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Conductivity of Lithium Salts in the Mixed Systems of High Permittivity Solvents and Low Viscosity Solvents

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Electrolytic conductivities of $LiClO_4$ and $LiPF_6$ have been investigated in the mixed systems of the high permittivity solvents and low viscosity solvents. Propylene carbonate (PC), sulfolane (S), and dimethyl sulfoxide (DMSO) were used as the high permittivity solvents, and 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF) as the low viscosity solvents. The conductivity of 1 mol dm^{-3} $LiClO_4$ has a maximum in the mixed solvent with 40—80 m/o ether for every system. The conductance improvement by solvent-blending was qualitatively described in terms of a favorable combination of high permittivity and low viscosity of each component. The maximum conductivity of 1 mol dm^{-3} $LiClO_4$ increased in the order of S<PC<DMSO for the systems containing THF. The difference in the order of maximum conductivity between DME and THF was interpreted by ion-solvent interactions, whose measure is generally expressed by the donor and acceptor properties of the solvent. The $LiPF_6$ solutions had much higher conductance than those of $LiClO_4$, especially in high DME concentration regions.

A large number of aprotic organic solvent/lithium (Li) salt combinations have been examined as electrolyte solutions for Li batteries.[1] One of the basic requirements for battery electrolytes is high ionic coductivity. The conductivity of the electrolyte solution is much influenced by the permittivity and the viscosity of the solvent. The former relates to dissociation of the salt and the latter affects the motion of charged particles, or ions. With respect to these, a solvent with high permittivity and low viscosity should be suitable for the conductive electrolyte.[2] In general, however, few solvents satisfy these requirements concurrently. Hence, mixed systems consisting of two solvents, i.e., a high permittivity solvent and a low viscosity solvent, have sometimes been used for practical batteries.[3–5]

Previously, we have reported on the characteristics of some mixed electrolyte systems consisting of a high permittivity solvent and a low viscosity solvent for primary and secondary Li batteries.[6–11] As was expected, high conductivities were observed in the mixed solvent systems, and the electrode characteristics were also excellent in the mixed electrolyte systems.[8,10–13] However, both the conductance behavior and the electrode characteristics changed in response to the kinds of the solvent and the electrolyte salt.

In the present work, conductance behavior in some mixed solvent systems has been compared with one another. The high permittivity solvents used here were propylene carbonate (PC), sulfolane (S) and dimethyl sulfoxide (DMSO), and the low viscosity solvents were 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF). The conductivities of $LiClO_4$ and $LiPF_6$ in the mixed systems are at first explained on the bases of the solvent permittivity and the solution viscosity. Differences in the conductance behavior among the systems are also discussed from the standpoint of the donor-acceptor properties of the solvents,[14,15] which concern the ion-solvent interactions to a great extent.

The structure of ionic solution with organic solvents has fairly been established by some workers,[16–18] but there have been few data on a comparison of the conductivities at moderate concentration of the salts.[19] This study concerns the conductivities at relatively high concentration (1 mol dm^{-3}). Thus the discussion will be rather qualitative, but be useful to develop the electrolyte of practical Li batteries.

Experimental

The purification of the solvents, PC, S, DME, and THF, was carried out as described previously.[9,11,19] DMSO was refluxed over CaH_2 and fractionally distilled.[20] The electrolytic salts were $LiClO_4$ (Ishizu Pharmaceutical) and $LiPF_6$ (Morita Chemical Industries). The solutions were prepared by dissolving the salts (normally 1 mol dm^{-3}) into the mixtures of the high permittivity solvents with the low viscosity solvents. These will be hereinafter represented by such formulas as "PC–DME/$LiClO_4$."

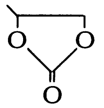
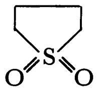
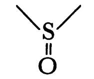
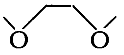
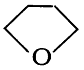
The conductivity of the electrolyte was measured with an AC impedance bridge (10 kHz). The relative permittivity (dielectric constant) of the solvent and the viscosity of the solution were determined by the same methods as described previously.[21] These measurements were carried out at 30 °C.

Results and Discussion

Table 1 shows the relative permittivity (ε_r), viscosity (η), donicity (DN) and acceptor number (AN) of the pure solvents. The values of DN and AN are those quoted from the literature.[1,14,15,24] PC, S, and DMSO have high permittivities as well as high viscosities. The ethers, DME and THF, are low viscosity-low permittivity solvents, whose η and ε_r are similar to each other.

Figure 1 shows the molar conductivity (Λ) of 1 mol dm^{-3} $LiClO_4$ in PC–DME, S–DME, and DMSO–DME as a function of the DME concentration (m/o) in the solvent. For every system, the conductivity in the mixed solvent was higher than that in the neat solvent. The molar conductivity became maximum at

Table 1. Selected Properties of the Solvents

Solvent	ε_r[a]	η[a]/10^{-3} Pa s	DN[b]	AN[b]
PC 	66.8	2.25	15.1	18.3
S 	42.5	9.87	14.8	19.0
DMSO 	47.8	1.75	29.8	19.3
DME 	6.92	0.40	24	(≈10)[c]
THF 	7.25	0.46	20.0	8.0

a) Measured at 30 °C. b) From references 1, 14, 15, and 24. c) 10.2 for diglyme (diethylene glycol dimethyl ether).

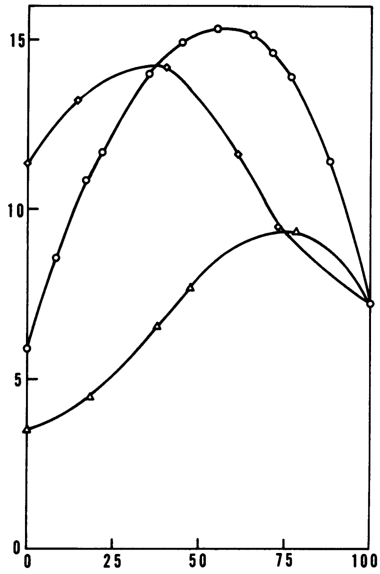


Fig. 1. Variation of the molar conductivity (Λ) of 1 mol dm^{-3} LiClO$_4$ with the solvent composition. ○: PC–DME, △: S–DME, ◇: DMSO–DME.

40—80 m/o DME. This conductivity enhancement is qualitatively explained by a favorable combination of high permittivity of PC, S, or DMSO with low viscosity of DME. The viscosity of the solution decreases with DME concentration. Thus, in the solution with relatively low DME content, the ionic mobility, or ionic conductance, increases with DME content in the solvents. On the other hand, the permittivity also decreases with DME content. This leads to an increase in the degree of ion association, which causes the conductivity to decrease, especially in the soltions with high DME content. Therefore, optimum solvent compositions are present for the conductance of these mixed electrolyte systems.

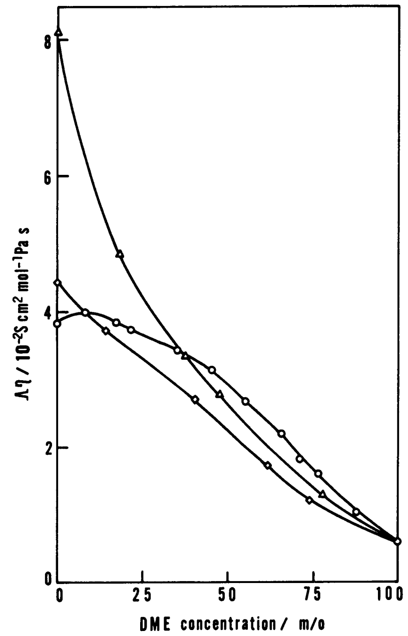


Fig. 2. Variation of the Walden product ($\Lambda\eta$) of 1 mol dm^{-3} LiClO$_4$ with the solvent composition. ○: PC–DME, △: S–DME, ◇: DMSO–DME.

Jansen and Yeager[25] have reported that the ion pair association constant K_a calculated by the Fuoss–Onsager theory was -1.0—-1.5 in PC(pure)/LiClO$_4$ at 25 °C. On the other hand, we have previously estimated the degree of association of LiClO$_4$ in the PC–DME and the PC–THF systems by using Bjerrum's equation.[9] The results showed that the degree of association would be very small (<0.1) in the solutions containing 0—40 v/o ethers, and that the ion association would significantly occur at the ether concentration range of 70 v/o or more. That is, it has been shown that the conductivity-solvent composition curves experimentally obtained in PC–DME/LiClO$_4$ and PC–THF/LiClO$_4$ were consistent with those calculated on the assumption that the conductivity is almost determined as the first approximation by the solution viscosity and the ion association.[9]

As shown in Fig. 1, there are some differences in the shape of the curve and in the DME concentration providing maximum conductivity among the three systems. This is first of all attributable to differences in the relative permittivity and the viscosity among PC, S, and DMSO. Figure 2 shows the Walden products ($\Lambda\eta$) of the 1 mol dm^{-3} LiClO$_4$ solutions as a function of DME concentration. The Walden products were approximately similar to one another in the solvents with DME concentration more than 40 m/o. The monotonous decrease of $\Lambda\eta$ with DME concentration in this region is related to the increase in ion association caused by increasing DME content in the solvents. If it is valid to assume that the conductivity is almost determined by the permittivity and the viscosity, differences in the Walden products among the solvent

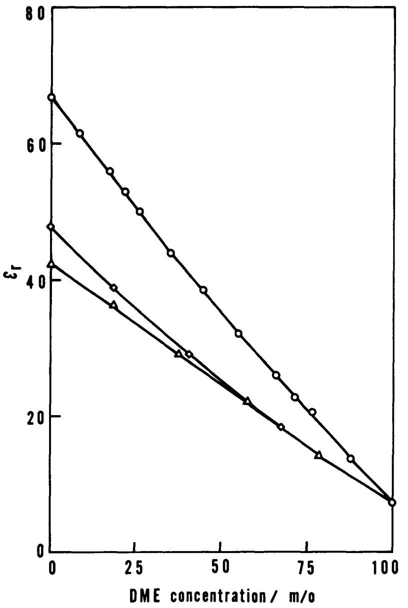


Fig. 3. Variation of the relative permittivity (ε_r) with the solvent composition.
○: PC-DME, △: S-DME, ◇: DMSO-DME.

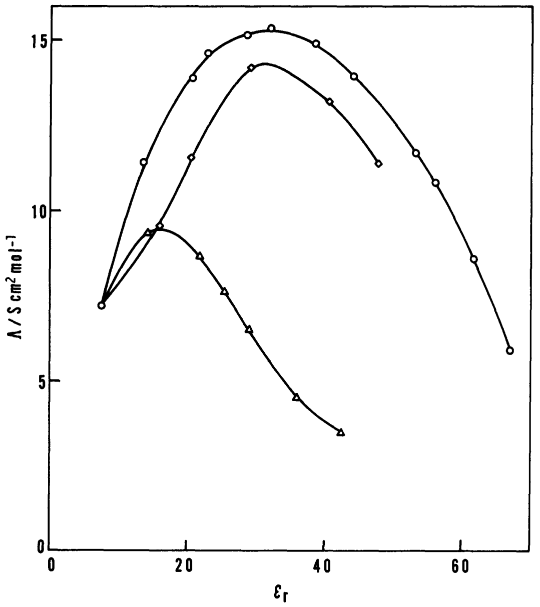


Fig. 4. Correlation between Λ of 1 mol dm^{-3} LiClO$_4$ and ε_r of the solvent.
○: PC-DME, △: S-DME, ◇: DMSO-DME.

systems would primarily originate in the permittivity of the solvent. The relative permittivities of the mixed solvents are shown in Fig. 3. In general, the permittivity of an binary system shows an additive property, i.e., a linear relationship between the permittivity and the composition. As shown in Fig. 3, the permittivity-composition curves for the present three systems bent downward. This is because the solvent compositions were represented by mole fractions. Relative permittivity can be assigned a significance in terms of the quantity per unit volume. In the present cases, the permittivities of the solvents varied almost linearly with the volume percent of the blended solvents.[9]

In Fig. 4, the molar conductivities of 1 mol dm^{-3} LiClO$_4$ solutions are plotted against the relative permittivities of the solvents. Since the permittivities had linear relationships to the solvent compositions, the Λ—ε_r relations also gave maximum values in the mixed systems. The ε_r providing the maximum Λ was about 30 in the systems of PC-DME and DMSO-DME, but it was 20 or less in S-DME. The relatively low Λ of 1 mol dm^{-3} LiClO$_4$ in S-DME might be attributable to the high viscosity of this system. Figure 5 shows the relation between the Walden products and the relative permittivities of the solvents. The differences in the $\Lambda\eta$—ε_r curves among the solvent systems originate probably in some characteristics of the systems, other than the permittivity and the viscosity, because the contributions of the latter parameters (ε_r and η) to the conductivity have already been reflected in the $\Lambda\eta$—ε_r relations. It must be taken into consideration that the dielectric saturation around ions[26] also affects the conductance behavior. However, this effect would be treated as a peculiar ion-solvent interaction. The ion-solvent interactions affecting the conductance behavior will be comprehensively discussed in the latter part of this section.

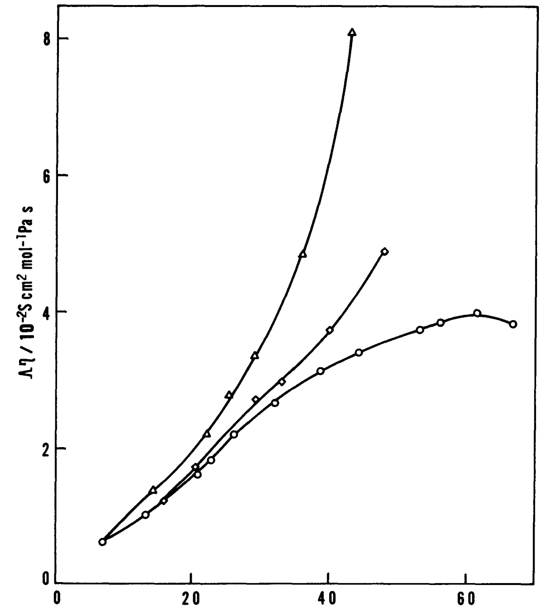


Fig. 5. Correlation between $\Lambda\eta$ of 1 mol dm^{-3} LiClO$_4$ and ε_r of the solvent.
○: PC-DME, △: S-DME, ◇: DMSO-DME.

In Fig. 5, the curve of DMSO-DME/LiClO$_4$ is almost consistent with that of PC-DME/LiClO$_4$ in the region of $\varepsilon_r<40$. The $\Lambda\eta$ in PC-DME tended to be unchangeable with increasing ε_r, especially in the high ε_r region. The $\Lambda\eta$ of DMSO-DME/LiClO$_4$ is higher than that of PC-DME/LiClO$_4$ in the DME concentration region of 20 m/o or lower (ε_r>40). In S-DME, the $\Lambda\eta$ markedly increased with ε_r in the higher ε_r region (>30), compared with the PC- or DMSO-based system. This is mainly caused by high viscosity of S, since $\Lambda\eta$ in S-DME is rather lower than that in PC-DME or DMSO-DME. However, from the other point of view, it is considered that the S-DME/ $LiClO_4$ system has relatively high conductance for its high viscosity.

The different $\Lambda\eta$—ε_r relations among the three systems in the low DME concentration (higher ε_r) region are explicable by the different donicities (*DN*) and acceptor numbers (*AN*) of PC, S, DMSO, and DME. According to Gutmann,[14,15] *DN* is defined as the negative ΔH-value in kcal mol^{-3} (1 cal=4.18 J) for the reaction (1) in 1,2-dichloroethane

$$D + SbCl_5 \longrightarrow D\cdot SbCl_5, \qquad (1)$$

where D denotes the solvent in question. As $SbCl_5$ is a strong electron-acceptor, *DN* is a measure of the nucleophilic property of the solvent. On the other hand, *AN* is derived from the chemical shift of ^{31}P NMR of Et_3PO in the solvent under consideration. *AN* is expressed by a relative value when that of hexane is defined as 0 and the δ-value of the $Et_3PO\cdot SbCl_5$ adduct in 1,2-dichloroethane is arbitrarily normalized as 100. Thus *AN* is a measure of the electrophilic property of the solvent.

As DME has higher *DN* than PC, specific solvation (selective coordination) of DME to Li^+ comes out in the PC-DME system.[7,17] The *DN* of DMSO is higher than those of PC and DME. Thus the specific solvation of DME to Li^+ would not be expected in the DMSO-DME system. On the other hand, DME in the S-DME system would preferentially coordinate to Li^+ as in PC-DME because of the relatively low *DN* of S. Nevertheless, the Λ in S-DME was rather low compared with that in PC-DME. This result suggests that the other interactions, e.g., anion-solvent and ion-ion interactions, in the two systems differ from each other. These will be briefly discussed later again.

In Fig. 6, the molar conductivity of 1 mol dm^{-3} $LiClO_4$ in PC-THF is compared with that in PC-DME. As ε_r and η of pure THF are similar to those of DME, the variations of ε_r and η in PC-THF are also similar to those in PC-DME.[9] However, the molar conductivity in PC-THF was relatively low. In both systems Li^+ is probably coordinated by the ethers in preference to PC. It is considered that the primary solvation number of DME per Li^+ is two in PC-DME,[7] and the number of THF is four in PC-THF.[27] That is, the ionic radius of the solvated Li^+ would be larger in PC-THF than in PC-DME since there is no great difference in molecular volume between THF and DME. It is considered that there is little difference in the degree of association between the two systems containing the same concentrations of the ethers. Thus the relatively large size of the Li^+-THF solvate would be responsible for the lower conductance in PC-THF than in PC-DME. An analogous explanation applies to the cases of S-DME and S-THF shown in Fig. 7. The S-THF/ $LiClO_4$ (1 mol dm^{-3}) system shows a conductivity maximum at THF concentration of about 60 m/o. However, the maximum value of the conductivity in S-THF is only 70% of that in S-DME. On the other hand, the conductance in DMSO-THF was appreciably high unlike the cases of PC-THF and S-THF (Fig. 8). The conductivity of $LiClO_4$ in the DMSO-THF system varied in a similar manner and in the same magnitude as in the DMSO-DME system, except for the composition region of fairly high ether concentration. This means that the ion-solvent interaction, or the solvation, in the two systems is almost equivalent to each other. As DMSO has higher *DN* than DME

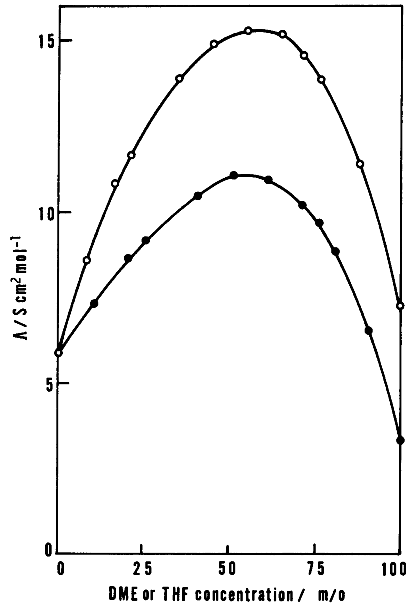


Fig. 6. Variation of Λ of 1 mol dm^{-3} $LiClO_4$ with the solvent composition.
○: PC-DME, ●: PC-THF.

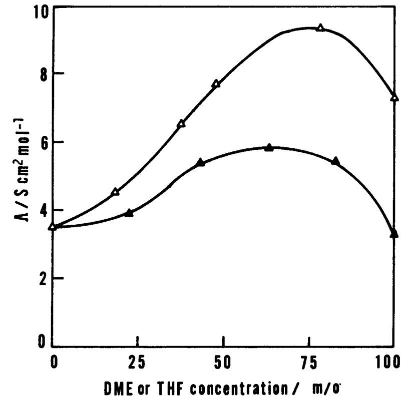


Fig. 7. Variation of Λ of 1 mol dm^{-3} $LiClO_4$ with the solvent composition.
△: S-DME, ▲: S-THF.

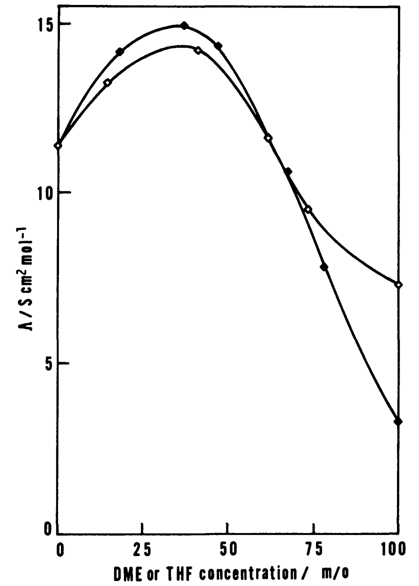


Fig. 8. Variation of Λ of 1 mol dm^{-3} $LiClO_4$ with the solvent composition.
◇: DMSO–DME, ◆: DMSO–THF.

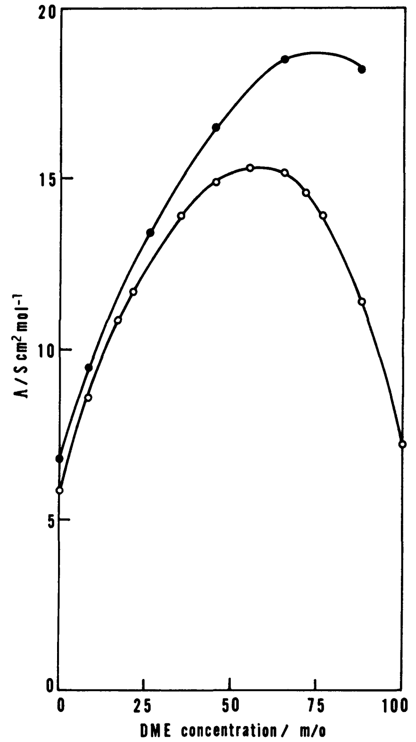


Fig. 9. Variation of Λ of 1 mol dm^{-3} $LiClO_4$ and $LiPF_6$ with the solvent composition.
○: PC–DME/$LiClO_4$, ●: PC–DME/$LiPF_6$.

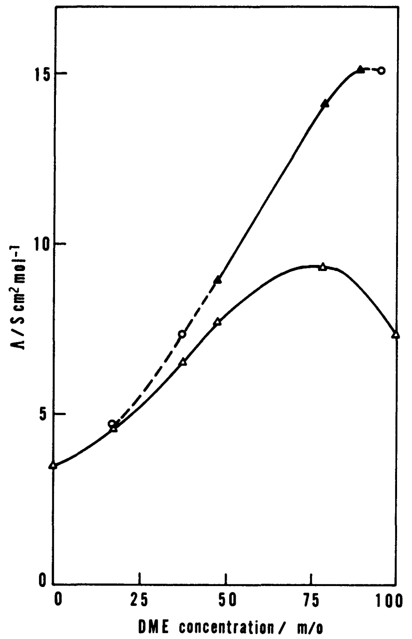


Fig. 10. Variation of Λ of 1 mol dm^{-3} $LiClO_4$ and $LiPF_6$ with the solvent composition.
△: S–DME/$LiClO_4$, ▲: S–DME/$LiPF_6$ (○: saturated $LiPF_6$).

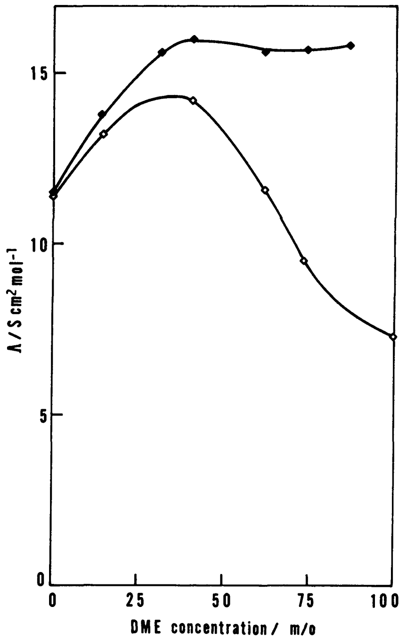


Fig. 11. Variation of Λ of 1 mol dm^{-3} $LiClO_4$ and $LiPF_6$ with the solvent composition.
◇: DMSO–DME/$LiClO_4$, ◆: DMSO–DME/$LiPF_6$.

or THF has, it is reasonable that DMSO coordinates preferentially to Li^+ in both systems. This description is consistent with the experimental results shown in Fig. 8. Besides the relatively low viscosity, the strong affinity of DMSO to Li^+, which leads to smaller size of solvated Li^+, might be related to the high conductance of $LiClO_4$ in neat DMSO compared with that in neat PC or S.

Influences of the anion on the conductance behavior of the Li salts were examined in PC–DME, S–DME, and DMSO–DME. Figures 9, 10, and 11 show the conductivity variations of 1 mol dm^{-3} $LiClO_4$ and $LiPF_6$. The solubility of $LiPF_6$ was rather low compared with that of $LiClO_4$. In S–DME, it was 1 mol

dm^{-3} or lower in the DME concentration range of $<$ 40 or $>$95 m/o. The conductivity-solvent composition curves of $LiPF_6$ were almost identical to those of $LiClO_4$ in the DME concentration range up to about 40 m/o. The $LiPF_6$ solutions with high DME content showed relatively high conductance. A similar manner to this has been observed in the ether based electrolytes such as DME,[28] THF,[29,30] and 1,3-dixolane (DOL)[30] containing $LiAsF_6$ which is an analogous compound to $LiPF_6$. The reason why $LiAsF_6$ has higer conductance than $LiClO_4$ in these ether solvents has not sufficiently clarified yet.[30] The ion association will take place to a considerable extent in the ether-based electrolytes because of the low permittivity of the solvent and the relatively high concentration of the electrolyte. It is considered that the size of anion and hence the charge density at the spherical surface of anion would influence the ion-pair formation. It has been found that the two types of ion pairs may be present in solutions of high concentration or of low permittivity, i.e., solvent separated ion pairs and solvated contact ion pairs.[16,31] These are represented by the following chemical equilibria

$$(Li^+)S_n + A^- \rightleftharpoons (Li^+)S_nA^- \tag{2}$$

$$(Li^+)S_n + A^- \rightleftharpoons (Li^+A^-)S_{n-m} + mS, \tag{3}$$

where S represents a solvent molecule and A^- an anion.[1,31] It is possible that redissociation of solvent separated ion pairs occurs because of the long range nature of the coulomb force, and that the resulting free ions contribute to ionic conductance.[1] In other words, the difference in the types of ion pairs would appear in the difference of the ionic behavior, e.g., the association constants in the conventional treatment. The PF_6^- anion would be larger than ClO_4^- in its geometry[19] and hence the surface charge density of PF_6^- would be lower than that of ClO_4^-. Thus, in analogy with the $LiAsF_6$ solutions,[30] the solvent separated ion pairs would be liable to come out in the $LiPF_6$ solutions, while the contact ion pairs would be subject to form in the $LiClO_4$ solutions. These descriptions will interpret the result that the conductivities of the $LiPF_6$ solutions with high DME content were much higher than those of the $LiClO_4$ solutions.

The charge-discharge cycle characteristics of the Li electrode in S-DME/$LiPF_6$[11] and in DMSO-DME/$LiPF_6$[22] were much superior to those in the solutions containing $LiClO_4$. The $LiPF_6$ solutions consisting of the mixture of a high permittivity solvent and a low viscosity ether, which show high electrolytic conductivities, are very impressive for the practical use as the electrolytes of rechargeable Li batteries working at ambient temperatures.

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