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# Review of PEO Based Composite Polymer Electrolytes[*]

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The present paper describes a short review of solid polymer electrolytes composed of high or low molecular weight poly(ethylene oxide), lithium salts and various types of nano and micro sized additives. The mechanism of ionic conductivity in the system is discussed in relation to the Lewis acid-base interaction between the components and the strategies of developing practical materials for lithium batteries are proposed.

**Key words**: poly(ethylene oxide), solid electrolytes, composite materials, lithium batteries

## Introduction

Ion conducting polymeric membranes have recently attracted considerable attention [1–7], due mainly to the possibility of their application in various electrochemical devices such as alkali metal batteries, electrochromic displays and sensors and fuel cells working at ambient and moderate temperatures.

In this type of electrolytes the polymer is often only an inert component assuring appropriate mechanical properties of the membrane, whereas the charge transport proceeds in a solvent immobilized in a polymeric matrix (gel electrolytes) or in the phase of molten salt of low glass transition temperature (rubbery electrolytes). There is also a group of solid polymer electrolytes, in which the chains of macromolecules play a key role in the ion transport. These kinds of materials were first studied by Wright *et al.* in 1973 [1], whereas the recognition of the potential of such systems for practical applications and much of the early development are credited to Armand and coworkers [2].

The "*legae artis*" polymer electrolyte is formed by the dissolution of a salt in an ion-coordinating macromolecule such as poly(ethylene oxide) (PEO) with high molecular weight of about $5\times10^6$ and 80% crystallinity. The main reason to choose this polymer host is because of the formation of stable complexes with many salts and the ability to possess higher conductivities than any other group of commercially available polymers. The oxygen atoms in this polymer have high electron donor power and a suitable interatomic separation, enabling them to form multiple intrapolymer coor-

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[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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dinate bonds with cations. The low barriers to bond rotation allow the segmental motion of the polymer chain, thus providing a mechanism for ion transport. Complex formation in $PEO_n$-salt (n – number of ether oxygen atoms per mole of salt) is governed by a competition between the solvation energy and the lattice energy of the polymer and the inorganic salt. Also low lattice energies of both the polymer and the salt have been found to improve the complex stability in the polymer electrolyte [3].

It has been found that the polymer and ion motions are coupled [8] and hence the presence of a flexible, amorphous polyether phase is essential for high ionic conductivity in polymeric electrolytes [9].

Most of the studies on polymer electrolytes are stimulated by the development of lithium batteries employing metallic lithium as anode and composite cathode capable of reversible lithium insertion and deinsertion (Figure 1).

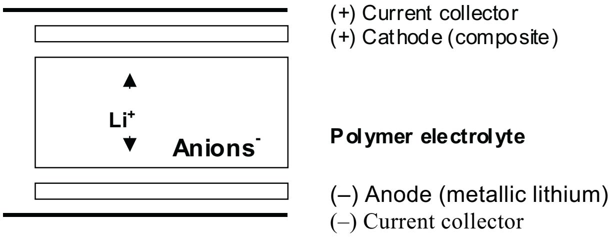


**Figure 1.** Lithium ion polymer battery.

These batteries are widely studied by various research groups, but still there are a number of problems which have to be solved before reaching the commercialization step. The main problems are the following:

(a) low cationic transference number (close to 0.1–0.3) of most conventional P(EO)-LiX polymer electrolytes,
(b) forming of highly resistive layers at the anode-electrolyte interface,
(c) high degree of crystallinity of PEO based electrolytes,
(d) conductivity at ambient temperature not high enough for application in batteries.

To avoid crystallization of polyether chains and improve the ambient temperature conductivity of electrolytes, a number of sophisticated polyethers have been developed in a laboratory scale. This includes molecular architecture based on random, block or comb-like copolymers, networks, interpenetrating networks and liquid crystals with PEO short segments.

The retardation of PEO crystallization by means of organic or inorganic additives is an alternative approach which allows to obtain amorphous matrices of good mechanical properties and stability over a wide temperature range [9–13].

In this paper the various types of composite electrolytes in which ceramic powders, hybrid inorganic-organic materials or high molecular weight polymers are added to PEO-salt complexes is reviewed. It will be demonstrated that these materials may offer at least partial solutions to all the main problems associated with the utilization of solid electrolytes in lithium batteries. We hope also to convince the readers that the interaction between additives and ions has a very important effect on the mechanism of conductivity in these systems.

## Ceramic Composite Polymer Electrolytes

Although it is in general agreement that ceramic particles play an important role in ion transport upon the addition of fillers, different trends in conductivity are observed. An increase, decrease or no change in conductivity have been reported in comparison to the analogous unfilled systems. This apparent inconsistency results from various factors, *e.g.*:

- materials (polymer, lithium salt, filler type, structure and size), and their concentration,
- preparation conditions, and thermal history of the polymer electrolytes.

These factors can also determine the different criteria which can be applied in order to classify ceramic composites. Many systems have been studied in order to understand the effect of ceramic particles on $Li^+$ transport properties. In order to clarify the general trends relevant to the composites based on PEO and their low molecular analogues, this chapter describes separately polymer electrolytes based on high molecular weight PEO and low molecular weight polyglycols.

## High Molecular Weight Composite PEO Based Electrolytes

In 1982 Weston and Steele [14] used $\alpha$-$Al_2O_3$ particles (grain size 40 $\mu$m) to improve the mechanical stability of a PEO-$LiClO_4$ electrolyte. Since then many different systems have been examined.

Previous studies on mixed-phase polymeric electrolytes containing conductive fillers such as NASICON [15],$\beta$-alumina and glassy fillers [16,17] have shown that these fillers do not contribute to the ionic conductivity of the mixed phase systems. Similar results were described by Scrosati and coworkers [18–21] for polymeric electrolytes containing $\beta$- and $\beta''$ aluminas. However, Skaarup *et al.* [22–24] reported that for composite systems containing high amounts of conducting fillers (exceeding 85 vol. %) the conductivity occurs via a dispersed phase and polymers act as binders for ceramic grains. The decrease in conductivity in comparison with pristine ceramic electrolytes is due to the dilution effect of the polymer host. Similar results demonstrating the contribution of the conducting filler to the conductivity of the mixed-phase electrolytes have been obtained by Stevens and Mellander [25] for systems containing PEO and $RbAg_4I_5$ or $KAg_4I_5$ as conductive ceramic additives. Due to the contradicting results obtained for ionically conducting fillers, nonconducting inorganic particles have been used as fillers.

Later, it was recognized that the addition of smaller inorganic filler particles (grain size 1–3 $\mu$m) led to an improvement in the mechanical properties and an increase in the ambient temperature conductivity of the electrolytes studied [26]. This increase results from a decrease in the electrolyte crystallinity as has been shown by

NMR [27], DSC [28,29], and Raman spectroscopy [30] as well as X-ray investigations [29,31]. The addition of small inorganic particles stiffens the electrolyte host [29]. The crystallinity of the system is observed to decrease. The effect of grain size distribution, particle concentration and surface area on the conductivity and phase structure of the composite electrolytes has been discussed [27,28,32]. Significant improvement in the conductivity of polymeric systems is usually obtained using fine-grained (1–2 $\mu$m) powders, with large effective surface areas and concentrations of 10–20 wt. %. For higher concentrations the formation of non-conducting particle aggregate regions is observed. This lowers the bulk conductivity of these electrolytes.

Scrosati and coworkers have been studying systems containing $\gamma$-$LiAlO_2$ as fillers. These authors have commented on the role of inorganic fillers in the improvement of the electrochemical stability of polymeric electrolytes and on the properties of the lithium electrode – composite polymeric electrolyte interface [10–34]. The highest ambient temperature conductivities measured for all the composite systems studied were ~$10^{-5}$ S/cm, *i.e.* lower than the conductivity reported for alkali metal salt complexes based on random oxymethylene linked poly(ethylene oxide) (OMPEO) which is believed to have the room temperature conductivity of the PEO amorphous phase. Some authors attribute this fact to a dilution effect due to the filler particles [10,23,35]. However, it has been shown by NMR [27] and DSC [28] that the addition of a stiff filler reduces the chain flexibility increasing the glass transition temperature of the amorphous phase. This in turn lowers the mobility of the charge carriers.

Krawiec *et al.* [36] reported a relationship between particle size of $Al_2O_3$ filler and conductivity. The composites of PEO with $LiBF_4$ showed an increase in ionic conductivity from $10^{-5}$ $S \cdot cm^{-1}$ to $10^{-4}$ $S \cdot cm^{-1}$ when substituting nanometer sized $Al_2O_3$ particles for micron sized particles. Similar results have been published by Croce *et al.* [37], with the addition of 10 wt. % of nano-sized $TiO_2$ or $Al_2O_3$ particles in P(EO)8:$LiClO_4$. An increase in conductivity has been seen at temperatures up to the melting point of the polymer complex. Above the melting point of the complex there is little, if any, effect of the filler on conductivity.

Dai *et al.* [38] showed that for highly concentrated PEO/LiI-based systems the addition of $Al_2O_3$ resulted in significant enhancement of lithium ion mobility and hence conductivity. They suggested that the enhanced conductivity in this highly concentrated salt system was due to a decrease in the crystalline or ordered phases of the salt complexes. They also observed that $Al_2O_3$ fillers suppress the formation of crystalline phases in $P(EO)_3LiI + Al_2O_3$ composite electrolytes. NMR results [39] implied that the presence of the ceramic filler improves $Li^+$ transport through grain boundaries parallel to the current flow in the electrolytes.

PEO complexes have been shown to have some remaining order even in the molten state [40] and sometimes, as in the case of PEO/LiI, high melting point polymer–salt compounds can be formed.

Through conductivity measurements Kumar and Scanlon [41] discovered that high-$M_w$ PEO-based composite electrolytes (PEO + $LiBF_4$ + $TiO_2$ or $ZrO_2$) can be maintained in an amorphous state below the PEO melting point after annealing, thus increasing conductivity. Higher annealing temperatures, longer heat-treatment times, and faster cooling rates from the annealing temperature promote a reduction in the crystalline phase of PEO in composite electrolytes.

Another promising method to enhance the ionic conductivity of PEO based polymer electrolytes is to incorporate lithium salts with low lattice energy and bulky anions such as lithium(bis)trifluoromethanesulfonate imide (LiTFSI or $Li(CF_3SO_3)_2N$), which are expected to slow down the recrystallization kinetics of PEO-LiTFSI complexes and thereby enhance the conductivity.

An interesting concept realized recently by Jayathilaka *et al.* [42] was to try to make use of both approaches. These authors incorporated nano-sized fillers into PEO-LiTFSI polymer salt complexes with a view to optimize the favorable physical properties mentioned above. At the same time they wished to understand the fundamental processes responsible for improved transport properties due to the incorporation of 10 wt. % of nano-porous $Al_2O_3$ into PEO-LiTFSI. The surfaces of the $Al_2O_3$ were activated with different Lewis acidity groups [42].

Connections with the surface chemistry of ceramic fillers and the ion transport and mechanical properties of composite electrolytes using nanometric $SiO_2$ functionalized by 2-[methoxy(polyethylenoxy)-propyl] trimethoxy silane have also been studied by Liu *et al.* [43]. Compared with untreated $SiO_2$ as the ceramic filler, there was noticeable improvement in ionic conductivity, in the stability of the Li/polymer electrolyte interface and in the mechanical properties.

A novel aspect, the anticrack effect of a whisker composite, has been discussed recently by Wen and coworkers [44]. The whisker aluminas were homogeneously dispersed in the $P(EO)_8$-$LiClO_4$ matrix and effectively prevented the formation of the microcracks.

It is now generally accepted that reduction in the crystallinity of high-$M_w$ PEO composite electrolytes upon the addition of ceramic fillers produces an increase in conductivity at temperatures below the melting point.

Composite electrolytes examined lastly by the Scrosati's group were: $P(EO)_8LiClO_4$ + 10 wt. % $TiO_2$ [37,45,46], $Al_2O_3$ [37,46], or $SiO_2$ [46], and $P(EO)_{30}LiClO_4$ + 10 wt. % $SiO_2$ [45]. The conductivity of the thus prepared composite electrolytes is consistently higher than that of filler-free electrolytes. In addition, a dramatic increase is observed in the ambient temperature conductivity of composite electrolytes after annealing at temperatures above the PEO crystalline-to-amorphous transition point. This conductivity increase is sustained for a 20 to 60 days period. However, no steady-state change in ambient-temperature conductivity was observed with filler-free electrolytes. X-ray diffraction data indicated that the structure of composite electrolytes was changed after annealing. $^7$Li NMR data showed that the increase in ionic conductivity of composite electrolytes after annealing is not attributable to an enhancement in polymer segmental motion, but more likely is due to a weakening of the polyether-cation interaction caused by filler particles. On the basis of this result, the authors concluded that the increase in ion conductivity of composite electrolytes at ambient temperature after annealing is due to the preservation of a high degree of disorder since small particles act as “solid plasticizers” to prevent PEO chain reorganization. It is not surprising that the term “solid plasticizer mechanism” can be found in the literature to describe the influence of ceramic particles on the ion transport properties of high molecular weight PEO [47].

The chronology, types of composite systems and the effect on conductivity from studies by several research groups are presented in Table 1.

**Table 1.** Effect of fillers on the ionic conductivity of high molecular weight PEO-based composite electrolytes.

| Ref./ (year) | PEO $M_w$ g/mol | Salt | Salt molar concentration | Filler[a] |  | Temp. |
|---|---|---|---|---|---|---|
|  |  |  |  | Characteristics | Effect on conductivity[b] | °C |
| [48]<br>(1986) | $5\times10^6$ | NaI | $P(EO)_xNaI(NASICON)_y$[c] | NASICON<br>$Na_{3.2}Zr_2Si_{2.2}P_{0.8}O_{12}$ | +[d] | 20–95 |
|  |  |  |  | cooling cycle | – | 25–90 |
| [49]<br>(1996) | $5\times10^6$ | $LiClO_4$ | 2.3 (Li:O = 1:10) | $AlCl_3$ (1.7–24.4 vol. %)<br>$\alpha Al_2O_3$ (2.6–33.9 vol.%)<br>< 5 μm | +[e] | 25 |
| [50] | $5\times10^6$ | $LiClO_4$ | 2.3 (Li:O = 1:10) | $AlBr_3$ (5–50 wt. %) | + | 0, 25 |
|  |  |  |  | $AlCl_3$ (5–50 wt.%) | + | 0, 25 |
|  |  |  |  |  | – | 100 |
|  |  |  |  | $\alpha Al_2O_3$ (5–50 wt.%, | + | 0, 25 |
|  |  |  |  | < 5μm) | – | 100 |
|  | OMPEO[f]<br>$4.1\times10^4$ | $LiClO_4$ | 1.1 (Li:O = 1:10) | $AlBr_3$ (5 wt. %) | + | 0, 25 |
|  |  |  |  | (50 wt. %) | – | 0, 25 |
|  |  |  |  | $AlCl_3$ (5–20 wt.%) | + | 0, 25 |
|  |  |  |  | (25–50 wt. %) | – | 0, 25 |
|  |  |  |  | (5, 10, 15, 25 wt.%) | – | 100 |
|  |  |  |  | (30, 40 wt.%) | + | 100 |
|  |  |  |  | (20, 50 wt.%) | 0 | 100 |
|  |  |  |  | $\alpha Al_2O_3$ (< 5μm) | – | 0 |
|  |  |  |  | (20–50 wt.%) | – | 25 |
|  |  |  |  | (5–50 wt.%) | 0 | 25 |
|  |  |  |  | (5–50 wt.%) | – | 100 |

[a]20 and 50 vol. %, [b]+ – increase, – – decrease, 0 – no effect, [c]x = 10, y = 0.5 or x = 10, y = 1, [d]in comparison with $(PVC)_1(NASICON)_1$, [e]($A1C1_3 > \alpha$-$A1_2O_3$ at same loading), [f]oxymethylene linked PEO.

## Low Molecular Weight Polymer Based Electrolytes

The discussion in the area of composite polymer electrolytes is quite intense, especially with the report of stable conductivity enhancements in PEO complexes even in the molten state [37,51]. However, the presence of ordered and amorphous phases presents considerable complications when interpreting the direct effects of filler on conductivity. The general consensus is that the dominant conductivity enhancement originates from a reduction in the amount of polymer crystallinity. Little information is available on the action of ceramic particles at the molecular level. The observation that ionic transport mainly occurs in the amorphous (liquid like) regions of these complexes [9] (a reasonable idea) suggests the use of low molecular weight liquid polymers (commonly named polyglycols) as model systems in fundamental studies of microscopic properties and transport processes.

**End groups effect**. It has been shown that the terminal OH groups significantly influence the degree of dissociation of the salt and thus the formation of new ion species in low molecular weight oligoether based model systems. These OH groups also influence the conductivity as was shown by Ferry and Tian [52] where complexes based on methyl terminated poly(propylene glycol) of molecular weight 4000 were compared to the normal OH terminated systems. Therefore, in order to discuss correlations observed in model low molecular weight polyether in relation to high molecular weight electrolytes, it is important that the effect of terminal OH end groups be studied.

Bernson and Lindgren have shown that the characteristic infrared modes of the OH end groups are affected upon complexation with alkali metal salts [53]. A low OH end group (PPG 4000) to ether oxygen ratio is found not to influence the properties of the electrolyte significantly. This would be logical to assume if there was a random distribution of metal ion to terminal OH group and ether oxygen contact ratios, or preferential metal ion to ether oxygen contacts. Bernson and Lindgren have shown that quite the opposite is true; in fact, that there is a strong preference for OH end group to metal ion coordination. Since the $O_{ether}/O_{OH}$ are of the same order of magnitude as the ether oxygen to metal ion ratios commonly used, the properties of these electrolytes should depend to a large extent on the metal ion to hydroxyl terminal group interactions.

The impact of large densities of polar end groups on ionic conductivity, and related ion interactions were investigated by directly comparing Raman and conductivity results on the normal OH-capped and methyl-capped complexes [52].

Prud'homme and coworkers [54,55] have suggested that the dramatic concentration dependency of the ionic conductivity can be attributed to a microphase separation occurring in electrolytes based on PPG (4000).

Despite all these efforts it is still under consideration as to whether different polyglycols are suitable model host polymers.

The aim of the work reported here was to test the hypothesis that non-conducting fillers can increase the conductivity of an amorphous polyether system.

Samples of composites using polyethylene glycols were first studied by Khan and co-workers [56]. Electrolytes prepared with $LiClO_4$ and fumed silica fillers in different polyglycols exhibit high room temperature ($>10^{-4}$ $S \cdot cm^{-1}$) conductivities, good processability and good mechanical stability.

Also Fan and Fedkiw [57] measured the conductivity of solution of PEGME and PEGDME electrolytes ($M_w$ from 200 to 400) containing lithium salts (imide and triflate anions) and their corresponding composite electrolytes containing fumed-silica particles (0 to 20 wt. %). At room temperature the ionic conductivity of such composite systems was as high as 1.5 $10^{-3}$ $S \cdot cm^{-1}$, and they exhibited a gel-like consistency but flow under shear. The electrochemical stability of the composites and their compatibility with lithium metal were also examined. A large potential window (~5.5 V) was found for lithium imide-based electrolytes. The passive film formed on lithium in contact with the composite electrolyte was relatively more stable and less resistive than that formed in contact with the parent solution electrolyte. These authors concluded that considering the advantages of processability and low volatility, these composites should be good candidates as electrolytes for lithium and lithium ion batteries.

A few groups suggested that there is support for the transport of cations on particle surfaces [58]. Phipps and Whitmore [59] measured surface transport on fused silica plates embedded in LiI and they found ion conductivity values parallel to the surface as high as 2 $S \cdot cm^{-1}$ at room temperature. This study opens the interesting possibility of surface assisted fast ion transport in composite polymer based materials.

The study of the system based on dimethyl capped low molecular weight PEO analogues has been continued by Fan and coworkers [60] in order to determine whether the fumed silica surface chemistry has an effect on the conductivity of composite electrolytes. In this review the rheological properties of the resulting composites are also examined to verify whether there exists a link between conductivity and viscosity. The properties of silica surfaces range from non-polar (alkyl-terminated) to highly polar (native fumed silica, OH terminated).

Fumed silica-based composite polymer electrolytes show almost complete decoupling between conductivity and rheology. The conductivity shows negligible dependence on the type of fumed silica surface group (silanol, alkyl, or PEO), and moreover, decreases only marginally even at high-solids content.

In contrast, rheological properties are strongly affected by the surface chemistry; in particular, mechanically stable composites (gels) were formed by fumed silicas with silanol or octyl surfaces dispersed in a polymer matrix.

These studies on low molecular weight polyglycols (PEGDME-500) were continued by Hou and Baker [61] by using cross-linkable composite electrolytes containing $LiClO_4$, fumed silica, and 10 wt. % methyl, butyl or octyl methacrylate.

The silicas used were chemically modified by attaching methacrylate groups to the silica surface through C8 and C3 ethers. Before cross-linking, the electrolytes were thixotropic and had ionic conductivities higher than $2 \times 10^{-4}$ $S \cdot cm^{-1}$. After ultraviolet (UV)-induced cross-linking, the electrolytes were rubbery and dimensionally stable, but the conductivities were unchanged. These authors presumed that mechanical properties of the composite electrolyte and its ionic conductivity are decoupled and can be optimized independently.

Composites of a lithium ion conducting ceramic $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ with a lithium salt and an amorphous polymer electrolyte matrix have been described by MacFarlane *et al.* [62]. Conductivity measurements were made as a function of the lithium ion conducting ceramic phase content in the composite. These results show that there is a significant increase in conductivity at approximately 40 vol. % of the ceramics. Enhanced conductivity was presumably due to enhanced $Li^+$ conduction.

A comparison of composites of small *versus* medium particle size fractions of the same ceramics have shown that the ceramic/polymer electrolyte interfacial impedance is a very significant contribution to the total (limiting low frequency) impedance of the material. Unfortunately, this composite was found to be strongly moisture sensitive.

In order to determine if the effect observed for PEO based systems was generally applicable to polyethers, Best and coworkers [63] have tried to reproduce the conductivity enhancement in completely amorphous polyether based composites using both $LiClO_4$ and $LiCF_3SO_3$. The base amorphous polymer material used was a polyether triol with molecular weight 5000 g/mol; it had ethylene oxide and propylene oxide units in a 3:1 ratio (3PEG). The conductivity of these composites was enhanced by a factor between 2 to 5 depending on composition and temperature.

Nairn *et al*. [64,65] studied composites based on lithium lanthanum titanate and lithium titanium phosphate ceramics combined with an amorphous ionically conducting polyether–salt complex. The ceramic component had particle sizes in the 10–100 $\mu$m range although individual grain sizes were likely considerably smaller than this. The properties of these materials indicated that higher conductivities, relative to the base polymer electrolyte, were possible. Nevertheless, it was evident that the interfacial region between the ceramics and the polymer would play a key role in the final properties of the ceramics.

Studying nanocomposite electrolytes of PEG and poly(methylene ethylene oxide) (PMEO) complexed with $LiClO_4$ and $LiCF_3SO_3$, Best *et al.* [66] showed that the incorporation of nanopowders (~20 nm) of $TiO_2$ and $Al_2O_3$ fails to influence the degree of ion association. This suggests that the number of charge carriers available for conduction in both polymers using both salts is not the source of any conductivity increase.

In some recent work of the Monash University group [67] the effects of $TiO_2$ on a completely amorphous polyether-based system have been reported. These authors showed, using NMR, FT-IR, impedance and positron spectroscopy, that the lithium ion environment was changed by the addition of a filler. Ceramic particles influence the disordered longitudinal acoustic modes (DLAM) in the case of an amorphous polyether; this suggests an interaction between the filler surface and the polymer. An increase in free volume upon addition of filler to an amorphous polyether–salt complex, coinciding with an apparent increase in polymer mobility is evidence of an ion conducting inter-phase region.

No large effect was seen in the ionic conductivity upon the addition of nanoparticles ($Al_2O_3$) to the amorphous PEO- LiTf and LiTFSI system studied by Johansson [68], apart from a small dilution effect. $SiO_2$ fillers of different particle sizes show very similar behavior. The authors indicated that only a minor enhancement of ionic conductivity is possible for nearly amorphous neat salt/polymer systems.

It was shown by Świerczyński *et al.* [69] that the addition of fumed silica to polymer electrolytes results in the formation of gel-like polymer materials. Despite the quasi-solid structure of these composite systems an increase in conductivity was observed for several salt concentrations of composite systems in comparison with the PEODME-$LiClO_4$ electrolytes which were the base systems. For other salt concentrations, the conductivities of the composite systems were found to be slightly higher or at least comparable to that measured for the unmodified PEODME-$LiClO_4$ electrolyte. At the lowest salt concentrations (*e.g.*, $10^{-5}$–$10^{-4}$ mol/kg PEODME), the conductivities of the PEODME-$LiClO_4$ electrolyte were higher.

This increase in conductivity was attributed to a reduction in the fraction of ion pairs as revealed by FT-IR experiments and Fuoss-Kraus-type analysis of the salt concentration dependence of the ionic conductivity.

## The Lewis Acid-Base Approach

A mechanism based on Lewis acid-base interactions was first developed by Wieczorek [70]. He suggested that the final conductivity of composite electrolytes depends on the equilibrium of the Lewis acid-base reactions involving a filler, a matrix polyether and alkali metal ions. Due to the complexity of these systems it would be difficult to theoretically predict the equilibrium of reactions. In his opinion only the hard-soft acid-base principle developed by Pearson [71,72] can be used to qualitatively predict the direction of a particular Lewis acid-base reaction and therefore would be helpful in choosing an appropriate filler which should be added to the polyether – alkali metal system in order to modify its structure and properties.

In a few papers [49,73,74] it has been proposed that changes in the microstructure and morphology of polyether-based electrolytes are due to various Lewis acid- Lewis base reactions occurring between Lewis base centers of the polyether (*i.e.*, polyether oxygen atoms), alkali metal cations (hard Lewis acids), and the Lewis (or Brønsted) base or acid character of the filler.

Wieczorek and coworkers [49] studied the effect of ceramic particles with Lewis acidic properties including $AlBr_3$ [51], $AlCl_3$ and $\alpha$-$Al_2O_3$ [49,50], on the ionic conductivity of electrolytes based on high-$M_w$ $P(EO)_{10}$ $LiClO_4$.

The increase in the conductivity upon addition of $\alpha$-$Al_2O_3$ into high-$M_w$ PEO electrolytes was ascribed to different acid-base interactions. The authors showed that filler particles could act as nucleation centers for the crystalline PEO. As a consequence polycrystalline microphases are formed, resulting in an enhanced disorder in composite electrolytes compared to filler-free electrolytes. The increase in disorder was evidenced by a decrease in the fraction of the crystalline phase upon addition of $\alpha$-$Al_2O_3$.

These authors postulated that aluminum halides such as $AlBr_3$ and $AlCl_3$ interact with $ClO_4$ anions leading to the formation of complex anions ($O_3ClOAlX_3^-$ with X = Br and Cl) that act as plasticizing agents for PEO matrixes, thus increasing the ionic conductivity. The plasticizing effect of aluminum halides was supported by the fact that composite electrolytes containing aluminum halides at low $AlCl_3$ concentration are amorphous. At high aluminum halide concentrations (> 25 wt. %) Lewis acids also interact with PEO leading to the formation of PEO-filler complexes; the polymeric electrolytes are stiffened and ionic conductivity is reduced.

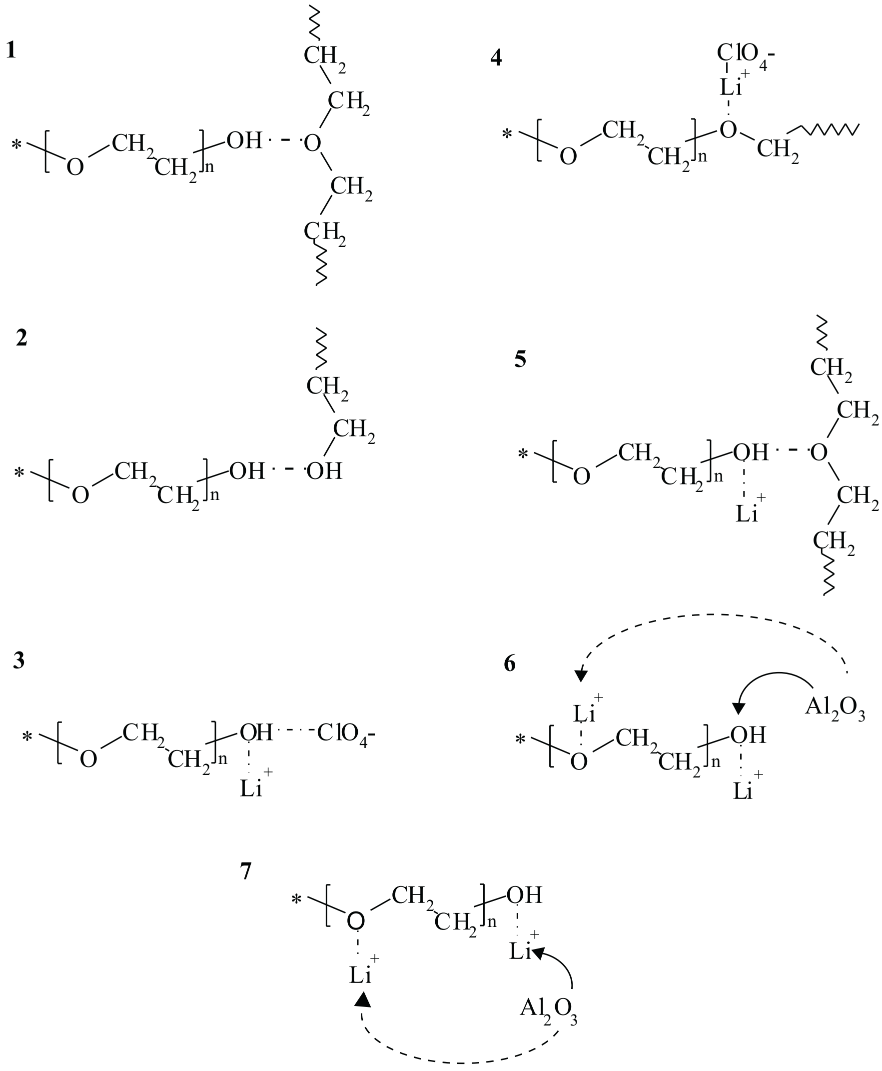
A study of Lewis acid interactions in amorphous PEO analogue matrix based systems has been proposed by Borkowska [75]. Using fully dissolved Lewis acid $AlBr_3$ it has been shown that the addition of a small amount (up to 5 wt. %) of $AlBr_3$ increases the electrolytic conductivity in comparison with the pure liquid polymer matrix-$LiClO_4$ electrolytes. Samples containing 1 mol of $LiClO_4$ per kg of polymer were used. For higher $AlBr_3$ concentrations stiffening of the polymer electrolyte was also observed which again results in a decrease in the ionic conductivity.

Lewis acid-base interactions in high-molecular weight $P(EO)_{20}$-$LiCF_3SO_3$, LiTf with 10-wt. % acidic, basic, or neutral surface activated $Al_2O_3$ fillers has been studied by Scrosati *et al*. [76]. A two orders of magnitude increase in room-temperature conductivity is observed upon the addition of acidic $Al_2O_3$ fillers. At temperatures below 60℃ the conductivity was ranked in the order acidic > neutral > filler-free > basic, with acidic the highest. However, at temperatures above 60°C, all fillers increased conductivity with neutral > acidic > basic > filler-free.

The OH acidic surface groups can H-bond with ether oxygen and oxygen on the anion. The basic $Al_2O_3$ has a surface modified with oxygen and forms transient crosslinking centers with the $Li^+$-polyether by Lewis acid-base interactions. Both acidic and basic surface groups coexist on neutral alumina, which interacts with anions through acidic sites by hydrogen bonding and with $Li^+$ through basic sites by Lewis acid-base interactions (see Scheme 1). Since hydrogen bonding is stronger than ion-dipole interactions, neutral alumina promotes salt dissociation most efficiently. The next efficiency is shown by acidic and basic fillers. In addition to promoting salt dissociation, the polar surface groups of the inorganic filler also act as crosslinking centers for PEO segments and for anions. Such interactions lower the PEO crystallization tendency (*i.e.*, the fillers act as "solid plasticizers") and thus promote a structure modification of polymer chains. Such a structure modification provides conducting pathways for $Li^+$ at the filler surface. This is consistent with an increase in Li transference number upon addition of fillers.

Jayathilaka *et al.* studied conductivity and thermal properties of high-$M_w$ $P(EO)_9LiN(CF_3SO_2)_2$ (LiTFSI) + 10 wt. % $A1_2O_3$ (acidic, basic, neutral, weakly acidic) electrolytes [42]. These authors agree that Lewis acid-base interactions between polymer chain, lithium salt and filler surface groups play a significant role in enhancing the ionic conductivity of both low- and high-molecular weight PEO-based composite electrolytes.

The presence of filler particles enhances the ionic conductivity substantially, and the degree of enhancement depends on the nature of the filler surface group and decreases as acidic > basic > neutral > weakly acidic. Jayathilaka *et al*. [42] believed that the filler particles do not interact directly with the PEO chains as revealed by the



**Scheme 1.** Types of interactions between the polymer matrix, salt and inorganic filler.

essentially unchanged $T_g$ values; this suggests that the main chain dynamics governing the ionic transport is unaffected.

These authors [42] noticed that the number of ion pairs remains essentially unchanged due to the presence of the filler particles and also with increasing temperature; this rules out the possibility of ion pair dissociation contributing to conductivity enhancement. Jayathilaka *et al.* proposed a qualitative model based on Lewis acid-base type interactions between filler surface groups, cations and anions in order to explain differences in the ionic conductivity enhancement caused by various surface groups. These authors propose that during migration lithium cations form temporary, weaker transient bonds with the oxygen atoms of the surface basic groups of alumina grains; these are very much similar to those with ether oxygen atoms. This fact promotes extra sites for the cations, which would, otherwise, be migrating only via forming and breaking coordination links with the ether oxygen atoms of the polyether chains.

The addition of surface modified micron sized $Al_2O_3$ results in a variation in conductivity, viscosity, ion-ion and ion-polymer interactions in polyglycol-$Al_2O_3$-$LiClO_4$ composite electrolytes in comparison with the pure polymer matrix-$LiClO_4$ system. The formation of different types of complexes in composite polyether electrolytes can be studied experimentally using FT-IR and Raman spectroscopy. Changes in the position and intensity of bands characteristic of groups or atoms involved in the Lewis acid-base reaction can be studied.

Taking into account the above discussion the final conductivity of composite electrolytes depends on the equilibrium of the Lewis acid-base reactions involving a filler, a polyethers matrix and alkali metal ions (with cations acting as Lewis acid centers and anions acting as Lewis base centers). Due to the complexity of these systems it would be difficult to theoretically predict the equilibrium of reactions on the basis of semiempirical thermodynamic correlations, such as donor-acceptor numbers, Drago-Wyland or Drago-Mark equations [71]. All of these approaches are specific to simple Lewis acid-base reactions. In our opinion only the hard-soft acid-base principle developed by Pearson [72] can be used to qualitatively predict the direction of the particular Lewis acid-base reaction and therefore would be helpful in choosing an appropriate filler which should be added to the polyether – alkali metal system in order to modify its ultrastructure and ionic conduction properties.

Therefore, in our opinion the aim of future work would be to find an appropriate filler with well determined Lewis acidity or basicity in order to apply the experimental data to semiempirical equations quantitatively describing the ionic interactions between components of the composite electrolytes.

## Composites with Organoaluminum Compounds

Although the formation of composites with various ceramic materials is an extremely simple and at the same time efficient method of modifying the mechanical and conducting properties of solid polymeric electrolytes based on PEO complexes, the application of this method on a production scale is connected, however, with some problems resulting from the agglomeration of inorganic particles in the polymeric matrix. It leads often to a pronounced inhomogenity and stiffening of the polymeric matrix which in turn affect its conducting properties and compatibility with electrode materials.

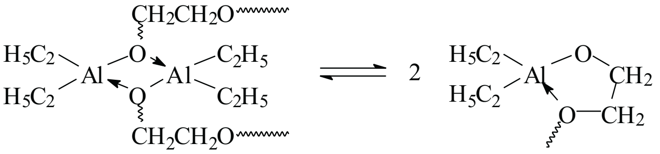
In order to avoid these problems we propose the use of appropriate organometallic compounds as protecting agents, which dissolve well in solvents used for the obtaining of films with PEO and which easily react both with water and impurities of an acidic character (often present in lithium salts) and the basic character typical for commercially available polyethers. The first class of additives developed in our laboratory was based on the diethylalkoxyaluminum compound obtained from the reaction of triethylaluminum and poly(ethylene glycol) methyl ether [77,78].

$$Al(C_2H_5)_3 + CH_3(OCH_2CH_2)_nOH \rightarrow 1/x[CH_3(OCH_2CH_2)_nOAl(C_2H_5)_2]_x + C_2H_6 \quad (1)$$

**8**

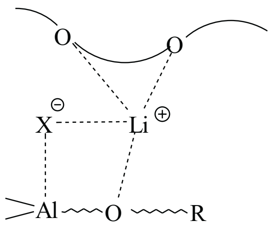
n = 2 3 7
x = 2 1.5 1.5

Cryoscopic molecular weight determinations show that the molecular weights of the **8**$_{n=2}$, **8**$_{n=3}$ and **8**$_{n=7}$ derivatives are 410, 375 and 640, respectively. This indicates that compound **8**$_{n=2}$ occurs as a dimer, and for compounds **8**$_{n=3}$ and **8**$_{n=7}$ an equilibrium establishes between the dimeric and monomeric forms with an intramolecular complexation of aluminum by the alkoxy group oxygen atoms.

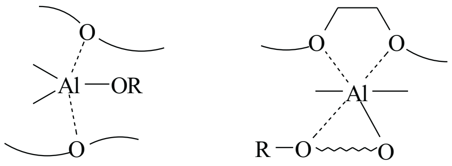


(2)

DSC studies indicate that the use of aluminum alkoxides as components of composite electrolytes profitably affects the morphology of the systems studied. A considerable decrease in the ability to crystallization of pristine PEO is observed. In the case of certain electrolytes with $LiClO_4$, and especially with $LiN(CF_3SO_2)_2$ the crystalline phase content does not exceed 10 wt. %. Furthermore, the short oxyethylene chains attached to aluminum act as internal plasticizers flexibilizing the amorphous phase, which results in low glass transition temperatures from –64 to –29°C. DSC, microscopic and X-ray studies indicate a strong endothermal transition in the amorphous phase at about 140°C which can be attributed to the dissociation of the mixed complex, in which aluminum alkoxides and PEO chains are linked via the lithium cation. The plausible structure of such a complex can be presented as follows:



Membranes of the electrolytes with several lithium salts are dimensionally stable, both at room temperature as well as that much higher than the melting point of the crystalline phase of pristine PEO and its complexes with salts, up to about 130°C. These good mechanical properties and thermal stability result probably from the transient crosslinking *via* lithium cations and the ability of polyethers to form coordination bonds with aluminum atoms. This results in the formation of structures of the character of a physical net, in which the aluminum atom may be complexed both by its own polyglycol fragments as well as by the PEO chains.

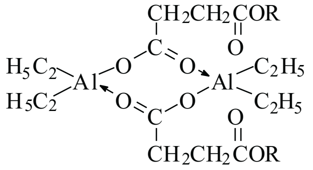


The membranes of electrolytes comprising aluminum alkoxides, when stored at 110℃ for several hundred hours, maintain their mechanical properties similarly as electrolytes stored at room temperature for 18 months. Thus, it can be stated that the organoaluminum compound added does not lead to the degradation of PEO, and even quite contrary, by probably forming stable complexes with it, inhibits its degradation.

The ambient temperature conductivity of composite electrolytes is over two orders of magnitude higher than that of non-modified PEO-$LiClO_4$ complexes. At an optimal composite composition (30–50 wt. % of $\mathbf{8}_{n=7}$) the conductivity values at room temperature are in the $5.2–5.4\times10^{-5}$ $S\cdot cm^{-1}$ range. These values are similar to those of the best dimensionally stable solid polymeric electrolytes, which do not contain low molecular weight plasticizers. It is interesting that $\mathbf{8}_{n=7}$ doped with $LiClO_4$ in the absence of PEO exhibits relatively low conductivity of $\sim10^{-7}$ $S\cdot cm^{-1}$ at 20℃ 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. The addition of water to the reaction mixture practically does not cause changes in the conducting properties of this system. The precipitation of a colloidal suspension forming a stable heterogeneous mixture is observed during the addition of water. In view of studies on the reactions of organoaluminum compounds with water it can be assumed that first hydrolysis of the aluminum-oxygen and aluminum-carbon bonds occurs, followed by condensation of aluminum-oxygen bonds leading to the formation of an alumoxane, similarly to sol-gel processes. Thus, at high water concentration (50 mol %) PEO composites with inorganic fillers can be formed *in situ* of the finely dispersed additive phase in the polymer matrix.

Initial impedance studies of composites comprising aluminum alkoxides $\mathbf{8}_{n=7}$ in a system of lithium electrodes indicate that the overall cell resistance measured 1 hour after assembling the cell only slightly increases within time (whereas in the absence of an organoaluminum compound an increase in resistance is very distinct). This suggests that in these systems the passivation layer formed does not give measurable capacitance effects and its resistance adds to the electrolyte resistance. The mechanism of the formation of passivation layers is not yet understood, but it seems that the passivation layers formed in the composite systems studied protect the lithium electrode against further corrosion.

The new generation of composite electrolytes is based on aluminum carboxylates **9** [78,79].



$R = CH_3(OCH_2CH_2)_n$—

$n = 1, 3, 7$

**9**

This type of organoaluminum modifiers in combination with PEO and lithium salts enable the obtaining of solid and gel polymeric electrolytes, which are chemically and mechanically stable up to *ca.* 100°C. The DSC studies indicate that the interactions between aluminum carboxylates and PEO are rather weak and the additive acts mainly as an oligomeric solvent, which hinders the crystallization of PEO chains. This effect is especially visible with lithium salts which form complexes with oxyethylene units both in PEO as well as in the modifier`s molecule like lithium perchlorate or lithium bis(trifluoromethanesulfone)imide. These electrolytes form a spatial net in which the $Li^+$ cations and aluminum atoms coupled by carboxylic bridges are the nodes. Such a structure causes the PEO chains to form crystallization nuclei with greater difficulty and after melting of the crystals the carboxylate modified electrolytes behave as an amorphous system over a wide temperature range. The optimal modifier content is 30–40 wt. %. The electrolytes containing such a share of the carboxylate show conductivities in the range of $1\text{–}7 \times 10^{-5}\ S \cdot cm^{-1}$ at ambient temperature and reach values in the range of $10^{-3}\ S \cdot cm^{-1}$ at 60–70°C. It should be noted that the addition of aluminum compounds causes an increase in the electrolyte conductivity not only at ambient temperature (which was observed in many composite electrolytes and was attributed to the changes in crystallinity of the PEO chains), but also at a temperature higher than the melting point of the PEO crystalline phase. The increase in the concentration of charge carriers and/or increase in their mobility due to a decrease in the concentration of ion aggregates may be the reason for this. The effect of carboxylate on the mobility of polymer chains is probably less important, since as is shown by DSC studies it is of no essential effect on the $T_g$ values of the electrolytes studied. These studies indicate, however that the modifiers can more effectively complex lithium salts than PEO, and thus increase the degree of their dissociation. The more effective complexation of lithium cations by short, fully amorphous oxyethylene segments of the modifier might be one of the reasons for this. The complexation of anions by electrophilic aluminum atoms present in the carboxylate molecule might be another possibility, but this hypothesis still requires verification.

This approach is at present systematically developed to derivatives of other metals (B, Ti) in order to optimize the acidic properties of the modifier and seeking of systems forming passivating films of good conductivity at the lithium-polymer interface.

## Blend Based Polymeric Electrolytes

The blending of two or more commercially available polymers in order to obtain new products of desirable properties is one of the simplest and widely applied concepts in the field of material science. Until now about 200 polymer pairs, which are totally miscible on a molecular scale, have been reported in the literature. By "total miscibility" is meant that the mixture of polymers does not show any specific features of its constituents. A necessary (but not sufficient) criterion for miscibility is a negative value of the free energy of mixing ($\Delta G_m$):

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{1}$$

The value of the combinatorial entropy of mixing ($\Delta S_m$) is usually positive and thus favors mixing. However, when the molecular weight of the polymers in the blend is high, the entropy of mixing becomes very small and negative and the $T\Delta S_m$ value is usually too small to have a substantial influence on the $\Delta G_m$ value. Thus, in most cases miscibility occurs in systems with negative values of the enthalpy of mixing ($\Delta H_m$). This might occur if the contribution from specific, favorable interactions (via hydrogen bonding or electrostatic forces) is greater than that from dispersive interactions [80,81].

Since this critical condition is satisfied rather rarely, most of the polymer mixtures show heterogeneity over the whole range of compositions and over a wide range of temperatures. One of the most popular approaches to the problem of polymer blends is to consider the component which is in excess as a matrix in which the second component is dispersed or exists in the form of scattered "islands". Systems of a stable, heterogeneous morphology (called "compatible blends") often show interesting properties which are not observed for homopolymers or miscible blends.

Many blends which consist of high molecular weight polymers and form homogeneous mixtures are less miscible at higher temperatures and above the lower critical separation temperature (LCST) phase separation may occur, according to a spinodal or binodal mechanism. Polymer miscibility is only observed for the amorphous phase. If one of the polymer blend components crystallizes, the amorphous material may be present in interfibrillar and interlamellar zones or segregate into domains in intraspherulittic regions and in interspherulittic contact zones [82].

Over the past few years a number of papers have been published which describe the application of polymer blends as matrices in polymer solid electrolytes [73,83–98]. The primary object of the former studies was to improve the mechanical properties of polyether-salt complexes, particularly at elevated temperatures. This strategy was originally disclosed by Tsuchida *et al.* [83] who studied the PEO-$LiClO_4$ system supported by poly(methacrylic acid). This system is fully miscible due to the formation of hydrogen bonds between both polymers. Although the thus prepared polymeric matrix is completely amorphous, the ionic conductivities of electrolytes obtained were poor because of strong interactions between polar groups hindering segmental motion. A similar system consisting of a PEO-$LiClO_4$ electrolyte mixed with poly(acrylic acid) [84] was found to be a more flexible conductor of ambient temperature conductivities approaching $10^{-5}$ S·cm$^{-1}$. The first electrolytes based on immiscible blends were described by Gray *et al.* [85]. They consisted of PEO/polystyrene and lithium salts. The mechanical properties of these electrolytes are far better than those for the pristine PEO based system. Conductivities are similar to those measured for a PEO-salt electrolyte for polystyrene concentration lower than 40% by weight. For higher concentrations the conductivities dropped. This was attributed by the authors to the formation of nonconductive polystyrene clusters in an electrolyte structure. At temperatures exceeding the melting point of the crystalline PEO (~70°C) the percolation limit corresponds to about 60% by weight of the nonconducting polymer concentration.

In our group we have focused attention on the conducting properties of blends comprising high molecular weight PEO ($M = 5 \times 10^6$ g/mol) and various polar polymers obtained by radical polymerization or copolymerization, acrylic or methacrylic acid esters, amides and nitriles [73,87–98]. In Table 2 are presented several examples illustrating the effect of these polymers on the conductivity, crystallinity and glass transition temperature of PEO complexes with $LiClO_4$. One can observe that despite the addition of a "nonconducting" component several electrolytes based on this type of blends exhibit much higher ambient and subambient ionic conductivities than pristine PEO-salt complexes. A maximum in the conductivity is usually observed for the samples containing 15–30 wt. % of the acrylic component.

**Table 2.** Crystallinity ($X_c$), glass transition temperature ($T_g$) and ambient conductivities ($\sigma_{298}$) of PEO-$LiClO_4$-acrylic polymer electrolytes[a].

| Acrylic polymer[b] | Concentration of acrylic polymer | $X_c$ | $T_g$ | $\sigma_{298}$ |
|---|---|---|---|---|
| | wt % | % | °C | S·cm$^{-1}$ |
| | 0 | 70 | –28 | $6.1\times10^{-7}$ |
| PMM | 20 | 31 | –27 | $1.5\times10^{-6}$ |
| | (20)[c] | 60 | –33 | – |
| *s*-PMM | 20 | | –27 | $1.4\times10^{-5}$ |
| *i*-PMM | 20 | 51 | –57 | $9.0\times10^{-5}$ |
| PAPG | 20 | | –70 | $1.0\times10^{-4}$ |
| PAA | 20 | 4 | –53, –32 | $2.5\times10^{-6}$ |
| PNNDMAA | 10 | 3 | –35 | $9.0\times10^{-6}$ |
| | 15 | 1 | –34 | $1.2\times10^{-5}$ |
| | 20 | 1 | –37 | $8.5\times10^{-6}$ |
| | 50 | 43 | –43 | $1.1\times10^{-7}$ |
| P(AN-*co*-MM) | 30 | 15 | –7 | $8.0\times10^{-5}$ |
| P(AA-*co*-$SO_2$) | 40 | | | $3.2\times10^{-5}$ |

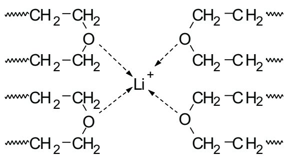
[a]samples doped with 10 mol % of $LiClO_4$ with respect to PEO monomeric unit, [b]PMM – atactic poly(methyl methacrylate), *s*-PMM – syndiotactic poly(methyl methacrylate), *i*-PMM – isotactic poly(methyl methacrylate), PAPG – poly{ethoxy[poly(propylene glycol)] acrylate}, PAA – polyacrylamide, PNNDMAA – poly(N,N-dimethylacrylamide), P(AN-*co*-MM) – copolymer of acrylonitrile (36 mol %) with methyl methacrylate (64 mol %), P(AA-*co*-$SO_2$) – copolymer of acrylamide (70 mol %) with sulfur dioxide (30 mol %), [c]value for undoped blend.

The phase structure of these electrolytes is not exactly known. Several observations indicate, however that some amount of nonconducting polymer can introduce a certain disorder into the system, reducing the crystallinity of PEO chains and hence increasing the concentration of the conducting amorphous phase. On the basis of DSC, FT-IR FT-Raman, SEM and X-ray dispersive studies, interactions were found to occur between lithium cations and the functional carbonyl group in acrylic polymers [98]. Therefore, in these systems lithium cations can be coupled to three types of ligands. These are counterions, which may form ion pairs or ion aggregates, oxygen atoms in polyether chains and carbonyl oxygen in acrylic polymers functional groups. The interaction between cations and macromolecular ligands leads to the formation of various types of complexes. They can be divided into three general categories.

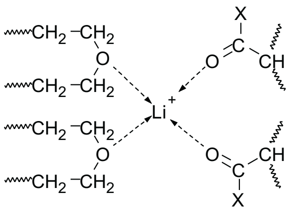
Type 1 complexes (**10**): PEO-$Li^+$-PEO complexes involving Lewis base ether oxygen atoms from polyether chains. These complexes incorporate transient crosslinks between polyether chains which stiffen the polyether matrix and reduce the charge carriers mobility.

Type 2 complexes (**11**): mixed PEO-Li+-acrylic polymer complexes involving oxygen atoms from polyether chain and carbonyl groups in the second polymeric component.

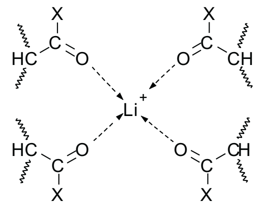
Type 3 complexes (**12**): acrylic polymer-Li+-acrylic polymer involving carbonyl functional groups. Examples of these complexes are schematically shown below.



**10**



X = OR, $NH_2$, $N(CH_3)_2$ **11**

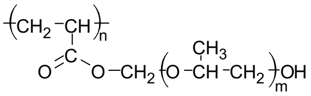


X = OR, $NH_2$, $N(CH_3)_2$ **12**

Complexes of type 1 and 2 occur mainly at small acrylic polymer content in the system. The interaction between both polymers *via* $Li^+$ in mixed complexes reduces the nucleation and crystallization growth rate of the crystallizable component. In some systems, for example PEO-$LiClO_4$ electrolytes doped with 15–20 wt. % of poly(N,N-dimethylacrylamide), the crystallization at ambient temperature is getting so slow that the portion of the nonconducting PEO crystalline phase does not exceed 1%. Type 2 complexes may be formed on the interface of both polymers or inside one of the phases when the systems forms miscible blends.

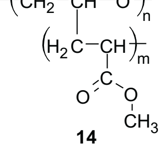
Information on the types of blends formed can be achieved by studying the glass transition temperature of these systems. The occurrence of immiscible blends is manifested by the presence of a highly flexible amorphous phase with glass transition temperature comparable to that of undoped PEO. This results from the decrease in the concentration of cations attached to the polyether chain and the density of transient crosslinks in the conducting phase. This is a system similar to nanocomposites with ceramic additives, in which the non-conducting core is surrounded by a layer of amorphous electrolyte of very flexible chains, due to which high ion mobility is achieved. Such dispersed systems form, among others, electrolytes containing polyacrylamide, poly(methyl methacrylate) of isotactic structure and a number of random copolymers of acrylonitrile and methyl methacrylate. The highest ambient temperature conductivities for this type of blend based electrolytes ($7–9\times10^{-5}$ $S\cdot cm^{-1}$) are significantly higher than the value estimated for fully amorphous type 1 complexes (**10**) ($\sim10^{-5}$ $S\cdot cm^{-1}$) of regular distribution of transient crosslinks.

In the case of miscible blends the glass transition temperature of the system is considerably higher, since it is an additive value resulting from the volumetric shares of the flexible polyether and stiff acrylic polymer chains. Such phenomena are observed among others in electrolytes containing atactic or syndiotactic poly(methyl methacrylate), methacrylamide and poly(N,N-dimethylacrylamide). These stiff chains are a barrier for ion mobility and therefore the conductivity of electrolytes based on miscible PEO blends ($10^{-6}–10^{-5}$ $S\cdot cm^{-1}$ at room temperature) is usually lower than that measured for immiscible systems. Systems developed in our group containing comb-like acrylic polymers with short oxyethylene segments in side chains, *e.g.* poly[ethoxy[poly(propylene glycol)] acrylate] (**13**) are an exemption.



**13**

In this system the flexible side chains act as a very efficient internal plasticizer, similarly as the hybrid systems **10**, **11**. Strong segmental motions of the polyether chain and acrylic component provide favorable conditions for fast ionic transport and the value of ambient conductivity approaches the value $10^{-4}$ $S\cdot cm^{-1}$. The high flexibility of the blends containing comb-like systems was confirmed by DSC experiments showing the $T_g$ value of –70°C, which is even lower than that for pristine PEO. A similar effect was achieved by us when a grafted PEO-poly(methyl methacrylate) copolymer (**14**) was used as polymeric matrix.



**14**

When exceeding a certain optimal concentration of the acrylic polymer, the PEO crystalline phase content in electrolytes based on acrylic polymer blends increases and may be even larger than that in pristine PEO-salt complexes. The reason for this is the formation of non-conducting type 3 complexes (**12**) and polyether fraction, which does not contain lithium cations and hence quickly undergoes crystallization. As a result, in systems of high acrylic polymer content a decrease in the concentration of amorphous type 1 and 2 complexes (**10** and **11**, respectively) in which the charge transfer is possible is observed, and the conducting properties of blends decrease.

One of the properties of the polymer additive, which may play an important role, is its polarity. A highly polar additive should increase the dielectric constant of the polymer host and hence its solvation ability and dissociation degree of the salt used as a dopant. We estimated the fraction of free $ClO_4^-$ anions for the polymer electrolytes based on PEO-$LiClO_4$ complexes modified by poly(N,N-dimethylacrylamide), on the basis of the changes in the shape and position of $\nu(ClO_4^-)$ band in FT-IR spectra. After separation of the observed signals in the 620–640 $cm^{-1}$ range into two contributions it was found that in the absence of the acrylic component the fraction of free anions at ambient temperature is about 75%. It increases up to 100% after addition of 25 wt. % of a polar polymeric additive. This suggests that the main contribution to the total bulk conductivity in this system may come from the high mobility of the anions, whereas the lithium cations trapped in complexes **11** and **12** move significantly slower.

Despite the relatively high conductivity of blend based electrolytes, the attempts to apply them in lithium batteries with a metallic lithium anode and $MnO_2$ composite cathode were not successful due to the formation of highly resistant layers at the Li-electrolyte interface. The cell open circuit voltage (OCV) was relatively high (3.2–3.5 V), however, the current densities obtained in the 10–20 $mA/cm^2$ range were considerably lower than could be expected on the basis of OCV and electrolyte ionic conductivity values.

It seems that this type of systems can find practical application as electrolytes in super-capacitors, whereas the hitherto attempts to utilize them in lithium batteries were unsuccessful due to the formation of highly resistant layers at the Li-electrolyte interface [70].

## Toward Single Cation Conductive Systems

In polymer electrolytes both cations and anions are mobile. However, only cations take part in the electrode reactions. Anions accumulate at the anode and become depleted at the cathode, since they can neither be formed nor discharged at the electrodes. This leads to the formation of high and low salt concentration regions at the interface during cell charging and discharging, which strongly limits the performance of electrochemical devices. The anion migration could be eliminated by the application of lithium polyelectrolytes bearing a negatively charged ion covalently attached to the polymer backbone, as a source of charge carriers. It turned out, however that solid lithium polyelectrolytes exist to low conductivity (usually in the range $10^{-6}$–$10^{-11}$ S/cm) to allow a reasonable current density in a lithium battery [5]. Therefore, most of the current attempts to obtain single cation highly conductive systems are based on the use of anion-trapping compounds as additives. In the literature studies of the use of cation receptors such as crown ethers, cryptands and calixarenes in low molecular weight non-aqueous solutions [96–100] as well as polymer electrolytes are more widely described. Anion receptors based on boron compounds were applied to the solutions of lithium salts in aprotic (inert) electrolytes based on low molecular weight solvents [104,105] as well as in gel polyelectrolytes [106]. Boron based aza ether compounds (borane, borate complexes) have been studied by McBreen and coworkers [107–110], using mainly near edge X-ray absorption fine structure spectroscopy (NEXAFS). They showed that the degree of complexation of $Cl^-$ or $I^-$ anions strongly depend on the structure of the boron compounds. Also the dramatic enhancement in ionic conductivity upon the addition of boron compounds has been noticed in these electrolytes.

Presently Wieczorek and coworkers are studying composites based on PEODME $M_w = 500$ triphenylborate complexes with different salts LiI, $LiCF_3SO_3$, LiNTFSI, $LiBH_4$ and $LiClO_4$.

Studies on the use of anion receptors in polymer electrolytes are very limited. Papers dealing with this subject are based on either theoretical predictions [111] or studies on the addition of boron family compounds, as well as cyclic or linear aza-ether structures with electron-withdrawing groups to oligoethers [107–110].

In our group we recently developed very efficient $I^-$ anion receptors, in which urea derivatives attached to calixarenes are employed as complexing ligands [112]. Introductory studies show that after addition of these compounds to PEO/LiI complexes it is possible to obtain electrolytes in which the $Li^+$ transference number is close to unity.

## Concluding Remarks

Polyether complexes with lithium salts are until now the only type of electrolytes which can be applied in rechargeable lithium batteries based on Li metal as anode and are regarded as the most promising candidates for the new storage system with high energy density. As a result of cooperation of 3M and Hydro-Quebec, a pilot production of cells of 10–15 Ah capacity was initiated. Cell voltage is in the range 2.6–2.8 V and specific power 400 W/kg. This battery is tested in vehicles of electrical propulsion. Similar prototypes are produced also in other industrial centers, *e.g.* in Europe within a mutual program of Electricité de France, Bolloré Technologies and Schneider Electrics. To achieve these parameters the cells should operate in the 60–80°C range for the conductivity values to be about $10^{-3}\,S \cdot cm^{-1}$. Under these conditions the application of composite electrolytes is the simplest method, from the technological point of view, for obtaining materials of appropriate mechanical properties and high chemical resistance. The addition of nanofillers or organometallic precursors that can form nanocomposites *in situ* increases the conductivity several-fold at 60–80°C, and prevents crystallization for at least several weeks at ambient temperature. Two other important advantages of these systems are an increase in the apparent $Li^+$ transference number, from low of ~0.1 (common for pristine PEO complexes) to ~0.6 and the formation of a stable, low resistance interface in contact with the metallic anode.

All these physical characteristics, once optimized, would make them suitable candidates for rechargeable solid state lithium polymer batteries. Although much attention has recently been focused on nano-composite polymer electrolyte systems by various groups, the mechanism of ionic conductivity enhancement and the role played by the nano-sized ceramic fillers such as $Al_2O_3$, $SiO_2$ and $TiO_2$ is still not well understood.

There is common agreement that there is a decrease in the polyether crystallinity and that the polyether flexibility changes due to the addition of filler particles. Usually, a less significant impact of fillers on conductivity is observed when polyethers are completely amorphous (*i.e.*, above the melting point). Knowledge of the structure, as in many other areas of material science, is an essential factor in building an understanding of the physical behavior, especially for the mechanism of ionic conductivity in complexes of polyethers. Transport mechanisms for ions in composite systems are highly dependent on the polymer host, ion types and the sizes and sorts of filler. However little is known about the mechanisms responsible for the changes in conductivity, role of the terminal groups of the polymer host in composite electrolytes and the salt concentration range where the filler acts as the conductivity enhancer.

The even more and more important problem is the better understanding of the lithium surface film formation, its composition and properties as a function of polymer electrolyte bulk and surface composition. Controlled formation and stabilization of the protective layer by chemical modification of the polymer electrolyte components may also enable the designing of cells operating at ambient and subambient temperature. To achieve appropriate conductivity values under these conditions, a polar organic solvent is additionally introduced to decrease the local viscosity of the system or obtain an electrolyte in the form of a gel. However, such an operation requires the necessity of changing the metal anode for a composite one, which causes a 15–20% reduction of specific energy or covering of the lithium electrode with a nanometric protective layer of high conductivity. There are some examples that such a layer can be formed by, *e.g.* selective sorption of ceramic materials on the lithium surface or by lithium sulfides afforded in the electrode reaction with organic polymers containing sulfur [113,114].

## Acknowledgments

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