Effects of Polymer Matrix and Salt Concentration on the Ionic Conductivity of Plasticized Polymer Electrolytes

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SYNOPSIS

Two polar polymers with different dielectric constants, poly(vinylidene fluoride) (PVDF) and poly (ethylene oxide) (PEO), were each blended with a chlorine-terminated poly(ethylene ether) (PEC) and one of the two salts, $LiBF_4$ and $LiCF_3CO_2$, to form PEC-plasticized polymer electrolytes. The room-temperature ionic conductivity of the PEC-plasticized polymer electrolytes reached a value as high as 10^{-4} S/cm. The room-temperature ionic conductivity of the PVDF-based polymer electrolytes displayed a stronger dependence on the PEC content than did the PEO-based polymer electrolytes. In PVDF/PEC/$LiBF_4$ polymer electrolytes, the dynamic ionic conductivity was less dependent on temperature and more dependent on the PEC content than it was in PEO/PEC/$LiBF_4$ polymer electrolytes. The highly plasticized PVDF-based polymer electrolyte film with a PEC content greater than CF4 (CF4 defined as the molar ratio of the repeat units of PEC to those of PVDF equal to 4) was self-supported and nonsticky, while the corresponding PEO-based polymer electrolyte film was sticky. In these highly plasticized PVDF-based polymer electrolytes, the curves of the room-temperature ionic conductivity vs. the salt concentration were convex because the number of carrier ions and the chain rigidity both increased with increase of the salt content. The maximum ionic conductivity at 30°C was independent of the PEC content, but it depended on the anion species of the lithium salts in these highly plasticized polymer electrolytes. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene oxide) (PEO) is the most favored solvating medium in studies of ionic conductivity in solid polymer electrolytes (SPE) because of its ability to combine effectively with the salt cations to form a homogeneous solution.[1] However, there are several disadvantages in using PEO. The major disadvantages are that PEO shows a high tendency to crystallize or to form crystalline complexes when long chains are used and that acceptable levels of ionic conductivity can only be obtained at temperatures above the melting point.[2] Ion transport in SPE can be aided by segmental motion of the polymer matrix, which, in turn, can be promoted by the preparation of new polymers and the addition of in-

organic additives and organic soluble additives.[2-8] These methods may suppress the crystalline phase and the glass transition temperature (T_g) and enhance the amorphous phase and the dielectric constant[7,8] of the polymer electrolytes. Polymer electrolytes with a high dielectric constant can reduce the energy required to dissociate the salt in the medium so that ionic conductivity can be promoted. A polymer with a high polarity usually has a high dielectric constant, ε.

In addition to PEO, polar polymers, such as poly(ethylene succinate)[9,10] (ε = 5.0–5.5), poly(β-propiolactone),[11] poly(ethylene adipate)[12] (ε = 5.2), poly(N-propylaziridine),[13] poly(alkylene sulfide),[14] and poly(vinylidene fluoride)[15,16] (ε = 8–13) have been used as the matrices in SPEs. The conductivities of these polymers, however, are poor. The dielectric constant of poly(vinylidene fluoride) (PVDF) is much higher than that of PEO (ε = 5), but the conductivity of PVDF/salt SPE is even lower

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than that of the corresponding PEO/salt SPE. This poor ionic conductivity might result from the high T_g and the high degree of crystallinity of PVDF. The addition of polar soluble organic additives has been used to improve the conductivity of the SPEs. Low molecular weight polar additives, e.g., N,N-dimethylformamide (DMF), ethylene carbonate (EC), and other additives, have been successfully dissolved in polymer to alter the physical and electrical properties of the matrix.[16-19] However, these kinds of additives are volatile at elevated temperatures. Liquid poly(ethylene glycol) (PEG), which is nonvolatile, has been added to the polymer electrolytes to produce a more stable system. However, the end groups of the PEG affect the ionic conductivity. Endo-acetylated PEG_{400} (molecular weight 400) has a lower viscosity than does PEG_{400}, but polymer electrolytes made with endo-acetylated PEG_{400} have a lower conductivity than do those made with PEG_{400}. This implies that conductivity is more sensitive to the polarity of the additives than to their viscosity. However, PEG with hydroxyl end groups is not suitable for battery application, since it reacts easily with lithium metal.

In this study, nonreactive polar chlorine atoms were used as a substitute for the hydroxyl groups in PEG. The chlorine-terminated poly(ethylene ether) (PEC) was expected to promote chain segmental motion and provide extra ion-transport channels in the PEC-rich phase to improve the ionic conductivity. Previous reports showed that unplasticized PVDF-based polymer electrolytes have a much lower conductivity than do the corresponding PEO-based polymer electrolytes, even though the dielectric constant of PVDF is much higher than that of PEO. We anticipated that the liquid PEC might have different effects on the conductivity of solid polymer electrolytes containing polymer matrices with different dielectric constants and different thermal transition temperatures (T_g and T_m). Therefore, in this study, PVDF and PEO were used as polymer matrices; the inorganic salt $LiBF_4$ (LB) and the organic salt $LiCF_3CO_2$ (LA), as electrolytes; and PEC, as a plasticizer.

EXPERIMENTAL

Preparation of Chlorine-terminated Poly(ethylene ether) (PEC)

Ten milliliters of $SOCl_2$ was added to 35 mL of PEG_{400}. After the mixture was refluxed for 4 days under dry nitrogen, it was placed in a vacuum oven

at 100°C for 48 h in order to remove all the volatile components. The liquid residue was PEC, which was identified by using Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. Both techniques confirmed that all the hydroxyl groups had been replaced by chlorine atoms.[16]

Preparation of PVDF/PEC, PVDF/PEC/LiBF₄, and PEO/PEO/LiBF₄ Films

PVDF, PEC, $LiBF_4$, and $LiCF_3CO_2$ are all commercially available. The solutions of polymer electrolytes were obtained by dissolving different amounts of these components in anhydrous N,N-dimethylacetamide (DMA) for the PVDF system and in acetonitrile for the PEO system. The weighing and mixing of the chemicals were performed in a dry box. The solutions were cast on surface-treated glass plates, and then the solvents were evaporated in a vacuum oven. The resulting polymer electrolyte films were stored in an electronic humidity-controlled desiccator before characterization. The glass plates were pretreated with a solution containing 1% $(CH_3)_3SiCl$ in $CHCl_3$. The salt concentrations in the polymer electrolytes were fixed at 16/1 and 4/1 of the molar ratios of the total monomeric units of the polymer matrix to the formula units of the salt. The mole number of the total monomeric units was the sum of the mole number of the monomeric units of PVDF or PEO and the number of units of PEC.

Nomenclature

FLBx and OLBx

FLBx and OLBx denote the polymer electrolytes containing the salt $LiBF_4$ and one of the two polymers PVDF and PEO, respectively, without the plasticizer PEC. "F" stands for PVDF; "O," for PEO; and LB, for $LiBF_4$. "x" is the molar ratio of the repeat unit of the polymer matrix to the formula unit of the salt.

FCmLBn and OCmLBn

The symbols "F," "O," and "LB" have the same meanings as in the above section. In addition, "C" stands for PEC; "m," for the molar ratio of the repeat unit of PVDF or PEO to that of PEC; and "n," for the molar ratio of the total polymeric repeat units (including PVDF, PEO, and PEC) to the formula unit of the salt.

Table I Thermal Transition Data of PVDF/PEC/LB (LB16) Polymer Electrolyte Films

Sample	Composition	T_g (°C)	T_m (°C)	ΔH_m (mJ/mg)
FLB16	"F" only, F/LB = 16	130.0	169.0	49.0
FC4LB16	F/C = 4, (F + C)/LB = 16	123.6	165.5	45.2
FC2LB16	F/C = 2, (F + C)/LB = 16	122.4	163.6	41.9
FC1LB16	F/C = 1, (F + C)/LB = 16	122.6	163.3	39.7
CF2LB16	C/F = 2, (C + F)/LB = 16	123.1	161.4	26.1
CF4LB16	C/F = 4, (C + F)/LB = 16	—	156.2	20.0

CFmLAn, CFmLBn, and COmLBn

All these symbols have the same meaning as those defined in the above section, except that "m" stands for the molar ratio of the repeat unit of PEC to that of PVDF or PEO, and LA stands for LiCF$_3$CO$_2$. In the two above sections, the first character stands for the component having the higher moles of repeat units in the polymer matrix.

LA and LB

LA represents the pure salt LiCF$_3$CO$_2$, and LB, the pure salt LiBF$_4$.

Characterization

Dynamic ionic conductivities and dielectric constants of the polymer electrolytes were obtained using a DuPont 2970 dielectric analyzer at 300 KHz. The measurement was scanned at 3°C/min in a dry nitrogen flow of 500 cc/min. Thermal transitions of the polymer electrolytes were characterized using a Seiko differential scanning calorimeter at 10°C/min in a nitrogen stream.

RESULTS AND DISCUSSION

Effects of Polymer Matrix

Thermal transition data for the PVDF/PEC/LB films are listed in Table I. The melting point (156–170°C) of the PVDF crystalline phase decreased as the PEC content increased. When the PEC content in the polymer electrolyte PVDF/PEC/LB16 films increased beyond the critical value of CF2 (the molar ratio of the repeat unit of PEC to that of PVDF equal to 2), there was a lower temperature subpeak near −12°C in the DSC curve of CF4LB16. This was the melting peak of the plasticizer PEC. As summarized in Table I, the ΔH_m of the PVDF melting decreased with increase in the PEC content. This indicates that PEC facilitated the formation of the PVDF amorphous phase while suppressing the crystalline phase in these SPEs. In the PEO-based polymer electrolyte system, increasing the PEC content showed the same effect as that in the PVDF system: It suppressed the crystalline phase and enhanced the amorphous phase.

As shown in Table II, the T_g's of the polymer electrolyte PEO/LB films without PEC were much lower than those of the corresponding PVDF/LB films. This means that the PEO polymer electrolytes were much more flexible than were the corresponding PVDF polymer electrolytes. The T_g's of the PEO/LB films with or without PEC were lower than −50°C. The amorphous phases of the PEO/PEC/LB16 and PEO/PEC/LB4 films in the temperature range 0–100°C of the dynamic ionic conductivity measurement were rubbery. The PEO-rich crystalline phase in the PEO/PEC/LB16 films started melting at about 20°C and reached a peak in the range of 30–50°C, as shown in Table II. The PEO–

Table II Thermal Transition Data of PEO/PEC/LB (LB16) Polymer Electrolyte Films

Sample	Composition	T_g (°C)	T_m (°C)	ΔH_m (mJ/mg)
OLB16	"O" only, O/LB = 16	−51.3	52.5	73.4
OC4LB16	O/C = 4, (O + C)/LB = 16	−47.9	50.4	64.2
OC2LB16	O/C = 2, (O + C)/LB = 16	−53.7	43.9	49.7
OC1LB16	O/C = 1, (O + C)/LB = 16	−55.5	40.4	40.1
CO2LB16	C/O = 2, (C + O)/LB = 16	−58.4	34.6	7.5
CO4LB16	C/O = 4, (C + O)/LB = 16	−61.1	31.1	3.2
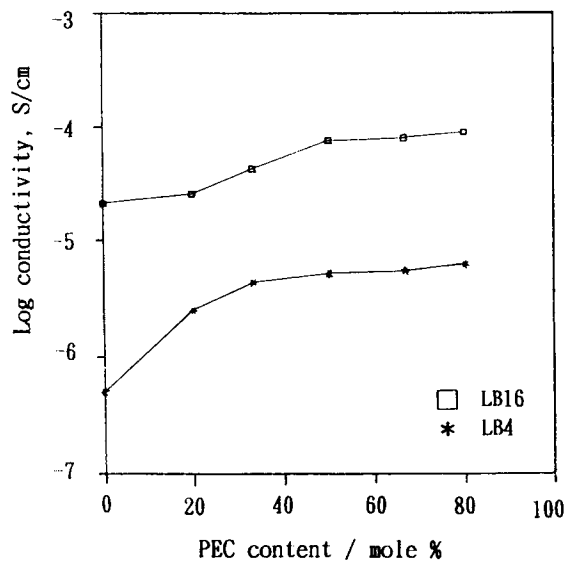
Figure 1 Dependence of ionic conductivity at 30°C on PEC content in PEO/PEC/LB polymer electrolytes.

Figure 2 Dependence of ionic conductivity at 30°C on PEC content in PVDF-based and PEO-based polymer electrolytes with constant $LiBF_4$ content (LB4).

salt complex crystalline phase of the PEO/PEC/LB4 films started melting from about 50°C, with a peak in the range of 100–115°C. The melting temperature of the PEO/PEC/LB films shifted to a lower temperature when more PEC was added to the polymer electrolytes. With a high PEC content in the polymer electrolytes, the PVDF-based film, e.g., CF4LB16, was self-supported and nonsticky, but the PEO-based film, e.g., CO4LB16, was sticky because of the low T_g of the PEO system.
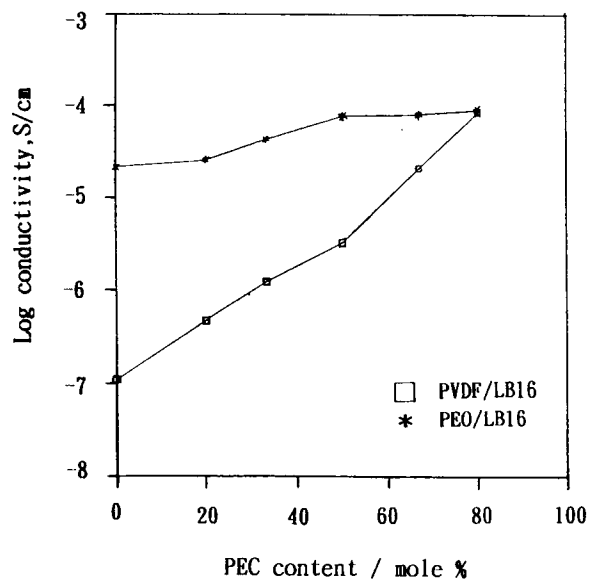
Dependence of the ionic conductivity at 30°C on the PEC content in the polymer electrolyte PEO/PEC/LB is illustrated in Figure 1. As the figure shows, the polymer electrolyte with a salt content of LB16 (lower concentration) had a higher ionic conductivity than that of the corresponding polymer electrolyte with a content of LB4. A higher concentration of $LiBF_4$ in the polymer electrolytes resulted in the appearance of more complex phases. This, in turn, produced a more rigid hybrid film and reduced ion mobility in the polymer matrix. Therefore, polymer electrolytes with a higher salt content exhibited a lower ionic conductivity. In the PEO/PEC/LB4 polymer electrolyte system, the addition of PEC initially resulted in an increase in ionic conductivity, which then leveled off when the PEC content (the molar ratio of the monomeric units of PEC to the sum of the monomeric units of PEO and PEC) reached 33%. The same result occurred with PEO/PEC/LB16, but the ionic conductivity leveled off at a higher PEC content of 50%.

Comparisons of the ionic conductivities of the hybrid films with the PEO matrix and the PVDF

matrix are shown in Figures 2 and 3. The dependence of ionic conductivity on PEC content in polymer electrolytes with the PVDF matrix was much stronger than it was in electrolytes with the PEO matrix. Figure 2 (with the fixed salt content LB4) shows that with a lower PEC content the ionic conductivities of the PEO system were higher than those of the corresponding PVDF system, but with a PEC content of higher than 55 mol %, the ionic conduc-

Figure 3 Dependence of ionic conductivity at 30°C on PEC content in PVDF-based and PEO-based polymer electrolytes with constant $LiBF_4$ content (LB16).

tivities of the PVDF system were higher than those of the corresponding PEO system. CF4LB4 (PEC content 80%) had an ionic conductivity of 4.4×10^{-5} S/cm and was nonsticky and self-supporting. In comparison, CO4LB4 had lower conductivity and was sticky. Figure 3 reveals that at a lower PEC content the ionic conductivities of the PEO system were much higher than those of the corresponding PVDF system, but at 80 mol % of the PEC concentration, the polymer electrolyte of the PVDF system had the same ionic conductivity as that of the PEO system, i.e., near 10^{-4} S/cm (8.2×10^{-5} S/cm for CF4LB16 and 8.8×10^{-5} S/cm for CO4LB16). CF4LB16 film was self-supporting and nonsticky, whereas CO4LB16 film was sticky. It might be useful for battery applications to blend CF4LB16 and CO4LB16 in order to maintain good contact between the SPE and the electrode during charge–recharge cycles and to provide mechanical stability. Figure 3 also shows that the room-temperature ionic conductivity of the PVDF/PEC/LB16 film was much more dependent on PEC content than was the conductivity of the PEO/PEC/LB16 film.

As shown in Figure 4, the dielectric constant (at 30°C and 300 kHz) of FLB16 (without PEC) was much lower than that of OLB16, although the dielectric constant of pristine PVDF is higher than that of pristine PEO. The T_g of the PVDF-based polymer electrolytes near 130°C was much higher than that of the PEO-based polymer electrolytes near −50°C. The PEO polymer chain is more flexible
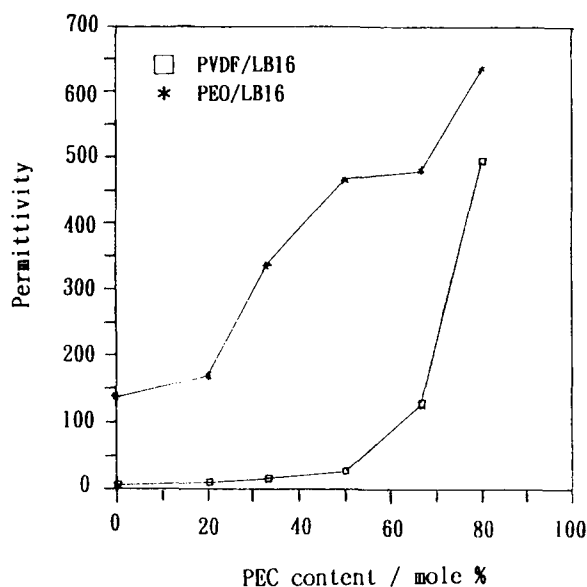
Figure 4 Dependence of permittivity at 30°C on PEC content in PVDF-based and PEO-based polymer electrolytes with constant LiBF$_4$ content (LB16).

than is the PVDF chain. The polarization in a dielectric may be produced by the induction effect and the orientation effect. The total molar polarizability, P_m, is the combination of the induced polarizability and the orientation polarizability. As shown in Figure 4, the dielectric constant of OLB16 (without PEC) at about 135 was much higher than that of the pristine PEO at 5.

It was apparent that the salt contributes greatly to the polarization of the polymer electrolyte in an electric field. However, the effect of the salt on the polarization of the polymer electrolyte FLB16 was negligible, as the dielectric constant of the polymer electrolyte was close to, or even slightly lower than, that of the pristine PVDF. The main difference between the PEO system and the PVDF system was that the PVDF system exhibited much higher T_g and T_m and a stronger coordination with the salt LiBF$_4$: The fluorine atoms in PVDF have greater electronegativity than that of the oxygen atoms in PEO. Therefore, the salt combined with PVDF more strongly than with PEO.

The combination of the chain flexibility of the polymer matrix and the interaction of the salt with the polymer matrix made the orientation of LiBF$_4$ in the PVDF-based films much more difficult than it was in the PEO-based films in an electric field. At 30°C, the amorphous phase of FLB16 film was in the glassy state, so the polymer chain movement and the orientation of the salt were both limited. Due to coordination with the salt, the PVDF chain mobility in the polymer electrolyte FLB16 was more difficult than in the pristine polymer, so orientation of the polymer chains in FLB16 film in an electric field was more difficult than was orientation in the pristine PVDF film.

The low dielectric constant of FLB16 at 30°C was probably due to induced polarization. At 30°C, the amorphous phase of the OLB16 polymer electrolyte film was in a rubbery state; the crystalline phase began to melt at 30°C, with a peak near 50°C. It is evident that the salt contributed greatly to the value of the dielectric constant, due to the orientation polarization at 30°C in the OLB16 film. As more PEC plasticizer was added to the polymer electrolyte, the crystalline phase was suppressed and the chain mobility was enhanced. Also, the orientation polarization of the polymer chains and the salts became easier, the value of the dielectric constant increased, and the room-temperature ionic conductivity of the polymer electrolytes also increased. Initially, the dielectric constant of the PVDF-based polymer electrolyte film rose slowly, but it increased rapidly when the PEC content was over 50 mol %.

However, the dielectric constant of the PEO/PEC/LB16 polymer electrolyte increased rapidly with increase of the plasticizer content.

The conductivity of the PVDF/PEC/LB16 film was much more sensitive to the increase of the PEC content than was the PEO/PEC/LB16 film. It is clear that, in addition to the dielectric constant, there was another factor that affected the ionic conductivity of the polymer electrolytes. It was mentioned above that the T_g and T_m of the PVDF-based polymer electrolytes were high and the interaction between the fluorine atoms of PVDF and lithium ions was stronger than that between the oxygen atoms of PEC and lithium ions, so that the weak-bond PEC–salt complex in the PVDF-based polymer electrolytes became a better conduction path. This explains why the ionic conductivity of the PVDF-based polymer electrolytes was much more sensitive to change in the PEC content than was the PEO-based polymer electrolytes.

The dynamic ionic conductivities of the polymer electrolytes PVDF/PEC/LB and PEO/PEC/LB in the temperature range of 0–100°C are shown in Figures 5–8. The conductivity of PVDF/PEC/LB polymer electrolyte films responded less sensitively to temperature but more sensitivity to PEC content than did the PEO/PEC/LB films. As mentioned before, PVDF-based polymer electrolytes exhibited a high T_g of about 130°C, below which the polymer electrolyte film was in a glassy state. On the other hand, in the PEO/PEC/LB films, the PEO-rich

crystalline phase and the PEO–salt complex crystalline phase melted below 100°C. The melting of the crystalline phase resulted in a significant change in morphology. Therefore, the effect of temperature on the conductivity of PEO/PEC/LB films was more significant than it was on the conductivity of the corresponding PVDF systems. In PEO/PEC/LB16 films, there was a marked change in conductivity in the temperature range of 20–40°C, while in PEO/PEC/LB4 films, the conductivity increased mildly in two ranges (from 20 to 40°C and from 75 to 100°C).

Effects of Salt Concentration

The curves of the room-temperature (30°C) ionic conductivity of highly plasticized polymer electrolytes vs. the salt concentration are shown in Figure 9 for CF4LAn and CF7LAn and in Figure 10 for CF4LBn and CF7LBn. Both sets of curves are convex. As shown in Figure 9, at the same salt concentration of LA25, the CF4LAn and CF7LAn films showed the same value for the highest ionic conductivity, 10^{-5} S/cm. In Figure 10, the dependence of the room-temperature ionic conductivity of CF7LBn films on the salt concentration was less than that of the ionic conductivity of CF4LBn films on the salt concentration of CF4LBn. At the salt concentration of LB25, both the CF4LBn and CF7LBn series exhibited the same maximum ionic conductivity of 10^{-4} S/cm. Thus, the PEC concen-
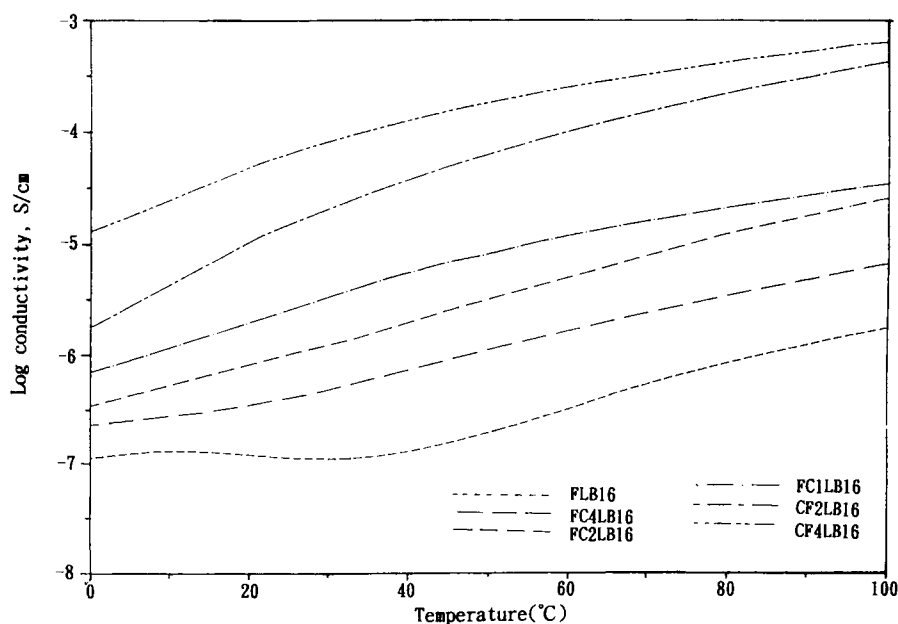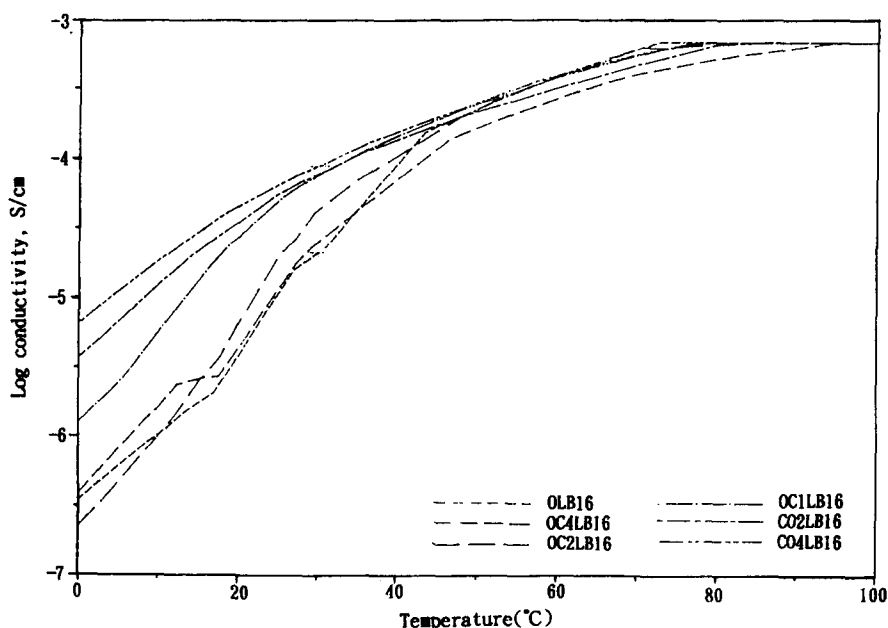

Figure 5 Dynamic ionic conductivity of polymer electrolytes at various ratios of PVDF/PEC with constant LiBF$_4$ content (LB16).
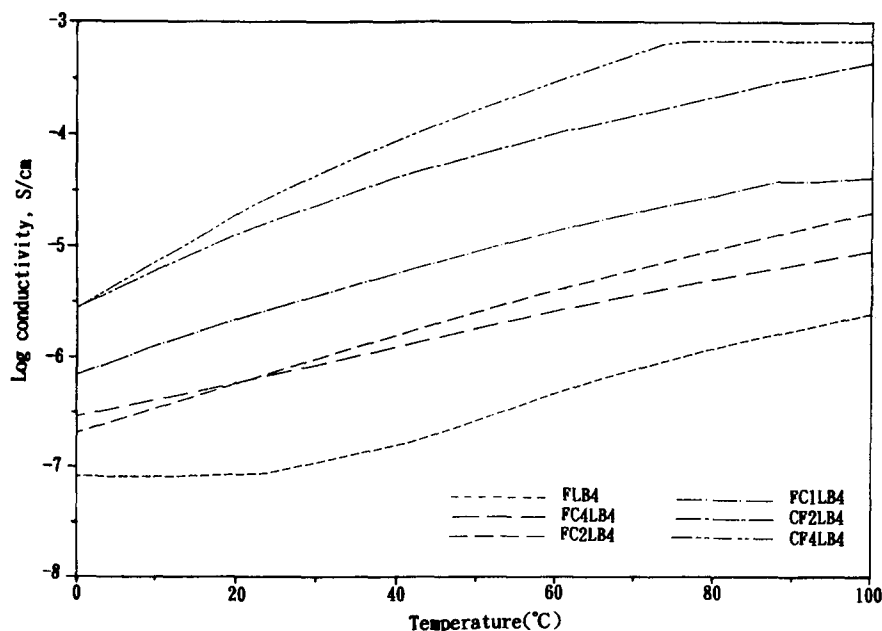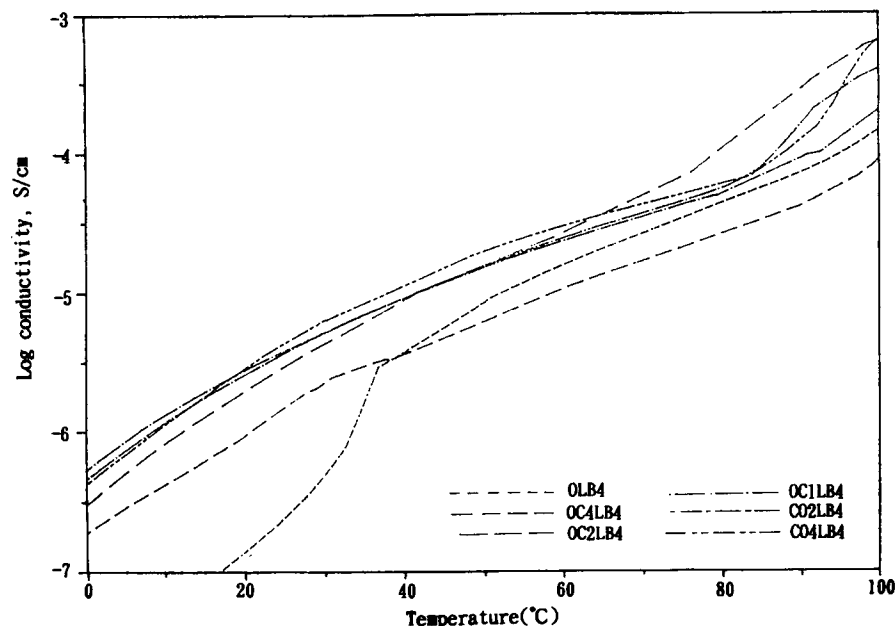
Figure 6   Dynamic ionic conductivity of polymer electrolytes at various ratios of PVDF/
PEC with constant $LiBF_4$ content (LB4).

tration had little effect on the maximum ionic conductivity of the highly plasticized polymer electrolytes with the same salt. The maximum ionic conductivity was salt species-dependent. This result shows that, when the PEC concentration in PVDF-based polymer electrolytes is high enough, the effect of PEC content on ionic conductivity is no longer important, except at low salt concentration. The curves of the room-temperature ionic conductivities vs. the salt content showed a bell-shaped profile. This might be because of an increase in both the carrier number and the matrix rigidity with increasing salt concentration. The increase in the film rigidity might result from the formation of physical

Figure 7   Dynamic ionic conductivity of polymer electrolytes at various ratios of PEO/
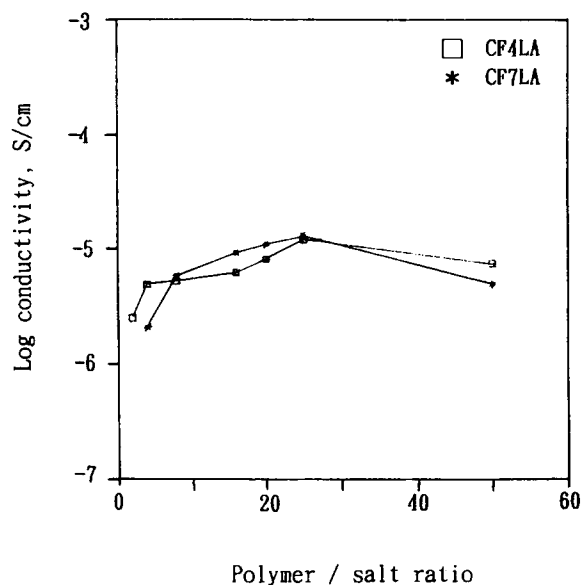PEC with constant $LiBF_4$ content (LB16).

Figure 8 Dynamic ionic conductivity of polymer electrolytes at various ratios of PEO/
PEC with constant LiBF$_4$ content (LB4).

crosslinking between fluorine atoms in PVDF or oxygen atoms in PEC and lithium ions. This rigidity hindered ion movement in the polymer electrolytes and reduced the room-temperature ionic conductivity.

PEC domain since the PEC-salt complex bond is weak in the PVDF-based polymer electrolytes. The chemical structure similarity and the low T_g and low T_m of the crystalline phase made the conductivity of plasticized PEO-based polymer electrolytes less sensitive to the PEC content.

CONCLUSION

The conductivity of the unplasticized PVDF/LB polymer electrolytes is much lower than that of the unplasticized PEO/LB polymer electrolytes. The PEC plasticizer in the polymer electrolytes can change the morphology and the conductivity of the polymer electrolytes. The dependence of room-temperature ionic conductivities of the plasticized PVDF-based polymer electrolytes on the PEC content was much more significant than that of the plasticized PEO-based polymer electrolytes on the PEC content. For PEC content in the plasticized polymer electrolytes higher than 55 mol %, the room-temperature conductivities of the plasticized PVDF/LB films are even higher than those of the corresponding PEO/LB films. At room temperature, the amorphous phase of PVDF-based polymer electrolytes was in the glassy state and that of PEO-based polymer electrolytes was in the rubbery state. In the plasticized PVDF-based polymer electrolytes, the PEC in the polymer electrolytes provided an excellent ion conduction path through the amorphous

Figure 9 Dependence of ionic conductivity at 30°C on LiBF$_3$CO$_2$ salt content at a constant ratio of PVDF/PEC = $\frac{1}{4}$ or $\frac{1}{7}$.
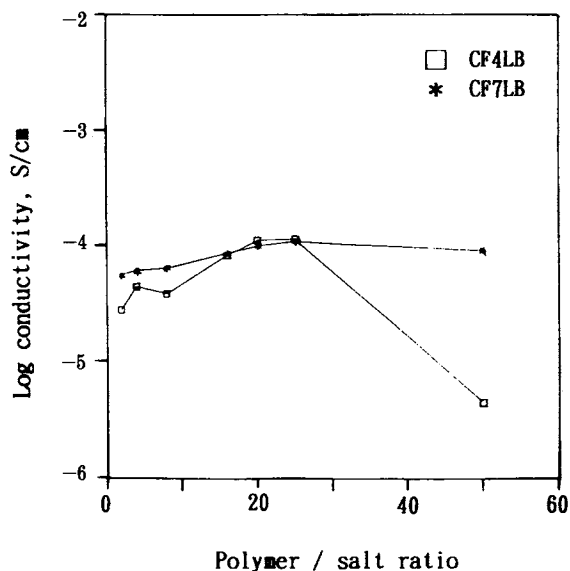
Figure 10 Dependence of ionic conductivity at 30°C on $LiBF_4$ salt content at a constant ratio of PVDF/PEC $= \frac{1}{4}$ or $\frac{1}{7}$.

The dynamic ionic conductivity of the plasticized PVDF-based polymer electrolyte was less temperature-dependent than that of the plasticized PEO-based polymer electrolytes. This was because the PEO-based films have low T_m's (below 100°C) and PVDF-based films have high T_m's, as high as 150°C. The maximum measurement temperature of the dynamic ionic conductivity was 100°C. Therefore, there was no significant phase transition in the plasticized PVDF-based polymer electrolytes. The highly PEC-plasticized PVDF-based polymer electrolytes showed a maximum room-temperature ionic conductivity as the salt increased. It was due to two different effects on the conductivity: an increased number of carrier ions and enhanced polymer chain rigidity with increased salt concentrations. The maximum ionic conductivity of the polymer electrolytes was independent of the PEC content, but was dependent on the anion species of the lithium salt.

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