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INTRODUCTION

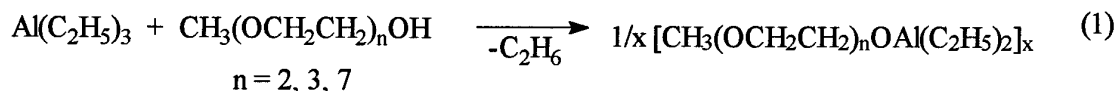
The formation of composites with different ceramic materials is one of the simplest method of improving the mechanical properties of solid polymeric electrolytes based on poly(ethylene oxide) (PEO) complexes. In some systems the addition of a ceramic substance also leads to an increase in the ambient temperature conductivity of electrolytes and stability of lithium electrode/polymer electrolyte interface. It was speculated that some inorganic substances like γ -LiAlO₂, zeolites, nanosize Al₂O₃ or glass powder of B₂O₃/Li₂O/Li₂SO₄ [1-4] react with moisture and other impurities yielding products inactive toward electrodes. The preliminary results presented by Scrosati et al. [5] permit to suggest that this mode of protecting the lithium electrode surface may be also effective in gel electrolytes of high ambient temperature conductivity.

The use of ceramic particles as components of electrolytes is connected, however, with some problems resulting from the homogeneous distribution of heterogeneous materials in the polymeric matrix, stiffening of the matrix, and also the presence of OH groups on the surface of the ceramic component which leads to initial passivation of the electrodes.

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In order to avoid these problems we propose the use of appropriate organometallic compounds as protecting agents, which dissolve well in solvents used for the obtaining of films with PEO and easily react both with water and impurities of an acidic character (often present in lithium salts) and basic character typical for commercially available polyethers.

From initial studies carried out previously [6] it appears that a diethylalkoxyaluminum compound obtained from the reaction of triethylaluminum and poly(ethylene glycol) methyl ether is a suitable component of the composite.



This compound clearly improved the ambient temperature conductivity of PEO complexes and could be used directly in the atmosphere of dry air. The simple method of synthesis along with the low price and availability of the substrates is an additional advantage of it.

Within this project we:

1. obtained and studied the structure of three diethylalkoxyaluminum derivatives obtained from poly(ethylene glycol) methyl ethers of $M_n = 120, 164$ and 350 ($n = 2, 3, 7$) and triethylaluminum.
2. studied the influence of these substances on the conductivity and thermal transformations of different PEO complexes, and compared the properties of these systems with those of composites containing inorganic modifiers ($\alpha\text{-Al}_2\text{O}_3, \text{AlCl}_3, \text{AlBr}_3$).
3. synthesized copolymers of ethylene oxide with propylene oxide in the presence of different organoaluminum catalysts and determined the conductivity of their complexes with some lithium salts.
4. determined the conductivity of systems: copolymer/ LiClO_4 /aluminum inorganic compounds ($\alpha\text{-Al}_2\text{O}_3, \text{AlCl}_3, \text{AlBr}_3$).
5. carried out initial synthesis of diethylaluminumcarboxylates and studied their effect on the conductivity of PEO - lithium salt complexes.

RESULTS AND DISCUSSION

Diethylpolyoxyethylenealuminum Synthesis and Characterization

The products (**A**) of the reaction of triethylaluminum and poly(ethylene glycol) methyl ethers of $n = 2, 3$ and 7 were obtained according to reaction 1. To a 250 ml reactor equipped with a reflux condenser, 15g of a 20 wt. % triethylaluminum solution in toluene was introduced in an inert gas atmosphere, and an equimolar amount of 10 wt. % poly (ethylene glycol) methyl ether (of $M_n = 120, 164$ and 350) toluene solutions was added dropwise at room temperature. The dropping in rate was controlled by measuring the amount of ethane evolved. The reaction mixture was then stirred for 30 minutes at room temperature and for 60 minutes at boiling point. After reaction completion the solvent was removed *in vacuo*.

Studies on the aluminum content indicated a very good correlation between the theoretical (Al_{theor}) and experimental (Al_{exp}) values.

	$A_{n=2}$	$A_{n=3}$	$A_{n=7}$
Al_{theor}	13.22	10.89	6.22
Al_{exp}	13.06	10.55	6.20

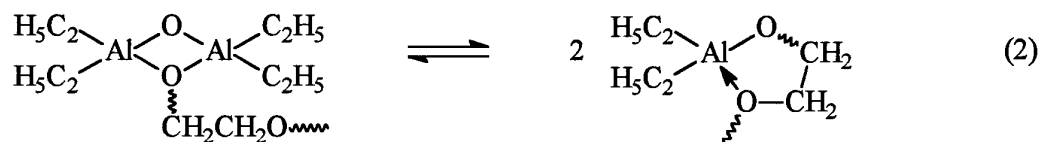
The 1H and ^{27}Al NMR spectra of compounds $A_{n=2}$, $A_{n=3}$ and $A_{n=7}$ contain the following signals:

$A_{n=2}$: 1H NMR: $\delta(CH_2Al)$ -0.28, (CH_3CH_2) , triplet) 0.94, (CH_3O) 3.32, $(OCH_2 + CH_2O)$, multiplet) 3.54–3.80 ppm. ^{27}Al NMR: δ (Al 4-coord.) 150, (Al 6-coord.) 9 ppm.

$A_{n=3}$: 1H NMR: $\delta(CH_2Al)$, quartet) -0.27, (CH_3CH_2) , triplet) 0.95, (CH_3O) 3.36, $(OCH_2 + CH_2O)$, multiplet) 3.51–3.81 ppm. ^{27}Al NMR: δ (Al 4-coord.) 150, (Al 6-coord.) 10 ppm.

$A_{n=7}$: 1H NMR: $\delta(CH_2Al)$ 0.05, (CH_3CH_2) 0.83, (CH_3O) 3.36, $(OCH_2 + CH_2O)$, multiplet) 3.61–3.64 ppm.

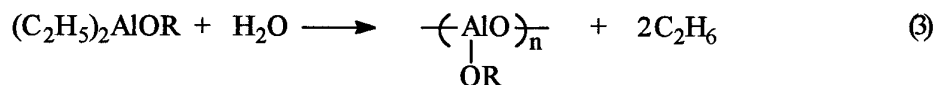
Cryoscopic molecular weight determinations show that the molecular weights of the $A_{n=2}$, $A_{n=3}$, $A_{n=7}$ derivatives are 410, 375 and 640, respectively. This indicates that compound $A_{n=2}$ occurs as a dimer, and in compounds $A_{n=3}$ and $A_{n=7}$ an equilibrium establishes between the dimeric form and monomeric form with an intramolecular complexation of aluminum by the alkoxy group oxygen atoms.



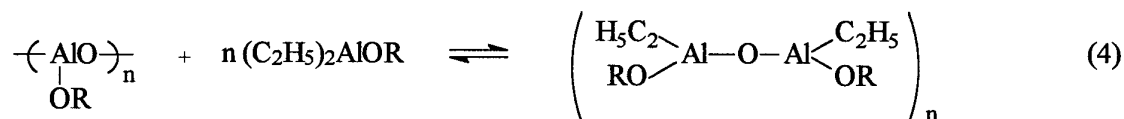
General characteristics

PEO blends with A and lithium salts.

The composite electrolytes were prepared by casting from acetonitrile. To a 8 wt. % acetonitrile solution of PEO, 20 wt. % solution of the organoaluminum compound and in some experiments 10 wt. % solutions of the salt were added. The whole was stirred by means of a magnetic stirrer at room temperature for 3 h. 15 cm³ samples were poured in the atmosphere of dry air onto glass plates or silicon coated paper covering an area of about 50 cm². The samples were left for the solvent to evaporate off. The acetonitrile residue was removed in a vacuum chamber at 50°C for 2 h. The films obtained were 0.2-0.3 mm thick and could be easily removed from the surface. Ethane evolution is observed during the mixing of the electrolyte components, which indicates a reaction to occur of the aluminum derivatives with moisture acidic impurities present in the system. This is accompanied by slight turbidity of the reaction mixture. The introduction of H₂O to the system in a 50 mol % amount with respect to that of aluminum leads to the occurrence of a finely dispersed phase which does not undergo agglomeration during further operations. At higher water concentration a white powder precipitated from the reaction mixture. The reaction mechanism of organoaluminum compounds with H₂O is still a matter of controversy [7]. At an equimolar amount of reactants highly associated oligomers of the general structure (ROAlO)_n are formed.



At Al/H₂O molar ratio 2:1 an equilibrium exists between this product and the so called alumoxanes.



All organoaluminum polymers easily form associates due to the acidic, three-coordinated aluminum atom and basic, two-coordinated oxygen atom.

Reactions with acids and bases also lead to hydrocarbon elimination and formation of derivatives, which undergo further association [8, 9].

The reactions mentioned proceed in liquid phase, but we did not observe evolution of gaseous products from the membranes obtained, even during storing for several weeks at 120 °C. No other degradation products are observed. The samples studied are dimensionally stable up to ~140 °C. DSC studies indicate that a strong endothermic transformation takes place at this temperature (Fig. 1). Microscopic and X-ray observations indicate that in the case of using LiClO₄ or LiCF₃SO₃ as dopants this is connected with melting of the crystalline phase, and in the case of LiN(CF₃SO₂)₂ with transformation in the amorphous phase. At this temperature dissociation probably occurs of Al←O coordination bonds in associates and complexes with PEO, which assure good mechanical properties of the system at lower temperatures. The addition of the organoaluminum compound causes a considerable decrease in the PEO crystalline phase content. In the case of some systems with LiClO₄ and LiN(CF₃SO₂)₂ the PEO crystalline phase content does not exceed 10 %. The glass transition temperature of blends are low, within the -64 - -29°C range. This probably results from the presence of long side chains in organoaluminum compounds, which act as a plasticizing agent. Such a morphologic structure seems to be very advantageous from the conductivity point of view, since a decrease in the crystalline phase content and increase in its flexibility cause an increase in ion mobility.

Conductivity of PEO blends with organoaluminum compounds and lithium salts

Studies on systems containing a PEO complex with LiClO₄ and organoaluminum compound A_{n=7} indicate that ambient temperature conductivity of composite electrolytes is over two orders of magnitude higher than that of non-modified PEO-LiClO₄ complexes. At an optimal composite composition (30-50 wt. %, A_{n=7}) the σ_{20} values are in the 5.2-5.4×10⁻⁵ S cm⁻¹ range (Fig. 2). It is interesting that A_{n=7} doped with LiClO₄ in the absence of PEO exhibits relatively low conductivity of ~10⁻⁷ S cm⁻¹ at 20 °C and that the composite conductivity clearly decreases when the organoaluminum compound content exceeds 60 wt. %. Therefore, it can be assumed that the role of the organoaluminum compound consists mainly in the modification of the PEO structure and not on the formation of a self conducting

phase. In the case of compounds of shorter side chains also the occurrence of a maximum of conductivity is observed at the organoaluminum compound content in the composite between 30 and 40 wt. %.

In Fig. 3 is presented a temperature dependence of conductivity for PEO blends containing 10 mol % LiClO₄ and 33 wt. % of compound A. The conductivity of blends with A_{n=3} and A_{n=7} is similar and at 20°C is slightly greater than 10⁻⁵ S/cm; the value of 10⁻³ S/cm is reached at ~60–70 °C. In the case of blends with A_{n=2} type of compounds, however, the conductivities are much smaller. The plasticizing effect is probably weaker in this case due to the too small length of the substituent at the aluminum atom. The temperature dependence of conductivity for many systems can be described by the equation:

$$\sigma = \sigma_0 \exp[-B/(T-T_0)]$$

where σ_0 , B and T_0 are fitted constants. This equation is related to the Vogel-Tamman-Fulcher (VTF) equation used to characterize the viscoelastic properties of polymers. The preexponential factor σ_0 is proportional to the square root of T, B is proportional to the activation energy and T_0 denotes the thermodynamic glass transition temperature. The parameters calculated for several copolymer electrolytes studied are listed in Table 1. The T_0 values calculated are very close to the real T_g values (± 10 K) obtained from DSC studies. The B parameter values for samples containing 10 mol % of the salt lie in the 450–800 K range and do not differ from the data published in the literature for other amorphous PEO based electrolytes of high ambient temperature conductivity [8, 9]. The B value increases when the salt concentration decreases.

Initial observations indicate that blends containing reaction products of A_{n=7} compounds with water exhibit a similar conductivity as the organic starting materials (Fig. 4), which indicates that condensation leading to the formation of organoaluminum compounds does not affect essentially the properties of the conducting phase. Similarly as in other systems, the conductivity values considerably increase upon the addition of strongly polar plasticizers, e.g. ethylene carbonate (Fig. 4).

In this case we obtained systems of ambient temperature conductivity typical like that for gel polymers, i.e. exceeding 10⁻³ S cm⁻¹. However, within time the organoaluminum compound present in the system reacts with cyclic carbonates and the system loses its good mechanical properties. In order to eliminate this problem an aluminum derivative of a dialkylaluminum carboxylate structure of the following formula has been synthesized:



PEO and Copolymer Composites with Inorganic Aluminum Derivatives.

DSC Studies

Figure 5 presents changes in the X_c for PEO-LiClO₄ based electrolytes containing α -Al₂O₃. The X_c values have been calculated in the same way as for pure PEO based blends. Composite electrolytes based on PEO or copolymer (Cop) and containing strong Lewis acids (e.g. AlCl₃, AlBr₃) are amorphous. Also Cop-LiClO₄ electrolytes with or without α -Al₂O₃ added are amorphous. X_c values calculated for PEO-LiClO₄- α -Al₂O₃ composite electrolytes are lower than that for the pristine PEO-LiClO₄ system. The melting peak of the crystalline PEO phase is shifted down to lower temperatures for PEO-LiClO₄- α -Al₂O₃ composite electrolytes in comparison with the PEO-LiClO₄ electrolyte.

Table 2 summarizes the T_g data measured by DSC for all composite systems. For most of the electrolytes the T_g values varied randomly with the additive concentration in the range between -30 and -40 °C. For PEO-LiClO₄- α -Al₂O₃ electrolytes the T_g values varied in a narrow temperature range (-34 to -38 °C) and are slightly lower than the T_g of the PEO-LiClO₄ electrolyte (-31 °C). For Cop-LiClO₄- α -Al₂O₃ electrolytes the T_g values are similar to that of the Cop-LiClO₄ electrolyte (-36 °C). Only for the sample containing 20 wt. % of α -Al₂O₃ the T_g value is higher (-26 °C). For PEO-LiClO₄-AlBr₃ electrolytes the T_g values are in the -33 to -39 °C range up to 30 wt. % of AlBr₃, and are slightly shifted to higher temperatures for samples containing 40 and 50 wt. %. For Cop-LiClO₄-AlBr₃ electrolytes T_g decreases to values between -45 and -55 °C for samples containing up to 25 wt. % of AlBr₃, and in this concentration range is lower than T_g for the COP-LiClO₄ electrolyte. For higher concentrations of AlBr₃ T_g increases up to -22 °C for samples containing 40 and 50 wt. % of AlBr₃. This suggests the formation of crosslinked structures which is not observed in electrolytes containing α -Al₂O₃. Similar trends as for systems with AlBr₃ were found for PEO or Cop based composite electrolytes with AlCl₃ additives (see Table 2). It should be noted that for composite electrolytes containing aluminum halides (up to the aluminum halide concentration ~30 wt. %) the T_g values are lower than for PEO-Al_yX₃ systems with analogous concentration of the aluminum halide. This observation as well as the lack of the melting peak of the complex phase at ~160 °C suggests that interactions between aluminum halides and polyether are limited in the presence of LiClO₄.

FT-IR studies

FT-IR studies are frequently used to analyze ion-ion interactions in polymeric electrolytes [12-14]. For these purposes the position and shape of the characteristic anion band is analyzed in more detail. In our case a Galactic Grams 386 software package was used to separate the $\nu(\text{ClO}_4^-)$ mode into two contributions with maxima in the 620-624 and 630-635 cm^{-1} ranges. Salomon et al. [14] suggest that the $\nu(\text{ClO}_4^-)$ band centered at 623 cm^{-1} can be attributed to the spectroscopically free ClO_4^- , whereas the band centered between 630 and 635 cm^{-1} is associated with the presence of contact-ion pairs. The "free" anion and contact-ion pairs bands have been fitted from the raw FT-IR data. The fractions of "free" anions and contact-ion pairs have 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 $\nu(\text{ClO}_4^-)$ vibrations. All band areas were normalized to the CH_2 stretch of polyethers. Figure 6 is an example of a fit of a Gaussian-Lorentzian peak to the experimental FT-IR data in the $\nu(\text{ClO}_4^-)$ region. As can be seen, the peak characteristic for "free" anions is much larger than that representing contact-ion pairs. In Table 3 the fraction of "free" ions calculated on the basis of FT-IR data is presented for various composite systems. For composite electrolytes containing $\alpha\text{-Al}_2\text{O}_3$ the fraction of "free ions" is higher than 80 %, which is higher than that for polyether- LiClO_4 electrolytes for which the fraction of "free" ions is equal to about 70 % [15]. 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 concentration of Lewis acid additives a broadening of the „free anion” peak centered at $\sim 623 \text{ cm}^{-1}$ was observed. However, based upon the fitting procedure, this peak could not be separated into two different contributions.

Table 4 summarizes the positions of the maximum of the C–O–C stretching vibrations 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 1090-1100 cm^{-1} range for the entire additive concentration range. This is close to the position of the maximum of the C–O–C stretching band for an amorphous polyether - LiClO_4 system (10 mol % of LiClO_4) (1095 cm^{-1}) [16]. The only exception is the Cop- 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 wt. % of AlBr_3 .

Conductivity Studies

Composite electrolytes with AlCl₃ additives

In Figure 7 conductivity isotherms (at 0, 25 and 100 °C) are shown for PEO-LiClO₄-AlCl₃ composite electrolytes. At 0 and 25 °C the conductivity significantly increases after the addition of up to 40 wt. % of AlCl₃ with a maximum for samples containing 15 wt. % of AlCl₃. At 100 °C conductivities measured for composite systems of the same AlCl₃ content are similar to the conductivity of the PEO-LiClO₄ electrolyte. The decrease in conductivity (of about one order of magnitude) in comparison with other composite systems was found for the samples containing 50 wt. % of AlCl₃.

In Figure 8 analogous conductivity isotherms are shown at 0, 25 and 100 °C for Cop-LiClO₄-AlCl₃ composite electrolytes. In this system an increase in conductivity was observed for samples containing up to 20 wt. % of AlCl₃. This is followed by a continuous decrease in conductivity for samples of higher AlCl₃ content. The highest conductivities correspond to the lowest T_g value (see Table 2) found from DSC investigations, whereas the decrease in conductivity is associated with an increase in T_g . At 100 °C the conductivity of the Cop-LiClO₄ electrolyte is higher than those measured for samples with the AlCl₃ additive.

Composite electrolytes with AlBr₃ additives

In Figure 9 conductivity isotherms obtained at 0 and 25 °C for composite PEO-LiClO₄-AlBr₃ electrolytes are presented. Similar to Figures 6 and 7, an increase in conductivity is observed for these composite systems relative to the (PEO)₁₀LiClO₄ electrolyte. An initial increase in conductivity with a maximum at 10 wt. % of AlBr₃ is followed by a small decrease for the sample with 15 wt. % of AlBr₃. For higher concentrations of AlBr₃ the conductivity increases.

In Figure 10 conductivity isotherms at 0 and 25 °C are shown for Cop-LiClO₄-AlBr₃ electrolytes. Conductivity increases with an increase in AlBr₃ concentration reaching a maximum for the sample with 25 wt. % of AlBr₃ and then decreases for electrolytes of higher AlBr₃ content. For the electrolyte containing 50 wt. % of AlBr₃ the conductivities are lower than that for the COP-LiClO₄ electrolyte. The decrease in conductivity observed for samples containing more than 25 wt. % of AlBr₃ corresponds to an increase in T_g (see Table 2) and shifting down of the maximum of the C-O-C band (see Table 4).

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

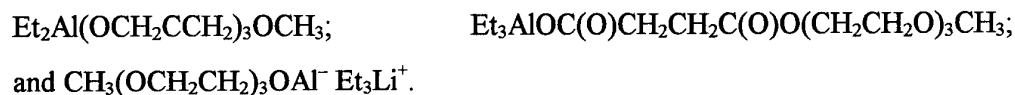
Composite electrolytes with α -Al₂O₃ additives

Figure 11 shows 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 wt. % of α -Al₂O₃ observed at 0 and 25 °C. It is worth noting that these conductivity maxima are observed for samples of the lowest degree of the PEO crystallinity (see Figure 4).

In Figure 12 conductivity isotherms obtained at 0, 25 and 100 °C for Cop-LiClO₄- α -Al₂O₃ electrolytes are presented. For Cop based electrolytes the addition of α -Al₂O₃ has rather a minor effect on the conductivity. An increase in conductivity relative to the Cop-LiClO₄ electrolyte is noticed for some of the composite electrolytes only at 0 °C. The shape of conductivity isotherms at 0 and 25 °C is qualitatively the same as previously described for PEO-LiClO₄- α -Al₂O₃ composite electrolytes (see Figure 9). The conductivity maxima occur at 10 and 25 wt. % of α -Al₂O₃. This corresponds to the samples with the lowest T_g (see Table 2).

Ethylene Oxide and Propylene Oxide Copolymers

Ethylene oxide and propylene oxide copolymers were synthesized in situ in the presence of organoaluminum catalysts:



The reactions were carried out at ambient temperature and at 50 °C for 45 h using 2 mol % of catalyst per sum of comonomers. In all the cases only oligomers were obtained in a yield not exceeding 40 wt. % (Table 5).

Since the catalytic systems studied did not lead to the obtaining of a high molecular weight copolymer, the copolymerization was carried out by the classic method in the presence of Vanderberg catalysts (triethylaluminum / acetylacetone / water; mole ratio 1:1:0.5). In Table 6 are presented the yields of copolymers carried out under different conditions. The necessity of purification from the catalyst of the copolymer obtained is a disadvantage of these systems.

The copolymer obtained by this method containing 16 mol % of PO monomeric units after purification and doping with an inorganic salt ($\text{CF}_3\text{SO}_3\text{Li}$, LiBF_4 , LiClO_4) exhibits ambient temperature conductivity exceeding 10^{-5} S/cm.

Thermal analysis of copolymers and electrolytes

DSC analysis showed that samples of copolymers stored for a long time at room temperature exhibit a small melting peak with maxima at 306 and 317 K. The melting of the samples is complicated by crystallization close to 285 K. The copolymer probably contains EO homosequences of different lengths, of which part is capable of forming a crystalline phase. Studies carried out for copolymer mixtures with $\text{CF}_3\text{SO}_3\text{Li}$ showed that samples containing 10 mol % of the salt were completely amorphous (Fig. 13). The copolymer glass transition temperature was equal to 208 K. In the presence of an inorganic salt the T_g value increases [$\text{P}(\text{EO})_{10}\text{CF}_3\text{SO}_3\text{Li}$ $T_g = 222$ K; $\text{P}(\text{EO})_{10}\text{LiClO}_4$ $T_g = 236$ K], since the interchain coordination by ions reduces the overall segmental mobility.

Conductivity

In Fig. 13 are presented changes of conductivity versus salt concentration for a copolymer doped with 10 mol % of LiBF_4 , $\text{CF}_3\text{SO}_3\text{Li}$ and CF_3COOLi at room temperature. As can be seen, at room temperature and at low salt content the highest conductivities are obtained for systems with LiBF_4 . At a 5 mol % content of the latter salt the ambient temperature conductivity reaches the value of 10^{-4} S/cm. Large changes in conductivity are observed in these systems even at small changes in the salt content. On the other hand, in systems with $\text{CF}_3\text{SO}_3\text{Li}$ the differences in the conductivity of electrolytes are small over a small salt content range (2 - 20 mol %). A considerable decrease in the electrolyte conductivity is observed at low (~ 1 mol %) or very high contents (~ 25 mol %). At very high salt content the conductivity of electrolytes containing that salt is lower than that of analogous electrolytes containing CF_3COOLi . In the case of electrolytes containing $\text{CF}_3\text{SO}_3\text{Li}$ and CF_3COOLi , the maximum ambient temperature conductivity appears at a salt content of ~ 10 mol %. In the case of certain salts, e.g. CF_3COOLi , the maximum location is shifted with a rise of temperature in the direction of higher salt content (Fig. 13).

The occurrence of a single or several conductivity maxima at salt content changes is a typical phenomenon observed in solid polymeric electrolytes. It results from complicated changes in the content of free ions, due to the establishing of a dynamic equilibrium between free ions, ion pairs and clusters containing ions and ion pairs.

Conclusions

1. The results obtained indicate that composites comprising PEO, lithium salt and alkylalkoxyaluminum compounds are characterized by very high conductivities. These are undoubtedly one of the most effective and cheapest solid polymer electrolytes.
2. These composites are characterized by good stability up to ~ 140 °C, small degree of crystallinity and high elasticity of the amorphous phase.
3. The conductivity of composites with α - Al_2O_3 is similar to that of systems containing organoaluminum compounds of short alkoxy chains $\text{A}_{n=2}$, but is clearly lower than that of composites containing plasticizing longer oxyethylene chains, $\text{A}_{n=3}$, $\text{A}_{n=7}$. In the case of composites comprising Al_2O_3 , the occurrence of local conductivity minimums and maximums is observed, which might be connected with non-uniform changes in the electrolyte crystallinity (Fig. 6), or various morphology of samples, which is difficult to control in heterogeneous systems. The T_g values for PEO- LiClO_4 - Al_2O_3 electrolytes varied in a narrow temperature range (-34 - -38 °C) and slightly lower than that value of the PEO- LiClO_4 electrolyte (-31 °C).
4. Composites with AlCl_3 and AlBr_3 turned out to be almost completely amorphous, of T_g values in the -30 - -41 °C range. The highest conductivities are obtained for composites containing about 10 wt. % of the aluminum compound (Figs 7 and 8), and they are comparable with the values obtained for compounds $\text{A}_{n=3}$ and $\text{A}_{n=7}$. Complexes between LiClO_4 and the organoaluminum compound are formed in these systems, which act as plasticizing salts. However, in these systems at temperatures above 50 °C ether cleavage reactions proceed leading to the formation of crosslinked structures and low molecular weight oligomers.
5. In the presence of some organoaluminum compounds it is possible to obtain amorphous ethylene oxide copolymers of ambient temperature conductivity $\sim 10^{-5}$ S/cm. The formation of composites, however, does not cause an improvement of the conducting properties and thus the use of these complicated polymers instead of PEO does not seem purposeful.

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Table 1. VTF Parameters for Some PEO-Organoaluminum (A_n) Composite Electrolytes

n	A_n wt. %	Salt ^a	σ_o S/cm	B K	T_o K	T_g K
2	40	LiClO ₄	4.99	766	227	
3	14	LiClO ₄	1.47	475	255	(248) ^b
3	33	LiClO ₄	2.11	515	228	
7	33	LiClO ₄	4.84	688	231	(239) ^b
7	60	LiClO ₄	2.18	563	230	
7	33	LiCF ₃ SO ₃	1.20	521	230	
3	33	LiN(CF ₃ SO ₂) ₂	2.38	587	228	(228) ^b
3	33	LiN(CF ₃ SO ₂) ₂ ^c	7.87	1090	212	(212) ^b

^a 10 mol % with respect to ethylene oxide monomeric units; ^b T_g determined by DSC; ^c 5 mol % with respect to ethylene oxide monomeric units.

Table 2. T_g values (in degree Celsius) obtained for various composite electrolytes.

Additive content wt. %	Copolymer based composite electrolytes			PEO based composite electrolytes		
	Al_2O_3	$AlCl_3$	$AlBr_3$	Al_2O_3	$AlCl_3$	$AlBr_3$
5	-33	-50	-44	-36	-39	-38
10	-37	-49	-41	-37	-37	-35
15	-30	-49	-42	-35	-41	-38
20	-26	-52	-46	-36	-39	-38
25	-36	-49	-55	-34	-38	-39
30	-31	-45	-28	-36	-35	-35
40	-35	-36	-22	-37	-34	-30
50	-33	-22	-22	-38	-34	-30

Table 3. Fraction of "free" ions calculated on the basis on FT-IR results for various composite electrolytes.

Additive concentration wt. %	Copolymer 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 $\nu(\text{ClO}_4^-)$ peak was observed

Table 4. Position of the maximum of C–O–C stretching band (in cm^{-1}) for various polyether based composite electrolytes.

Additive concentration wt. %	Copolymer based composite electrolytes			PEO based composite electrolytes		
	Al_2O_3	AlCl_3	AlBr_3	Al_2O_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

Table 5. Copolymerization of Ethylene Oxide (EO) and Propylene Oxide (PO) in Situ^a.

Catalytic system	H ₂ O	Yield	Average length of oxirane sequence ^b
	mol %	wt. %	
CH ₃ (OCH ₂ CH ₂) ₃ OAlEt ₃ Li ⁺	----	8	3
CH ₃ (OCH ₂ CH ₂) ₃ OAlEt ₂	0.5	40	6
	0.5 ^c	8	3
	----	39	5
Et ₂ AlOC(O)CH ₂ CH ₂ OC(O)(CH ₂ CH ₂ O) ₃ CH ₃	----	20	6

^a catalyst: 2 mol %; temp. 50 °C; time 45 h; EO/PO = 1,

^b determined on the basis of ¹H NMR

^c room temperature

Table 6. Copolymerization of ethylene oxide (EO) and propylene oxide (PO) ^a

EO content in monomer feed mol %	Copolymer		
	Yield wt. %	EO m.u. content mol %	$[\eta]^b$ dl/g
0	95	0	-
20	90	24	1.48
40	92	48	-
50	88	56	1.31
60	90	66	-
80	97	84	1.59

^a Catalyst: triethylaluminum/acetylacetonate/water (mole ratio 1:1:0.5), 5 mol % with respect to the amount of EO + PO in feed; solvent: toluene; temp.: 30 °C; 24 h < t < 48 h.

^b In chloroform at 25 °C

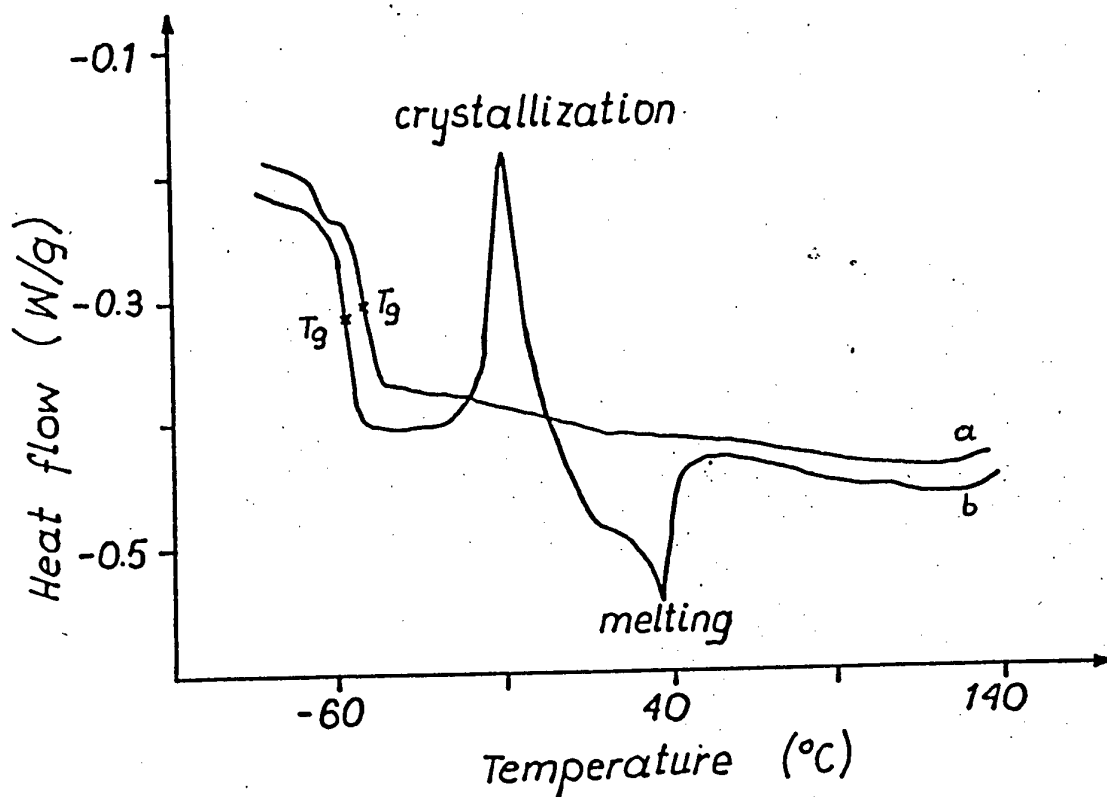
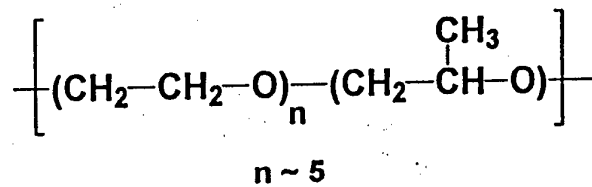


Figure 1. DSC curves for electrolytes: a. PEO - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ - organometallic compound
 b. PEO - LiCF_3SO_3 - organometallic compound

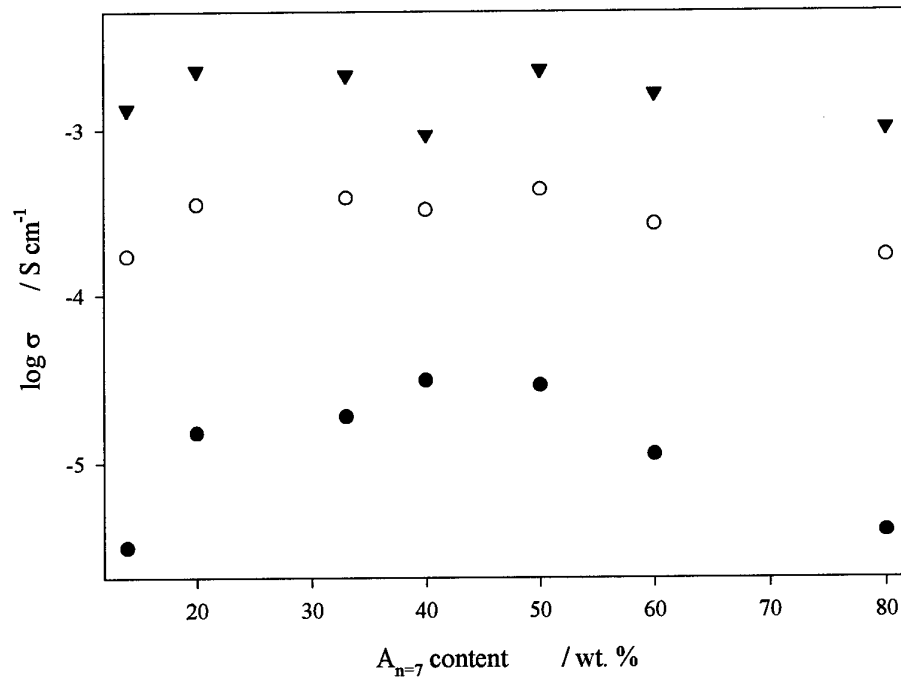


Figure 2

Ionic conductivity isotherms of PEO-LiClO₄-(organoaluminum compound) blends depending on the organoaluminum compound ($A_{n=7}$) content. (●) - 20 °C; (○) - 50 °C; (▼) - 90 °C.

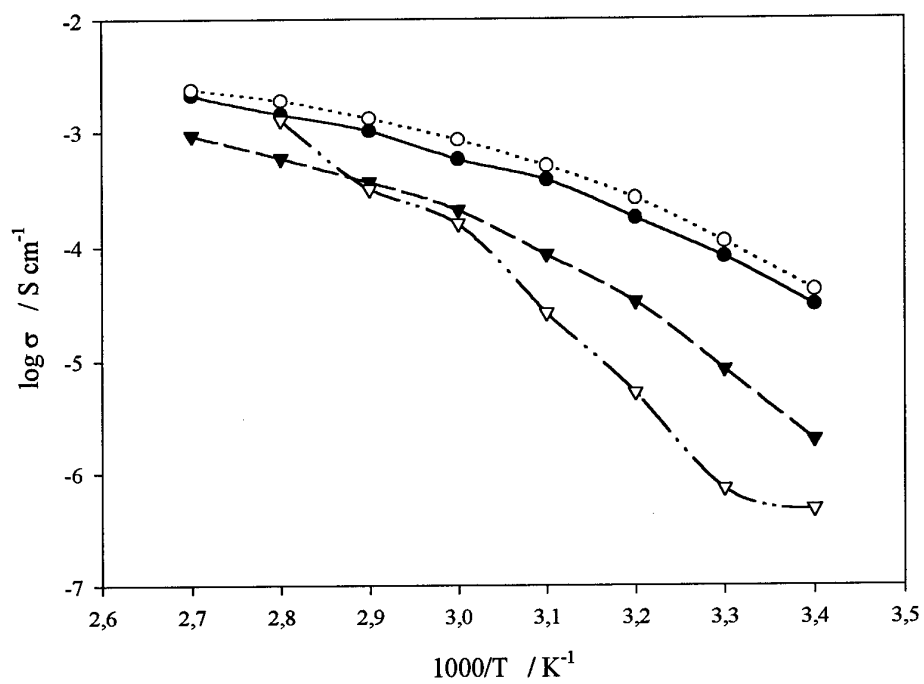


Figure 3

Ionic conductivity as a function of inverse temperature for $\text{P(EO)}_{10}\text{LiClO}_4$ - (▽) and its blends with 33 wt. % of $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OAl}(\text{C}_2\text{H}_5)_2$, where: (▼) - $n = 2$, (●) - $n = 7$, (○) - $n = 3$.

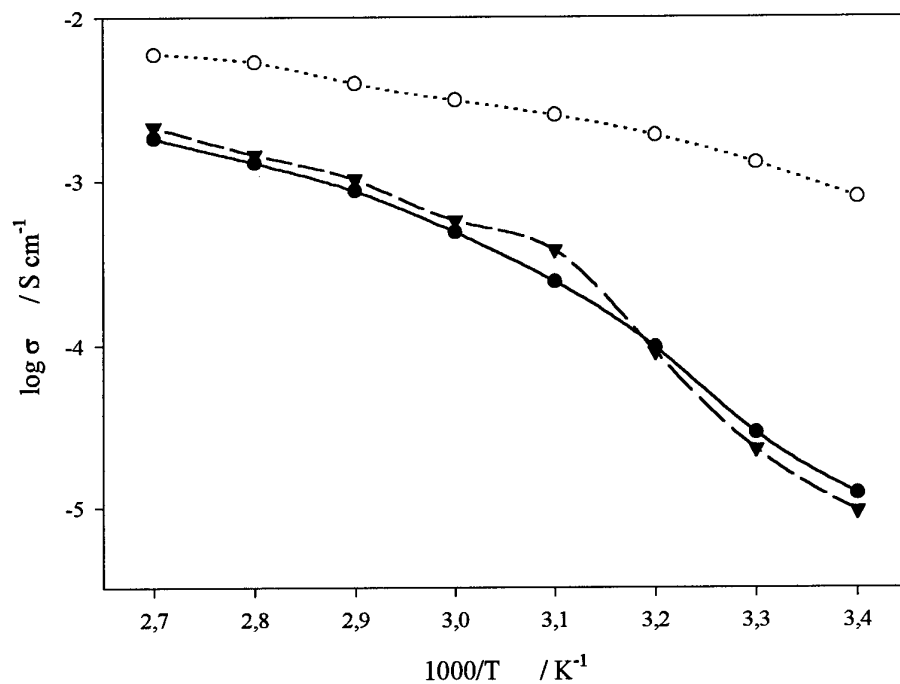


Figure 4

Ionic conductivity as a function of inverse temperature for P(EO)₁₀LiClO₄ blends with CH₃(OCH₂CH₂)_nOAl(C₂H₅)₂ (A); where (○) - 16 wt % of A_{n=3} and 51 wt % of ethylene carbonate; (●) - 33 wt % of A_{n=7}; (▼) - 20 wt % of (A_{n=7} and H₂O in a 1:1 mole ratio).

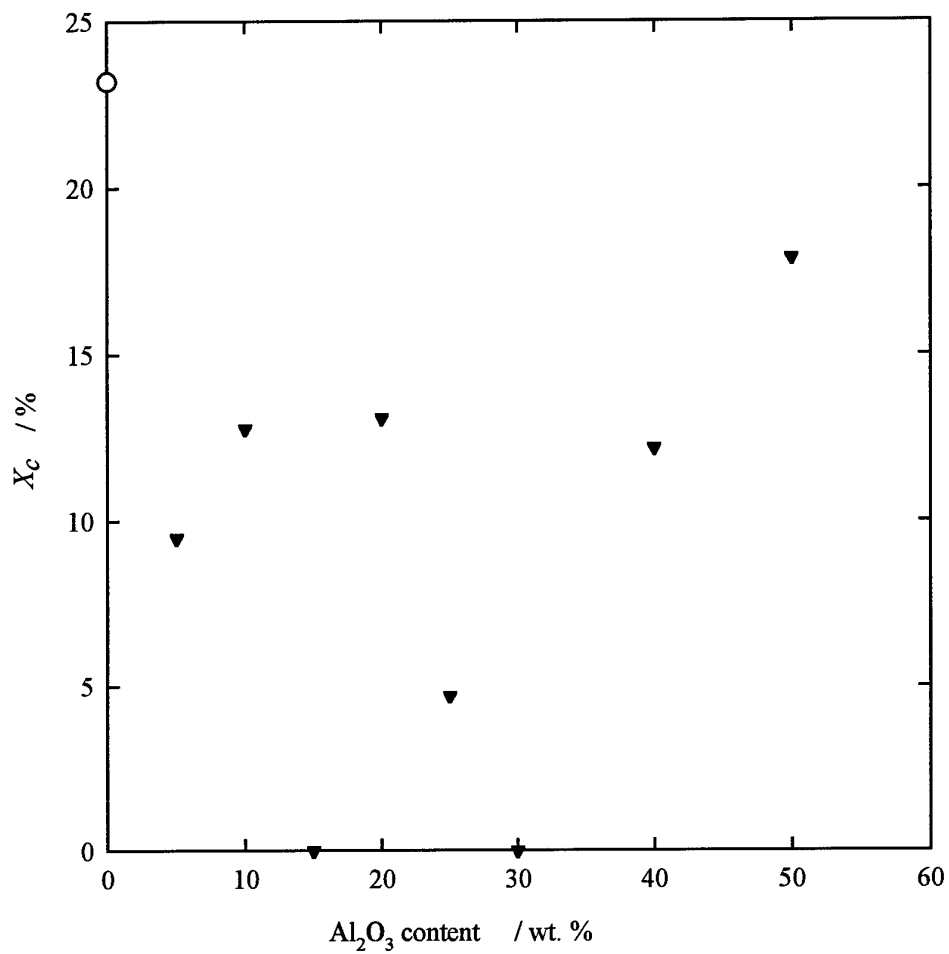


Figure 5
Changes in the X_c versus filler (Al_2O_3) concentration for composite polymeric electrolytes based on the PEO- LiClO_4 system. [o] represents X_c for the basic PEO- LiClO_4 system with 10 mol % of LiClO_4

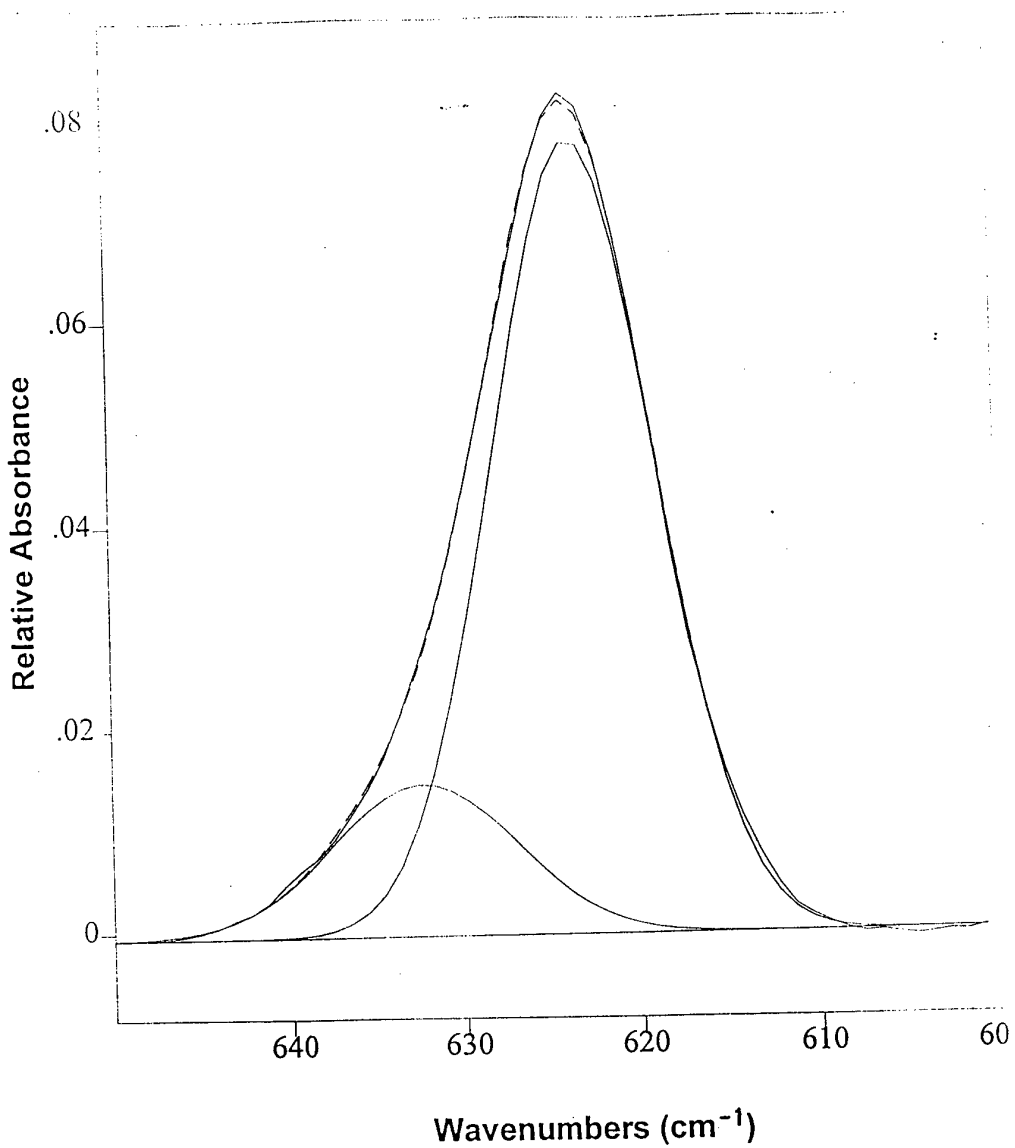


Figure 6.

Peak fitting for the $\nu(\text{ClO}_4^-)$ FT-IR region for the Cop-LiClO₄-Al₂O₃ (5 wt. %) sample at 25 °C. Dashed line represents experimental IR data. Solid line are represents experimental IR data. Solid lines are fits of Lorentzian-Gaussian type function to experimental data.

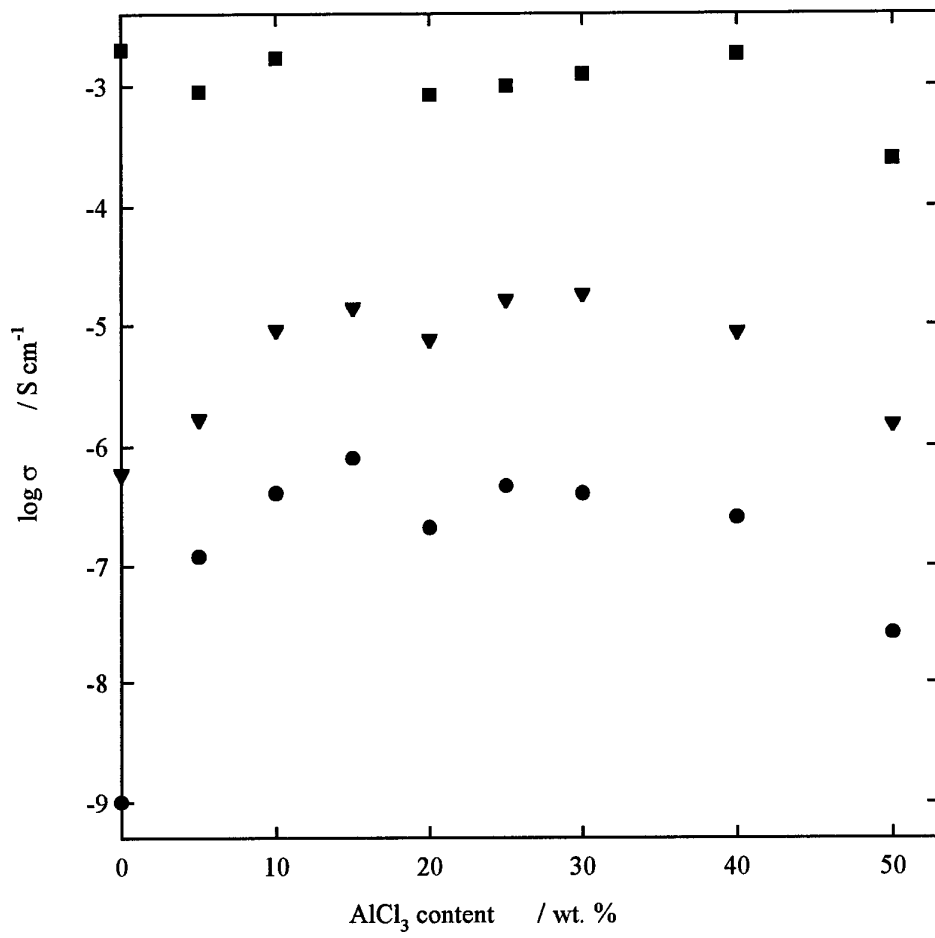


Figure 7
Isotherms of ionic conductivity of PEO-LiClO₄ versus AlCl_3 content
with 10 mol % of LiClO₄. (●) 0 °C; (▼) 25 °C; (■) 100 °C

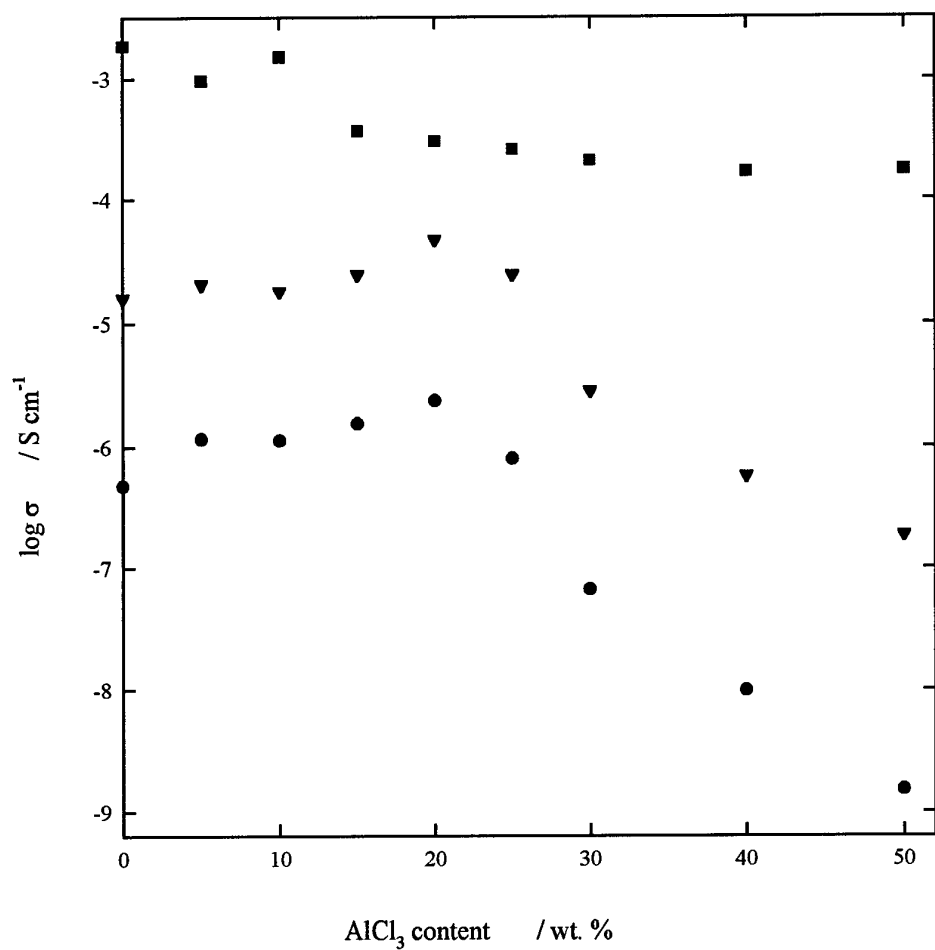


Figure 8
Isotherms of ionic conductivity of $\text{Cop-LiClO}_4\text{-AlCl}_3$ versus wt. % of AlCl_3 of AlCl_3 with 10 mol % of LiClO_4 . (●) 0 °C; (▼) 25 °C; (■) 100 °C

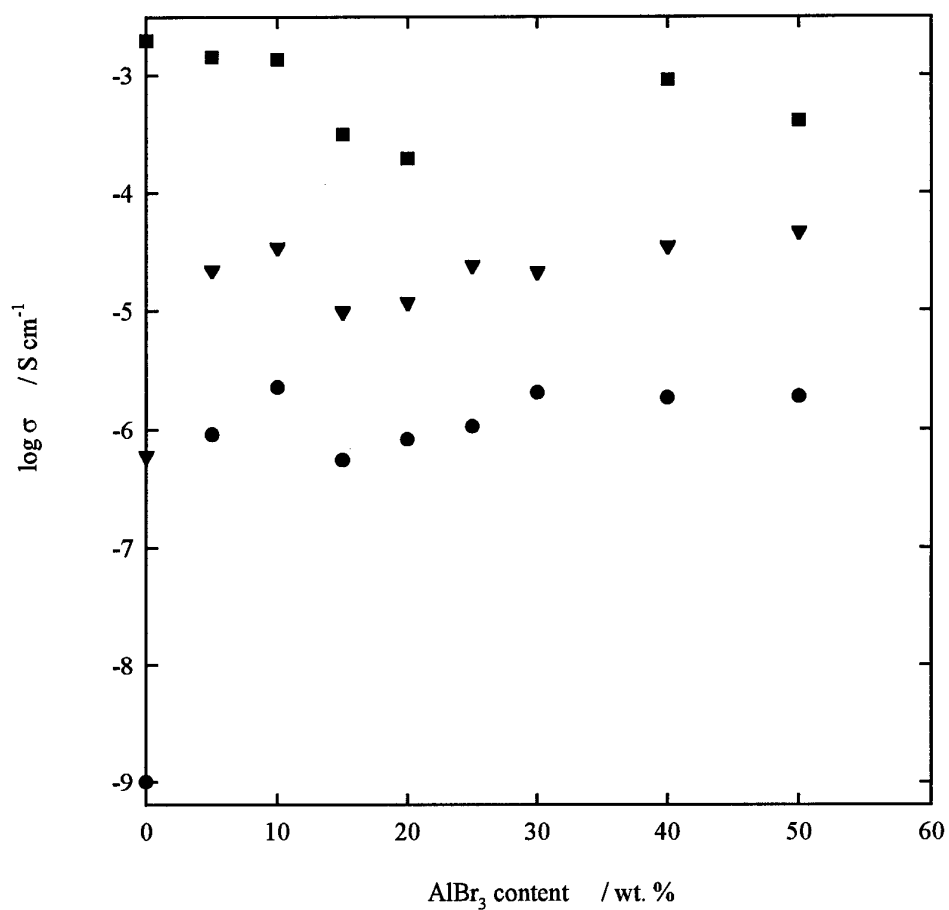


Figure 9
Isotherms of ionic conductivity of $\text{PEO-LiClO}_4\text{-AlBr}_3$ versus AlBr_3 content
with 10 mol % of LiClO_4 . (●) 0 °C; (▼) 25 °C; (■) 100 °C

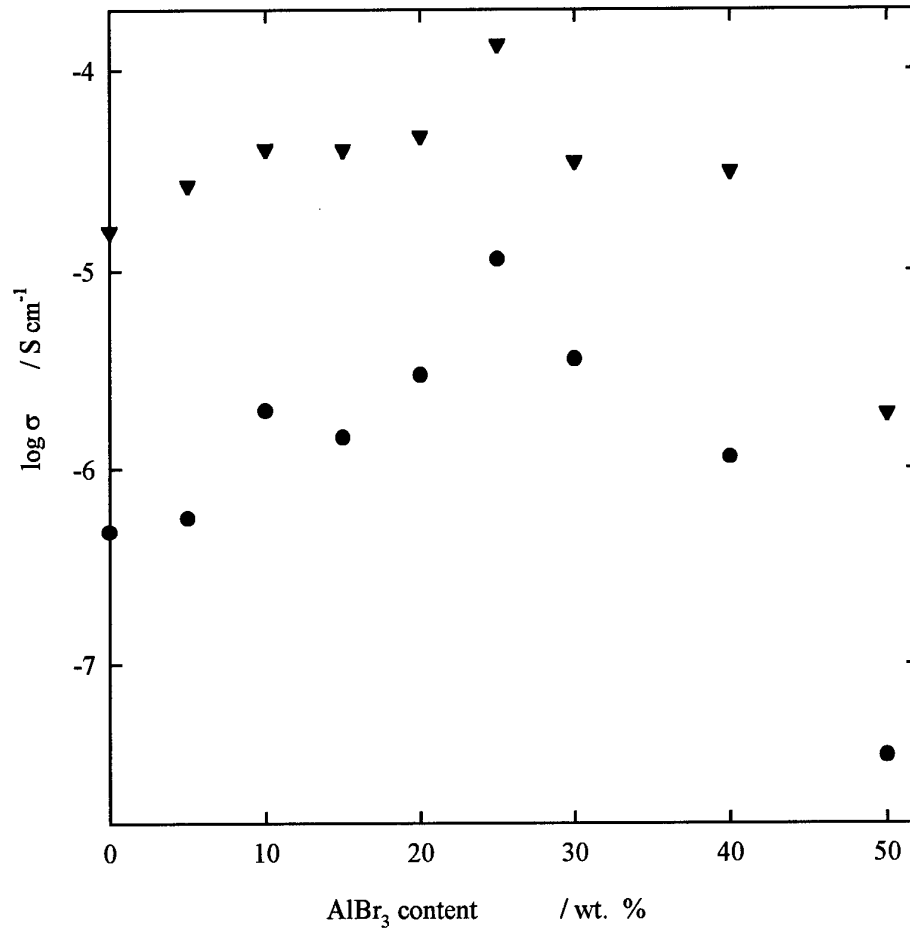


Figure 10

Isotherms of ionic conductivity of $\text{CoP-LiClO}_4\text{-AlBr}_3$ versus wt. % of AlCl_3 of AlBr_3 with 10 mol % of LiClO_4 . (●) 0°C ; (▼) 25°C .

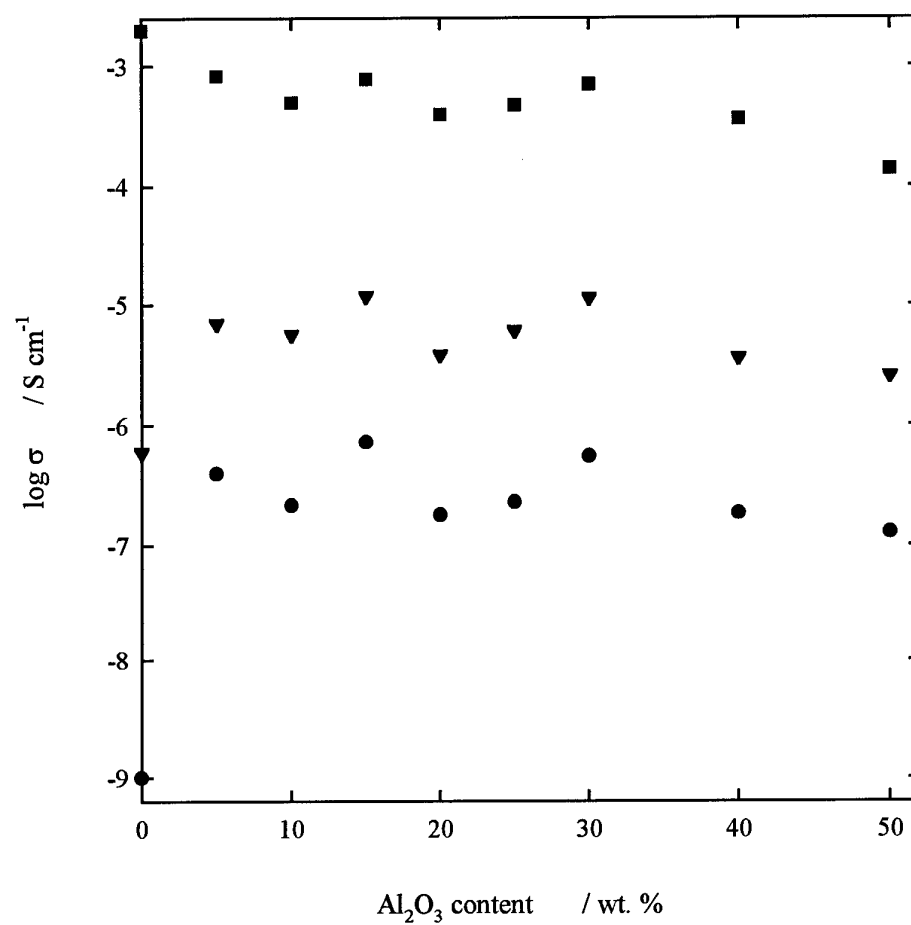


Figure 11
Isotherms of ionic conductivity of PEO-LiClO₄-Al₂O₃ versus Al₂O₃ content with 10 mol % of LiClO₄. (●) 0 °C; (▼) 25 °C; (■) 100 °C

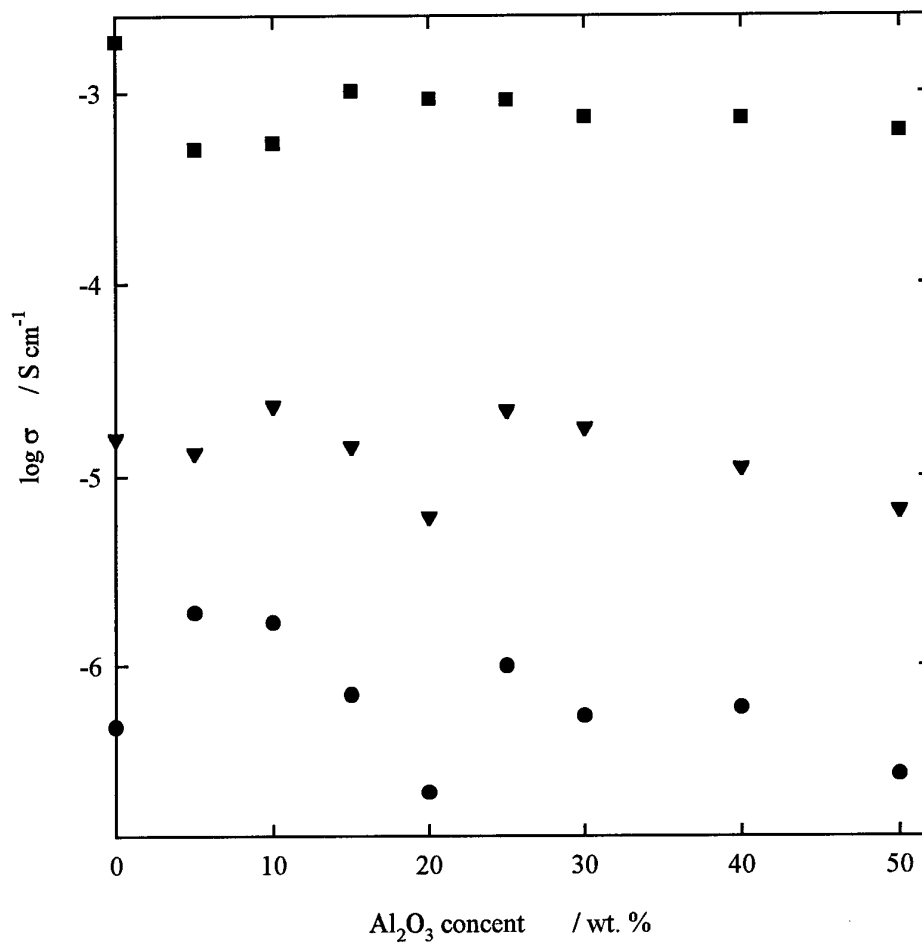


Figure 12
Isotherms of ionic conductivity of $\text{Cop-LiClO}_4\text{-Al}_2\text{O}_3$ versus Al_2O_3
content with 10 mol % of LiClO_4 . (●) 0 °C; (▼) 25 °C; (■) 100 °C

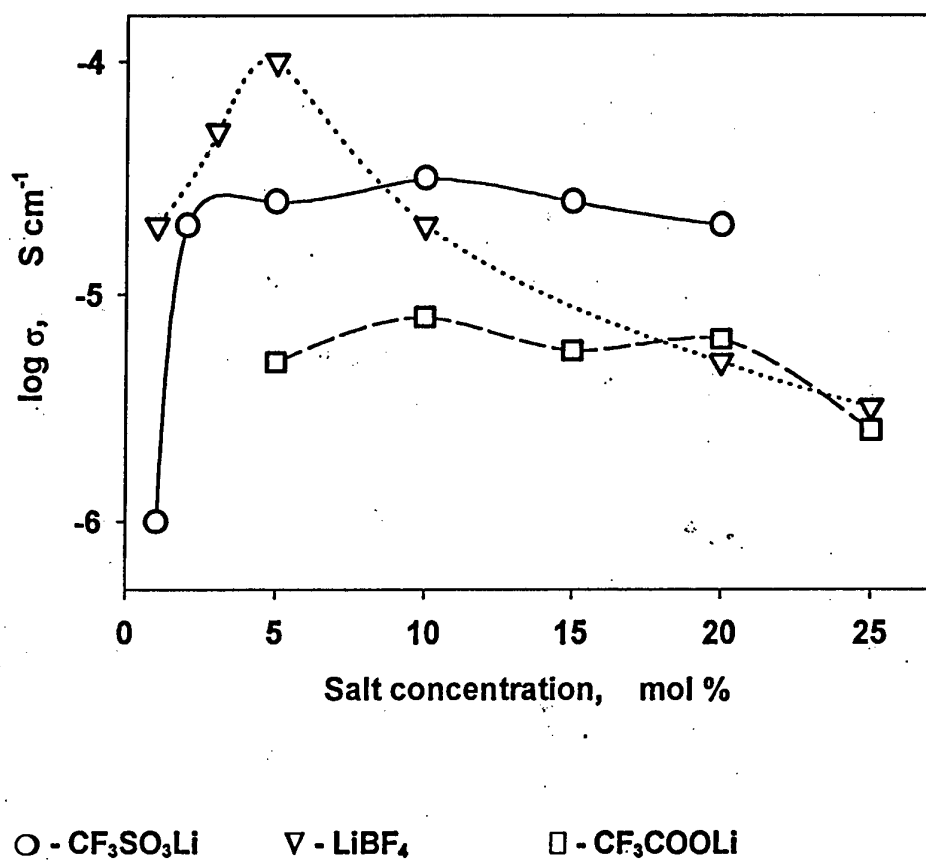


Figure 13. Changes of conductivity versus salt content for poly(ethylene oxide-co-propylene oxide) electrolytes doped with lithium salts at ambient temperature.