/DMC and TFPC/DMC mixed electrolyte systems.

The current density dependence of the cell using amorphous carbon as the anode was influenced by the properties of the interface between the electrolyte and electrode. In the system using a TFPC 100% solution in particular, the interfacial impedance was very high, causing a great effect on current density dependence. This is probably due to the property of the surface film on to the carbon anode, which contains trifluoromethyl group. For the TFPC/DMC system, the interfacial impedance is lower than that in the TFPC 100% system, because both TFPC and DMC solvate to lithium ions and therefore, the surface film of this system was formed from both TFPC and DMC.

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