Solid polymer electrolytes based on ethylene oxide polymers

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Dedicated to Professor Stanisław Penczek on the occasion of his 80th birthday

Abstract: Solid salt solutions in poly(ethylene oxide) have been intensively studied in view of their practical application in lithium batteries and other electrochemical devices. Many attempts of modifying the polymer matrix chemical structure and morphology have been undertaken to improve the conducting properties of these systems and increase the ion transport selectivity. The basic strategies developed in the last three decades have been presented in the paper, especially synthesis methods of new ethylene oxide copolymers, characterization of electrolytes comprising poly(ethylene oxide) blends and composites and attempts of obtaining polyelectrolytes bearing inbuilt ethylene oxide monomeric units segments.

Keywords: polymer electrolytes, ionic conductivity, ethylene oxide, copolymers, blends, composites.

Polimery tlenku etylenu stosowane w stałych elektrolitach

Streszczenie: Stałe roztwory soli w poli(tlenku etylenu) są od szeregu lat intensywnie badane pod kątem ich wykorzystania w bateriach litowych i innych urządzeniach elektrochemicznych. Aby poprawić właściwości przewodzące takich układów i zwiększyć selektywność transportu jonów, podejmuje się liczne próby modyfikacji struktury chemicznej i morfologii matrycy polimerowej. W pracy przedstawiono podstawowe strategie rozwinięte w ostatnich 3 dekadach, a zwłaszcza metody syntezy nowych kopolimerów tlenku etylenu, charakterystykę elektrolitów zawierających mieszaniny lub kompozyty poli(tlenku etylenu) oraz próby otrzymania polielektrolitów z wbudowanymi segmentami merów tlenku etylenu.

Słowa kluczowe: elektrolity polimerowe, przewodnictwo jonowe, tlenek etylenu, kopolimery, mieszaniny, kompozyty.

INTRODUCTION

Ethylene oxide (EO) is a reactive cyclic ether, which undergoes polymerization in the presence of initiators of both nucleophilic as well as electrophilic character. Polymerization products of relatively small molar mass (200—10 000 g/mol), commonly called poly(ethylene glycol) (PEG), used among others as components of drugs, cosmetics, polar stationary phases for gas chromatography and lubricating coating for various surfaces in aqueous and non-aqueous environment, are of the greatest practical importance. Segments built of EO monomeric units (m.u.) constitute the hydrophilic component in various types of surfactants and other more advanced materials of amphiphilic character, which in aqueous medium may form micelles and larger aggregates utilized as drug or photosensitizer carriers for photodynamic therapy. On the market is also present poly(ethylene oxide) (PEO) of high molar mass ($100 \cdot 10^3$—$8\,000 \cdot 10^3$ g/mol) produced by coordination polymerization catalyzed with magnesium, calcium or strontium derivatives. Due to good solubility in water they are used as thickeners, flocculating agents, and water retention aids or binding agents, especially in paper and textile industries. They are also valuable thermoplastic materials that can be extruded, injection molded and cast from organic solvents [1].

The presence of oxygen atoms in the PEO main chain causes that this polymer can relatively easily complex cations and form solid solutions with many salts and acids [2—4].

In the late 1970 the pioneer works of Wright and Armand *et al.* [5—7] appeared, in which it was shown that this type of complexes are capable to transport ions in solid phase and a conception of their practical application as electrolytes in electrochemical devices was presented. Most of the early studies on PEO complexes were stimulated by the development of lithium batteries with high energy density with a lithium or lithium alloy anode and cathode made from transition metal derivatives of layered structure (*e.g.* V_6O_{13}) capable of reversible lithium cations intercalation. These types of batteries were inten-

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sively studied by various research group and several prototypes of 10—15 Ah capacity, cell voltage in the range 2.6—3.0 V and specific power around 400 W/kg were constructed [8, 9]. Solid electrolytes based on PEO have been also considered as replacement for liquid electrolytes for several other electrochemical devices such as portable power source, variable transmission ("smart") windows, sensors and displays [10—13], especially for miniaturized systems in which cells may be no thicker than 20—100 μm.

The main advantages of PEO as matrix in polymer electrolytes are its good mechanical properties at ambient temperature, ease of fabrication of thin films of desired size, its ability to ensure proper electrode-electrolyte contact, high electron-donor power to form coordinated bond with cations and low barrier to segmental motion of polymer chain in amorphous phase providing a suitable condition for ion movements. The mechanism of ion motions may involve the formation of time-dependent pathways in polymer matrix, the short-range transport of ions temporarily attached to polymer chain and ion hopping between ionic cluster or coordination center (Fig. 1).

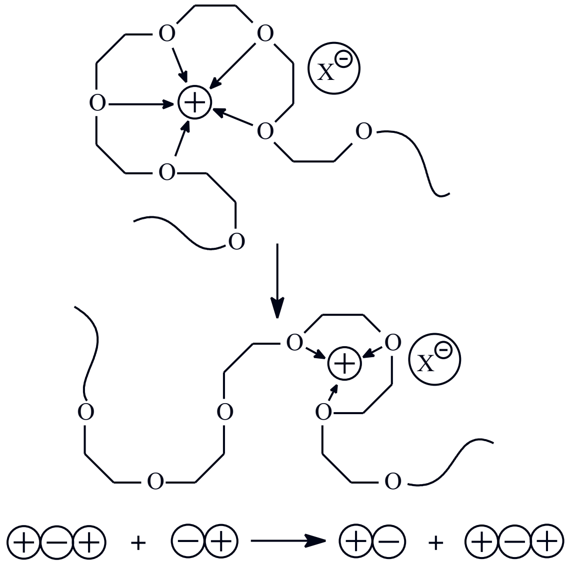


Fig. 1. Ion transportation in PEO

Polymer and ion motions are coupled and hence the presence of a flexible amorphous phase of a suitable distance between coordination centers is essential for high ionic conductivity [14]. Unfortunately, PEO is prone to crystallization and formation of stoichiometric crystalline phases with salts, both of which reduce electrolyte conductivity because the crystalline domains are basically electrical insulators [14, 15]. Here the conductivities of PEO — salt system at ambient temperature are in the range 10^{-7}—10^{-8} S/cm, which is too low for most applications. For example, for electrolytes working in lithium batteries the conductivities exceeding 10^{-4} S/cm are required and to achieve that threshold the cell should operate at temperature higher than melting point of PEO crystalline phase (65 °C).

It should be noticed that in solid solutions of salts in PEO, cations and anions are both mobile, however, only cations take part in electrode reactions during charge/discharge cycles. In the working cell anions accumulate at the anode and become depleted at the cathode since they can neither be formed nor discharged at the electrodes. It leads to the concentration polarization that strongly limits the performance of electrochemical devices. Furthermore, the anions movements are faster since their interaction with polymeric matrix is weaker than that of cationic species which are solvated by oxygen atoms in PEO matrix. The selectivity of charge transportation is characterized by the value of cation transfer number t_+ which is given by the following expression [eq. (1)]:

$$t_+ = D_+ / (D_+ + D_-) \tag{1}$$

where: D_+ and D_- — the cationic and anionic diffusion coefficients, respectively.

The values of t_+ reported for PEO complexes with inorganic salts applied in lithium batteries are typically in the range 0.05—0.30. In some systems, however, the anions mobility can be significantly reduced and it was shown that better battery performance might be exhibited by polymer electrolytes of t_+ close to 1 than those possessing an order of magnitude higher total conductivity but poorer t_+ [16].

Therefore, one of the most important strategic goals in the field of solid polymer electrolytes is the development of amorphous polymeric materials of improved conductivity at ambient temperature and high lithium transference numbers.

The objective of this work is to review briefly some of the approaches adopted in the last 3 decades to improve the conducting properties of EO polymers. This includes the preparation of various kind of EO copolymers and composite electrolytes in which PEO was mixed with inorganic, organic or hybrid inorganic-organic additives to suppress the tendency of polymer chain toward crystallization and/or reduce the anions mobility. We will show also several examples of successful application of PEG in the synthesis of polyelectrolytes and anion traps.

ETHYLENE OXIDE COPOLYMERS APPLIED IN SOLID ELECTROLYTES

It is well known that copolymers usually exhibit much lower tendency toward crystallization than homopolymers. This prompted many research groups to obtain solid polyether type solvents in which short EO segments are separated by other m.u. that do not enter the crystalline lattice of PEO. The products of PEG condensation with dimethyldichlorosilane [17] and methylene bromide [18, 19] were the first fully amorphous EO linear copolymers applied in electrolyte synthesis [eqs. (2, 3)].

$$\begin{array}{c} n\,HO(CH_2CH_2O)_mH \;+\; (CH_3)_2SiCl_2 \\ \downarrow \\ [O(CH_2CH_2O)_mSi(CH_3)_2]_n \;+\; 2\,HCl \end{array} \qquad (2)$$

$$\begin{array}{c} n\,NaO(CH_2CH_2O)_mNa \;+\; n\,CH_2Br_2 \\ \downarrow \\ [O(CH_2CH_2O)_mCH_2]_n \;+\; 2n\,NaBr \end{array} \qquad (3)$$

The procedures elaborated allowed to quite precisely control the length of EO m.u. homo sequences and determine the effect of its length on conducting properties. The highest conductivity was characterized by materials, in which the length of EO m.u. sequences was from 5 to 7. It is assumed that in such segments the number of oxygen atoms is sufficient to effectively complex lithium cations, and simultaneously, they are too short to form a crystalline phase. In optimal systems, after doping with lithium salts, electrolytes were obtained in which the ambient temperature conductivity was in the $1—5\cdot10^{-5}$ S/cm range. The EO copolymerization with other epoxides catalyzed with alkylalumoxanes, *i.e.* products of partial hydrolysis of trialkylaluminum compounds [20—22] leading to random copolymers of general structure [Formula (I)] appeared also to be a very effective method of synthesis of amorphous matrices of good conducting properties.

$$[(CH_2CH_2O)M(CH_2CH(R)O)] \qquad (I)$$
$$R = CH_3,\ C_6H_{13},\ C_6H_5,\ CH_2Cl,\ CH_2OCH_3,\ CH_2OC_4H_9,\ \textit{etc.}$$

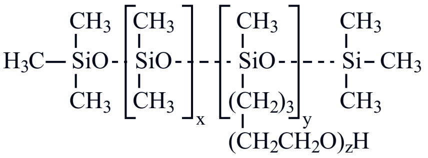
The copolymer with propylene oxide (PO), in which the EO m.u./PO m.u. molar ratio was *ca.* 5 showed the most interesting properties. At this proportion the products obtained were completely amorphous, and the presence of side methyl groups lead, additionally, to internal plastification. Electrolytes obtained from this copolymer were found for glass transition temperature below –70 °C, whereas the T_g values for analogous systems obtained with PEO were by 30 to 40 degrees larger. The lack of crystalline phase and high flexibility of the conducting amorphous phase enabled fast ion transport and at appropriate selection of lithium salt, ambient temperature conductivity of *ca.* $1\cdot10^{-4}$ S/cm could be obtained, *i.e.* by 3 to 4 orders of magnitude higher than that for PEO complexes [22].

Poly(1,3-dioxolanes) [23] and linear EO copolymers with sulfur dioxide or carbon dioxide [24—26] have been also used as solid solvents for lithium salts. It turned out, however, that the number of EO m.u. in repeating units is too small to achieve high conductivity after doping.

Unfortunately, the mechanical strength of highly conducting electrolytes employing linear copolymers is often poor. Most of them creep under the pressure applied in electrochemical devices leading to short circuiting effects at temperature exceeding 40—50 °C.

The formation of crosslinked network structures based on PEG and trifunctional EO oligomers has been extensively used to produce more mechanically stable materials. The most common approach was based on polyaddition reactions with isocyanates leading to polyurethane structures [11, 27—32].

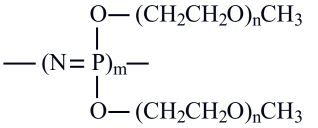
The immobilization of EO segments in network structure reduces, however, their mobility, which results in some sacrifice of conductivity unless the degree of crosslinking is limited and repeating units are used which are themselves very flexible. The most pronounced effect was achieved using EO segments attached to the short polysiloxane chains as polyols (II).



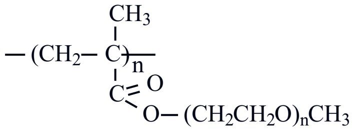
$$H_3C-\overset{CH_3}{\underset{CH_3}{Si}}O-\left[\overset{CH_3}{\underset{CH_3}{Si}}O-\right]_x-\left[\overset{CH_3}{\underset{(CH_2)_3-(CH_2CH_2O)_zH}{Si}}O-\right]_y-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3 \qquad (II)$$

The conductivities exceeding 10^{-5} S/cm at room temperature for the systems doped with $LiClO_4$ were reported and electrolytes were mechanically stable up to 120 °C [28, 30].

Branched copolymers, which short ion coordinating segments containing 5 to 22 EO m.u. are attached to the inert polymer backbones, have been also very intensively studied. The early studies have been focused on comb-like derivatives of polyphosphazenes [32, 33] (III), polymethacrylates [34, 35] (IV) and triblock styrene-butadiene-styrene copolymers [29].



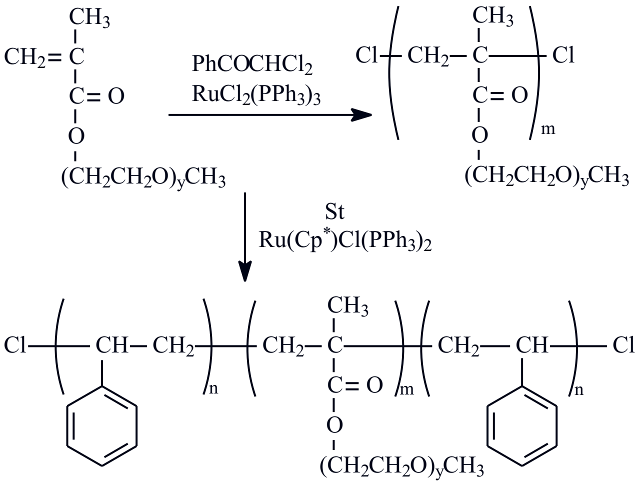
$$-(N=\overset{O-(CH_2CH_2O)_nCH_3}{\underset{O-(CH_2CH_2O)_nCH_3}{P}})_m- \qquad (III)$$



$$-(CH_2-\overset{CH_3}{\underset{C(=O)O-(CH_2CH_2O)_nCH_3}{C}})_n- \qquad (IV)$$

The polymers bearing short side oxyethylene segments combined with lithium salts form amorphous electrolytes of ambient temperature conductivity in the range $10^{-5}—10^{-6}$ S/cm.

To achieve a proper balance between conductivity and mechanical properties, attempts were made to use block copolymers composed of stiff polystyrene segment and elastic conducting segments derived from poly(ethylene glycol) methyl ether methacrylate. Therein the copolymer should exhibit microphase separation with the hard segment domain and the ion conducting continuous phase. The first copolymers of this type were obtained by the living anionic polymerization method [36], but the molar masses of the products obtained were too small for them to form membranes of satisfactory mechanical pro-

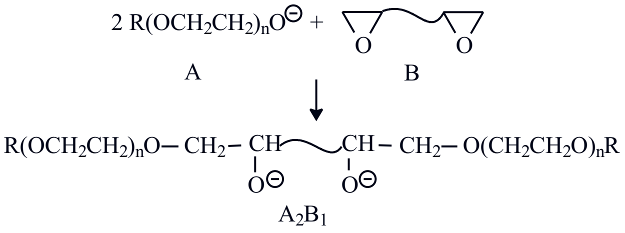


(4)

perties. Controlled radical polymerization methods appeared to be more effective, especially when applying ruthenium (II) complexes and bifuctional initiator [37, 38] [eq. (4)].

This method allows to obtain polymers of M_w over 100 000. Studies of the products obtained by means of the transmission electron microscope technique showed that phase separation with continuous phase of PEO segment forming a network structure is formed when the content of EO m.u. exceeded 70 mol. %. These copolymers doped with $LiClO_4$ exhibited high ionic conductivity of $2 \cdot 10^{-4}$ S/cm at 30 °C. The electrolyte forms free standing films of tensile strength around 5 MPa. The electrochemical test in $LiCoO_2$/copolymer electrolyte/Li cell showed the high discharge capacity at discharge rate 0.1 C (over 100 mAh/g against theoretical 140 mAh/g, which does not change after 100 cycles). Moreover, the electrolyte was electrochemically stable up to 4.5 V.

The methods of anionic and/or controlled radical polymerization have been utilized also for the synthesis of star branched EO copolymers. The procedure developed in the Centre for Molecular and Macromolecular Studies of Polish Academy of Sciences (Łódź, Poland) in the group of Professor Stanislaw Penczek is an example of a purely anionic process [39]. According to this method, in the first stage living EO oligomers are obtained in the classic anionic polymerization initiated with alkoxides, or in the reaction of metallic potassium with PEG mono ethers. In the next step the living oligomers are subjected to the reaction with diepoxides. The reaction between these reagents leads first to the formation of an A_2B_1 type reactive oligomer, which gradually increases the number of arms as a result of further addition reactions of primary and secondary alkoxide centers to epoxide groups [eq. (5)].

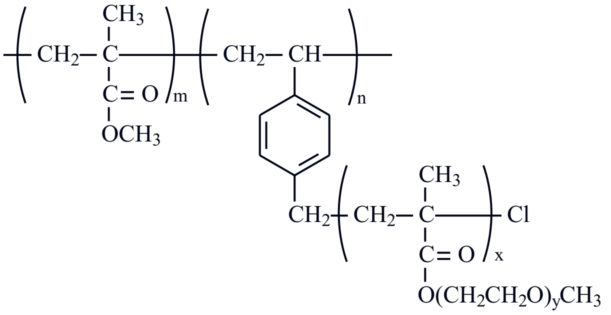


(5)

A_xB_y type reactive stars are formed from the reaction, to which further arms can be added as a result of EO anionic polymerization. Products bearing from several to 100 arms can be obtained, depending on the method of carrying out the reaction. The morphology of these polymers depends essentially on the EO homosequences length. Products, in which conducting segments contain 20 or more EO m.u. are semicrystalline, but after doping with lithium salts the crystalline phase disappears.

The mobility of ether segments in branched structures is smaller than that in the linear polymers amorphous phase, but at appropriate selection of the kind of salt and its concentration, amorphous electrolytes are obtained, the conductivity of which at low temperature is about 50 times higher than that of analogous systems with PEO [40].

In the synthetic approach based on radical polymerization, grafting of methacrylate chains with oxyethylene side chains by ATRP technique has been applied, utilizing reactive chlorine atoms in *p*-chloromethylstyrene m.u. (V) [41].

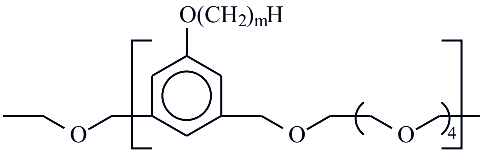


(V)

A number of other solutions are known, in which the anionic polymerization technique is combined with that of controlled radical polymerization [42], and also other methods, in which condensation of trifunctional monomers is utilized [43—45].

Binary structures with amorphous conducting pathways containing EO segments can be generated in these systems, showing ambient temperature conductivities reaching 10^{-4} S/cm.

With a view to creating highly conducting pathways, several amphiphilic polymers were synthesized in which short EO segments were separated by monomeric units bearing long aliphatic side chains [46—49]. Systems



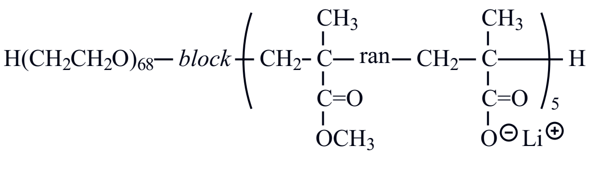
(VI)

based on poly[2,5,8,11,14-pentaoxapentadecamethylene(5-alkyloxy-1,3-phenylene)] (VI) have been the most extensively studied ones.

This polymer, after doping with lithium salt, adopts regular crystalline structures in which side chains interdigitate in a hexagonal layer between polyether helices into which cations are encapsulated. Anions lie in the inter-lamellar spaces.

The melting temperature of hydrophobic side chain is in the range 25—45 °C and above this temperature the system forms liquid crystalline smectic phases. Some of these materials have low temperature dependence of conductivity over 10^{-3} S/cm at 20—110 °C. Subambient measurements to –10 °C gave a conductivity of $4 \cdot 10^{-5}$ S/cm. These spectacular conducting properties are attributed to the specific mechanism of conduction which involves Li^+ hopping between neutral aggregates such as ion pairs or double ion pairs within the channels of diameter ~1 nm (see Fig. 1).

The similar mechanism of ions transportation was suggested also for systems based on other highly polar polymeric matrices like polyethers [50], polyacrylonitrile [51] or acrylonitrile copolymers [52], which do not dissolve lithium salts but are able to stabilize amorphous ionic clusters. In these systems (called polymer in salt) the concentration of salts is very high (70—90 wt. %), however, some of these systems form flexible membranes exhibiting glass transition temperature lower than that of parent organic polymers. Unfortunately, most of them are thermodynamically unstable and separation of polymer and salts occurs with elapse of time which has a negative effect on conducting properties [53]. Recently, these systems were significantly improved by application of block copolymers of PEO with random copolymer of methyl methacrylate with lithium methacrylate (VII) [54, 55].

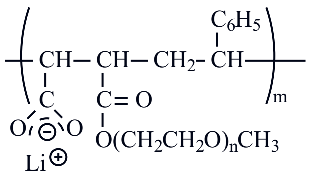


$$\mathrm{H(CH_2CH_2O)_{68}}-\mathit{block}-\left(\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{C(=O)OCH_3}}{\mathrm{C}}}-\mathrm{ran}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{C(=O)O^{\ominus}Li^{\oplus}}}{\mathrm{C}}}\right)_5-\mathrm{H} \qquad \text{(VII)}$$

The block copolymer microphase separates into spherical domains of acrylic components dispersed in PEO matrix. This material combines with lithium *bis*(oxalate)borate salt ($LiBC_4O_8$) to form elastic amorphous membrane of ambient temperature conductivity exceeding 10^{-5} S/cm and lithium transference number of 0.9. The preliminary tests in lithium batteries showed that electrolyte membrane also has good electrochemical stability during Li plating/stripping cycles.

POLYELECTROLYTES

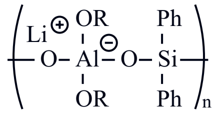
To improve the cation transport number several research groups have utilized the polyelectrolytes in which anionic groups are chemically bonded to the polymer back bone with alkali metal counter ions. The dielectric constant of solid polyelectrolytes is too low to ensure high degree of dissociation and ambient temperature conductivities have been very low, usually well below 10^{-6} S/cm. For instance, the polyelectrolytes bearing immobilized carboxylic anions of the following structure (VIII):



$$\left(\underset{\mathrm{COO^{\ominus}Li^{\oplus}}}{\mathrm{CH}}-\underset{\mathrm{C(=O)O(CH_2CH_2O)_nCH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{C_6H_5}}{\mathrm{CH}}\right)_m \qquad \text{(VIII)}$$

exhibit ambient conductivity in the range 10^{-9}—10^{-6} S/cm depending on the side-chain length [56]. However, at 90 °C the conductivity of electrolytes containing 7—22 EO m.u. differs only slightly and exceeds 10^{-5} S/cm which is regarded as border line for practical application. Somewhat better results were obtained by Ryu *et al.* [57] by using triblock systems: poly(lauryl methacrylate)-*block*-poly(lithium methacrylate)-*block*-poly[(oxyethylene)$_n$ methacrylate], system which approaches the 10^{-5} S/cm level at 70 °C.

Large hopes are now connected with hybrid polyelectrolytes, in which negative charges are localized on four-coordinative aluminum or boron atoms in $[AlO_4]^-$, $[BO_4]^-$, $[BC_4]^-$ type m.u., which are linked with EO segments, like for example in structure IX [58—60].



$$\left(\mathrm{Li^{\oplus}}\ \mathrm{O}-\overset{\mathrm{OR}}{\underset{\mathrm{OR}}{\mathrm{Al^{\ominus}}}}-\mathrm{O}-\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{Si}}}\right)_n \qquad \text{(IX)}$$

$R = CH_3(OCH_2CH_2)_n-$ n = 3, 7.2, 11.8

The ionic conductivity as high as 10^{-4}—10^{-5} S/cm at 25 °C were reported for the best materials of this class. Unfortunately, some of them contained low molecular weight contaminants which reduce the transference number below 1. However, it indicated a promising approach.

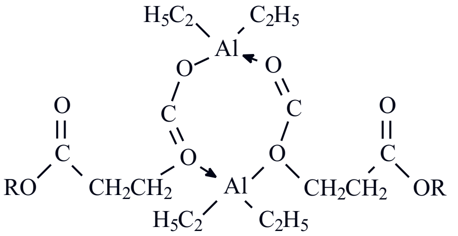
PEO BLENDS AND COMPOSITES

Very often additional components are added to EO polymers and lithium salts based polymer electrolytes, to improve their mechanical and conducting properties [61—63]. Most often these are inorganic fillers, such as aluminum, titanium or silicon oxides. The addition of small inorganic particles stiffens the polymeric matrix increasing the glass temperature of amorphous phase [64]. This in turn lowers the mobility of the charge carriers, however, several authors reported significant improvement in the ambient temperature conductivity (up to 10^{-4}—10^{-5} S/cm) of PEO complexes upon addition of 10—20 wt. % of ceramic components [61—68]. For higher concentration of fillers, the non-conducting phases are formed, which hinders the ionic movements. An increase in conductivity has been seen at temperatures up to the melting point of polymer complex. Above the melting point of crystalline phase there is little, if any, effect of the filler on conductivity. The improvement of ambient temperature conductivity of PEO is attributed mainly to the changes in morphology of electrolytes since the interaction with fine grained ceramic powders (especially nano-size fillers) strongly reduce the tendency of EO segments toward crystallization. Solid state ^{7}Li NMR studies [69] showed that in some systems fillers cause a weakening of the polyether-cation interaction which introduces a higher degree of disorder and provides better conditions for Li^+ transportation. It is assumed that acidic centers present the filler surface play a key role causing binding of fillers with the polymer matrix forming fast pathways for cation transport [61—63, 70—73]. Great interest is put forward to composites with substances, which dissolve in the polymer matrix and form stable complexes with anions [eq. (6)].

$$Li^+A^- + MtX_n \rightarrow Li^+ + AMtX_n^- \qquad (6)$$

Such interaction leads to an increase in the lithium salt degree of dissociation and to an increase in the anion size, and thus a decrease in its mobility.

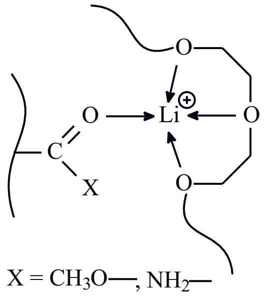
Initially, strong inorganic Lewis acids, such as aluminum or boron halogens were applied as complexing agents [56, 71, 72, 74, 75], but these acids interacted very strongly with the polyether matrix, often causing its decomposition, and also undergo dissociation with the formation of mobile anions, such as $AlCl_4^-$ or BF_4^-. Therefore, recently mainly organic boron derivatives of strong acidic properties resulting from the presence of fluorine atoms in organic substituents [74—79], or at boron atom [80] have been applied as anion receptors. In the presence of these additives, a considerable increase in conductivity of electrolytes and increase of lithium cations transference numbers to the 0.7—0.8 values were observed. Aluminum diethyl carboxylates containing oxyethylene side chains (X) appeared to be still more effective anion traps [81, 82].


(X)

R = $CH_3(OCH_2CH_2)_7$–

On the basis of electrochemical studies and nuclei diffusion rate measurements by means of solid state NMR technique it has been shown that after addition of 33 wt. % of this modifier to the PEO/CF_3SO_3Li complexes, the t_+ value at 50 °C reaches the value of 0.995, which suggests practically complete immobilization of triflate anions. Self-diffusion coefficient value for lithium cation is equal to $2.4 \cdot 10^{-6}$ cm^2/s. It was proved that in the studied system lithium salts form complexes with aluminum compounds which are stable up to about 110 °C. Furthermore, aluminum derivatives favorably affect the mechanical properties of conducting membranes also at elevated temperature. The role of anion receptors can be also fulfilled by supramolecular compounds such as cyclic azaethers, calixarenes or calixpyrroles [83—85].

A distinct improvement of the polymer matrices mechanical properties can be also achieved by the addition to the system of some organic polymers. The optimal content of additive is usually 15—30 wt. %. At this concentration range, polymers of low polarity, such as, *e.g*. polystyrene, practically do not affect a change in conductivity [36, 86]. However, in systems with more polar additives obtained by polymerization or copolymerization of acrylic or methacrylic acid esters, amides and nitriles, very often significant improvement of ambient and subambient conductivity is observed [62, 64, 71, 87—91]. The phase structure of these materials is not exactly known, however, on the basis of FT-IR, FT-Raman, DSC and X-ray dispersive studies, interactions were found to occur between both polymers *via* lithium cations which are linked to oxygen atoms in polyether matrix and the functional carbonyl group in acrylic polymers (XI).


(XI)

X = CH_3O—, NH_2—

The formation of mixed PEO-Li^+-acrylic polymer complexes reduce the crystallization rate of polyether chains and creates fast ion conducting pathways. The most significant effect was observed among others in electrolytes containing poly(methyl methacrylate) of isotactic structure, polyacrylamide and a number of copolymers of acrylonitrile with methyl methacrylate which tend to form separate phases. The highest ambient temperature conductivities reported for this type of electrolytes are 7—$9 \cdot 10^{-5}$ S/cm.

Several acrylic polymers like poly(methacrylic acid), poly(acrylic acid) or atactic poly(methyl methacrylate) which are fully or partially miscible with PEO also favor the formation of amorphous electrolytes, however, the flexibility of conducting phase and thus ion mobility is reduced because of the strong interaction between chains hindering segmental motion [61, 89, 92]. This disadvantage may be overcome by applying acrylic polymers with short flexible side chains *e.g.* poly{ethoxy[poly(propylene glycol)]acrylate} [93] or flexible polar main chains, *e.g.* epoxidized natural rubber [94], which provide favorable conditions for fast ionic transport and the value of ambient conductivity approaches the value 10^{-4} S/cm.

CONCLUSIONS

Solid polymer electrolytes constitute a bridge between on the one hand inorganic solid or molten electrolytes and on another conventional liquid electrolytes in which ions solvated by low molecular weight polar molecules can undergo long-range displacements.

The examples presented show that we are now able to obtain materials of good mechanical properties, ambient temperature ionic conductivity in the 10^{-4}—10^{-5} S/cm range and cation transference number above 0.8, but still there are a number of problems which have to be solved before reaching the commercialization step. One of the key issues is the better understanding of the phenomena occurring at the electrolyte-electrode interphase and promote the formation of protecting layers of low resistivity by the proper selection of electrolyte composition. Another important factor is the cost of conducting membranes. With this respect, the copolymers and polyelectrolytes of sophisticated architecture are rather too exotic to be applied as practical materials. Therefore, most of the current studies in the field of polymer electrolytes are focused rather on physicochemical modification of commercially available polymers and formation of multicomponent systems containing polymeric matrices, inorganic fillers saturated with solutions of lithium salts in polar organic solvents.

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