Novel solid polymer electrolytes based on poly(trimethylene carbonate) and lithium hexafluoroantimonate

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Abstract

The results of the characterization of a polymer electrolyte system based on the poly(trimethylene carbonate) host matrix, with lithium hexafluoroantimonate as guest salt, are described in this study. Electrolytes with lithium salt compositions with values of n between 5 and 100 (where n represents the total number of monomeric cation-coordinating units - $(O=COCH_2CH_2CH_2O)$- per lithium ion) were prepared by co-dissolution and deposition from acetonitrile. The solvent-casting technique was used to prepare flexible, transparent and self-supporting films of electrolytes which were characterized by measurements of conductivity, cyclic voltammetry, differential scanning calorimetry and thermogravimetry.

Keywords: polymer electrolytes; lithium hexafluoroantimonate; conductivity; thermal stability.

1. Introduction

Since the publication of the earliest studies of substances recognized as solid polymer electrolytes (SPEs) in 1973 [1], this sub-domain of the solid electrolyte class of materials has benefitted from the attention of researchers with diverse scientific backgrounds. The practical result has been the application of a remarkable variety of development strategies with the common objective of producing electrolytes with appropriate chemical, electrochemical, thermal and mechanical properties for applications in sensors, displays or advanced batteries [2 – 8].

While first-generation SPEs were based on commercial souces of poly(ethylene oxide) (abbreviated as PEO) or PEO-derived host matrices, subsequent studies were directed towards the improvement of polymer host network, the development of salts with improved characteristics and the use of conductivity-enhancing additives. 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 amorphous matrices. The exploration of block co-polymer hosts [10], sol-gel derived hybrid materials [11] and inter-penetrating [12] or inter-connecting [13] polymer blends may be considered to have been motivated by this discovery.

Recently nano-dimensioned inorganic fillers [14] have also been added to electrolyte formulations to inhibit polymer spherulite growth. In view of the commercially-driven nature of research in this domain, restrictions arising from the need to produce stable interfaces, pass stringent safety tests and limit production costs, while simultaneously achieving adequate levels of ionic conductivity, led to the proposal of novel plasticized matrices [15-19]. Unfortunately, while the use of moderate plasticizer content leads to improved polymer segment mobility and contributes to increased salt dissociation and higher ionic conductivity, the presence of excessive quantities of plasticizer in electrolyte formulation may also re-introduce the problems of electrolyte leakage and electrode interfacial instability [20], the same practical deficiencies that solid electrolytes were expected to eliminate.

In this paper a novel polymer-salt combination has been characterized. The polymer component has been demonstrated to provide good thermal, mechanical and electrochemical stability [21-24]. The solubilization of lithium hexafluoroantimonate in the polycarbonate host has been shown to provide access to electrolyte compositions with encouraging electrochemical and physical characteristics.

2. Experimental

2.1. Materials

High molar mass p(TMC) (3×10^5 g.mol^{-1}), prepared by catalyzed bulk polymerization and characterized by gel permeation chromatography, was provided by Shell Chemicals, Houston, TX, USA. The purified host polymer, received in the form of an elastomeric, transparent solid, was subjected to argon/vacuum purge cycles at 70ºC for a period of about 7 days. Lithium hexafluoroantimonate (Alfa Aesar, 99%) was provided as a pure, dry solid, packed under nitrogen, and was used without further purification. Acetonitrile (Aldrich, anhydrous 99,9%) was dried over molecular sieves prior to use. All manipulations of host polymer, salt and electrolyte samples were carried out within high-integrity dry argon-filled gloveboxes.

2.2. Sample preparation

Homogeneous solutions of p(TMC) and lithium hexafluoroantimonate were prepared by adding known masses of polymer and lithium salt to a small conical flask. A convenient volume of acetonitrile was added as solvent and the contents of the flask were stirred for a period of at least 48 hours within a dry argon-filled preparative glovebox. The resulting viscous solutions were decanted into glass rings seated on glass plates and the solvent was removed slowly inside an

isolated chamber within the preparative glovebox. The atmosphere of this evaporating chamber was recirculated through a column of molecular seives to effect a controlled evaporation of the casting solvent and form self-supporting films of approximately 150 μm thickness. These electrolyte films were subjected to a final drying procedure during which the oven temperature was raised from 30°C to 60°C over a period of 3 days. During this period the tube oven was periodically evacuated and purged with dry argon.

The SPE formulation with a host matrix composed of p(TMC) and lithium guest salt such that the ratio of oxygen and carbonate coordinating units in the sample was 15, in accordance with current practice in this domain, was identified as $TMC_{15} LiSbF_6$.

2.3. Measurements

Total ionic conductivities of electrolyte samples were determined using a constant-volume support [25] with gold ion-blocking electrodes located within a Buchi TO 50 oven. A calibrated type K thermocouple positioned close to the electrolyte film was used to measure the sample temperature with a precision of about ±0.2°C. Impedance measurements were carried out at frequencies between 96kHz and 500mHz with a Solartron 1250 FRA and 1286 ECI, over a temperature range of 20°C to 90°C. Measurements of conductivity were effected during heating cycles. The reproducibility of recorded conductivities was demonstrated by comparing the results obtained for different electrolyte samples removed from the same film and subjected to precisely-reproduced assembly and characterization procedures. Repeated measurements on samples confirmed that reproducibility was better than 5%. The experimental procedure adopted confirmed the correct operation of the cell support used to effect measurements and the mechanical stability of the sample films.

Polymer electrolyte sections were removed from dry films and subjected to thermal analysis under a flowing argon atmosphere between –40°C and 350°C and at a heating rate of 5°C.min^{-1} using a Mettler DSC 821e. All samples were presented for analysis in 40 μL aluminium cans with perforated lids to permit the release and removal of decomposition products.

Samples for thermogravimetric studies were prepared in a similar manner, transferred to open platinum crucibles and analyzed using a Rheometric Scientific TG 1000 thermobalance operating under a flowing argon atmosphere. A heating rate of 10°C.min^{-1} was used to analyze all the electrolyte samples.

Evaluation of the electrochemical stability window of electrolyte compositions was carried out under an argon atmosphere using a two-electrode cell configuration. The preparation of a 25μm

diameter gold microelectrode surface by the conventional polishing routine was completed outside the drybox. The microelectrode was then washed with THF, dried with a hot-air blower and transferred to the drybox. The cell assembly was initiated by locating a clean lithium disk counter electrode (Aldrich, 99.9%, 10mm diameter, 1mm thick) on a stainless steel current collector. A thin-film sample of electrolyte was centered over the counter electrode. A small volume (0.20μL) of THF was placed on the microelectrode surface prior to location on the electrolyte surface. Firm contact between the cell components was secured by means of a clamp. The use of THF to soften the electrolyte was necessary to achieve a reproducible microelectrode/electrolyte interfacial contact. An Autolab PGSTAT-12 (Eco Chemie) was used to record voltammograms at a scan rate of 100mV/s. Measurements were conducted at room temperature within a Faraday cage located inside the measurement glovebox.

3. Results and discussion

3.1. Thermal behavior of electrolytes

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 complexes with guest salts or to phase-separate and form spherulites. In contrast, the undoped p(TMC) matrix is a completely amorphous material with a glass transition temperature (T_g) of –18ºC and a thermal stability limit (T_d) of about 200ºC. All the previously characterized p(TMC)-based electrolyte systems were found to be completely amorphous over a wide range of salt compositions. The mechanical properties of these systems are however clearly influenced by the choice of guest salt. In the $(TMC)_n LiSbF_6$ electrolyte system the value of T_g was found to be effectively independent of n at low salt content (Figure 1), similar to the behavior of electrolytes of the $(TMC)_n LiTFSI$ (lithium trifluoromethanesulphonyl imide) system [23]. This latter salt continues to be considered one of the most promising guest species for SPEs, precisely because of its capability to reduce the T_g of host polymers. In contrast to p(TMC)-based systems containing lithium perchlorate or lithium triflate, both the lithium trifluoromethanesulphonyl imide and lithium hexafluoroantimonate-doped electrolytes show a marked plasticizing effect at high salt content (see inset of Figure 1). While the variation of the T_gs of electrolytes based on lithium perchlorate and lithium triflate passes through a minimum and then rises at high salt content, the T_g of electrolytes containing both lithium trifluoromethanesulphonyl imide and lithium hexafluoroantimonate continue to decrease with increasing salt content. At compositions of n less than 5, neither of these systems

have adequate mechanical properties to satisfy separator functions of a dual electrolyte/separator cell component.

The onset temperature of thermal degradation of electrolyte samples was observed to decrease with an increase in the salt content of electrolytes. In this respect the lithium hexafluoroantimonate-based electrolyte was found to show improved thermal stability relative to electrolytes containing both lithium triflate and lithium perchlorate with similar compositions, as demonstrated by the inclusion of Figure 2. Lithium perchlorate-based electrolytes suffer exothermic degradation at moderate temperatures while the lithium hexafluoroantimonate, lithium trifluoromethanesulphonyl imide and lithium triflate-based systems degrade endothermally. In commercial devices, such as primary or secondary cells, this aspect of the electrolyte thermal performance is clearly of critical importance, particularly in relation to the practical consequences of severe cell abuse where overheating may be expected.

3.2. Ionic conductivity of electrolytes

The conductivity behavior of electrolytes with composition of n between 5 and 100 is reported in Figures 3 and 4. From the data presented in Figure 3b) it is immediately apparent that the conductivity is almost independent of composition in the range of n between about 10 and 5. The variation of conductivity with salt may be more clearly seen in the conductivity isotherms of Figure 4. All the electrolytes based on the p(TMC) host matrix show an increase of total ionic conductivity as the salt content is increased (or n is reduced) and in this respect the lithium hexafluoroantimonate system behaves in a manner consistent with previously characterized systems. This variation of conductivity is explained in terms of an increase in the number of charge carriers available for ionic transport. While in most electrolyte systems the conductivity passes through a readily-identified maximum and then decreases at higher salt content, in the lithium hexafluoroantimonate electrolyte system this effect is not observed. In this respect this system demonstrates a behavior similar to that of $(TMC)_n LiTFSI$. Once again, this observation is consistent with the suggestion that the guest salt exercises a strongly plasticizing effect on the host polymer. From Figure 4 we conclude that from the point-of-view of electrolyte conductivity, no further advantage results from the presence of salt compositions greater than about n = 12. In view of the decrease of thermal stability that arises as a consequence of higher salt content, in this system the thermal stability may effectively dictate the optimum electrolyte composition.

3.3. Electrochemical stability

The electrochemical stability of the lithium hexafluoroantimonate electrolyte system was determined by microelectrode cyclic voltammetry over the potential range 0V to 6V. The potential limit for the electrolyte system 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. On the cathode sweep several low current peaks were observed and attributed to the reduction of decomposition products that were formed at the anodic limit. This attribution of peaks was based on a series of experiments in which the anodic limit was successively reduced and the effect on the voltammogram observed. The overall stability of the electrolytes is good with no electrochemical oxidation occurring at potentials less than 5V. This result is in accordance with expectations that arise from studies of alkyl carbonate-based Kynar gel electrolytes [26] or liquid electrolytes containing asymmetric alkyl carbonates [27, 28] and confirm the applicability of this electrolyte composition in practical primary and secondary cells which typically operate within range from 3 to 4 volts.

4. Conclusions

The electrolyte system based on p(TMC) doped with lithium hexafluoroantimonate is a promising addition to the existing series of electrolytes using this amorphous host. Over the composition range of n between 5 and 15, the electrochemical, mechanical and thermal properties are appropriate for dual-function electrolyte/separator components and these materials may find future application in commercial devices. In particular, the thermal degradation of these electrolyte compositions occurs with a controlled endothermic process that suggests that safety requirements will be readily satisfied. Both the conductivity and thermal behavior observed confirm that this salt exercises a plasticizing effect on the p(TMC) host polymer and the conductivities reported for electrolytes in the range of n between 5 and 10 encourage further development of this system. Electrochemical stability studies are consistent with previous results obtained with other members of this electrolyte series [29] and indicate that appropriate performance may be expected.

5. Bibliography

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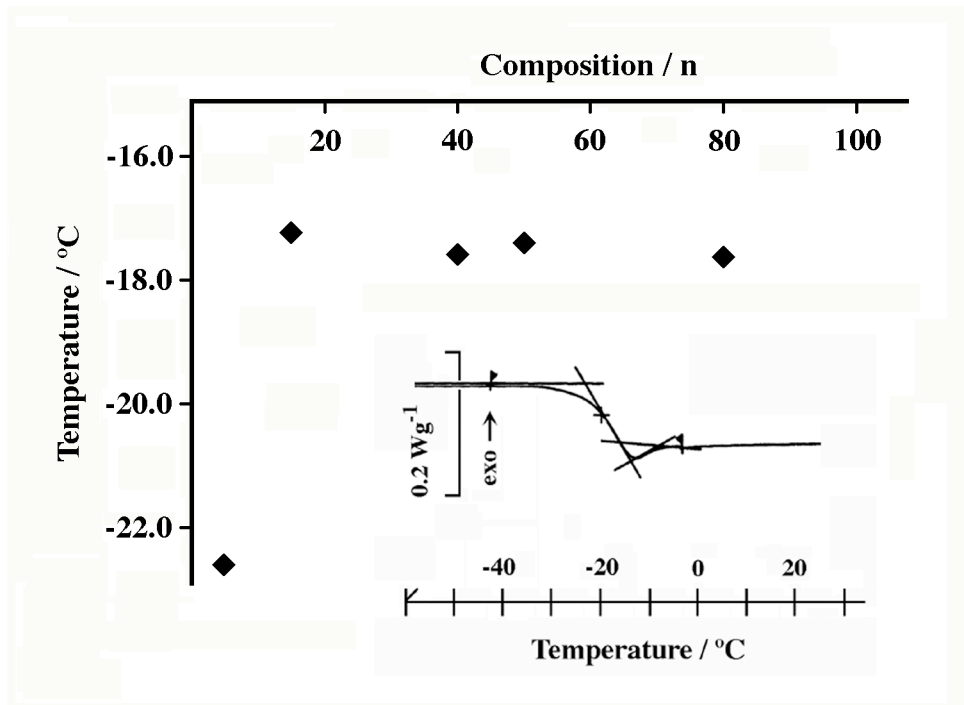[29] D. N. Januário, M. Sc. Thesis, University of Minho, Braga (2004).

Fig 1. Variation of glass transition temperature (T_g) with electrolyte composition. Inset shows behavior of n = 5 electrolyte composition.
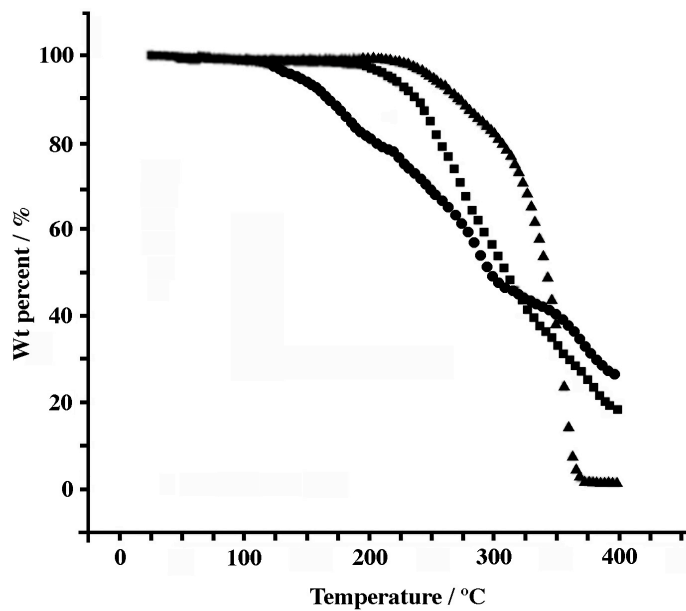

Fig 2. Thermal decomposition of selected electrolyte compositions $(TMC)_n$ $LiSbF_6$ where n = 5 ●, 30 ■ and 100 ▲.
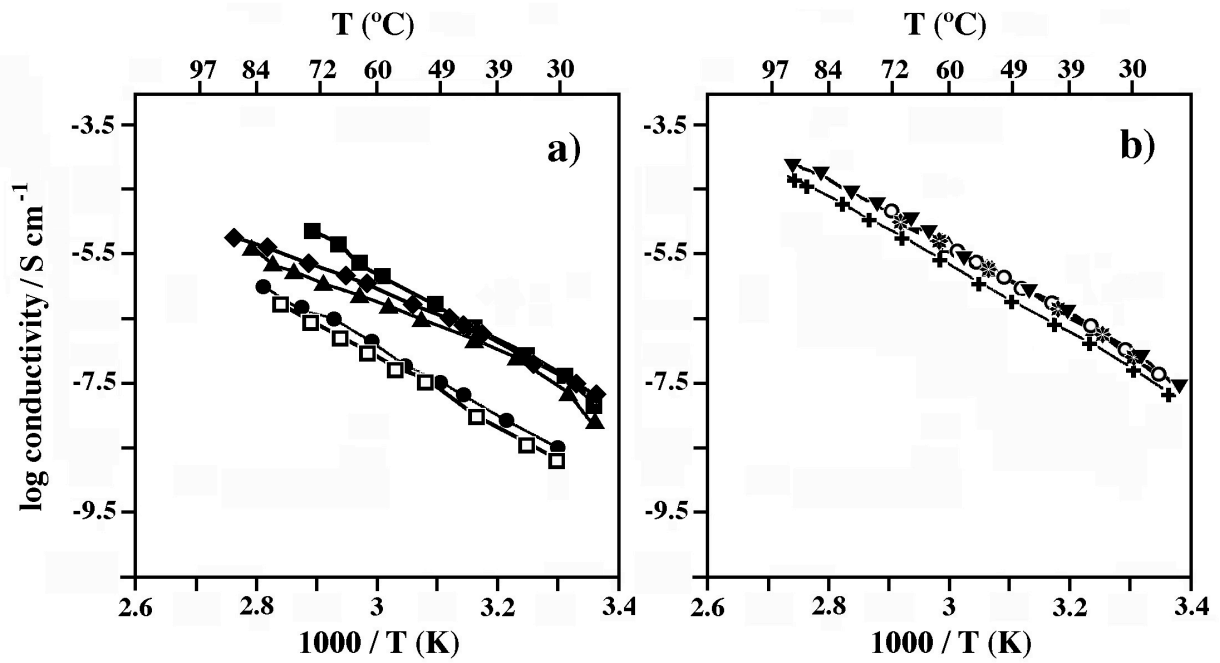
Fig 3. Variation of ionic conductivity with 1/T for selected electrolyte compositions
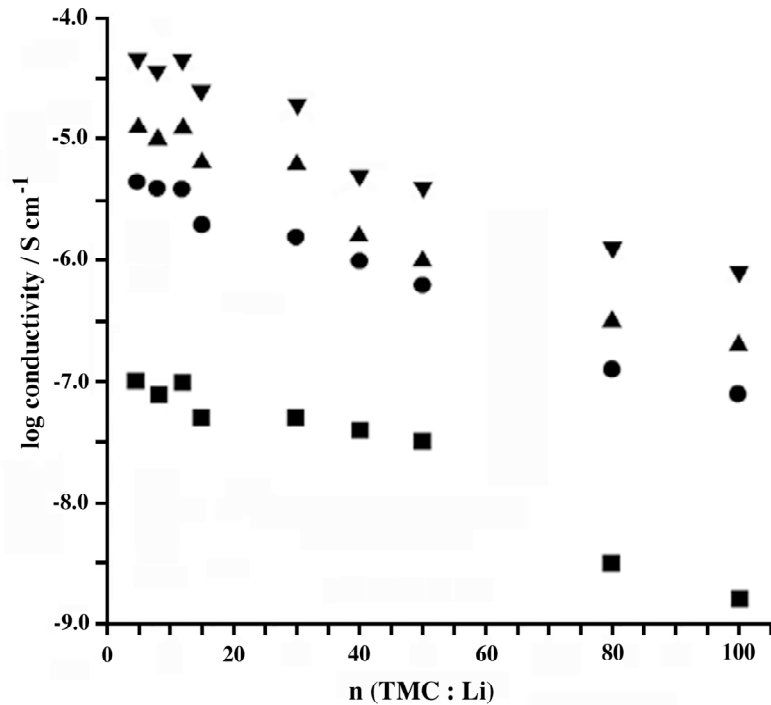(TMC)$_n$ LiSbF$_6$ (n = 5 ◯, 8 ✳, 12 ▼, 15 ✚, 30 ■, 40 ◆, 50 ▲, 80 ● and 100 ◻)

Fig 4. Conductivity isotherms for the (TMC)$_n$ LiSbF$_6$ system
(30ºC ■, 60ºC ●, 70ºC ▲ and 85ºC ▼)