

Synthesis and characterization of amorphous poly(ethylene oxide) /poly(trimethylene carbonate) polymer blend electrolytes

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Abstract

Solid Polymer Electrolytes (SPEs) have been proposed as substitutes for conventional non-aqueous electrolytes in various electrochemical devices. These promising materials may be of interest in various practical devices including batteries, sensors and electrochromic displays as they can offer high performance in terms of specific energy and specific power (batteries), safe operation, form flexibility in device architecture and low manufacturing costs.

Many different host polymers have been characterized over the last 30 years, however a relatively un-explored strategy involves the use of interpenetrating blends incorporating two or more polymers. Electrolyte systems based on interpenetrating blends of known host polymers, poly(ethylene oxide) and poly(trimethylene carbonate), doped with lithium perchlorate, were prepared by co-dissolution in acetonitrile. This combination of polymer components results in the formation of a material that may be applicable in batteries and electrochromic devices.

The results of characterization of polymer electrolyte systems based on interpenetrating blends of amorphous poly(ethylene oxide) and poly(trimethylene carbonate) host matrices, with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as guest salt, are described in this study. Electrolytes with compositions of n between 5 and 15 (where n represents the total number of cation-coordinating units per lithium ion) were obtained as flexible, transparent and free-standing films that were characterized by measurements of conductivity, cyclic voltammetry, differential scanning calorimetry and thermogravimetry.

Keywords: blends, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), amorphous poly(ethylene oxide)

1. Introduction

Solid polymer electrolytes are complexes formed between ionic salts and polymers with electron-donor atoms, such as linear high molecular weight poly(oxyethylene) (PEO) [1, 2]. SPEs were recognized by Armand et al. [3] as potential substitutes for non-aqueous liquid electrolytes in rechargeable lithium batteries. Among the perceived advantages of these materials are good electrochemical properties, a reduction in both safety-related problems and environmental concerns, and virtual elimination of electrolyte leakage problems. These electrolytes may perform a multifunctional role in practical devices as separator, adhesive and cell sealant in electrochemical devices. Li⁺-based SPEs are considered to be attractive materials for application in various devices including galvanic cells, electrochromic displays and sensors [4]. The application of PEO-based electrolytes in commercial solid-state electrochemical devices has unfortunately been delayed by two main drawbacks: their poor processability and a marked tendency to crystallize. The latter aspect of SPE behaviour is particularly limiting. PEO/salt complexes are usually crystalline, but pristine or un-doped PEO is itself already semi-crystalline. To overcome the disadvantages associated with conventional PEO-based SPEs, three distinct strategies have been applied over the last two decades. Authors have explored the consequences of changes to the host polymer architecture, to the choice of the anion present in the guest salt and the results of the addition of plasticizers [1].

In general, salts with a polarizing cation and a large anion with a well-delocalized charge distribution, and therefore also with low lattice energy, are the most suitable for use in SPEs [5,6]. Lithium perchlorate (LiClO₄) remains a common choice of guest salt, in spite of the safety concerns raised by several authors. Both lithium trifluoromethanesulfonate (or triflate) (LiCF₃SO₃) and lithium tetrafluoroborate (LiBF₄) have also been extensively applied in this context [1]. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) has attracted particular attention as a guest species in SPEs and in a wide variety of host polymers provides good conductivity performance. In common with other salts that contain large polarizable anions, LiTFSI has a low lattice energy and a low tendency to form ion-pairs, leading to enhanced ionic mobility. This salt also performs as a plasticizer in polyether electrolytes by increasing free-volume and suppressing the inherent tendency of certain polymer hosts to crystallize.

While first-generation SPEs were based on commercial sources of PEO-derived host matrices, subsequent studies evolved to the development of novel polymer host networks, the incorporation of salts with improved characteristics and the inclusion of conductivity-enhancing additives in the electrolyte formulation. The almost universal acceptance of evidence that ionic conductivity increases with the amorphous content of the host polymer [9] provided a new impetus to the development of novel amorphous matrices. The exploration of block copolymer hosts [10], sol-gel derived hybrid materials [11] and inter-penetrating [12] or interconnecting [13] polymer blends may be considered to have been motivated by the perception that improved conductivity would result from an decrease in host crystallinity.

In this study the preparation and characterization of SPEs systems based on interpenetrating blends of amorphous poly[oxymethylene-oligo(oxyethylene)] and

poly(trimethylene carbonate) host matrices, with lithium bis (trifluoromethane sulfonyl) imide) as guest salts, are described.

2. Experimental

2.1 Materials

High molar mass p(TMC) (3×10^5 g mol⁻¹, Shell Chemicals, Houston, TX, USA) was dried by argon/vacuum purge cycles at 70°C for 7 days. No further purification of the polymer matrix was carried

out. Amorphous poly(ethylene oxide) synthesized according to the procedure described elsewhere [4,5] was also dried by argon/vacuum purge cycles at 90°C for 5 days.

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (Aldrich 99,95%) was dried under vacuum at 180 and 190°C, for 7 days and then 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, electrolyte samples and the assembly of the conductivity cell were carried out under a dry argon atmosphere.

2.2 Sample preparation

Homogeneous solutions of aPEO, pTMC and LiTFSI were prepared by stirring known masses of polymers, lithium salt and a convenient volume of acetonitrile, in a small conical flask. The components of the electrolyte formulation were stirred for a period of at least 48 h within a dry argon-filled preparative glovebox. The resulting homogeneous solutions were decanted into glass rings 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.

In accordance with the conventional notation, a host matrix composed of 5 wt% p(TMC) and 95 wt% a-PEO was represented as a-PEO_{95%}/ p(TMC)_{5%}. Electrolytes with LiTFSI compositions of n between 5 and 15 and a p(TMC) content of between 5 and 15 wt% of the electrolyte formulation, were prepared as self-supporting films. An electrolyte with a combined ratio of oxygen and carbonate coordinating sites to guest lithium cations of 15, and a host matrix composed of 5 wt% p(TMC) and 95 wt% a-pEO was identified as (a-pEO_{95%}/pTMC_{5%})₁₅LiTFSI.

2.3. Measurements

2.3.1 Thermal analysis of polymer electrolyte samples

Samples for thermogravimetric characterization were transferred to open platinum crucibles and analyzed using a Rheometric Scientific TG 1000 thermobalance operating under a flowing argon atmosphere between 30°C and 700°C. A heating rate of 10°C.min⁻¹ was used to analyze 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 DSC analysis in 40 μL aluminium cans with perforated lids to permit the release and removal of the decomposition products.

The evaluation of glass transition temperatures was performed on a Mettler DSC 821e instrument over the temperature range from -60°C to 20°C at 10°C.min⁻¹. Samples with a mass of about 5-10 mg were located in aluminium pans with perforated lids.

2.3.2 Impedance spectroscopy

The conductivity of electrolyte samples was determined using a constant volume support equipped with gold blocking electrodes installed in a Buchi TO 50 oven located within an argon-filled glovebox. 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 65kHz and 500mHz using an Autolab PGSTAT-12 (Eco Chemie), over a temperature range from 20 to 90°C. Measurement of conductivity was performed during heating cycles.

2.3.3 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 25µm 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 disk counter electrode (10 mm diameter, 1mm thick, Aldrich, 99.9% purity) on a stainless steel current collector. A thin-film sample of electrolyte was centered over the counter electrode and the cell assembly completed by locating and supporting the microelectrode in the centre of the sample disk. 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 100mVs⁻¹. Measurements were conducted at room temperature within a Faraday cage located inside the measurement glovebox.

3. Results and discussion

3.1. Thermal analysis of the polymer electrolytes

The results of thermal analysis of the electrolyte samples are illustrated in Figure 2. These results confirm the non-crystalline character of all the samples studied and this behaviour is also verified by other systems based on pTMC/PEO [12,13]. In this study the beneficial effect of pTMC component on the PEO matrix is confirmed by the suppression of the characteristic poly(ethylene oxide) melting peak at about 60°C. One of the most restrictive aspects of commercial PEO and PEO-derived host networks is related to the tendency of this host matrix to form crystalline regions within the electrolyte bulk. In contrast, the undoped p(TMC) matrix is a completely amorphous material with a glass transition temperature (T_g) of -18°C and a thermal stability limit

(Td) of at least 200°C. All the previously characterized p(TMC)-based electrolyte systems were found to be completely amorphous over a wide range of salt compositions [14]. As expected, aPEO based electrolyte systems were also found to be amorphous [15, 16]. The incorporation of the pTMC component into the aPEO matrix contributes to this system by significantly improving the mechanical performance of the polymer blends. Electrolytes prepared with a broad range of salt composition were very transparent and flexible, well-adapted as multi-functional components in optical devices.

The variation of glass transition temperature with electrolyte formulation, illustrated in figure 3, shows an increase in Tg with increasing salt content. The lowest Tg of all the formulations included in the study was found in the blends with n=15. In electrolytes with high salt content the Tg of the (aPEO_{x%}/pTMC_{y%})_nLiTFSI samples increases markedly with salt concentration. As the Tg of a polymer is defined as the temperature above which local chain segmental motion begins, this result 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 LiClO₄ salt [18], and with LiBF₄ salt [17]. Even after more than 20 years of development the lithium trifluoromethanesulphonyl imide salt [19] is still considered to be one of the most promising guest species for SPEs, precisely because of its capability to reduce the Tg of semi-crystalline host polymers. In contrast to p(TMC)-based systems containing lithium perchlorate [18] or lithium triflate [20], both the lithium trifluoromethanesulphonyl imide and lithium hexafluoroantimonate [14,21] doped electrolytes show a marked plasticizing effect at high salt content.

Referring to figure 3, it is apparent that an increase in pTMC content gives rise to a shift of the Tg to higher temperatures. The Tg is also clearly influenced by salt concentration, and once again, with increasing salt content the Tg is shifted to higher temperatures. The sample with the lowest Tg of all the electrolyte formulations studied is (a-pEO_{95%}/pTMC_{5%})₁₅LiTFSI.

The thermal decomposition of electrolyte samples was characterized by TGA (Figure 4), using the conventional procedure of extrapolation of baseline and curve tangent to identify the temperature associated with the initiation of sample weight loss. In this electrolyte system the presence of the guest salt apparently stabilizes the polymer network. Thermal decomposition of the salt-rich electrolyte compositions occurs at temperatures between 150 and 200°C. The TGA curves also reveal that decomposition takes place in two distinct steps. Even at the 420°C temperature the samples are not fully decomposed and a significant amount of residue still remains (about 10 % of the original sample mass). In the case of the sample with formulation (a-pEO_{95%}/pTMC_{5%})_nLiTFSI, included in Figure 4(c), thermal decomposition starts virtually from room temperature and, after an initial mass loss of about 5 %, the TGA curve is subject to major loss of mass at 350 °C and at about 420 °C. Between this temperature and 750 °C no further mass losses occur. Electrolytes with higher salt concentration showed greater thermal stability as demonstrated by Figure 4. From this figure it is also possible to conclude that the pTMC content also influences the initial weight loss temperature. Degradation occurs at lower temperatures in samples with lower pTMC contents, suggesting that the addition of pTMC also improves the thermal stability of the network.

The composition (a-pEO_{95%}/pTMC_{5%})₁₅LiTFSI was found to show the lowest degradation temperature, at about 155°C, confirming that the system has adequate thermal stability for commercial applications in devices.

3.2. Impedance spectroscopy

Electrolytes within the range of salt compositions with n from 5 to 15 show a variation of \log (conductivity) that is continuous and almost linear with respect to $1/T$. This behaviour is typical of amorphous polymer electrolytes and contrasts with that of semi-crystalline materials based on the commercial PEO host matrix that generally show two linear segments with a change of gradient close to the melting temperature of PEO spherulites. The non-linear variation observed with the a-pEO/pTMC blend system studied has been frequently reported for systems with predominantly amorphous character, and this behaviour is expected from the information obtained from DSC characterization.

From the results presented in Figure 5, we may conclude that the most conducting electrolyte of the all the formulations systems studied is located at $n=5$. These results also confirm that the electrolyte with composition $(a\text{-pEO}_{90\%}/\text{pTMC}_{10\%})_5$ LiTFSI, supports the highest ionic conductivity ($2.05 \times 10^{-3} \text{ Scm}^{-1}$, at 95°C) with an ambient temperature conductivity of approximately $1.35 \times 10^{-4} \text{ Scm}^{-1}$. This sample presents an ionic conductivity higher than either pure component polymer system at room temperature $1.20 \times 10^{-4} \text{ Scm}^{-1}$ for a-PEO [22] and about $1 \times 10^{-7} \text{ Scm}^{-1}$ for pTMC [14]. The addition of pTMC to a-pEO up to about 10% produces an increase in ionic conductivity, simultaneously improving both the mechanical properties and the transparency of the electrolyte films obtained. This behaviour is similar to that reported for the same interpenetrating blend systems doped with lithium perchlorate, once again resulting in an improvement of the ionic conductivity obtained. For the $(a\text{-pEO}_{X\%}/\text{pTMC}_{Y\%})_n$ LiClO₄ system the highest ionic conductivity was observed with the $(a\text{-pEO}_{90\%}/\text{pTMC}_{10\%})_5$ LiClO₄ composition, with an ambient temperature conductivity of approximately $1.13 \times 10^{-4} \text{ Scm}^{-1}$ and $6.61 \times 10^{-4} \text{ Scm}^{-1}$ at 63°C . This observation leads us to conclude that the LiTFSI salt has a greater plasticizing effect on the blended matrix in agreement with the observations reported for other solid polymer electrolyte system [14, 22, 23].

3.3. Electrochemical stability

The electrochemical stability of the $(a\text{pEO}_{85\%}/\text{pTMC}_{15\%})_5$ LiTFSI and $(a\text{pEO}_{90\%}/\text{pTMC}_{10\%})_{15}$ LiTFSI electrolytes was determined by microelectrode cyclic voltammetry over the potential range -2.0 to 6.5 V (Figure 6). 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 volts. During the return sweep in the cathodic direction three low intensity current peaks were detected at approximately 1, 3 and 4 V versus Li/Li⁺ and were attributed to the reduction of decomposition products that were formed at the anodic limit.

As can be observed in the Figure 6, 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 potential window confirms the applicability of this electrolyte composition in practical primary and secondary cells.

4. Conclusions

Interpenetrating blends of amorphous poly(ethylene oxide) and poly(trimethylene carbonate) matrices doped with LiTFSI were obtained as transparent, flexible, free-standing films with good mechanical properties. The formulation of electrolytes with PEO and pTMC provides access to a small, but significant, improvement in ionic conductivity. Although conductivity levels are still only moderate, 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 multi-functional components to the practical requirements of the device.

The stability of this electrolyte system permits 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 the electrolyte compositions characterized in this study.

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Figure 1- Polymer electrolyte film obtained with composition $(a\text{-pEO}_{15\%}/\text{pTMC}_{85\%})_{12}$ LiTFSI.

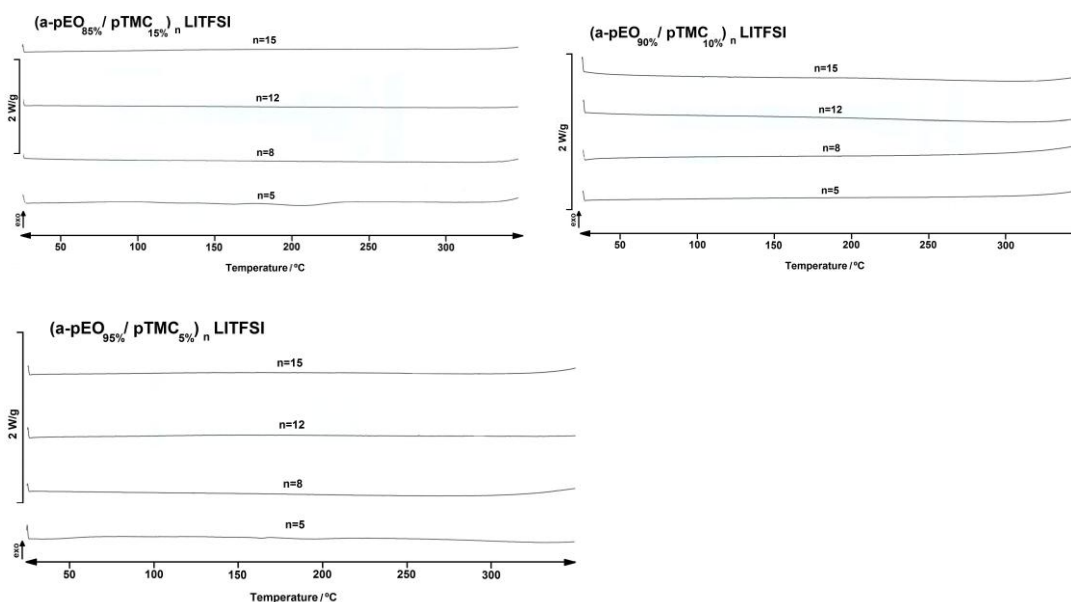


Figure 2 - DSC curves of $(a\text{-pEO}_{X\%}/\text{pTMC}_{Y\%})_n$ LiTFSI electrolyte systems.

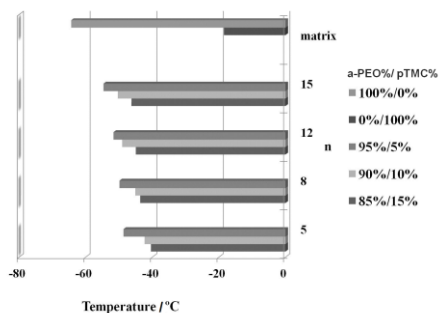


Figure 3 – Effect of electrolyte formulation on glass transition temperature.

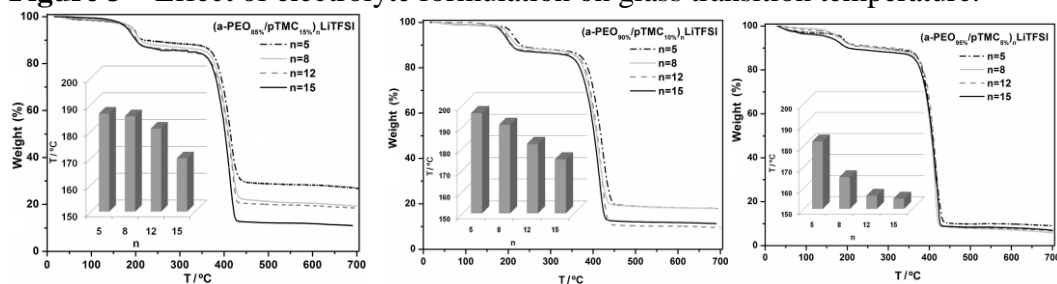


Figure 4 - TGA curves of $(a\text{-PEO}_{x\%}/p\text{TMC}_{y\%})_n$ LiTFSI electrolyte systems as a function of composition; inset degradation temperatures of each sample.

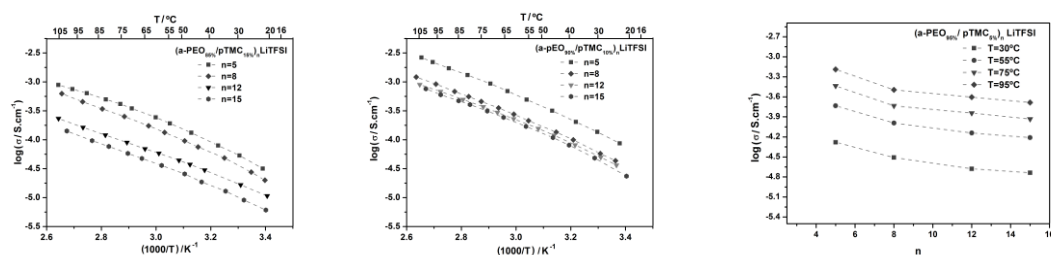


Figure 5A - Conductivity curves of $(a\text{-PEO}_{x\%}/p\text{TMC}_{y\%})_n$ LiTFSI electrolyte systems as a function of temperature; **B** - Isotherms of $(a\text{-PEO}_{x\%}/p\text{TMC}_{y\%})_n$ LiTFSI electrolyte systems.

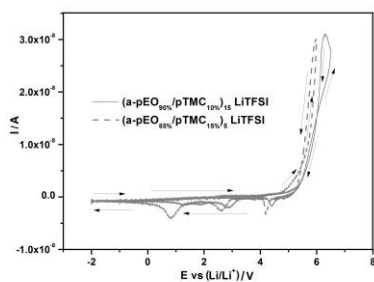


Figure 6 - Voltammogram of the $(a\text{PEO}_{85\%}/p\text{TMC}_{15\%})_5\text{LiTFSI}$ and $(a\text{PEO}_{90\%}/p\text{TMC}_{10\%})_{15}\text{LiTFSI}$ at a $25\ \mu\text{m}$ diameter gold microelectrode versus Li/Li^+ . Initial sweep direction is anodic and sweep rate is $100\ \text{mVs}^{-1}$.