

IDENTIFICATION OF PEO - M(SO₃Cl)_x (M = Li, LiAl, Ca) POLYMER ELECTROLYTES

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Keywords: organic chemistry, PEO, PolyEthylene Oxides, polymer electrolytes, solid electrolytes, amorphous electrolytes, electrolyte films, oxohalide salts, plasticisers, crystallinity, PC, propylene carbonate, DME, DiMethoxyEthane, ionic conductivity, impedance spectroscopy, vibrational spectroscopy

Abstract: Preparation and electrochemical characterisation of (PEO)_nM(SO₃Cl)_x (M = Li, LiAl, Ca, X = 1, 2 and 4) polymer electrolytes is reported. Variation of the polymer electrolyte conductivity with temperature is correlated to the corresponding microstructural characteristics (degree of crystallinity). In the paper also the preparation and microstructural and electrochemical characterisation of (PEO)_nLiAl(SO₃Cl)₄ (n = 2 - 12) polymer electrolytes containing a mixture of plasticisers, i.e. propylene carbonate (PC) and 1,2-dimethoxyethane (DME), is presented. The effect of plasticiser mixture on polymer crystallinity and its electrical conductivity at various temperatures is studied using X-ray powder diffractometer analysis, differential scanning calorimetry in combination with impedance spectroscopy. The dependence of the glass transition temperature, crystallinity and conductivity of the (PEO/PC/DME)_nLiAl(SO₃Cl)₄ polymer electrolytes on salt concentration is measured and discussed.

Identifikacija polimernih elektrolitov PEO - M(SO₃Cl)_x (M=Li, LiAl, Ca)

Ključne besede: kemija organska, PEO polietilen oksidi, elektroliti polimerni, elektroliti trdni, elektroliti amorfni, plasti elektrolitske, soli oksohalidne, mehčala, kristaliničnost, PC propilen karbonat, DME dimetoksietan, prevodnost ionska, spektroskopija imedančna, spektroskopija vibracijska

Povzetek: V prispevku poročamo o pripravi in karakterizaciji trdnih polimernih elektrolitov (PEO)_nM(SO₃Cl)_x (M = Li, LiAl, Ca, X = 1, 2 and 4). Študirali smo, kakšen je vpliv kristaliničnosti in temperature na spremembo specifične ionske prevodnosti polimernih filmov. V delu poročamo tudi o pripravi mikrostrukturnih in elektrokemijskih lastnostih z mehčali modificiranih trdnih polimernih elektrolitov (PEO/PC/DME)_nLiAl(SO₃Cl)₄ (n = 2 - 12). Kot mehčalo smo uporabili mešanico propilen karbonata (PC) in 1,2-dimetoksietana (DME).

Mikrostrukturne in električne lastnosti polimernih trdnih elektrolitov smo študirali z rentgensko praškovno analizo (X-ray), diferenčno termično analizo (DSC) in imedančno spektroskopijo.

INTRODUCTION

The rapid development of the present technology poses particular urgency to the need for new, more efficient and less polluting power source systems /1, 2/. For instance, high energy density, rechargeable batteries are today needed to replace bulky lead-acid batteries for the development of long range electric vehicles with improvements in the air quality of large urban areas. Advanced, environmentally friendly batteries would be also highly welcome in the electronic consumer market where they could replace the nickel-cadmium batteries or, even, the most common zinc-carbon dry cells, with the final goal of limiting the risk associated to their waste disposal. However, the development of ambient temperatures, high-energy batteries is today a major task and, accordingly, many laboratories throughout the world are carrying out research aimed to reach this important goal /1, 2/. The so far most promising approach has been that directed to the development of lithium batteries. These batteries offer a superior energy content in respect to that delivered by more conventional electrochemical storage systems. In its most essential structure, a lithium battery is formed by a

lithium-based anode, a lithium ion conducting electrolyte and a lithium-ion-accepting cathode material. In synthesis, the overall discharge process involves the dissolution of lithium ions at the anode, their migration across the electrolyte and their insertion within the crystal structure of the host compound, while the compensating electrons travel in the external circuit of the same hosting compound, Fig. 1.

As the anode material in the batteries, generally metal lithium is used. Lithium is a very reactive metal which is attacked by almost any electrolyte material. In fact, corrosion reactions may induce the growth of passivation layers on electrode surface which may ultimately lead to a cell failure /1, 9-11/. One way which has been proposed for overcoming this problem is that of replacing the metal lithium by insertion compounds B_nC_m (coke or graphite insertion compounds; B_nC_m lithium sink negative electrode is capable of accepting and exchanging large quantities of lithium ions, *rocking chair batteries* /1, 2, 3/).

The insertion cathodes most commonly used in lithium batteries are inorganic compounds, such as transition metal dichalcogenides and oxides, which are characterised by layered or tunnel structures capable of providing channels for the easy access and fast mobility of

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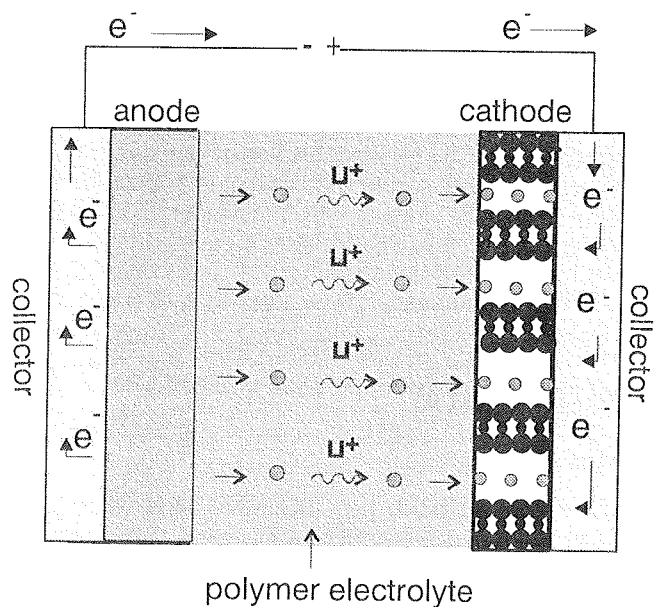


Fig.1. Schematic illustration of discharge process on the Li/AzBy battery (from ref. (1)).

lithium ions (insertion AzBy compounds having an open structure capable of accepting and releasing "x" number of lithium ions per AzBy mole, /1, 2, 3/).

Any liquid or solid conducting material characterized by fast lithium ion transport can be used as a proper electrolyte medium for these batteries /1 -3, 5-8, 12-15/. An important class of electrolyte which has been proposed and characterised in the most recent years are ionically conducting polymer membranes "polymer electrolytes". The potential uses of ion-conducting polymer electrolytes are numerous: e.g. they have been used to replace aggressive and dangerous liquid electrolytes in primary and rechargeable batteries and could be used in other electrochemical devices (sensors, electrochromic windows, electrochromic displays, etc.) /8/. However, polymer electrolytes offer many revolutionary properties, e.g., easiness of fabrication, high electrochemical and chemical stability, their elasticity compensates for quite big changes in volume during the electrochemical reaction both on anode and on cathode. Additionally, polymer electrolytes have two functions: to act as electrolyte and well as separator which prevents contact (electric short cut) between anode and cathode. The battery may be constructed in new forms such as a thin, flexible sandwich or plastic layers which may be shaped to fit any desirable empty space of the addressed device /1, 2, 8/. Due to these unique advantages, the development of lithium polymer batteries is today strongly supported and many are the ongoing projects aiming at their commercial production for the electric vehicle and the electronic consumer markets /1 - 8, 12-16/. Obviously, the polymer electrolyte is the key component of these new plastic-like batteries and thus the characteristics and properties of the most promising types of these electrolytes will be discussed and evaluated.

Ionically Conducting Polymer Electrolytes

Polymer electrolytes are ionically conducting materials formed by incorporating different salts into polymers /1, 2, 4-8, 12-16/. High molecular ($M = 10^5 - 10^6$) poly(ethylene oxide), PEO, is one of the most popular and studied polymer hosts for such electrolytes. A long polar PEO chain is an excellent solvent for most ionic salts

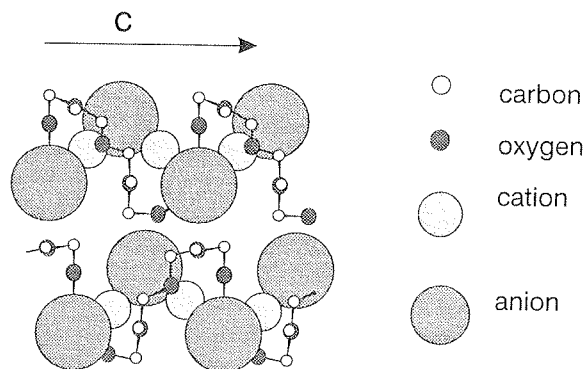


Fig.2. Schematic illustration of structure of PEO - MX complex (from ref. /5/).

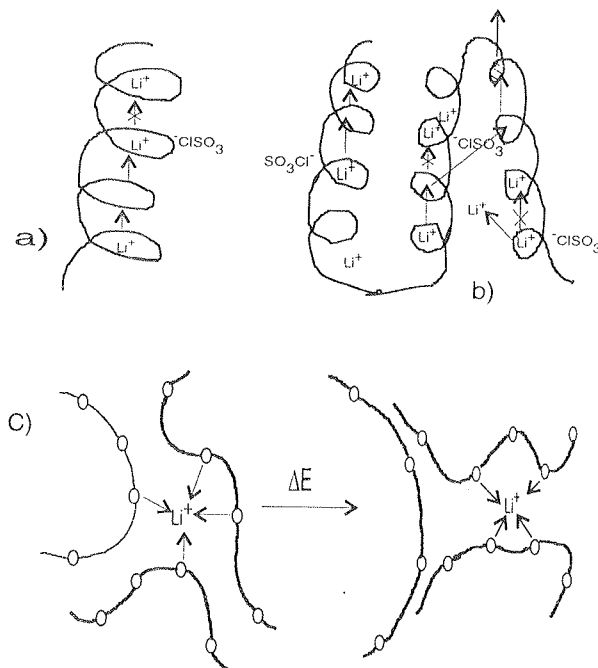


Fig.3. A pictorial representation of the migration of a metal ion (in our case lithium ion) in the polymer electrolyte.

- the lithium cations in the electrolyte move by "hopping" mechanism through the polymer channels (lithium ions jump from one co-ordination site into a vacant hole)
- in the crystalline phase lithium ions jump from one co-ordination site into a vacant hole or go to the amorphous phase where migration of a lithium ion assisted by polymer segmental motion.
- migration of a lithium ion assisted by polymer segmental motion.

(MX); MX salts are dissolved by the presence of polar ether groups (-O-) /1, 2, 4, 5, 7, 8/. It will be mainly stressed that the formation of the electrolyte (i.e. polymer - salt complex) occurs via the co-ordination of the metal ions (M⁺) by the oxygen atoms of the polymer chains, with a basic structure involving the folding of the chains around the M⁺ cations with their consequent separation from the anions (X⁻), Fig 2. The effective structure of solid PEO - MX systems may be much more complicated (involving single ions, ion - pairs and ion - clusters) /1, 2, 4, 7, 8/. However, the ionic transport in the solid polymer electrolyte is strongly related to the cation - ether oxygen coordination bonds (the stronger are these interactions the lower is the cation mobility) and to the freedom of polymer chains movements and to their rearrangements /8, 13, 14/. Local relaxation and sequential motions of polymer host chains become essential to confer high ionic conductivity to the electrolyte /2, 6-8/, Fig. 3c, Fig. 3b. At lower temperature (below PEO melting temperature (T_m) e.g. T_m < 60 °C), where the crystallinity of the electrolyte increases, the chain flexibility is hindered and the conductivity drops by several orders of magnitude, passing from ca. 10⁻⁴ Ω⁻¹ cm⁻¹ at 80 °C to ca. 10⁻⁸ Ω⁻¹ cm⁻¹ /2, 5, 8, 13, 14/. Above glass transition temperature (T_g) the cations in the electrolyte move through the polymer channels by "hopping" mechanism and the contribution of polymer chain flexibility is markedly reduced, Fig. 3a.

Electrical and electrochemical characterisation of (PEO)_nM(SO₃Cl)_x (M = Li, LiAl, Ca) polymer electrolytes

A number of poly(ethylene oxide), PEO-salt complexes are known to be electrochemically stable and exhibit high ionic conductivities at higher temperatures /2, 5, 8/. Alkali and alkali earth salts (Cl⁻, Br⁻, I⁻, SCN⁻, ClO₄⁻, BF₄⁻, AsF₆⁻) are the most frequently used for the preparation of polymer electrolytes because of high practical interest (especially high voltage of the Li / Li⁺ and Ca / Ca²⁺ couple) /12, 17/. Most of these complexes are polycrystalline, and therefore poor ion conductors near ambient temperature /2, 5, 8/.

Oxohalides are a class of salts, used as dopants, that have been very often studied and have usually shown good electrochemical characteristics (good conductivity, good stability of polymer electrolytes, etc.). A great deal of data has been recorded on LiCF₃SO₃, LiC(SO₂CF₃)₃, and LiN(SO₂CF₃)₂ /2, 5, 15/. Several years ago we used another (S, O, Cl) - based lithium salt, LiAl(SO₃Cl)₄, to alleviate the voltage delay effect of Li/SOCl₂ batteries /9-11/. In the present paper we check the characteristics of LiAl(SO₃Cl)₄ and related salts (LiSO₃Cl, Ca(SO₃Cl)₂) as dopants in a PEO matrix. We report on the preparation, electrochemical and microstructural characterisation of the (PEO)_nM(SO₃Cl)_x (M = Li, LiAl, Ca, X = 1, 2 and 4) polymer electrolytes.

Most PEO-based electrolytes have good mechanical strength and achieve high conductivity at about 100 °C (ca. 10⁻³ - 10⁻⁴ S cm⁻¹) (1, 2, 4, 5). However, they suffer from low conductivity values below 60 °C because of high crystallinity. The incorporation of a plasticiser into

the electrolyte composition usually reduces the crystallinity and therefore improves the conductivity of PEO-based electrolytes at room temperature /6-8, 14/. In this paper the preparation and characterisation of a solid polymer electrolyte with a composition of (PEO/plasticiser)_nLiAl(SO₃Cl)₄ is described and discussed. A mixture of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) is used as the plasticiser. The characterisation of polymer electrolytes focuses on the correlation between the electrochemical (conductivity) and physical characteristics of electrolytes with and without plasticisers.

EXPERIMENTAL

Reagents

Chlorosulphuric acid, p.a. (Kemika), and AlCl₃, p.a. (Fluka), were used without further drying or purification. LiCl, p.a., and CaCl₂, p.a. (Fluka), were vacuum dried before use (at 180 °C for 4 days). Thionyl chloride, purum (Fluka), was distilled at atmospheric pressure and the fraction boiling at 76 °C collected and used. PEO (relative molar mass M_w = 10⁶, Aldrich) was vacuum-dried before use (for 48 hours at 50 ± 2 °C). The PC and DME were cleaned with vacuum distillation and the middle fractions were used. Acetonitrile (Aldrich) and N,N-dimethylacetamide (Aldrich) were used as received after drying over 4 Å molecular sieves.

Li, Ca and LiAl-chlorosulphates were synthesised using a procedure described elsewhere /9-12/. The reaction yield was tested by X-ray and EXAFS analysis /8, 12, 13/.

Polymer films were prepared in an argon-filled Braun dry box. The relative humidity in the dry box was below 20 ppm. A two-solvent technique was used to prepare the (PEO)_nM(SO₃Cl)_x (M = Li, Ca, LiAl, X = 1, 2 and 4) electrolytes, the preparation procedure was described elsewhere /8, 12, 13/. The polymer films were prepared by casting the solutions (PEO)_nM(SO₃Cl)_x on a Teflon sheet. The excess solvent was evaporated and the films were finally dried under vacuum (<0.1 torr) at 50 ± 1 °C for 8 hours. A series of as-cast (PEO)_nM(SO₃Cl)_x mixtures, with n = 4 and n = 8 (where n = [EO / M⁺] ratio, M⁺ = Li⁺, Ca²⁺, (0.5 Li⁺ : 0.5 Al³⁺)), were prepared. In the case of mixed salts (e.g. LiAl(SO₃Cl)₄) the number "n" is related to the sum of the cations. The average film thickness was around 150 μm.

The (PEO/plasticiser)_nLiAl(SO₃Cl)₄ electrolyte was prepared by mixing 20 % PEO and 80 % PC /DME mixture. The mixing volume ratio between the PC (Fluka) and the DME (Fluka) was 70:30. The LiAl(SO₃Cl)₄ was dissolved in PC/DME mixtures before being added to the polymer solution. The mass ratio between the PEO and the PC/DME was the same in all solutions. Polymer films were prepared by casting the (PEO/PC/DME)_nLiAl(SO₃Cl)₄ solutions on a Teflon plate and evaporating the excess solvents and plasticisers in a vacuum until a film was formed, the more detail preparation procedure was described elsewhere /8, 14/. A series of as-cast (PEO/PC/DME)_nLiAl(SO₃Cl)₄

films with n between 2 and 12 was prepared, where $n = [\text{EO} / \text{M}^+]$ and $\text{M}^+ = \text{Li}^+, \text{Al}^{3+}$. EO is related to the PEO ether unit ($-\text{CH}_2\text{CH}_2-\text{O}-$) only, while the number " n " denotes the sum of all cations in the mixed salts. The average film thickness was c. 100 μm .

X-ray analysis of synthesised Li, Ca and LiAl - Chlorosulfates salts, $(\text{PEO})_n\text{M}(\text{SO}_3\text{Cl})_x$, and of $(\text{PEO}/\text{PC}/\text{DME})_n\text{LiAl}(\text{SO}_3\text{Cl})_4$ electrolytes was made using a Philips 1710 X-ray powder diffractometer using $\text{CuK}\alpha$ radiation with 2θ ranging from 5° to 65° in 0.025 steps with 1 s per step.

Differential scanning calorimetric (DSC) measurements were carried out with a Perkin-Elmer DSC7 calorimeter. For determination of glass transition temperature (T_g) the samples were heated at a rate of $20^\circ\text{C}/\text{min}$ from -80°C to 100°C . The melting point (T_m) of pure PEO, $(\text{PEO})_n\text{M}(\text{SO}_3\text{Cl})_x$ and of $(\text{PEO}/\text{PC}/\text{DME})_n\text{LiAl}(\text{SO}_3\text{Cl})_4$ complexes was determined from temperature scans performed at a rate of $10^\circ\text{C}/\text{min}$ from 25°C to 250°C .

The films intended for impedance response measurements were mounted between two gold (blocking) electrodes with a surface area of 0.5 cm^2 . The electrodes were spring-loaded to maintain a good and reproducible contact with the polymer films. The cell used for conductivity (impedance) measurements was enclosed in a hermetically sealed glass tube supplied with electrical leads /8, 13/. The temperature dependence of the conductivity of the polymer films was measured using an aluminium furnace, constructed in the laboratory, equipped with a Parr - 4843 thermoregulator and two Fe/constantan thermocouples. Measurements were taken in the range from 24 to 110°C at intervals of approximately $10^\circ\text{C} \pm 1^\circ\text{C}$.

Impedance response measurements in the frequency range from 1 MHz to 20 Hz were taken using a Hewlett Packard 4284A LCR meter. Below 20 Hz impedance responses were measured using a Solartron 1250 Frequency Response Analyzer and a 1286 Electrochemical Interface.

RESULTS AND DISCUSSION

Polymer $(\text{PEO})_n\text{M}(\text{SO}_3\text{Cl})_x$ electrolytes, $M = \text{Li}, \text{Ca}, \text{LiAl}$

From the literature /2, 5/ we know that the size of anions and cations in an inorganic salt influences the crystallinity of the host PEO. In Fig. 5 the effect of different cations ($\text{Li}^+, \text{Ca}^{2+}, \text{Li}^+\text{Al}^{3+}$) in the presence of the same anion (SO_3Cl^-) on the crystallinity of the $(\text{PEO})_8\text{M}(\text{SO}_3\text{Cl})_x$ electrolyte is shown. From a comparison of diffraction patterns it can be seen that the crystallinity of the electrolytes decreases by more than 85% with respect to the undoped PEO (here the intensity of the PEO peak at $23^\circ 2\theta$ was taken as the reference value). The decrease of the crystallinity with the addition of salts is usually related to the plasticising effect of salts on PEO /2, 5, 8, 13/.

Both the shape of the impedance response and its dependence on voltage bias (Fig. 4) confirm that all the

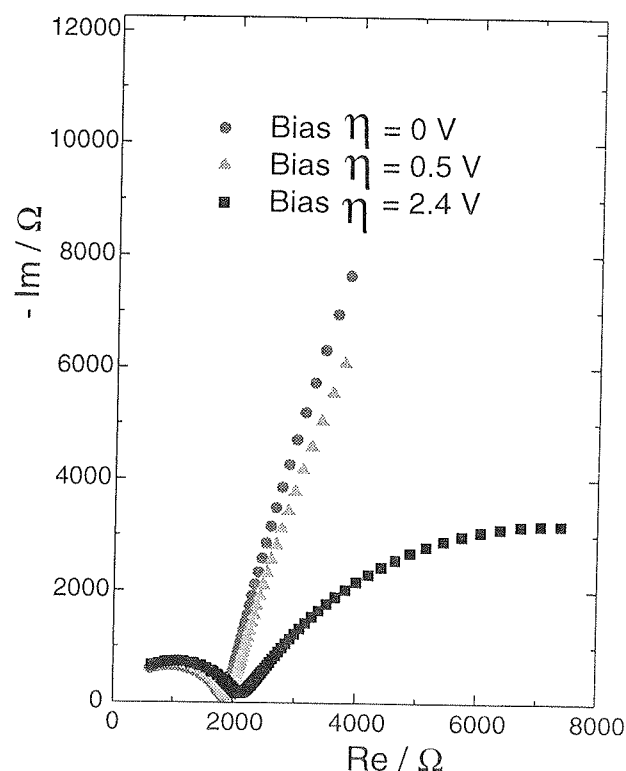


Fig. 4. A complex-plane plot of typical impedance spectra measured in the frequency range from 1 MHz to 20 Hz.

polymer films studied, i.e. $(\text{PEO})_n\text{M}(\text{SO}_3\text{Cl})_x$, $n = 8, n = 4$ ($M = \text{Li}, \text{Ca}, \text{LiAl}$), are ionic conductors /8, 13, 14/. The high-frequency arc represents the bulk film ionic conductivity, while the low-frequency part has a shape typical for an interface between an ionic conductor and a blocking electrode /8, 13, 14/ (in the present case Au electrodes were used).

Different cations ($\text{Li}^+, \text{Ca}^{2+}, \text{Li}^+\text{Al}^{3+}$) of chlorosulfates at the same concentration ($n=8$) exhibit different conductivities (Fig. 6). The highest conductivity across the whole temperature range was observed with the $\text{LiAl}(\text{SO}_3\text{Cl})_4$ salt. This is not the result that would be expected if conductivity were only related to the ratio between the amount of crystalline and amorphous phases. According to this criterion, the most amorphous $(\text{PEO})_8\text{Ca}(\text{SO}_3\text{Cl})_2$ electrolyte (see Fig. 5) should have the highest conductivity. Apparently the small, highly polarisable cations, such as Li^+ and Ca^{2+} , are trapped in strong electrostatic bonds with the ether linkages on the polymer chain /8, 13/. Notice that a full explanation of the enhanced conductivity of mixed salts should also take into account the anion contribution which could be a very complicated task. However, it is obvious that the number of SO_3Cl^- anions plays a very important role in the overall conductivity of the polymer electrolytes (LiSO_3Cl salt with one SO_3Cl^- anion exhibit the lowest conductivity compared to $\text{Ca}(\text{SO}_3\text{Cl})_2$ with 2 SO_3Cl^- anions with the medium one and $\text{LiAl}(\text{SO}_3\text{Cl})_4$ salt with 4 SO_3Cl^- anions with the highest conductivity).

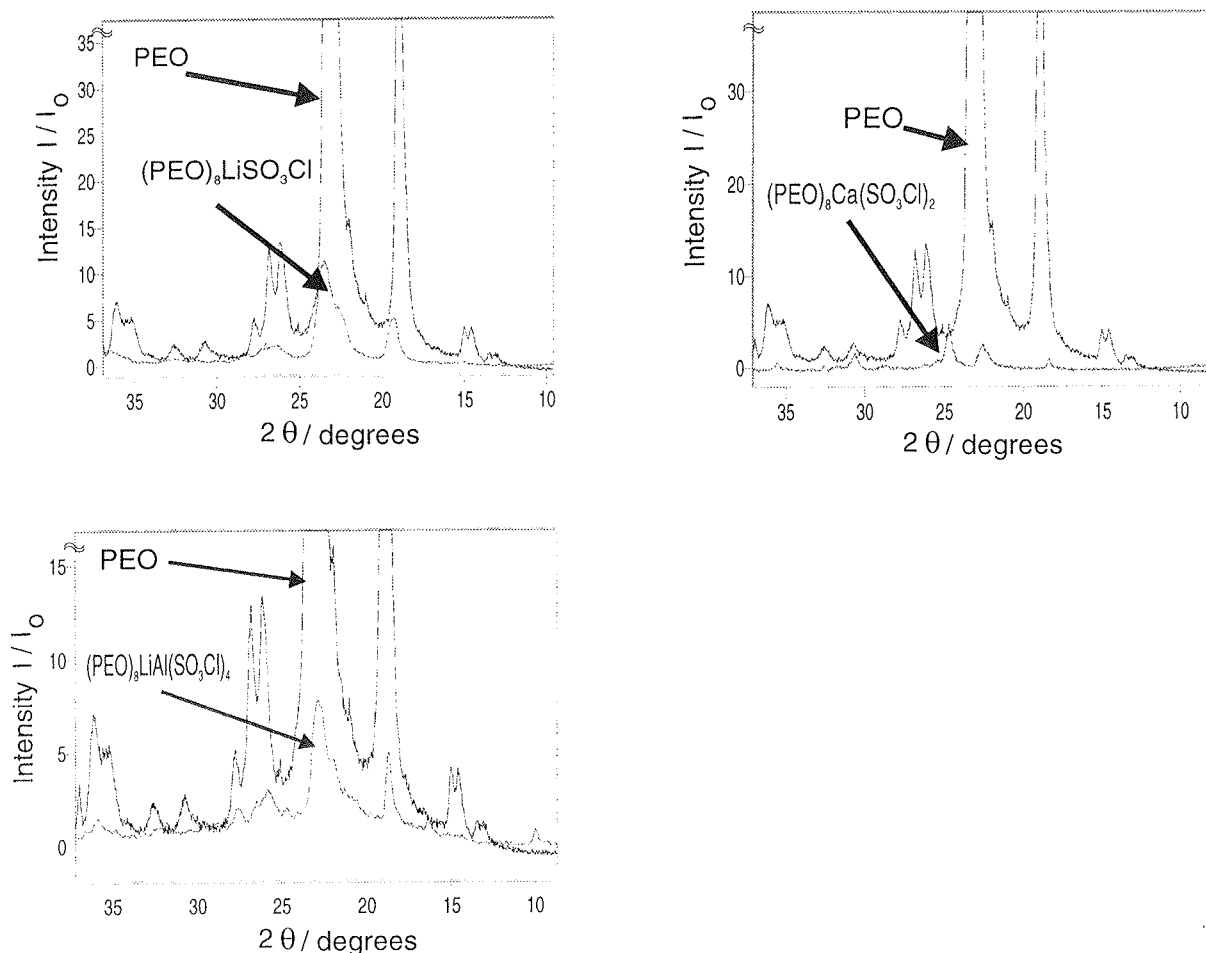


Fig. 5. The effect of LiSO₃Cl, Ca(SO₃Cl)₂, LiAl(SO₃Cl)₄ salts on the crystallinity of the (PEO)₈MSO₃Cl, M = Li, Ca, LiAl electrolyte.

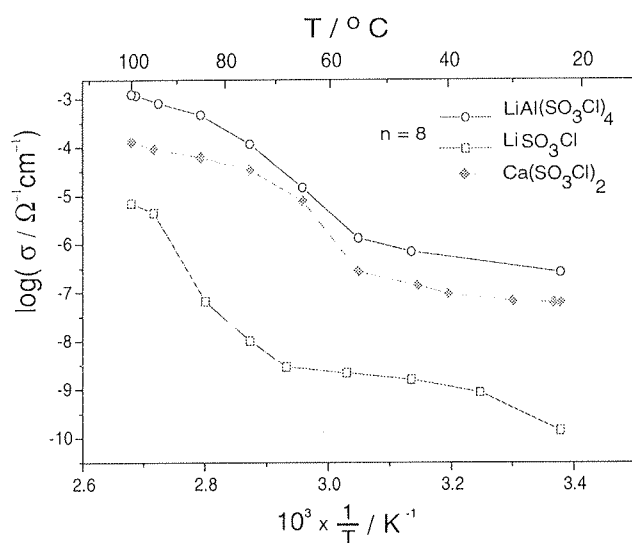


Fig. 6. Arrhenius plots for (PEO)_nMSO₃Cl polymer electrolytes doped with different MSO₃Cl salts (M = (Li⁺, Ca²⁺, Li⁺Al³⁺)). In all cases n = 8.

Characterisation of (PEO/PC/DME)_nLiAl(SO₃Cl)₄ polymer electrolytes

The most widely studied (PEO)_nMX polymer electrolytes (MX = LiClO₄, LiCF₃SO₃, LiBF₄, M(SO₃Cl)_x (M = Ca, Li, LiAl), etc.) are materials more or less polycrystalline at room temperature /1, 2, 5, 8, 13/. Only above ca. 65 °C, where the pure PEO portion of the heterogeneous complex melts, do these electrolytes show a significant increase in conductivity. An important and frequently used way of overcoming the polycrystalline character of the (PEO)_nMX electrolytes is to incorporate plasticisers into PEO /2, 5, 6-8/. Fig. 7 shows that the presence of a combination of two plasticisers (PC and DME) in PEO reduces the crystallinity of high-molecular PEO (M = 10⁶) by more than 50 %. Using size exclusion chromatography (SEC) we found that during the vacuum drying of (PEO/ PC/DME) solutions a certain amount of the plasticiser vaporises /8, 14/. In the final dry undoped (the same was later found for Li-salt doped) films the mass ratio between PEO and the PC/DME mixture increased to c. 65:35 (from the initial 20:80 ratio in the solution /8, 14/). The reduction of the crystallinity of PEO/PC/DME films and the presence of both PC and DME in the final

dry doped and undoped PEO/PC/DME films could also be confirmed using Raman and FTIR spectroscopy /8, 14/. X-ray powder diffractometer analysis shows that the (PEO/PC/DME)₁₂LiAl(SO₃Cl)₄ polymer electrolyte is still crystalline, while at higher concentrations of the LiAl(SO₃Cl)₄ salt the crystallinity rapidly decreases /8, 14/. When the concentration of the LiAl(SO₃Cl)₄ salt reaches $n = 3$, the electrolyte is already entirely amorphous, as evidenced by the total absence of Bragg peaks, Fig. 7.

A similar dependence of crystallinity on salt concentration was observed by DSC measurements /8, 14/. As the concentration of the LiAl(SO₃Cl)₄ salt increases, the endotherm in the temperature range 25 °C to 100 °C shifts to lower temperatures. For example, the melting

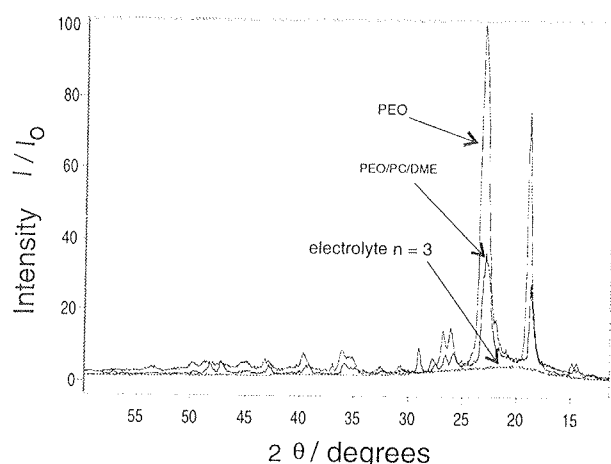


Fig. 7. X-ray powder spectra of undoped PEO and (PEO/PC/DME) polymer films and doped (PEO/PC/DME)_nLiAl(SO₃Cl)₄, $n = 3$ polymer electrolytes

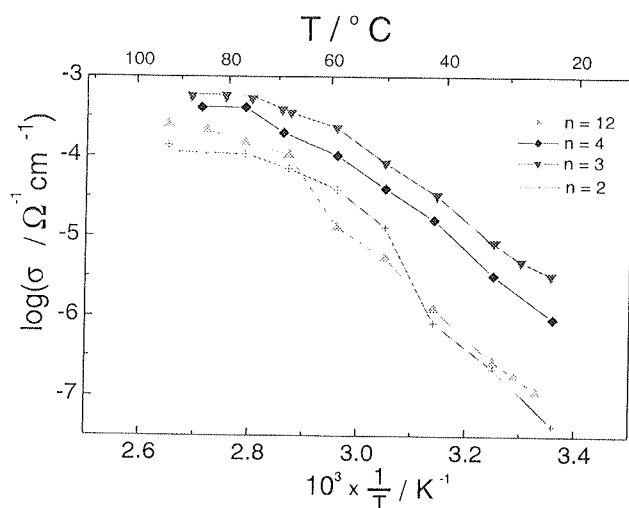


Fig. 8. Temperature dependence of conductivity of the (PEO/PC/DME)_nLiAl(SO₃Cl)₄ polymer electrolytes with salt content $n = 12, 4, 3$ and 2 .

point of undoped PEO is 67 °C, the endothermic maximum of the (PEO/PC/DME)₁₂LiAl(SO₃Cl)₄ electrolyte appears at 59 °C, while for (PEO/PC/DME)₃LiAl(SO₃Cl)₃ it occurs at 36 °C (Table 1). From the literature we know that in this temperature range the uncomplexed PEO and/or the lower - melting complex forms are melts /18/. We reported previously that also the ratio between the height and the width of the low endothermic maximum changes with salt concentration /8, 14/. The samples with low concentrations have a narrower and more symmetrical endotherms, while the samples with high concentrations of the LiAl(SO₃Cl)₄ salts ($n = 3$, $n = 2$) have a broad asymmetric endotherm, or even exhibit no endotherms, indicating that at these salt concentrations the polymer electrolytes are amorphous /8, 14/. From the SEM micrograph it is clear that the amorphous electrolytes ($n = 3$) also retain their mechanical stability (it is possible to peel them off Teflon plates) /8, 14/.

As expected, the presence of LiAl(SO₃Cl)₄ salt in (PEO/PC/DME)_nLiAl(SO₃Cl)₄, (with $n = 2$ to 12) electrolytes causes a shift of the glass transition temperature (T_g) to higher temperatures /2, 5, 8, 13/. For pure PEO T_g has a value of -59 °C while for the amorphous complex (PEO/PC/DME)₂LiAl(SO₃Cl)₄ the value is -23 °C (Table 1). We assume that in our case it is the cation-ether oxygen interaction which is reducing the thermal mobility of polymer chains.

Table 1: Glass transition temperature (T_g) and melting point (T_m) of the low temperature complex of selected (PEO)_nLiAl(SO₃Cl)₄ and (PEO/PC/DME)_nLiAl(SO₃Cl)₄ polymer electrolytes.

$n=[EO/Li^+Al^{3+}]$	$T_g/^\circ C$	$T_m/^\circ C$
PEO	-59	67
$n=8$	-49	65
$n=4$	-38	60
(PEO/PC/DME)	-62	68
$n=12$	-47	59
$n=4$	-36	49
$n=3$	-25	36
$n=2$	-23	/

K. M. Abraham et al. and M. Alamgir et al. suggested that LiClO₄ solvated with PC molecules interacts with the CN⁻ group in polyacrylonitrile (PAN) or with the Cl⁻ group in PVC /19, 20/. However, the structure of plasticised electrolytes is not well understood. Our present knowledge is consistent with structures in which Li⁺ and Al³⁺ are complexed by both the polymer network (PEO) and the solvents (PC, DME) /8, 14/. The fact that the Li⁺ and Al³⁺ ions are solvated with PC and/or

DME molecules should lead to a decrease in the ion-etheric oxygen interaction with respect to the interaction of unsolvated ions because the solvated ions have a lower surface charge density. Furthermore, the relatively high dielectric constant (ϵ (0.5 PC : 0.5 DME) = 41 at 20 °C [17] while ϵ (PEO) = 5) probably prevents the formation of large cation-anion complexes (triplets and quartets) [8, 14]. We presume that both effects lead to increased ion conductivity (see further text). Note, however, that at given temperature these effects cannot be detected separately from the effect of polymer segmental mobility by the plasticiser which also essentially contributes to the conductivity increase. We reported previously [8, 13], that the plasticiser modifies the shape of the Arrhenius curve. The modified polymer electrolyte exhibits better ionic conductivity at lower temperatures (20 - 60 °C), while at higher temperatures ($T > 60$ °C) the polymer without plasticiser shows better conductivity. Based on this result, we assume that at lower temperatures the interactions between the mobile cations and the ether oxygen are smaller if the plasticiser is present (the surface charge density is smaller). At high temperatures, the interaction between cations and ether oxygen is reduced to a great extent, due to temperature-activated chain mobility. In this case the smaller cations (unsolvated Li⁺, Al³⁺) exhibit higher mobility than the cations solvated with the plasticiser, and hence the higher average conductivity of the electrolyte without the plasticiser at higher temperatures. Of, course, the overall ionic conductivity is also determined by the concentration and mobility of anions [13]. In this work it is assumed that their contribution is the same in all polymer electrolytes studied. The dependence of the ionic conductivity of the studied doped polymers on salt concentration is shown in Fig. 8. At all temperatures the ionic conductivity increases until a salt concentration of $n = 3$ is reached; further addition of salt leads to a decrease in conductivity. It seems probable that this decrease occurs due to formation of non-conducting (electrically neutral) cation - anion pairs, because at high concentrations the average distance between cations and anions is significantly reduced [8, 21]. In addition, the associates themselves hinder the transport of the remaining free ions. It should be noted that the salt concentration has a stronger impact on conductivity at lower temperatures than at higher temperatures [8, 14]. This seems reasonable because at higher temperatures the thermal mobility of polymer chains is greatly increased and the properties change from solid-like to liquid-like. Correspondingly, the slope of Arrhenius plots is less (cf. Fig. 8).

CONCLUSIONS

1. At room temperature, (PEO)_nM(SO₃Cl)_x, $n = 8$, (M = Li, LiAl, Ca) polymer electrolytes are semi-crystalline, containing both amorphous and crystalline regions. The crystallinity and conductivity of polymer solid electrolytes are considerably affected by the type of cation in the chlorosulphate salts as well as the number of SO₃Cl⁻ groups. The highest ionic conductivity was shown by the salt containing both Li⁺ and Al³⁺ cations and 4 SO₃Cl⁻ group compared to 1 or 2 SO₃Cl⁻ group in the LiSO₃Cl or Ca(SO₃Cl)₂ salts.

2. Preparation of a (PEO/PC/DME)_nLiAl(SO₃Cl)₄ polymer electrolyte was described.

Using X-ray powder diffractometer analysis it was shown that a substantial amount of PC and DME plasticisers remains incorporated in final dry polymer electrolyte films and that the PC/DME combination reduces the crystallinity of PEO by more than 50%.

As expected, the crystallinity of (PEO/PC/DME)_nLiAl(SO₃Cl)₄ polymer electrolytes decreases with increasing LiAl(SO₃Cl)₄ salt concentration. At $n \leq 3$, the polymer electrolyte films were shown to be entirely amorphous.

The amorphous electrolytes ($n = 3$) remain mechanically stable.

With increasing salt concentration the T_g values of the polymer electrolytes studied increases, i.e. the polymer chains become increasingly rigid, presumably due to a cation - ether oxygen interaction.

The PEO/PC/DME polymer electrolyte exhibits better ionic conductivity at lower temperatures (20 - 60 °C), while at higher temperatures ($T > 60$ °C) the polymer without plasticiser shows better conductivity. With respect to salt concentration the conductivity exhibits a maximum value at $n = 3$.

Acknowledgement

Financial support from the Ministry of Science and Technology of the Republic of Slovenia is gratefully acknowledged.

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Prispelo (Arrived): 23.6.1998

Sprejeto (Accepted): 7.7.1998