Composite Polyether Electrolytes with Lewis Acid Type Additives

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The effects of AlBr$_3$, AlCl$_3$, and α-Al$_2$O$_3$ on the conductivity and ultrastructure of electrolytes based on LiClO$_4$ and polyethers have been studied. The results obtained are analyzed in terms of Lewis acid−base interactions occurring between various chemical moieties within these composite systems. It is shown that aluminum halides form complexes with ClO$_4^-$ anion acting as plasticizing agents for polyether matrixes. However, aluminum halides interact also with polyethers leading to the formation of polyether−aluminum halide complexes, thus stiffening polymeric electrolytes. It is shown that for low additive concentrations the addition of Lewis acid results in a decrease in the degree of crystallinity of poly(ethylene oxide)-based electrolytes; this is followed by an increase in the conductivity. A significant increase in conductivity was obtained at 0 and 25 °C for samples containing up to 25 mass % of aluminum halides or α-Al$_2$O$_3$. For samples containing more than 30 mass % of the additive, the effect of the stiffening of polymer hosts dominates (and is confirmed by the increase in T_g values observed from DSC experiments) and the conductivity decreases.

Introduction

Starting from the late 1970s, polymer solid electrolytes based on polyether matrixes have attracted considerable attention in the scientific community, especially in the fields of polymer chemistry and physics, solid-state electrochemistry, and energy storage technology. This interest arises from the possibility of applications of polymer ionic conductors in energy storage systems, electrochromic windows, and fuel cells or sensors operating from subambient to moderate temperatures.[1] To improve electrolyte efficiency, various methods have been applied to modify the structure and morphology of polyether hosts. These investigations have been directed toward decreasing the crystallinity and increasing the rate of structural relaxation in the polyether while maintaining good, stable mechanical and electrochemical properties over the entire operational temperature range of the electrolyte. One of the most successful approaches has been to prepare composite polyether-based electrolytes, i.e., blends of polyether ([mainly poly(ethylene oxide) (PEO)] with other high molecular weight polar polymers[2,3] or inorganic ceramic additives such as aluminas,[4−6] silica,[7] or zeolites.[8] Composite polyether electrolytes exhibit improved temperature stability in comparison with the pure polyether-based electrolytes.[5,8,9] It has also been demonstrated by Scrosati and co-workers[9,10] that the addition of inorganic fillers such as LiAlO$_2$ or zeolites improves electrochemical stability of the electrolyte and facilitates electrode−electrolyte charge transfer. In such systems ambient and subambient temperature conductivities are enhanced compared to pure polyether-based systems due to the lowering of the polymer host crystallinity.[3,4] Moreover, in some completely amorphous systems based on oxymethylene-linked PEO (OM-PEO) the improvement of conductivity was also observed after

the addition of highly polar polymers such as poly(acrylamide)[11] or poly(*N,N*-dimethylacrylamide).[12] This effect was attributed to the formation of fast ion conducting pathways on the interface between polymer fillers and polyether−alkali metal salt complexes.[6,11,12] The presence of this highly conductive phase is due to the formation of mixed complexes between polyether, alkali metal salts, and functional groups of the polymer type additives. Such interactions lower the transient cross-link density in the highly conductive phase which is confirmed by a decrease in the glass transition temperature (T_g). Therefore, this phase exhibits higher flexibility than pure polyether-alkali metal salt electrolytes. This is contrary to previous results obtained for composite systems with alumina or silica additives in which the stiffening of the polymer host after the addition of the filler was observed.[7]

Despite a common agreement on the decrease of polyether crystallinity and changes in the polyether flexibility caused by the addition of organic or inorganic fillers, little is known about the mechanisms responsible for these changes. In recent papers[6,12−14] it has been proposed that changes in the microstructure and morphology of polyether-based electrolytes are due to the various Lewis acid−Lewis base reactions occurring between Lewis base centers of the polyether (i.e., polyether oxygens), alkali metal cations (hard Lewis acids), and the Lewis (or Brønsted) base or acid centers of the filler such as the carbonyl groups of poly(acrylamide)s or the surface groups of Al$_2$O$_3$. Such an approach has been successfully applied to explain changes in the phase structure and morphology of composite polyether−alkali metal salt systems containing aluminas, silica, or poly(acrylamide)s as additives.[6,12−14]

In this report effects of the addition of strong Lewis acids, like AlCl$_3$ and AlBr$_3$, on the conductivity, structure (crystallinity and flexibility of polyether chains), and morphology of PEO−LiClO$_4$- and OMPEO−LiClO$_4$-based electrolytes is examined. The results obtained are compared to properties of composite polyether-based electrolytes containing α-Al$_2$O$_3$. It is demonstrated that the conductivity of polyether-based systems can be

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enhanced by the addition of Lewis acids or α-Al$_2$O$_3$, which in turn can be related to changes in the microstructure of the polymer host.

Experimental Section

Sample Preparation. PEO (Aldrich, reagent grade, $M_w = 5 \times 10^6$), AlBr$_3$ (Aldrich, reagent grade), and AlCl$_3$ (Aldrich, reagent grade) have been used without further purification and after drying under vacuum ($<10^{-4}$ Torr) at 50−70 °C for 48 h. α-Al$_2$O$_3$ (grain sizes <5 mm) was prepared according to a procedure described elsewhere.[4,6] The synthesis of OMPEO followed that of Nicholas et al.[15] The resulting transparent elastomers were dried under vacuum for 48 h before synthesizing the polymer electrolyte. Acetonitrile (Aldrich, reagent grade) was doubly distilled and stored over type 4 Å molecular sieves. All of the steps in the preparation procedure were performed in an argon-filled drybox (moisture concentration lower than 20 ppm). LiClO$_4$ (Aldrich, reagent grade) was dried under vacuum ($<10^{-4}$ Torr) at 120 °C prior to incorporation. The concentration of LiClO$_4$ was equal to 10 mol % with respect to the ether oxygen concentration. The solid components were mixed in appropriate amounts in a small glass reactor, and then acetonitrile was added to form an approximately 5 mass % suspension with respect to all solid components. The mixture was magnetically stirred until a homogeneous suspension was obtained. Excess acetonitrile was removed by vacuum distillation. The composite electrolytes obtained were dried under vacuum ($<10^{-4}$ Torr) for 48−72 h at 60 °C. The concentration of AlBr$_3$, AlCl$_3$, and α-Al$_2$O$_3$ varied between 5 and 50 mass %.

DSC Studies. DSC data were obtained between −110 and 150 °C using a DuPont TA 2910 scanning calorimeter with a low-temperature measuring head and liquid nitrogen-cooled heating element. Approximately 15 mg samples in aluminum pans were stabilized by slow cooling to −110 °C and then heated at 10 °C/min to 200 °C. An empty aluminum pan was used as a reference.

Conductivity Measurements. Ionic conductivity was determined using the complex impedance method in the temperature range 0−100 °C. The samples were sandwiched between stainless steel blocking electrodes and placed in a temperature-controlled oven. The impedance measurements were carried out on a computer-interfaced HP 4192 impedance analyzer over the frequency range 5−13 MHz. The peak-to-peak voltage in impedance experiments was equal to 1 V. The reproducibility of impedance spectroscopy results was checked by multiple experiments performed at room temperature. All results for samples of the same composition do not differ by more than 10%.

FT-IR Experiments. Infrared absorption spectra were recorded on a computer-interfaced Nicolet FT-IR system 4.4 instrument with a wavenumber resolution of 2 cm^{-1} in the frequency range from 4000 to 400 cm^{-1}. Thin-film electrolyte foils were sandwiched between two NaCl plates and placed in the FT-IR temperature-controlled cell; the accuracy of the temperature was estimated to be ±1 °C.

Gel Permeation Chromatography (GPC) Experiments. GPC was used to determine the molecular weight distribution of the polyethers. Measurements were carried out on a Waters 590 instrument equipped with a Model R-401 DRI detector. The detector was connected to an IBM compatible microcomputer for data acquisition. The system was operated with four PL-gel columns with 100 000, 1000, 500, and with 100 Å pore sizes at 25 °C and with tetrahydrofuran (THF) as the eluent.

TABLE 1: GPC Data for Polyether-AlX$_3$ (X = Cl, Br) Systems

sample	M_w	M_n	M_w/M_n	% soluble phase
OMPEO	4.1×10^4	2.5×10^4	1.66	100
OMPEO−20 mass % AlCl$_3$	2.7×10^3	1.2×10^3	2.18	95
OMPEO−50 mass % AlCl$_3$	5.6×10^2	5.4×10^2	1.03	21
OMPEO−20 mass % AlBr$_3$	4.9×10^3	2.9×10^3	1.68	92
OMPEO−50 mass % AlBr$_3$	8.4×10^2	5.7×10^2	1.49	75
PEO−20 mass % AlCl$_3$	7.3×10^2	4.7×10^2	1.55	2
PEO−50 mass % AlCl$_3$	7.2×10^2	4.2×10^2	1.72	1
PEO−20 mass % AlBr$_3$	4.4×10^2	2.6×10^2	1.70	14
PEO−50 mass % AlBr$_3$	8.1×10^3	4.5×10^3	1.82	40

Polystyrene (Pressure Chemical Co. and Polymer Laboratories) was used as a standard. A universal calibration was used.

Results

PEO−Al$_y$X$_3$ Electrolytes (y = 1, 2; X = O, Br, Cl). *GPC Studies.* Before examining the properties of polymeric electrolytes containing LiClO$_4$ as a dopant salt, some initial studies were carried out using a mixture of aluminum halides (AlCl$_3$, AlBr$_3$) or α-Al$_2$O$_3$ with polyethers (PEO, OMPEO).

To check whether interaction between polyether chains and aluminum halides leads to the degradation or cross-linking of polymer chains, the PEO−Al$_y$X$_3$ samples were extracted with THF and subjected to GPC studies. The results of these measurements are presented in Table 1. In all cases the formation of a THF insoluble fraction was observed after the addition of aluminum halides. As was expected, the presence of a low molecular weight fraction, soluble in THF ($M_w = 5 \times 10^2$ to 1×10^4), has also been detected (see Table 1). In the two PEO−AlCl$_3$ samples the fraction of soluble phase is only 1−2 mass %. The molecular weight of this fraction is $M_n = \sim 4.5 \times 10^2$ and $M_w = \sim 7.0 \times 10^2$. In the PEO systems containing AlBr$_3$ the fraction of soluble phase is higher (14−40 mass %), and its average molecular weight found from chromatographic experiments is between 2.5×10^2 and 4.5×10^3. In the analogous systems based on OMPEO, the fraction of soluble phase is in the range 20−95 mass % and the molecular weight of this fraction is much lower than that for the pure OMPEO (see Table 1). On the basis of GPC results, it can be assumed that the chain scission processes occur in polyether−aluminum halide systems. However, in the PEO-based blends most of the products of such polyether−Lewis acids interactions form high molecular weight aggregates probably of a cross-linked structure.

DSC Studies. Figure 1 presents DSC curves obtained for the PEO−AlBr$_3$ system (10 mass % of AlBr$_3$ (Figure 1b), 50 mass % of AlBr$_3$ (Figure 1c)) and pure PEO (Figure 1a). After the addition of AlBr$_3$ an increase in T_g is observed from −52 °C for the pure PEO to about −30 to −20 °C for the PEO−AlBr$_3$ system, which suggests significant reduction in the chain mobility of PEO. The melting peak of the crystalline PEO phase is smaller for both the PEO−AlBr$_3$ and PEO−AlCl$_3$ systems, and its onset temperature is shifted down compared to the case of pure PEO. In addition, a sharp endothermic peak is observed at 155−160 °C. A similar phase transition is noticed for other systems containing AlBr$_3$ and AlCl$_3$. For these systems an increase in T_g is observed with an increase in the filler concentration; values of T_g level off in the range −20 to −25 °C for systems with the highest filler concentration.

Figure 2 presents changes in the fraction of the crystalline PEO phase (X_c) as a function of the Al$_y$X$_3$ concentration. The fraction of crystalline phase has been calculated as a ratio of
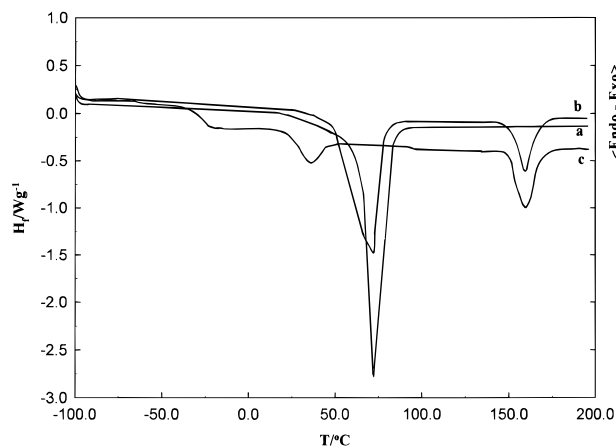
Figure 1. DSC traces obtained for (a) undoped PEO, (b) PEO−AlBr$_3$ system (10 mass % AlBr$_3$), and (c) PEO−AlBr$_3$ system (50 mass % AlBr$_3$).
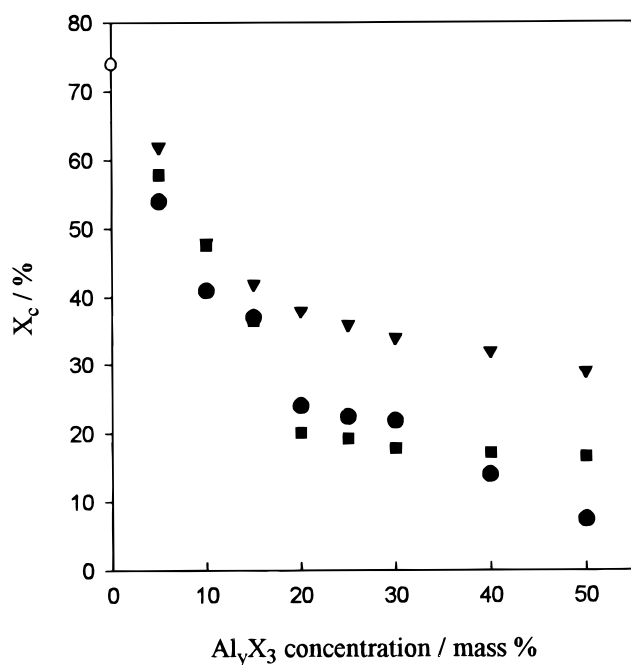

Figure 2. Changes in the X_c versus filler concentration [(▼) α-Al$_2$O$_3$, (■) AlCl$_3$, (●) AlBr$_3$] for PEO blends (without salt). (○) represents X_c for the pure PEO used.

the heat of melting found from DSC results for the PEO−Al$_y$X$_3$ system to the heat of melting of the crystalline PEO phase (213 J/g[16]). For all of the systems studied X_c decreases with an increase in the concentration of the aluminum additive. The most significant change is observed for filler concentrations ≤20 mass %. For higher filler concentration X_c levels off. The fraction of the crystalline PEO phase decreases from 74% for pure PEO to about 30% for systems with more than 20 mass % of α-Al$_2$O$_3$ and to about 10−15% for systems with more than 20 mass % of AlBr$_3$ and AlCl$_3$ additives.

Conductivity Studies. Figure 3 presents temperature dependencies of conductivity obtained for PEO−Al$_y$X$_3$ electrolytes (5, 20, and 50 mass % of Al$_y$X$_3$). For systems containing aluminum halides conductivity increases with an increase in the aluminum halide concentration. An opposite trend is observed for samples containing α-Al$_2$O$_3$ as an additive. For most of the systems studied there is an abrupt change in the conductivity at around 60 °C, which corresponds to the melting point of the crystalline PEO phase. For all of these electrolytes except PEO−AlBr$_3$ (50 mass %) the room temperature (rt) conductivities (measured
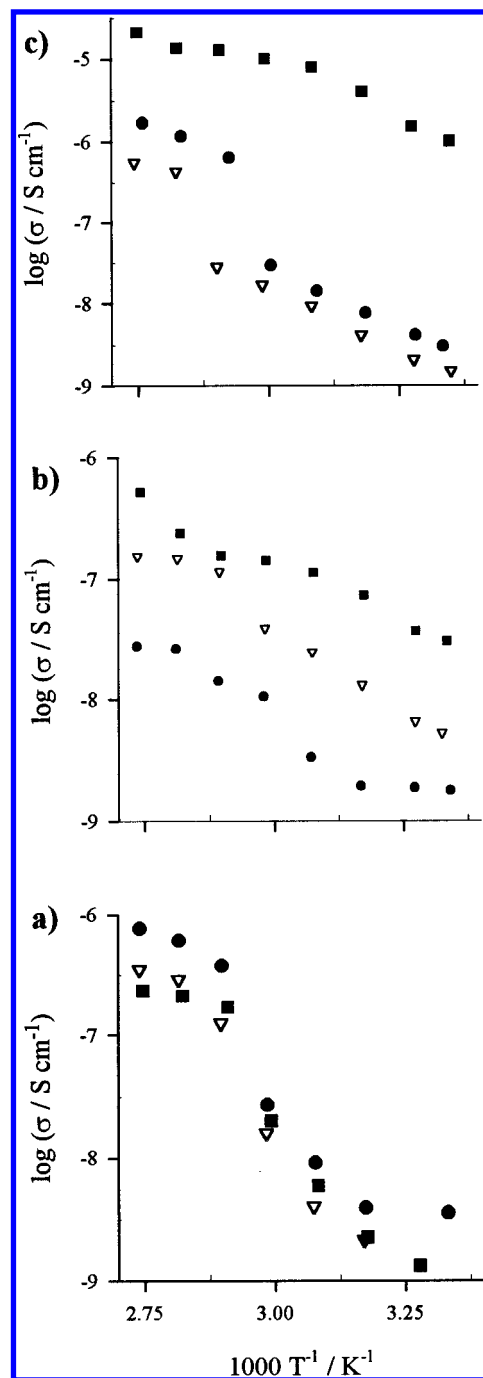

Figure 3. Changes in the conductivity versus reciprocal temperature for PEO−Al$_y$X$_3$ electrolytes: (a) α-Al$_2$O$_3$, (b) AlCl$_3$, and (c) AlBr$_3$. Samples containing (●) 5 mass %, (▽) 20 mass %, and (■) 50 mass % of Al$_y$X$_3$.

at 25 °C) are much lower than that for the (PEO)$_{10}$LiClO$_4$ electrolyte (6 × 10^{-7} S/cm). For the PEO−AlBr$_3$ (50 mass %) system the ambient temperature conductivities exceed 10^{-6} S/cm, and the ionic conductivity increases with temperature up to 10^{-4} S/cm at 100 °C. The latter observation suggests the possibility of the creation of charge carriers in systems with high aluminum halide concentration. For systems with low aluminum halide concentration the contribution of the PEO−Al$_y$X$_3$ component to the bulk conductivity of the composite PEO−LiClO$_4$−Al$_y$X$_3$ electrolytes should be assumed as negligible.

Composite Polyether-Based Electrolytes. *DSC Studies.* The X_c values obtained for composite electrolytes have been calculated in the same way as for pure PEO-based blends

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described in the previous section. Composite electrolytes based on PEO or OMPEO and containing strong Lewis acids (e.g., $AlCl_3$, $AlBr_3$) are amorphous. Also, OMPEO$-$LiClO$_4$ electrolytes with or without α-Al$_2$O$_3$ added are amorphous. X_c values calculated for PEO$-$LiClO$_4-\alpha$-Al$_2$O$_3$ composite electrolytes are lower than for the pristine PEO$-$LiClO$_4$ system. The melting peak of the crystalline PEO phase is shifted to lower temperatures for PEO$-$LiClO$_4-\alpha$-Al$_2$O$_3$ composite electrolytes compared with the PEO$-$LiClO$_4$ electrolyte.

For most of the electrolytes the T_g values varied randomly in the range between -30 and -40 °C with an increase in the additive concentration. For PEO$-$LiClO$_4-\alpha$-Al$_2$O$_3$ electrolytes the T_g values varied in a narrow temperature range (-34 to -38 °C) and are slightly lower than that of the PEO$-$LiClO$_4$ electrolyte (-31 °C). For OMPEO$-$LiClO$_4-\alpha$-Al$_2$O$_3$ electrolytes the T_g values are similar to that of the OMPEO$-$LiClO$_4$ electrolyte (-36 °C). Only for the sample containing 20 mass % of α-Al$_2$O$_3$ T_g is higher (-26 °C). For PEO$-$LiClO$_4-$AlBr$_3$ electrolytes the T_g values are in the range -33 to -39 °C up to 30 mass % of AlBr$_3$ and are slightly shifted to higher temperatures for samples containing 40 and 50 mass %. For OMPEO$-$LiClO$_4-$AlBr$_3$ electrolytes T_g decreases to values between -45 and -55 °C for samples containing up to 25 mass % of AlBr$_3$ and in this concentration range is lower than T_g for the OMPEO$-$LiClO$_4$ electrolyte. For higher AlBr$_3$ concentration T_g increases up to -22 °C for samples containing 40 and 50 mass % of AlBr$_3$. This suggests the formation of cross-linked structures above some critical concentration of a strong Lewis acid, which is not observed in electrolytes containing α-Al$_2$O$_3$. Similar trends as for systems with AlBr$_3$ were found for PEO- or OMPEO-based composite electrolytes with AlCl$_3$ additives. It should be noted that for composite electrolytes containing aluminum halides (up to the aluminum halide concentration $\sim$30 mass %) the T_g values are lower than for PEO$-$Al$_y$X$_3$ systems with an analogous aluminum halide concentration. This observation as well as the lack of the melting peak of the complex phase at $\sim$160 °C suggests that interactions between aluminum halides and polyether are limited in the presence of LiClO$_4$.

FT-IR Studies. FT-IR studies are frequently used to analyze ion$-$ion interactions in polymeric electrolytes.[17$-$19] For these purposes the position and shape of the characteristic anion band are analyzed in more detail. In our case a Galactic Grams 386 software package was used to separate the ν(ClO$_4^-$) mode into two contributions with maxima in the 620$-$624 and 630$-$635 cm^{-1} ranges. Salomon et al.[19] suggest that the ν(ClO$_4^-$) band centered at 623 cm^{-1} can be attributed to spectroscopically free ClO$_4^-$ anions whereas the band centered between 630 and 635 cm^{-1} is associated with the presence of contact-ion pairs. The bands associated with "free" anions and contact-ion pairs have been fitted from the raw FT-IR data. The fraction of "free" anions and contact-ion pairs has been calculated as the ratio of the area under the peaks attributed respectively to "free" anions and contact-ion pairs to the total area for the ν(ClO$_4^-$) vibrations. All band areas were normalized to the CH$_2$ stretch of polyethers. Figure 4 is an example of a fit of a Gaussian$-$Lorentzian peak to the experimental FT-IR data in the ν(ClO$_4^-$) region. As can be seen, the peak characteristic for "free" anions is much larger than that representing contact-ion pairs. In Table 2 the fraction of "free" anions calculated on the basis of FT-IR data is presented for various composite systems. For composite electrolytes containing α-Al$_2$O$_3$ the fraction of "free anions" is higher than 80%, which is higher than that for polyether$-$LiClO$_4$ electrolytes for which the fraction of "free" anions is equal to
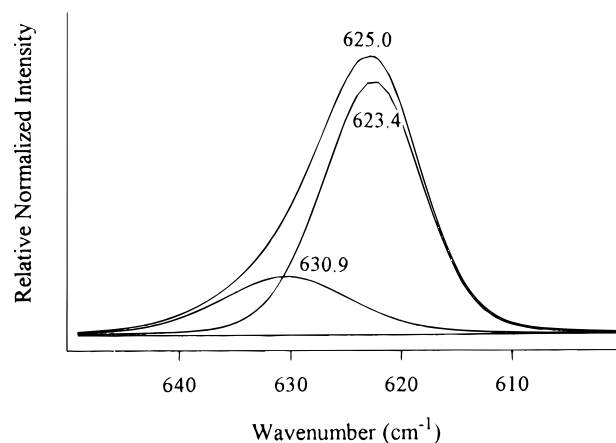

Figure 4. Peak fitting for the ν(ClO$_4^-$) FT-IR region for the OMPEO$-$LiClO$_4-$Al$_2$O$_3$ (5 mass %) sample at 25 °C.

TABLE 2: Fraction of "Free" Anions Calculated on the Basis of FT-IR Results for Various Composite Electrolytes

additive concn (mass %)	OMPEO-based composite electrolytes			PEO-based composite electrolytes		
	Al$_2$O$_3$	AlCl$_3$	AlBr$_3$	Al$_2$O$_3$	AlCl$_3$	AlBr$_3$
5	0.82	~1	0.96	0.95	~1	0.95
10	0.82	~1	~1	0.99	~1	0.9
15	0.97	~1	~1	0.96	~1	0.96
20	0.90	~1[a]	~1[a]	0.97	~1[a]	0.89[a]
25	0.89	~1[a]	0.89[a]	0.91	~1[a]	~1[a]
30	0.87	~1[a]	~1[a]	0.91	~1[a]	~1[a]
40	0.86	~1[a]	0.89[a]	0.89	~1[a]	0.86[a]
50	0.82	~1[a]	~1[a]	0.88	~1[a]	~1[a]

[a] For these samples broadening of the ν(ClO$_4^-$) peak was observed.

TABLE 3: Position of the Maximum of C$-$O$-$C Stretching Band (in cm^{-1}) for Various Polyether-Based Composite Electrolytes

additive concn (mass %)	OMPEO-based composite electrolytes			PEO-based composite electrolytes		
	Al$_2$O$_3$	AlCl$_3$	AlBr$_3$	Al$_2$O$_3$	AlCl$_3$	AlBr$_3$
5	1091	1095	1094	1092	1096	1094
10	1095	1097	1095	1093	1093	1093
15	1092	1092	1096	1095	1093	1093
20	1092	1096	1095	1093	1094	1094
25	1092	1101	1094	1090	1091	1097
30	1091	1098	1092	1091	1095	1090
40	1096	1096	1085	1092	1092	1094
50	1095	1094	1081	1092	1097	1094

about 70%.[12] In IR spectra obtained for electrolytes with AlBr$_3$ and AlCl$_3$ additives the band characteristic for contact-ion pairs is not observed. It should be noted that for high Lewis acid additives concentration a broadening of the "free anion" peak centered at $\sim$623 cm^{-1} was observed.

Table 3 summarizes the positions of the maximum of C$-$O$-$C stretching band for various composite electrolytes as a function of the concentration of each additive. For most of the electrolytes studied the position of the C$-$O$-$C stretching maxima found for composite electrolytes remains in the range 1090$-$1100 cm^{-1} for the entire additive concentration range. This is close to the position of the maximum, 1095 cm^{-1}, of the C$-$O$-$C stretching band for an amorphous polyether$-$LiClO$_4$ system (10 mol % of LiClO$_4$).[11] The only exception is the OMPEO$-$LiClO$_4-$AlBr$_3$ system for which the maximum in the C$-$O$-$C band shifts to lower frequencies for samples containing more than 30 mass % of AlBr$_3$.

Conductivity Studies. a. Composite Electrolytes with AlCl$_3$ Additives. In Figure 5 conductivity isotherms (at 0, 25, and
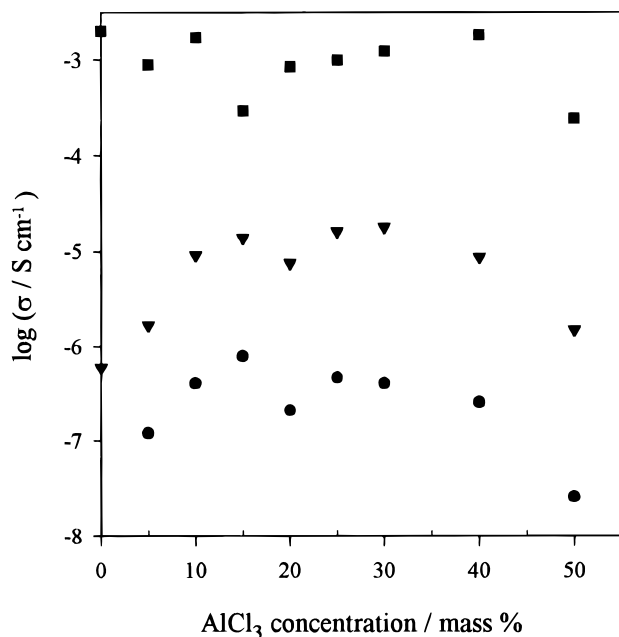
Figure 5. Isotherms of ionic conductivity of PEO−LiClO₄−AlCl₃ versus AlCl₃ concentration with 10 mol % of LiClO₄: (●) 0, (▼) 25, and (■) 100 °C.
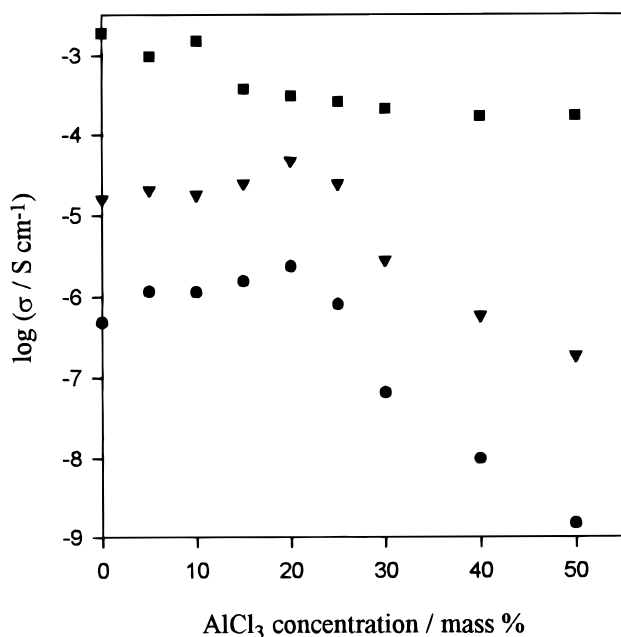

Figure 7. Isotherms of ionic conductivity of PEO−LiClO₄−AlBr₃ versus AlBr₃ concentration with 10 mol % of LiClO₄: (●) 0 and (▼) 25 °C.

Figure 6. Isotherms of ionic conductivity of OMPEO−LiClO₄−AlCl₃ versus AlCl₃ concentration with 10 mol % of LiClO₄: (●) 0, (▼) 25, and (■) 100 °C.

100 °C) are shown for PEO−LiClO₄−AlCl₃ composite electrolytes. At 0 and 25 °C conductivity significantly increases after the addition of up to 40 mass % of AlCl₃ with a maximum for the samples containing 15 mass % of AlCl₃. At 100 °C the conductivities measured for composite systems of various AlCl₃ concentration are similar to the conductivity of the PEO−LiClO₄ electrolyte. In comparison with other composite systems a significant (order of magnitude) decrease in conductivity was found for the samples containing 50 mass % of AlCl₃.

In Figure 6 analogous conductivity isotherms obtained at 0, 25, and 100 °C for OMPEO−LiClO₄−AlCl₃ composite electrolytes are presented. In this system an increase in the conductivity was observed for samples containing up to 20 mass % of AlCl₃. This is followed by a continuous decrease in
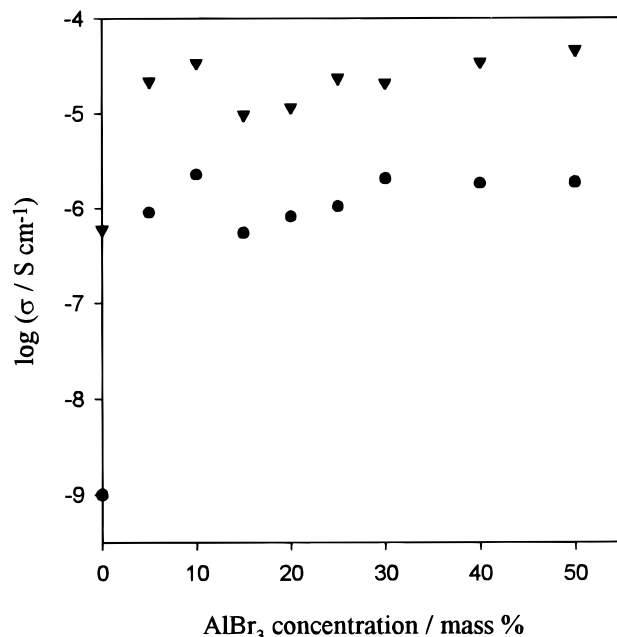
conductivity for samples of higher AlCl₃ concentration. The highest conductivities correspond to the lowest T_g value found from DSC experiments, whereas the decrease in conductivity is associated with an increase in T_g. At 100 °C the conductivity of the OMPEO−LiClO₄ electrolyte is higher than those measured for samples with the AlCl₃ additive.

b. Composite Electrolytes with AlBr₃ Additives. In Figure 7 conductivity isotherms obtained at 0 and 25 °C for composite PEO−LiClO₄−AlBr₃ electrolytes are presented. Similar to Figures 5 and 6, an increase in conductivity is observed for these composite systems relative to the (PEO)₁₀LiClO₄ electrolyte. An initial increase in conductivity with maximum at 10 mass % of AlBr₃ is followed by a small decrease for the sample with 15 mass % of AlBr₃. For higher AlBr₃ concentration the conductivity increases.

In Figure 8 conductivity isotherms at 0 and 25 °C are shown for OMPEO−LiClO₄−AlBr₃ electrolytes. Conductivity increases with an increase in AlBr₃ concentration, reaching a maximum for the sample with 25 mass % of AlBr₃, and then decreases for electrolytes of higher AlBr₃ concentration. For the electrolyte containing 50 mass % of AlBr₃ the conductivities are lower than that for the basic OMPEO−LiClO₄ electrolyte. The decrease in conductivity observed for samples containing more than 25 mass % of AlBr₃ corresponds to an increase in T_g and shifting down of the maximum of the C−O−C band (see Table 3).

Most of the samples containing AlBr₃ was unstable at around 100 °C, and therefore the conductivities measured at this temperature range were not reproducible.

c. Composite Electrolytes with α-Al₂O₃ Additives. Figure 9 shows the conductivity isotherms obtained at 0, 25, and 100 °C for composite PEO−LiClO₄−α-Al₂O₃ electrolytes. At 0 and 25 °C the conductivities measured for composite electrolytes are higher than that for the (PEO)₁₀LiClO₄ electrolyte, whereas at 100 °C the addition of α-Al₂O₃ results in a decrease in the conductivity of the (PEO)₁₀LiClO₄ electrolyte. At all temperatures the conductivities measured for composite electrolytes are similar, with two small maxima for samples containing 15 and 30 mass % of α-Al₂O₃ observed at 0 and 25 °C. Note that
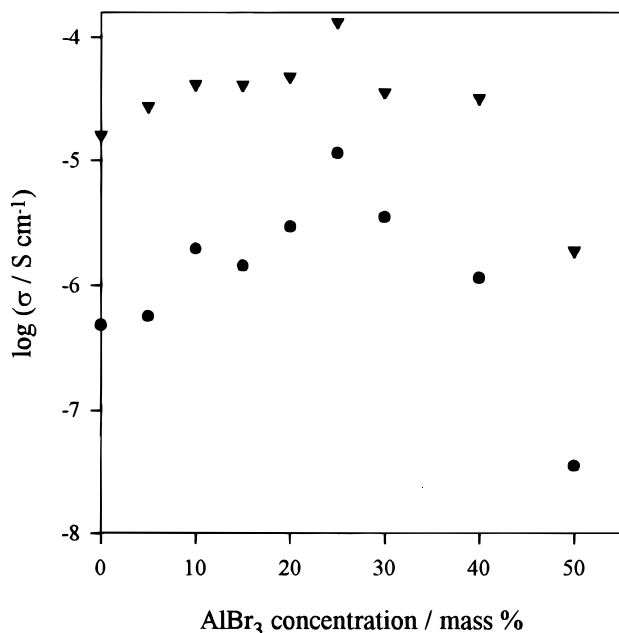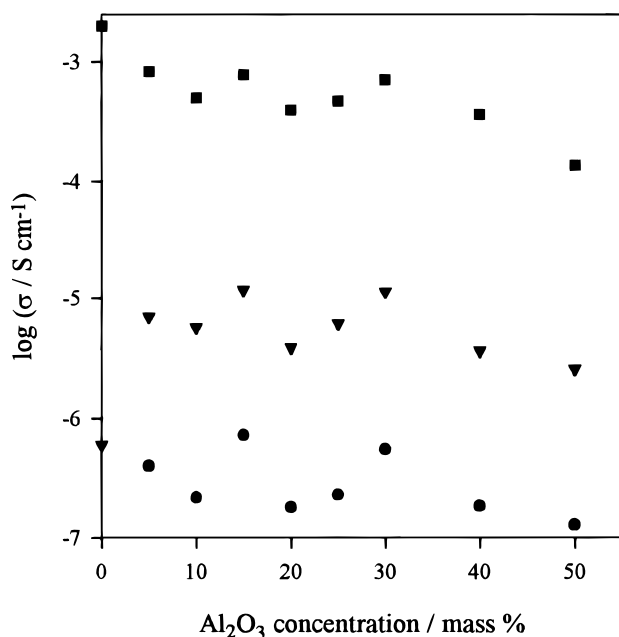
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Figure 8. Isotherms of ionic conductivity of OMPEO−LiClO$_4$−AlBr$_3$ versus AlBr$_3$ concentration with 10 mol % of LiClO$_4$: (●) 0 and (▼) 25 °C.

Figure 10. Isotherms of ionic conductivity of OMPEO−LiClO$_4$−Al$_2$O$_3$ versus Al$_2$O$_3$ concentration with 10 mol % of LiClO$_4$: (●) 0, (▼) 25, and (■) 100 °C.

Discussion

Acid−Base Interactions. As has been pointed out in the Introduction, a number of the chemical moieties of the composite polyether electrolyte are of either a Lewis acid or a Lewis base character.[20] PEO, OMPEO, and ClO$_4^-$, anions are Lewis bases since they have lone electron pairs on the ether oxygens. AlCl$_3$ and AlBr$_3$ are known as strong Lewis acids. In the case of the α-Al$_2$O$_3$ surface, Al Lewis acid centers and surface Lewis base oxygen centers coexist.[20] Since the Li$^+$ cation is a hard acid,[20] there is a possibility of various acid−base interactions in these composite systems. The final ultrastructure and hence the conductivity of composite polyether based systems are a result of an equilibrium between various Lewis acid−base reactions.

DSC studies of PEO−Al$_y$X$_3$ blends have shown that aluminum halides are capable of the formation of crystalline complexes with pure PEO whose melting point is in the range 155−160 °C (see Figure 1). The formation of these complexes hinders the flexibility of polyether chains, resulting in an increase in T_g as well as a reduction in X_c. DSC and GPC studies showed that interactions between polyethers and aluminum halides result not only in the degradation of polyether chains (see Table 1) but also in the formation of highly cross-linked structures (see Table 1 and DSC data). The degradation reaction of polyethers influenced by the presence of strong Lewis acids occurs according to reaction 1.[21]

Figure 9. Isotherms of ionic conductivity of PEO−LiClO$_4$−Al$_2$O$_3$ versus Al$_2$O$_3$ concentration with 10 mol % of LiClO$_4$: (●) 0, (▼) 25, and (■) 100 °C.

these conductivity maxima are observed for samples of the lowest degree of the PEO crystallinity. In Figure 10 conductivity isotherms obtained at 0, 25, and 100 °C for OMPEO− LiClO$_4$−α-Al$_2$O$_3$ electrolytes are presented. For OMPEO-based electrolytes the addition of α-Al$_2$O$_3$ has rather a minor effect on the conductivity. An increase in conductivity relative to the OMPEO−LiClO$_4$ electrolyte is noticed for some of the composite electrolytes only at 0 °C. The shape of the conductivity isotherms at 0 and 25 °C is qualitatively the same as previously described for PEO−LiClO$_4$−α-Al$_2$O$_3$ composite electrolytes (see Figure 9). The conductivity maxima occur at 10 and 25 mass % of α-Al$_2$O$_3$. This corresponds to the samples with the lowest T_g.
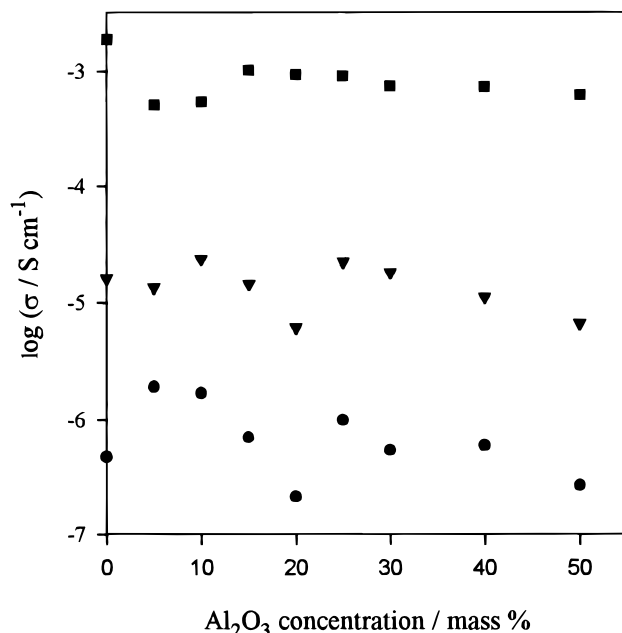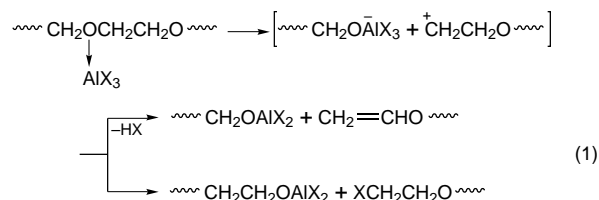
The formation of cross-linked structures might result from the association of dichloroaluminum alcoholates as well as the reaction between carbocations and unsaturated ethers formed according to reaction 1. The hydrogen chloride or hydrogen bromide generated in the latter reactions reacts with aluminum

halides (according to reaction 2) leading to the formation of charge carriers.

$$HX + AlX_3 \rightarrow H^+ + AlX_4^- \qquad (2)$$
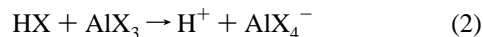
This reaction seems to be particularly important for systems containing high AlBr$_3$ concentration for which ambient conductivities higher than 10^{-6} S/cm have been measured.

The generation of additional charge carriers is not observed in the composite electrolytes with α-Al$_2$O$_3$ additive. Since α-Al$_2$O$_3$ is a weaker Lewis acid than aluminum halides, its interaction with PEO leads neither to the formation of cross-linked structures nor to the degradation of polyether chains. These weaker interactions are manifested by the lack of crystalline complex phases in the PEO−α-Al$_2$O$_3$ blends (DSC results) as well as by the constant T_g values obtained for these systems as a function of the additive concentration.

It appears that in the heterogeneous PEO−α-Al$_2$O$_3$ blends α-Al$_2$O$_3$ molecules can act as nucleation centers for the crystalline PEO. Since there are a large number of these centers, the crystallization process proceeds faster due to a higher nucleation rate, and as a consequence polycrystalline microphases are formed, resulting in greater disorder in the new solid. As can be seen from Figure 2, the fraction of the PEO crystalline phase is lower for systems containing strong Lewis acids (AlBr$_3$, AlCl$_3$) than for the amphoteric α-Al$_2$O$_3$. After the initial drop the X_c levels off for higher additive concentration.

After the addition of LiClO$_4$ aluminum halides start to act as plasticization agents in composite polymeric electrolytes. From DSC measurements for up to ∼25 mass % of aluminum halide the T_g values measured for polyether-based composite electrolytes are lower than for PEO−LiClO$_4$ as well as for PEO−Al$_y$X$_3$ systems. It should be emphasized that all composite electrolytes containing aluminum halides are amorphous. It is suggested that the plasticization effect of aluminum halides is a result of reaction 3:

$$ClO_4^- + Li^+ + AlX_3 \rightarrow O_3ClOAlX_3^- + Li^+ \qquad (3)$$
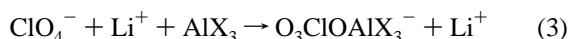
The possibility of this reaction is confirmed by FT-IR data showing a change in the shape of the $\nu(ClO_4^-)$ band upon the addition of aluminum halide to composite electrolytes. A broadening of this peak connected with a shift of the peak maximum to higher wavenumbers is observed. The peak, however, could not be resolved into two parts corresponding to "free anions" and contact-ion pairs. It is well-known that large anions such as N(CF$_3$SO$_2$)$_2^-$ often act as plasticizers for polyether electrolytes,[1,2] leading to an increase in the ambient temperature conductivity and decrease in the fraction of the polyether crystalline phase.

Conducting Properties. Composite electrolytes containing up to 25 mass % of aluminum halides exhibit ambient and subambient temperature conductivities higher than the PEO−LiClO$_4$ electrolyte. This enhancement in conductivity is more pronounced for samples based on PEO. In these electrolytes an increase in conductivity results from both a decrease in X_c and a decrease in T_g, whereas for amorphous OMPEO-based electrolytes only the latter effect is important. For aluminum halide concentration higher than 25 mass % a stiffening of the polyether chains is observed due to the formation of complexes between aluminum halides and polyethers; cross-linked structures result and the ionic conductivity decreases. The decrease in conductivity is more pronounced for OMPEO-based electrolytes. An exception is the PEO−LiClO$_4$−AlBr$_3$ system for which the formation of additional charge carriers (reaction 2)

has a greater effect than the reduction in the mobility of polyether chains (Figure 7). The degradation processes mentioned in the previous section are much faster at higher temperatures where the reproducibility of the conductivity data is lower (Figures 7 and 8).

The degradation phenomena are not observed for composite systems containing α-Al$_2$O$_3$ which are mechanically and thermally stable up to 100 °C. Also, a different composition dependence for conductivity has been observed for composite systems containing α-Al$_2$O$_3$. An initial increase in conductivity is followed by a decrease for the α-Al$_2$O$_3$ concentration range 10−20 mass %; a further increase in conductivity is followed by a gradual decrease for α-Al$_2$O$_3$ concentration higher than 30 mass %. Two conductivity maxima are observed for both the OMPEO- and PEO-based systems. We attribute such behavior to the amphoteric character of α-Al$_2$O$_3$. For low α-Al$_2$O$_3$ concentration α-Al$_2$O$_3$ acts as a Lewis acid lowering the fraction of the PEO crystalline phase (Figure 2). For α-Al$_2$O$_3$ concentration above 10 mass % there is no further change in the X_c (Figure 2). The first conductivity maximum measured for the PEO−α-Al$_2$O$_3$−LiClO$_4$ system appears at the α-Al$_2$O$_3$ concentration for which the plateau on the X_c versus mass fraction of α-Al$_2$O$_3$ is reached (compare Figure 2 with Figure 9). For the α-Al$_2$O$_3$ concentration higher than 30 mass %, a small increase in the fraction of the pure crystalline PEO phase and a decrease in T_g for the PEO−LiClO$_4$−α-Al$_2$O$_3$ electrolytes were noticed. This effect as well as the presence of the second conductivity maximum can probably be explained by an increase in the anion mobility since cations are bonded to both the polyether and base centers of α-Al$_2$O$_3$. Similar trends in the compositional dependence of conductivity are observed for the OMPEO−LiClO$_4$−α-Al$_2$O$_3$ electrolytes.

Despite significant differences in acid−base interactions, the effect of the strong Lewis acids (AlCl$_3$, AlBr$_3$) and α-Al$_2$O$_3$ in changing the conductivity of polyether based electrolytes is similar. The addition of small amounts of these compounds (15−20 mass %) results in a significant increase in conductivity at about 0 °C. In the case of amorphous OMPEO−LiClO$_4$ electrolytes this increase does not exceed an order of magnitude (with the conductivity maximum of ∼5 × 10^{-6} S/cm). In the case of PEO-based electrolytes an increase in conductivity of about 2−3 orders of magnitude is observed which most probably results from a decrease in X_c. At 25 °C the addition of aluminum compounds has a much smaller effect on the conductivity of polyether-based electrolytes, and at ∼100 °C these additives result in a decrease in the conductivity of polyether-based electrolytes.

Note that 0 °C is around 1.2−1.3 T_g for the composite electrolytes studied. (T_g values cover the range from 220 to 240 K.) According to the mode coupling theory in this temperature range changes in the diffusion mechanism are to be expected. Below 1.3−1.2T_g the segmental motions of polymer chains start to freeze, and therefore any differences in the flexibility of various polymer matrixes used are not evident in the ionic conductivity.[22] Movements of ions are primarily due to the thermally activated hopping and cations are the dominant mobile species.[22] In our composite electrolytes the addition of both aluminum halides and α-Al$_2$O$_3$ should result in an increase in the concentration of mobile Li$^+$ cations as well as in the concentration of sites available for cations. At temperatures higher than 1.3T_g, transport of ions is connected with the segmental motions of polymer chains and ionic transport is predominantly due to ClO$_4^-$ anions.[22,23] At these temperatures the addition of a strong Lewis acid results in an
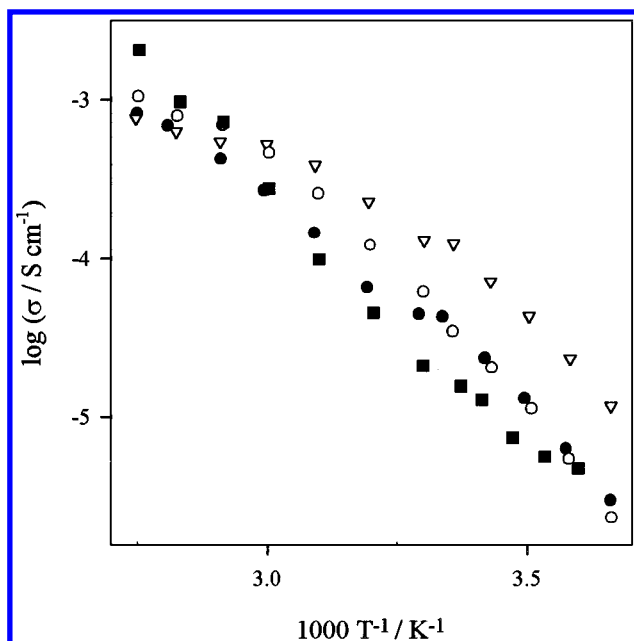
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Figure 11. Comparison of the temperature dependence of conductivity for: (●) (PEO)$_{10}$LiClO$_4$ electrolytes (M_w of PEO equal to 1000), (○) (PEO)$_{10}$LiClO$_4$−AlBr$_3$ (10 mass %), (▽) (OMPEO)$_{10}$LiClO$_4$−AlBr$_3$ (25 mass %), and (■) model Lewis acid type electrolyte.

increase in the fraction of free anions (Table 2) which act as plasticizing agents for the polyether host. On the other hand, the complexation of anions by Lewis acids should lower the anion mobility and thus the bulk conductivity of the electrolyte. The last effect seems to be more important at elevated temperatures.

For composite electrolytes containing AlCl$_3$ a maximum in conductivity is observed for equimolar concentrations of AlCl$_3$ and LiClO$_4$. A further increase in the AlCl$_3$ concentration leads to a reaction between aluminum halide and the polyether which results in stiffening of the polyether matrix and lowering of the conductivity. In the case of systems with AlBr$_3$ additives such an effect is not easy to observed since, as was shown in the previous section, interactions between polyether and AlBr$_3$ lead to the creation of additional charge carriers.

One can argue that the increase in conductivity observed in composite electrolytes containing aluminum halides can also be due to the degradation of the polyether host in the presence of strong Lewis acids. However, in PEO-based composite electrolytes the fraction of the low molecular weight phase is low (Table 1), and its effect on the conductivity of composite electrolytes should be mainly due to its plasticizing effect. Conductivities for composite polyether electrolytes with AlBr$_3$ or AlCl$_3$ additives should still be lower than that for low molecular weight polyethers doped with LiClO$_4$. In Figure 11 a comparison is made between the temperature dependence of conductivity for the (PEO)$_{10}$LiClO$_4$ electrolyte ($M_w = 1 \times 10^3$), the PEO−LiClO$_4$−10 mass % of AlBr$_3$ electrolyte (~15 mass % of low molecular weight fraction, $M_w \sim 1 \times 10^3$), and the OMPEO−LiClO$_4$−25 mass % of AlBr$_3$ electrolyte (~90 mass % of low molecular weight fraction, $M_w \sim 4 \times 10^3$). Up to 70 °C the conductivities of the OMPEO−LiClO$_4$−AlBr$_3$ system are higher than for the low molecular weight (PEO)$_{10}$LiClO$_4$ electrolyte. The PEO−LiClO$_4$−AlBr$_3$ system exhibits higher conductivities than the low molecular weight (PEO)$_{10}$LiClO$_4$ electrolyte at temperatures higher than 30 °C. At lower temperatures the conductivities of both systems are comparable. On the basis of the above results, it can be concluded that the plasticizing effect of the low molecular weight polyether is not

the only reason for changes in the conductivity of composite polyether electrolytes. Also, the contribution of these components to the bulk conductivity of composite PEO−LiClO$_4$−Al$_y$X$_3$ electrolytes cannot explain the enhancement of conductivity; this is due to low conductivities measured for most of the PEO−Al$_y$X$_3$ electrolytes (Figure 3).

It should also be emphasized that alkoxy aluminum compounds which can be formed as a result of chain degradation reactions do not enhance the conductivity of the PEO-based electrolytes. As an example, the temperature dependence of the conductivity measured for the composite PEO electrolyte containing 25 mass % of the alkyl aluminum compound − [CH$_3$(OCH$_2$CH$_2$)$_3$O−AlCl$_2$]$_n$ is shown in Figure 11. The alkylaluminum compound was obtained according to reaction 4.

$$n\mathrm{C_2H_5AlCl_2} + n\mathrm{CH_3(OCH_2CH_2)_3OH} \rightarrow$$
$$n\mathrm{C_2H_6} + [\mathrm{CH_3(OCH_2CH_2)_3OAlCl_2}]_n \ \ (4)$$
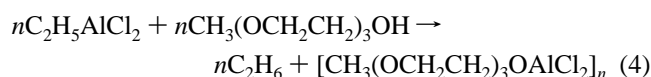
As can be seen from Figure 11, the ionic conductivities measured for composite electrolytes containing this alkylaluminum compound are 2−3 times lower than for other systems, at temperatures below 60 °C.

Conclusions

It has been shown that the conductivity of polyether-based solid electrolytes can be modified by the addition of various Lewis acids. Aluminum halides (AlCl$_3$, AlBr$_3$) interact with ClO$_4^-$ anions leading to the formation of complex anions acting as plasticizers for polyether hosts. Such an effect was not observed for samples with α-Al$_2$O$_3$ additives. The Lewis acids are capable of the formation of complexes with polyether hosts which leads to a decrease in the flexibility of polyether chains manifested by an increase in T_g. These interactions lead to either the degradation of polyether chains or the formation of cross-linked structures as observed on the basis of GPC and DSC experiments. An enhancement in ambient and subambient temperature conductivity for samples with low Lewis acids or α-Al$_2$O$_3$ concentrations is observed. However strong interactions between polyether Lewis base centers and acid type additives result in an increase in the T_g and a subsequent lowering of the conductivity for composite electrolytes of high AlBr$_3$ or AlCl$_3$ concentration. At 100 °C the addition of aluminum compounds leads to a decrease in the conductivity of polyether−LiClO$_4$ electrolytes. No degradation or cross-linking reactions are observed for composite systems containing α-Al$_2$O$_3$ for which an increase in ambient and subambient temperature conductivities compared to the polyether−LiClO$_4$ electrolytes is also observed.

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