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ORIGINAL PAPER

Synthesis and electrochemical characterization of aPEO-based polymer electrolytes

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Abstract In this paper, the preparation and purification of an amorphous polymer network, poly[oxymethylene-oligo (oxyethylene)], designated as aPEO, are described. The flexible CH_2CH_2O segments in this host polymer combine appropriate mechanical properties, over a critical temperature range from −20 to 60 °C, with labile salt-host interactions. The intensity of these interactions is sufficient to permit solubilisation of the guest salt in the host polymer while permitting adequate mobility of ionic guest species. We also report the preparation and characterisation of a novel polymer electrolyte based on this host polymer with lithium tetrafluoroborate, $LiBF_4$, as guest salt. Electrolyte samples are thermally stable up to approximately 250 °C and completely amorphous above room temperature. The electrolyte composition determines the glass transition temperature of electrolytes and was found to vary between −50.8 and −62.4 °C. The electrolyte composition that supports the maximum room temperature conductivity of this electrolyte system is $n=5$ (2.10×10^{-5} S cm^{-1} at 25 °C). The electrochemical stability domain of the sample with $n=5$ spans about 5 V measured against a Li/Li^+ reference. This new electrolyte system represents a promising alternative to $LiCF_3SO_3$ and $LiClO_4$-doped PEO analogues.

Keywords SPEs · Poly[oxymethylene-oligo (oxyethylene)] · Lithium tetrafluoroborate · Electrochemical analysis · Thermal analysis

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Introduction

Solid polymer electrolytes based on poly(ethylene oxide) (PEO) and salt dissolved in a polymer matrix are well developed and widely studied materials [1–5]. Many new electrolyte systems have been described over the last few years in a continuing effort to prepare SPEs with adequate properties for use in practical devices. Unfortunately, the rather modest ionic conductivity of known systems continues to restrict the application of these materials as components in commercial products. In order to increase conductivity, different polymer matrix architectures [6], liquid plasticising components [7, 8], ceramic fillers [9], plasticising salts [10], as well as ionic liquids have been evaluated [11].

Zhang et al. [12] have demonstrated that $LiBF_4$-based non-aqueous electrolytes are a good alternative to other lithium-based components in low temperature Li-ion batteries with improved performance. The $LiBF_4$ salt may be an appropriate choice for a low temperature electrolyte of a Li-ion cell if a solvent system that has low freezing temperature, high-solubility towards $LiBF_4$, and good electrochemical compatibility with a graphite anode can be found.

In this study, we have prepared a novel polymer electrolyte based on aPEO and lithium tetrafluoroborate $LiBF_4$. This choice of polymer component was motivated

by the favourable mechanical properties of amorphous poly [oxymethylene-oligo(oxyethylene)]. Thin polymer electrolyte samples were prepared by solvent casting and the resulting transparent membranes were obtained as self-supporting films. In the present study the thermal stability, ionic conductivity and electrochemical stability of samples with a wide range of $LiBF_4$ concentrations have been analysed.

Experimental

Materials

Lithium tetrafluoroborate ($LiBF_4$, Aldrich, 99.998%) was used without further purification and stored prior to use in a high integrity, dry argon-filled glovebox. Acetonitrile (Aldrich, HPLC grade) was dried over molecular sieves (Aldrich, 4A). All subsequent manipulations of salt, solvent, electrolyte samples and measurements were carried out under a dry argon atmosphere.

Synthesis of the matrix

The synthesis of poly[oxymethylene-oligo(oxyethylene)] was carried out using a procedure similar to that previously described by other authors [13]. Finely ground KOH (40 g) was mixed with dry CH_2Cl_2 (Aldrich Chromasolv for HPLC, 20 mL) under nitrogen at room temperature within a three-necked round-bottomed flask equipped with a liquid addition funnel and a condenser. The mixture was stirred into a slurry using a high-torque overhead motor (Heidolph, RZR 2020) and 20-mL PEG400 (Aldrich) were added quickly and stirring was continued.

The reaction mixture turned a lemon yellow colour and an increase in viscosity was apparent almost immediately. The temperature of the reaction mixture rose abruptly after the addition of the PEG400 and remained constant for the first 15 min of the reaction. During this period, the viscosity of the reaction mixture became so high that further addition of 5 mL aliquots of CH_2Cl_2 became necessary.

Occasional addition of solvent was continued to maintain the viscosity of the reaction volume approximately constant. Typically about 100–150 mL CH_2Cl_2 was added over a period of 5 h. Finally, a volume of 200–250 mL of CH_2Cl_2 was added to quench the reaction.

A further 700 mL of CH_2Cl_2 was added and the reaction mixture was filtered at a water pump to separate un-reacted KOH from the polymer component. The filtrate was reduced in volume by evaporation under reduced pressure to isolate a rubbery transparent polymer with a slight yellow coloration.

The sample (≈5 g) was then purified by dissolution with stirring in a volume of 100 mL toluene (Acros Organics, water of <30 ppm) and re-precipitated by addition of about 27 mL hexane (LabScan, 99% HPLC). The mixture was heated to re-dissolve the polymer and allowed to cool again to re-precipitate high-molecular-mass polymer. The precipitated polymer was isolated by decantation and evaporated to dryness. The objective of this procedure was to eliminate any insoluble polymer and to remove the low molecular mass oligomers by retention in the mixed solvent fraction.

The solid polymer obtained from this preliminary treatment was subjected to further purification by tangential flow filtration. A dilute aqueous solution of the polymer was prepared and recirculated through a membrane (OMEGA TM Filtron Technology Corp.) using a mini-Ultrasette filter with a flow rate adjusted to permit about 150 mL of waste fraction to be removed from the filtrate port per hour. This critical stage of the purification procedure typically took about 24 h.

The aqueous solution was finally extracted with a similar volume of CH_2Cl_2. The polymer was isolated by reduction to dryness on a rotary evaporator and stored in a dessicator over P_2O_5, for a period of about 30 days with periodic purging and dessicant renewal, to eliminate residual water.

Sample preparation

Homogeneous solutions of aPEO and Lithium tetrafluoroborate were prepared by stirring known masses of polymer, lithium salt and a convenient volume of acetonitrile, in a small conical flask. The components were stirred for a period of at least 48 h within a dry argon-filled preparative glovebox. The resulting solutions were decanted into glass rings seated on teflon plates and the solvent was removed slowly by evaporation to form films of approximately 150-μm thickness. Residual solvent was removed by drying using argon purge/heating cycles at 60 °C.

Measurements

Gel permeation chromatography of the matrix

A sample of polymer was analysed using conventional gel permeation chromatography (GPC) with a 0.01-M lithium bromide solution in *N*,*N*′-dimethylformamide as eluent. A single solution of the sample was prepared by adding 15 mL of eluent to 30 mg of sample and warming to 80 °C, with shaking, for 90 min. The sample was dissolved completely and filtered through a glass fibre pad into auto sampler vials. A Polymer Laboratories PL-GPC 120 equipped with a refractive index detector and a PS-AL-MT autosampler, and a set flow rate of 1.0 mL min^{-1} was used to perform the analysis. Data were collected and

analysed using Polymer Laboratories "Cirrus" software. A Polymer Laboratories PolarGel guard plus and two polarGel-M 30 cm columns operating at 80 °C were used.

Nuclear magnetic resonance spectroscopy of the matrix

The nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker Avance II 400 (^{1}H, 400 MHz and ^{13}C, 100 MHz) at room temperature and $CDCl_3$ was used as solvent. The chemical shifts are expressed in δ (ppm) from TMS.

Thermal analysis of the polymer electrolytes

Selected samples for thermogravimetric studies were transferred to open platinum crucibles and analysed using a Rheometric Scientific TG 1000 thermobalance operating under a flowing argon atmosphere between 30 and 700 °C. A heating rate of 10 °C min^{-1} was used to characterise all polymer samples. Polymer electrolyte sections were removed from cast films and subjected to DSC analysis under a flowing argon atmosphere between 25 and 350 °C at a heating rate of 5 °C min^{-1} using a Mettler DSC 821e instrument. All samples were presented for analysis in 40-μL aluminium cans with perforated lids to permit the release and removal of the decomposition products.

Studies performed on a Q200 DSC from TA Instruments over the temperature range of −90 to 40 °C permitted evaluation of the glass transition temperatures of electrolyte compositions. Samples of 5–10 mg were located in hermetically sealed aluminium pans. The analytical procedure includes a cooling ramp to −90 °C at a rate of 10 °C min^{-1}, an isothermal period of 30 min at −90 °C and a heating ramp up to 40 °C at a rate of 10 °C min^{-1}. A constant nitrogen flow of 50 mL min^{-1}, was supplied to the DSC cell in order to avoid condensation of water at low temperature.

Impedance spectroscopy

The ionic conductivity of samples was determined using a constant volume support equipped with gold blocking electrodes located within a Buchi TO 50 oven. The sample temperature was evaluated by means of a type K thermocouple placed close to the electrolyte film and impedance measurements were carried out at frequencies between 65 kHz and 500 mHz using an Autolab PGSTAT-12 (Eco Chemie), over a temperature range from 20 to 90 °C. Measurement of conductivity was performed during heating cycles.

Electrochemical stability

Evaluation of the electrochemical stability window of the polymer was carried out within a dry argon-filled glovebox using a two-electrode cell configuration with a gold microelectrode as working electrode. The preparation of the 25-μm diameter gold microelectrode surface by the conventional polishing routine was completed outside the glovebox. The microelectrode was then washed with THF, dried with a hot-air blower and transferred into the glovebox. Cell assembly was initiated by locating a freshly cleaned lithium disc counter electrode (10 mm in diameter, 1-mm thick, Aldrich, 99.9% purity) on a stainless steel current collector. A thin-film sample of electrolyte was centred over the counter electrode and the cell assembly completed by locating and supporting the microelectrode in the centre of the sample disc. The assembly was held together firmly with a clamp and electrical contacts were made to the Autolab PGSTAT-12 (Eco Chemie) used to record voltammograms at a scan rate of 100 mV s^{-1}. Measurements were conducted at room temperature within a Faraday cage located inside the measurement glovebox.

Results and discussion

M_w distribution from GPC

Results for weight distribution (M_w), and polydispersity (d) are included in Table 1. GPC curves of aPEO in Fig. 1 show a single peak and confirm the efficiency of the purification procedure applied. Previous preparations of this polymer host have shown a small peak at low molecular weight attributable to ring polymers and a large peak at high molecular weight attributable to linear chains [14, 15]. Using the purification procedure described in this paper an improved control of the molecular weight distribution of the polymer was possible. As the ionic mobility in the electrolyte is determined by the characteristics of the polymer host, an improvement in the electrolyte conductivity and mechanical properties is achieved by appropriate synthesis and purification of the polymer component.

Nuclear magnetic resonance spectroscopy (NMR)

The ^{1}H and ^{13}C NMR spectrum obtained with the host polymer matrix were similar to those reported previously for high-molecular-weight polymers [16]. In the ^{1}H NMR

Table 1 Weight distribution and polydispersity of aPEO

Sample	M_w	d
aPEO (sample 1)	118,000	3.6
aPEO (sample 2)	115,000	3.7
aPEO (sample 3)	115,000	3.8

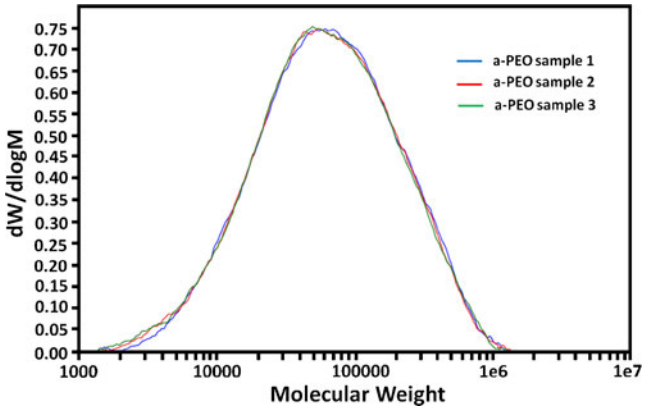

Fig. 1 GPC curves of aPEO samples

spectrum (not show) the alkyl protons are observed as a multiplet at δ=3.62–3.72 ppm and the proton of the hydroxyl group as a singlet at δ=4.73 ppm. In the ^{13}C NMR spectrum (not show) six different alkyl carbon atoms are observed (δ=66.84, 70.29, 70.42, 70.52, 70.62, and 95.52 ppm) linked to oxygen atoms [17].

Thermal behaviour of electrolytes

The results of thermal analysis of electrolyte samples, illustrated in Fig. 2, confirmed that samples with n between 40 and 8 were totally amorphous. At high salt concentration (n=2.5 and 5) an endothermic peak is observed at approximately 101 °C. This observation is consistent with the presence of a salt-polymer complex. The studies reported by Chiodelli et al. [18] and Zahurak et al. [19] for the PEO_nLiBF_4 system, propose the existence of a crystalline complex situated at $2<n<4$ and n=3.5, respectively, with fusion, in both cases, being recorded at about 150 °C.

The thermal decomposition of electrolyte samples was studied by TGA (Fig. 3), using the conventional extrapolation of baseline and curve tangent to identify the temperature associated with the initiation of sample weight loss. The guest salt clearly destabilises the polymer network at compositions greater than n=8 and electrolytes with higher salt concentration were found to be thermally less stable.

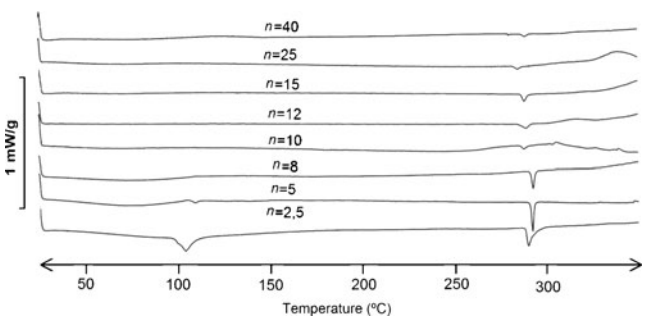

Fig. 2 DSC thermograms of selected $aPEO_nLiBF_4$ electrolytes

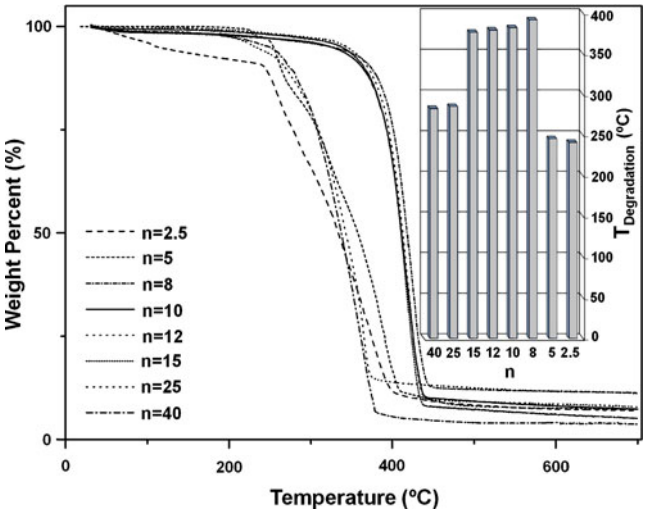

Fig. 3 TGA curves of selected $aPEO_nLiBF_4$ electrolytes. Inset illustrates the variation of the extrapolated onset of degradation temperatures from TGA results

Figure 4 confirms that the glass transition temperature (T_g) of the doped polymer electrolyte samples increases with salt concentration. In electrolytes with high salt content the T_g of the $aPEO_nLiBF_4$ samples increases markedly with salt concentration. As the T_g of a polymer is defined as the temperature above which local segmental motion begins, the trend observed confirms the existence of interactions of significant intensity between the Li^+ ions and the host matrix in the most concentrated samples. A similar observation was previously reported for other systems based on aPEO with guest $LiClO_4$ salt [20]. This variation was different from that previously observed in studies of an electrolyte based on the PEO host matrix and p(TMC) host matrix with the same guest salt [21]. In these systems T_g decreased with increasing salt content.

Ionic conductivity of electrolytes

The ionic conductivities of selected polymer electrolytes over the temperature range from 25 to 90 °C and as a function of salt content are illustrated in Fig. 5. These electrolytes show a variation of conductivity that is almost

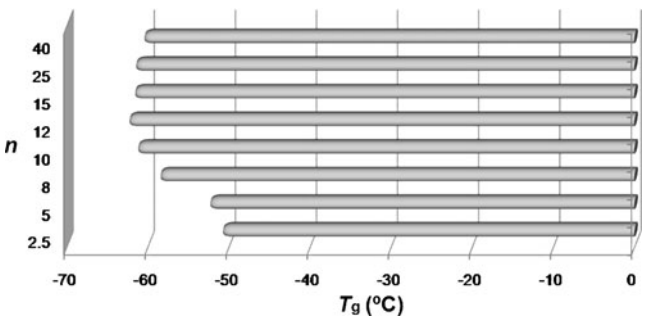

Fig. 4 T_g of selected $aPEO_nLiBF_4$ electrolytes

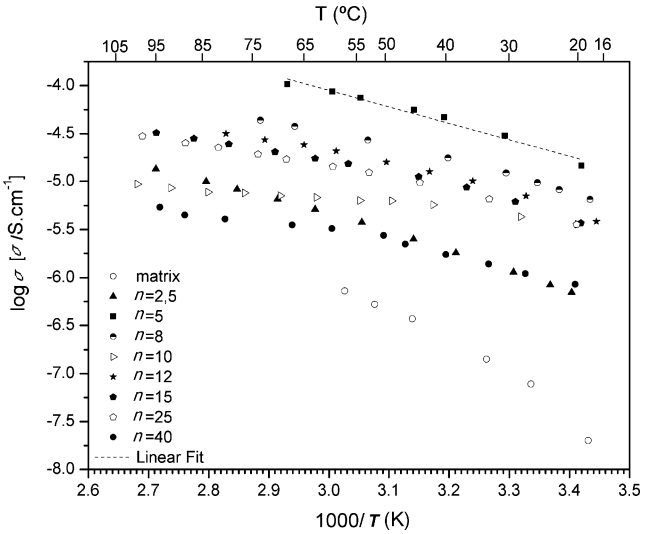

Fig. 5 Variation of ionic conductivity with $1/T$ for selected electrolyte compositions of $aPEO_nLiBF_4$

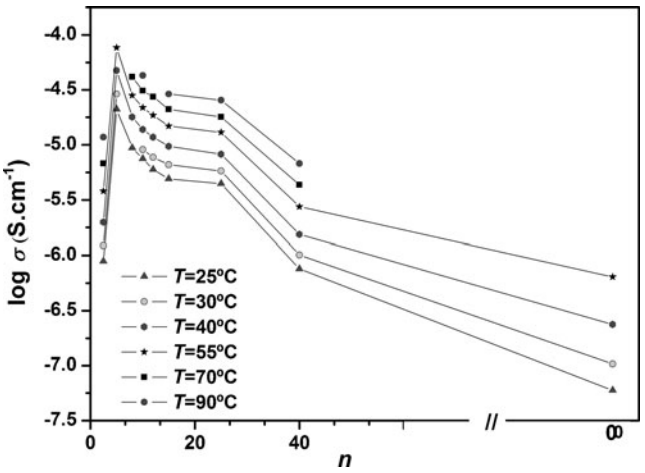

Fig. 6 Conductivity isotherms of the $aPEO_nLiBF_4$ electrolytes

linear with respect to $1/T$ over a range of electrolyte compositions with n from 2.5 to 40. This behaviour is characteristic of amorphous polymer electrolytes and contrasts with that of semi-crystalline materials based on the PEO host matrix which generally show two distinct regions of linear variation with a change in gradient associated with fusion of the crystalline polymer component [18, 22]. From the results presented in Fig. 5, we conclude that the most conducting sample of the series is $aPEO_5LiBF_4$. At about 55 °C, this electrolyte presents the highest conductivity of all the samples investigated (7.66×10^{-5} S cm^{-1}) and at ambient temperature the ionic conductivity presented is approximately 2.10×10^{-5} S cm^{-1}. These results are comparable with those reported by Chiodelli et al. [18] and Armand et al. [22] for the PEO_nLiBF_4 system and by Silva et al. [21] based on the p(TMC) host matrix.

Electrolytes based on aPEO doped with $LiBF_4$ have higher conductivity than electrolytes based on this host polymer matrix but including other guest salts [13, 20, 23]. These results are considered to be a consequence of optimisation of the preparation of the amorphous host polymer and the choice of guest salt species.

For amorphous materials the ionic conductivity measured above glass transition temperature is no longer represented by the Arrhenius law, as can be observed for the fitting in Fig. 5. The experimental results are better represented by an empirical relationship as VTF model. This model is related to the transport properties obtained from the free volume concept, taking in account the structured relaxation time. This time is the mean life time for the movement of a structure unit over a distance equivalent to its size [24].

The values of ionic conductivity and activation energies for the matrix aPEO and for composition $aPEO_5LiBF_4$ are 70.6 kJ mol^{-1}, 1.253×10^{-6} S cm^{-1} (at 70 °C) and 32.8 kJ mol^{-1}, 1.091×10^{-4} S cm^{-1} (at 70 °C), respectively. The activation energy for ionic conductivity decreased with the presence of salt, this is in agreement with the fact that the amount of ions in the polymer electrolyte increases and the energy barrier to the ion transport decreases, leading to a decrease in the activation energy [25].

The conductivity isotherms derived from these results are included in Fig. 6 and confirm that the composition dependence of this electrolyte system is similar to that reported for other aPEO systems [17, 20, 23, 24]. The electrolyte conductivity rises from very low values in the undoped polymer host as mobile ionic species are added and as n decreases in $aPEO_nLiBF_4$. The maximum conductivity was found at a composition of about $n=5$, and then falls rapidly in electrolytes with greater salt content. This behaviour is consistent with a decrease in the flexibility of the host polymer chain segments,

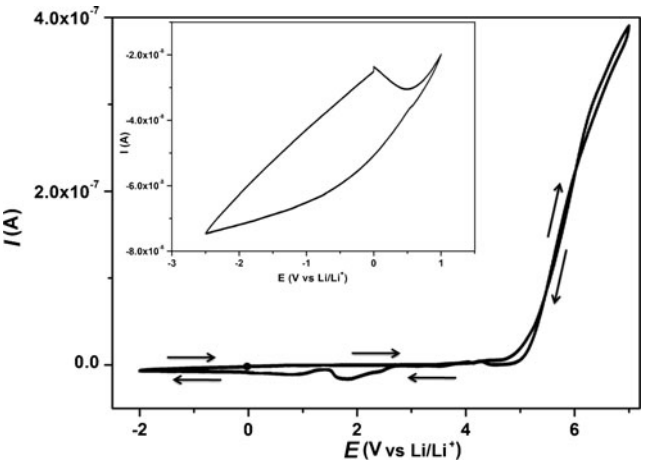

Fig. 7 Voltammogram of $aPEO_5LiBF_4$ electrolyte at a 25-μm diameter gold microelectrode versus Li/Li^+. Initial sweep direction is anodic and sweep rate is 100 mV s^{-1}

confirmed by an increase in the T_g of the electrolyte matrix. Since the publication of results obtained by Berthier et al. [26] it has been recognised that ionic mobility in polymer electrolytes is closely correlated with the viscoelastic properties of the host polymer and so the value of T_g of polymer/salt compositions is of crucial importance. The observed increase in T_g at lower values of n can be explained by an increase in the number of bridging interactions that take place between adjacent polymer chains and guest salt species, generally designated as "ionic cross-linking" and that contribute to a reduction in the mobility of ionic species. A further reduction in conductivity results from the increased tendency to form ion pairs and aggregates in concentrated electrolyte compositions in the low-dielectric constant medium.

Electrochemical stability

The electrochemical stability of the $aPEO_5LiBF_4$ electrolyte was determined by microelectrode cyclic voltammetry over the potential range of −2.0 to 7.0 V (Fig. 7). The potential limit for the electrochemical stability of the electrolyte composition was determined as the potential at which a rapid rise in current was observed and where the current continued to increase as the potential was swept in the same direction. The sweep was initiated at zero potential toward the anodic limit. After detecting an anodic peak the sweep direction was inverted and continued to a limit of −2 V. During the cathodic sweep a low intensity current peak was detected at approximately 2.0 V versus Li/Li^+ and attributed to the reduction of decomposition products that were formed at the anodic limit.

As can be observed in Fig. 7, the current flow in these electrolytes started at approximately 5 V versus Li/Li^+ indicating that the SPE would be electrochemically stable up to about 5 V in the anodic region. This means that the overall redox stability of the electrolyte spans more that 7 V, an indication that this material displays an acceptable stability window for an application in a solid state electrochemical device.

Conclusions

The aPEO host matrix with lithium tetrafluoroborate guest salt, introduced in this study, has been shown to provide a suitable basis for the preparation of solvent-free electrolytes with encouraging conductivity performance.

In the range of compositions characterised the electrolyte with the highest ionic conductivity is found at a composition of $n=5$, a behaviour similar to that reported in the system where lithium perchlorate was added to the aPEO matrix [17].

This electrolyte system presents good mechanical and electrochemical properties permitting a favourable prediction of its applicability in commercial devices. Although optical transparency is not a property directly relevant to the electrolyte performance, in applications in electrochromic display devices, this is an additional advantage shown by all compositions characterised in this study.

A new study of interpenetrating blends of poly(trimethylene carbonate) and amorphous poly(ethylene oxide) matrices doped with different lithium salts has been initiated. These polymer blends are obtained as transparent, flexible, free-standing films with good mechanical properties. The addition of aPEO to this electrolyte formulation provides access to improved ionic conductivity. The attractive thermal and mechanical features of these electrolytes suggest that further optimization studies are worth pursuing. It seems likely that electrolyte formulations for specific applications may benefit from tailoring physical/chemical properties of multifunctional components to practical requirements of the device.

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