

비활성 세라믹 분말이 고분자 전해질의 전기적, 기계적 특성에 미치는 영향

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Effect of the Inert Ceramic Powder on the Electrical and Mechanical Properties of the Polymer Electrolytes

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초 록 : 폴리에틸렌 옥사이드(PEO)/리튬 삼불화메탄 술포네이트(LiCF₃SO₃) 착체에 평균 직경 1 μ m인 미세 세라믹 분말(γ -LiAlO₂)을 혼합하여 얻은 복합체 고분자 전해질의 특성을 형태학 및 기계적 성질의 관점에서 고찰하였다. 균일하게 분산된 세라믹 분말은 상온에서 고체 고분자 전해질의 전기적, 기계적 성질을 크게 향상시키는 것으로 관찰되었으며, 그 조성에 따라 그 특성이 변하였다. 본 연구에서 조사된 복합체 고분자 전해질의 경우, 상온에서 최대 이온 전도도를 나타내는 LiAlO₂의 최적 함량은 약 20%인 것으로 나타났다.

Abstract : The characteristics of composite polymer electrolytes obtained by adding a fine ceramic powder(γ -LiAlO₂) with a diameter of 1 μ m to a poly(ethylene oxide)/lithium trifluoromethane sulfonate (LiCF₃SO₃) complex are described in terms of morphological and mechanical behavior. The addition of uniformly dispersed ceramic powder greatly improves the electrical and mechanical properties of solid polymer electrolytes at ambient temperature. For the composite polymer electrolytes under this study, the optimum composition of the γ -LiAlO₂ in the composite for maximum ionic conductivity was found to be 20 wt%.

1. Introduction

An intriguing and potentially technologically useful class of solid polymer electrolytes consisting of alkali salts dissolved in polymer has recently received a great deal of attention^{1,2)}. Much of the effort to date has focused on poly(ethylene oxide)(PEO) as the host. These polymer electrolyte systems, however, exhibit the poor ambient temperature conductivity and mechanical stability. The above problems pose a serious threat to ambient temperature

electrochemical device applications, most notably batteries.

One point of concern in the development of new polymer electrolytes lies in the fact that high conductivity is necessarily associated with an amorphous phase of the polymer complexes²⁾. It is also of importance to improve the mechanical properties of the amorphous polymer electrolytes, since the direct use of the polymers may give rise to those problems commonly met in conventional liquid electrolyte systems, such as leakage and loss of electrode

to electrolyte contacts^{2,3}).

Many systems are based on low molecular weight PEO grafted a high T_g polymer backbone that imparts mechanical stability to the material⁴⁻⁸). Formation of networks by radiation or chemical cross-linking can also greatly improve the mechanical properties, but it may lead to excessive rigidity of the polymer chain with a consequent decay in conductivity^{9,10}).

Alternatively, the physical approach appears more appropriate in this respect. It is well known that the addition of inert filler is a useful tool to increase the electrical and mechanical properties of solid electrolytes^{11,12}). In this paper, we report the characteristics of composite polymer electrolytes prepared by the addition of lithium aluminate(γ -LiAlO₂) to lithium ion conducting polymer complexes. The mechanical and electrical properties of solid polymer electrolytes were proved to be greatly enhanced by addition of an inert ceramic powder. The ionic conductivity behavior of composite polymer electrolyte was discussed in terms of the increased topological disorder introduced by the ceramic powder.

2. Experimental

Materials

PEO with molecular weight 100,000 and LiCF₃SO₃ were supplied by Aldrich Chemical Co. Ltd and the salt was dried at 100°C in a vacuum oven overnight before use. Lithium aluminate(LiAlO₂) was confirmed to have a phase composition of 5% α and 95% γ from X-ray powder diffraction, and their mean particle diameter was found to be about 1 μ m from scanning electron microscope. Appropriate amounts of PEO and LiCF₃SO₃ to give an O:Li ratio 10:1 in the complex were dissolved in acetonitrile, and the solution was stirred for 12 hr at 80°C. A predetermined amount of LiAlO₂ powder was then added and the solution was stirred vigorously. When the complete homogenization of mixture had occurred, the solution was cast on a flat Teflon plate by

allowing slow evaporation of solvent. Residual solvent was removed by heating under vacuum. In our study, we prepared (PEO)₁₀LiCF₃SO₃/LiAlO₂ composite polymer electrolytes having four different LiAlO₂ compositions, namely 0, 10, 20 and 30 wt% of the LiAlO₂. The subscript "10" in (PEO)₁₀ refers to the molar ratio of monomer units to LiCF₃SO₃, i.e., [EO unit]/[LiCF₃SO₃]=10.

Conductivity Measurement

Film of the order of 200 μ m in thickness was sandwiched between the two disk-like stainless steel(12 mm in diameter). A.C impedance measurement was made on the cell with a Hewlett-Packard 4192 LF vector impedance meter over a frequency range of 5 Hz-13MHz. The ionic conductivity(σ) was obtained from the bulk resistance(R_b) found in the complex impedance diagram as shown in Figure 1, i.e.,

$$\sigma = \frac{t}{R_b A}$$

where t is the thickness and A is the surface area of the sample film.

DSC(Differential Scanning Calorimetry)

The DSC studies were carried out to determine the glass transition or melting temperature of the polymer electrolyte using a Du Pont 9900 instrument. Samples were loaded in hermetically-sealed aluminum pans and measurements were taken over a temperature range of -100 to 150°C at a heating rate of 10°C/min. The temperature was calibrated at the melting point of indium metal. The recorded T_g was taken as the inflection point and T_m was given as the peak point of the melting endotherm.

Durometer Hardness

The evaluation of the mechanical stability of composite polymer electrolytes has been carried out by measuring the relative hardness of materials with durometer hardness tester(type A). The test method was based on the penetra-

tion of a specific indenter forced into the material. The indenter was spring loaded and the point of the indenter was produced through the hole in the base. The test specimens were prepared with a diameter of 13 mm and thickness of the order of 10–15mm. The test was carried out by first placing a specimen on a flat surface. The pressure foot of the instrument was pressed onto the specimen and the hardness was read within 1 sec after the pressure foot was in firm contact with the specimen. We made five measurements of hardness at different positions on the specimen at least 3 mm apart and determined the arithmetic mean.

Morphology

A thin film(50–100 μ m thickness) of composite polymer electrolyte was deposited on a microscope slide and the morphology of film was observed by scanning electron microscope. The spherulitic structure was also observed by using the cross polarizing optical microscope at room temperature.

3. Results and Discussion

Figure 2 shows the scanning electron micrographs of the composite polymer electrolytes. It is found that the ceramic powders are uniformly distributed within complex when a LiAlO₂ composition is 10 wt%, but the powder agglomeration is observed in the complex containing 30 wt% of LiAlO₂, that is to say, the composite polymer electrolyte having a high LiAlO₂ content may exhibit a tendency to separate into phase. From this result, it can be said that a low particle content should be maintained to assure a highly distribution of the powder though the polymer matrix.

The DSC results of composite polymer electrolytes are summarized in Table 1, and the example of these DSC thermograms is shown in Figure 3. The enthalpy of melting(ΔH_m) is represented as that per unit weight of PEO and the crystallinity was estimated from the

ratio of the experimentally determined ΔH_m to the value of 203 J/g reported in the literature for the enthalpy of melting of 100% crystalline PEO¹³⁾. The crystallinity is significantly reduced with increasing the LiAlO₂ composition upto 20 wt%, but the crystallinity is slightly increased again at 30 wt% LiAlO₂. If too much LiAlO₂ is added, substantially homogeneous composite do not result as shown in Figure 1, and therefore it can not effectively hinder the crystallization of the polymer chain. The variation in T_g of composite polymer electrolytes is paralleled by a change in crystallinity, as the inert filler is added. The effect of LiAlO₂ content on T_g is striking, because the T_g value of composite decreases with the increase in the amount of the inert ceramic powder in spite of the increase in rigidity. The decline

Table 1. DSC results of the composite polymer electrolytes [(PEO)₁₀LiCF₃SO₃/LiAlO₂]

LiAlO ₂ (wt%)	T _g (°C)	T _m (°C)	ΔH_m (J/g)	crystallinity
0	-33.1	71.7	79.4	0.39
10	-35.9	71.4	43.0	0.21
20	-41.7	70.5	37.1	0.18
30	-37.3	68.1	39.5	0.19

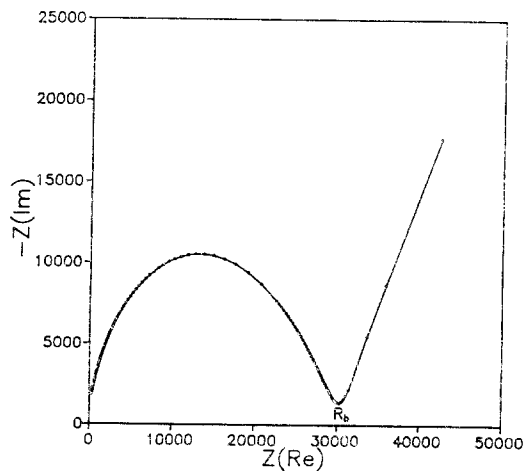
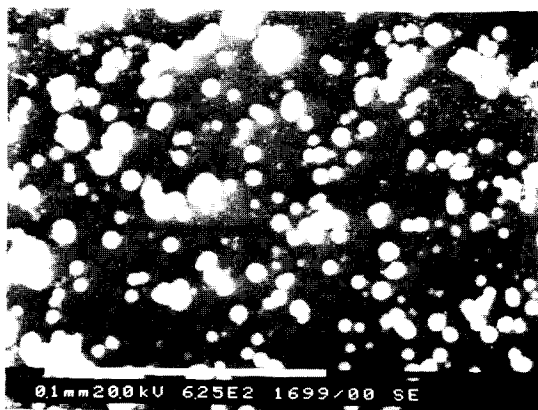
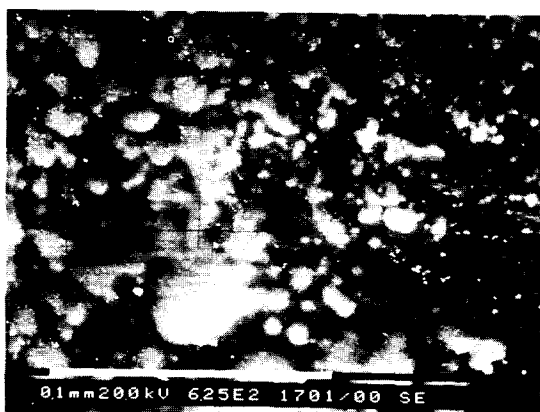


Fig. 1. Complex impedance spectrum of the (PEO)₁₀LiCF₃SO₃/LiAlO₂(20wt%) composite polymer electrolyte at 25°C



(a)



(b)

Fig. 2. Scanning electron micrographs of the $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3/\text{LiAlO}_2$ composite polymer electrolytes (a) 10 wt% LiAlO_2 (b) 30 wt% LiAlO_2

in T_g may be associated with the decrease in crystallinity of composite polymer electrolyte as the LiAlO_2 content is increased. As the LiAlO_2 is added, the amorphous region in the complex is increased, and it results in dilution of salt in the amorphous region of the complex. Therefore reduction in segmental motion due to the interaction between ether oxygen atoms and ions in polymer electrolytes becomes weaker compared to pure $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ complex. The uniformly distributed inert ceramic powder is also thought to be able to effectively hinder the formation of transient

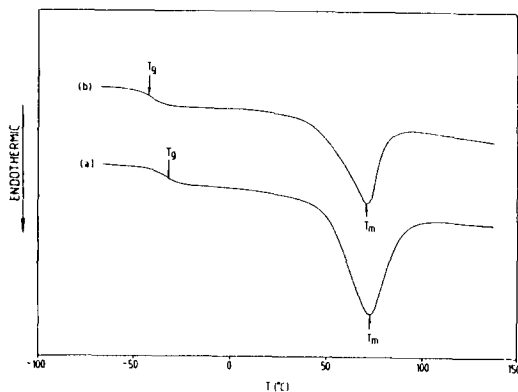


Fig. 3. Profiles of DSC curves of composite polymer electrolyte (a) $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ (b) $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3/\text{LiAlO}_2(20 \text{ wt} \%)$

crosslinking between PEO segments occurred in $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ complex. The slight increase in T_g at 30 wt% LiAlO_2 may be due to the fact that ununiformly dispersed ceramic powder can not effectively increase the amorphous region in complex as is already shown in crystallinity data. These results suggest that the amount of ceramic filler may be critical to reduce the crystallinity of solid polymer electrolytes without reduction of segmental motion, and its composition be about 20 wt% in this study.

The optical micrographs of spherulitic texture of composite polymer electrolyte films are shown in Figure 4. For pure PEO, the spherulites are observed to unciate sporadically and grow radially until they impinge upon each other at straight boundaries as shown in Figure 4-(a). The size of individual spherulite ranges from a $10\mu\text{m}$ to $200\mu\text{m}$ in diameter depending on the LiAlO_2 composition. The uncomplexed PEO film which has no salt and ceramic powder tends to spawn large spherulites due to the high degree of crystallinity. For the $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ complex, the spherulite size is significantly decreased compared to uncomplexed PEO film. This result is due to the fact that the interaction of lithium ion with

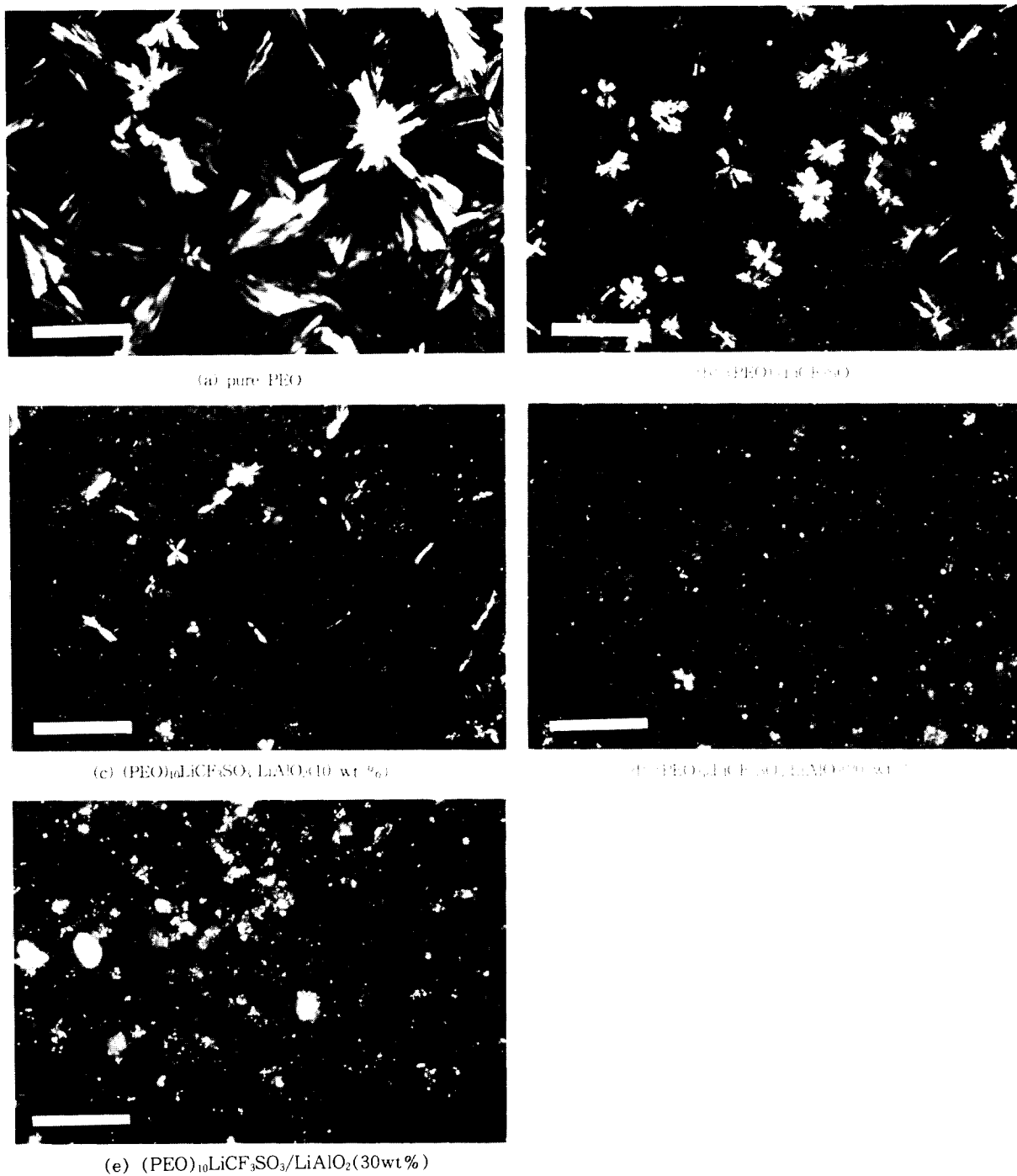


Fig. 4. Optical micrographs of the spherulitic texture viewed between crossed polarizers for the $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3/\text{LiAlO}_2$ composite polymer electrolyte films at various LiAlO_2 compositions(The bar in the lower left indicates $100\mu\text{m}$)

- (a) pure PEO (b) $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ (c) $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3/\text{LiAlO}_2(10 \text{ wt}\%)$
 (d) $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3/\text{LiAlO}_2(20 \text{ wt}\%)$ (e) $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3/\text{LiAlO}_2(30 \text{ wt}\%)$

polar oxygen atoms in the complex suppresses the segmental motion of PEO and this suppression also inhibits the crystallization of PEO segments with the incorporation of LiCF_3SO_3 . When the LiAlO_2 powders are added to the $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ complex, the spherulite size is further reduced. Especially, for the composite electrolyte film of 20 wt% LiAlO_2 , the maltese cross texture can not be observed, since the crystallite size is very small. This phenomenon presumably arises from random distribution of inert ceramic powder which may introduce the topological disorder to the complex. The unclenation density slightly increases at 30 wt% LiAlO_2 composition, which is consistent result with the above DSC analysis on crystallinity. That is to say, a reasonably high concentration of the ceramic powder is necessary to reduce the crystallinity of the polymer host, but the concentration should be remain low enough to prevent phase discontinuities in the composite polymer electrolytes.

The temperature variation of the conductivities for composite polymer electrolytes having a different LiAlO_2 composition is shown in Figure 5. The σ vs temperature profiles of the composite electrolytes except for a complex having 30 wt% LiAlO_2 show a marked improvement in conductivity compared with that of pure $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ at the temperature lower than 70°C , i.e., in the semi-crystalline (amorphous and crystalline) region of the complexes. This result may be due to the fact that the addition of small ceramic powder enhances the degree of amorphicity of the polymer electrolyte as explained in the above DSC and optical microscopy analysis. The effects are considered to arise from the topological disorder introduced the complexes by adding the inert ceramic powder. This result leads to the fact that the number of charge carriers contributing to the ionic conductivity in the amorphous phase increases with LiAlO_2 content at a given salt concentration since the ions are virtually immobilized in the crystalline

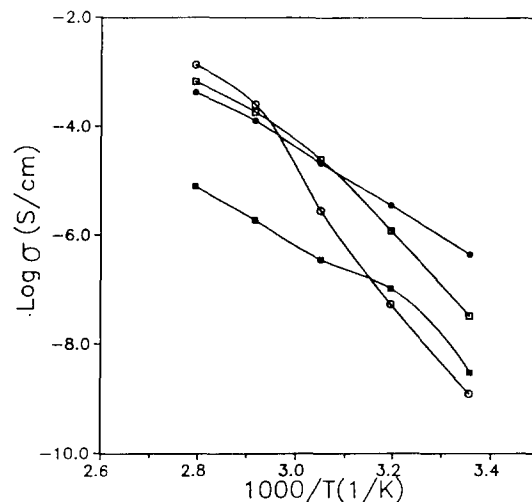


Fig. 5. Temperature dependence of the ionic conductivity for the $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3/\text{LiAlO}_2$ composite polymer electrolytes having the various LiAlO_2 compositions

○ : 0wt%, □ : 10wt%, ● : 20wt%, ■ : 30wt%

phase¹⁴, and therefore the larger concentration of mobile amorphous phase can give rise to the larger conductivity than in pure polymer electrolyte ($\text{PEO}/\text{LiCF}_3\text{SO}_3$). However, the conductivity of the composite electrolytes is not higher than that of the $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ electrolyte in the homogeneous amorphous region of the complex, i.e., the temperature higher than melting point of the complex. This result suggests that the addition of LiAlO_2 powder can not improve the ionic conductivity of the completely amorphous polymer electrolytes due to the increase of the rigidity (or, decrease of the ionic mobility) in the amorphous region.

The influence of the ceramic powder content on the ionic conductivity at a given temperature is shown in Figure 6. It is found that the conductivity passes a maximum at temperature lower than 70°C . These maxima are displaced to a lower LiAlO_2 composition as the temperature is increased. At the temperature lower than 70°C , the LiAlO_2 powder added up to the critical composition for maintaining the random distribution effectively hinders the

crystallization of the polymer chain as explained above, and resulting in a increase of ionic conductivity with LiAlO_2 content up to the critical concentration. The LiAlO_2 concentration for the maximum conductivity is lowered with temperature, as the fraction of crystalline phase is decreased. On the other hand, at higher temperature having completely amorphous structure, the addition of ceramic powder is useless and even negative due to the restriction of ionic motion. In summary, the described results provide conclusive indications that addition of the ceramic powder in the optimum content prevents the crystallization of the polymer electrolyte and the influence of inert ceramic powder on ionic conductivity behavior is weakened as the amorphous region of complex(or temperature) is increased. For the materials under this study, the optimum in composition appears to be 20 wt% LiAlO_2 at room temperature.

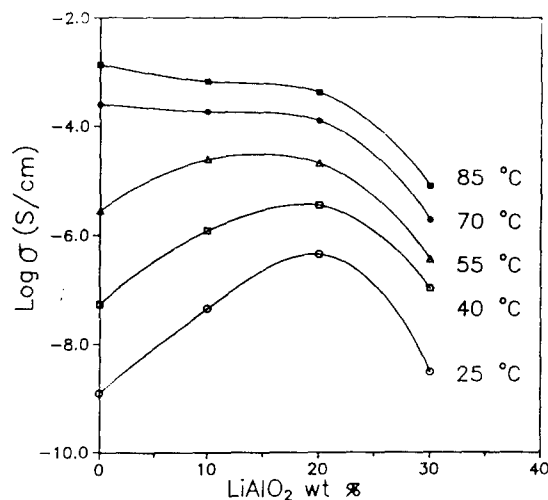


Fig. 6. Isothermal variation of the ionic conductivity with the LiAlO_2 composition for the $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3/\text{LiAlO}_2$ composite polymer electrolytes having the various LiAlO_2 compositions (○ : 25°C, □ : 40°C, △ : 55°C, ● : 70°C, ■ : 85°C)

Table 2 shows the durometer hardness measurements, given as the dimensionless Shore (type A) hardness. The indentation hardness

is known to be related to the rigidity and resistance to deformation. From the data in Table 2, it is clearly seen that the composite polymer electrolytes show a more stable mechanical behavior than the pure complex, and the indentation hardness of composite polymer electrolytes is increased as the content of ceramic powder increases. The strength properties such as tensile modulus, tensile strength and impact resistance are even more dependent on the size and dispersion of the filler particles, and also on the adhesion and interfacial contacts of the two phases than deformational property such as indentation hardness. Therefore the indentation hardness is expected to continuously increase with LiAlO_2 content in spite of non-uniform distribution in composite polymer electrolyte having 30 wt% LiAlO_2 .

Table 2. The results of durometer hardness measurement

LiAlO_2 wt%	Hardness*(type A)
0	64.8
10	74.6
20	80.2
30	82.7

*The hardness values represent the arithmetic mean of five measurements at different positions on the specimen

4. Conclusion

The addition of inert ceramic powder ($\gamma\text{-LiAlO}_2$) having a mean particle size of $1\mu\text{m}$ increased the mechanical stability of the material with greatly enhancing its conductivity at ambient temperature. The enhancement of ionic conductivity is related to the fact that composite polymer electrolyte prepared by adding ceramic powder contains more potential charge carriers (i.e., mobile cations and anions) in amorphous polymer phase than does pure $\text{PEO}/\text{LiCF}_3\text{SO}_3$ system. The increase of amorphicity was considered to arise from the topological disorder introduced into the com-

plexes by adding the ceramic powders. A reasonably high concentration of ceramic fillers is necessary to affect the crystallinity of the complex, however, the concentration should be low enough to prevent phase discontinuities. The optimum in composition is proved to be 20 wt% in terms of the electrical and mechanical properties improvement in our polymer electrolyte systems.

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