Electrochemical and thermal properties of polymer electrolytes based on poly(epichlorohydrin-co-ethylene oxide-co-allyl glycidyl ether)

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Abstract

A series of novel electrolytes based on the terpolymer host, poly(epichlorohydrin-co-ethylene oxide-co-allyl glycidyl ether) with lithium perchlorate and lithium bis(trifluoromethanesulfonyl)imide have been prepared and characterized by conductivity measurements, cyclic voltammetry at a gold microelectrode and thermal analysis.

Electrolyte compositions, represented as p(EEO-AGE)LiX(wt%), were produced with lithium salt compositions between 0,1 and 12 wt% (where wt% indicates amount of lithium salt present in the epichlorohydrin-co-ethylene oxide-co-allyl glycidyl host matrix). The guest salt and host polymer were dissolved in tetrahydrofuran and cast to produce thin, free-standing electrolyte films.

The p(EEO-AGE)_nLiX(wt%) (X=ClO₄ and TFSI) electrolytes showed encouraging levels of ionic conductivity and acceptable thermal stability. Electrolytes based on this host polymer were obtained as completely amorphous films with good mechanical properties.

Keywords: solid polymer electrolytes, poly(epichlorohydrin-co-ethylene oxide-co-allyl glycidyl ether).

1. Introduction

Secondary lithium batteries are sophisticated energy storage devices that have received considerable attention over the last 30 years. As a result of their superior energy and power density, and the absence of a “memory” effect, solid-state lithium ion batteries [1-3] have become the preferred power source for many portable applications. The search for solid polymer electrolytes (SPEs) with high ionic conductivity and good mechanical, electrochemical and thermal stability continues to provide a challenge to many research groups [4]. The development of a successful solid-state lithium polymer battery is dependent upon the choice of a suitable host polymer matrix. Solvent-free solid polymer electrolytes used in prototype rechargeable lithium polymer batteries are mainly poly(ethylene oxide) (PEO) – based polymers containing lithium salts [5-9]. In spite of the considerable investment in this domain, and variety of the strategies applied, the low room temperature conductivity exhibited by solvent-free, PEO-based polymer electrolytes modified by ceramic fillers, polymer blending [10], additives and polar plasticizers, have not yet provided an adequate basis for commercial systems. Many of these materials suffer from the disadvantage that the ionic conductivity necessary for practical applications can only be reached at higher-than-ambient temperatures, due to the high degree of crystallinity inherent in this host matrix at room temperature.

With the objective of developing highly conductive solid polymer electrolytes, we prepared solid polymer electrolytes based on the commercially available p(EEO-AGE) (Scheme 1) and lithium salts, which showed encouraging total ionic conductivity. The advantage that favors the LiTFSI-based system arises due to its greater charge distribution, superior thermal stability, low energy barrier to the conformational mobility of the anion and a higher degree of ionic dissociation of the salt. These factors combine to make this salt one of the most promising candidates for applications in commercial devices. In view

of the advantages of LiTFSI, relative to LiClO₄ [11], it seemed appropriate to study the behaviour of this former salt in the p(EEO-AGE) host matrix. The choice of this host polymer was determined by the lower halogen content of the terpolymer relative to the epichlorohydrin/ethylene oxide copolymer. The lower halogen content provides a higher degree of backbone flexibility and this may be expected to improve low temperature electrolyte performance. Initially the possibility of using suitable agents to cross-link the host matrix through the cure sites on the polymer backbone and improve the mechanical properties of the resulting electrolytes was also considered, however as adequate dimensional stability over the range of temperatures of interest was obtained this strategy of development was not pursued.

An important consequence of using this terpolymer is that there are three different locations where interactions between the polymer and guest ion species may take place. Without prior knowledge of the distribution of guest salt between these sites it is not possible to use the conventional SPE notation that expresses the ratio of monomer units to lithium salt in the electrolyte. To avoid this problem the salt composition has been given as wt% of the salt in the polymer electrolyte.

2. Experimental

2.1. Materials

The elastomeric host polymer, commercially designated as Hydrin TX3 (Zeon Chemicals, Japan), was dried before use at 90°C, under vacuum, for a period of about 7-10 days. The molecular structure of this material, as supplied by Zeon, is shown in Scheme 1. Both Lithium perchlorate (Aldrich, 99.99 %) and Lithium bis(trifluoromethanesulfonyl)imide were dried under vacuum at 180°C and 190°C, respectively, for 7 days and then stored in a

high integrity, dry argon-filled glovebox. All subsequent manipulations of salts, electrolyte samples and cell assembly were carried out under a dry argon atmosphere.

Scheme – Chemical structure of terpolymer designated as Hydrin TX3.

2.2. Preparation of the p(EEO-AGE)_nLiClO₄ and p(EEO-AGE)_nLiTFSI samples

Homogeneous solutions of p(EEO-AGE) and lithium salts in THF (Aldrich, anhydrous 99.9 %) were prepared by adding known masses of polymer and lithium salt to a small conical flask. A convenient volume of THF was transferred to the flask and the components were stirred for a period of at least 48 hours within a dry argon-filled preparative glovebox. The resulting homogeneous viscous solutions were cast into glass rings on glass plates and the solvent was then removed slowly within an isolated chamber inside a preparative glovebox. The atmosphere of the chamber was recirculated through a column of molecular sieves to effect a slow evaporation of the solvent and form films of about 150µm thickness. These films were subsequently transferred to a Buchi TO51 oven and over a period of 3 days the temperature of the films was raised from 30 to 60°C. During this period the tube oven was periodically evacuated and purged with dry argon. In this preliminary study sample compositions of (LiClO₄) and (LiTFSI) were characterized.

2.3. Experimental techniques

Ionic conductivity. The total ionic conductivity of the p(EEO-AGE)LiX(wt%) electrolytes was determined by locating an electrolyte disk between two 10mm diameter ion-blocking gold electrodes (Goodfellow, > 99.95%) to form a symmetrical cell. The

electrode/p(EEO)LiX(wt%)/electrode assembly was secured in a suitable constant-volume support [12] and installed in a Buchi TO51 tube oven. A calibrated type K thermocouple was placed close to electrolyte disk to measure the sample temperature. Bulk conductivities of electrolyte samples were obtained during heating cycles using the complex plane impedance technique (Schlumberger Solartron 1250 frequency response analyzer and 1286 electrochemical interface) between 25 and 100 °C and at approximately 7 °C intervals.

Thermal analysis. Polymer electrolyte sections were removed from dry films and subjected to thermal analysis under a flowing argon atmosphere between 25 and 300°C and at a heating rate of 5°C.min⁻¹ using a Mettler DSC 821e. Samples were transferred to 40μL aluminium cans with perforated lids within a dry argon-filled glovebox. Samples for thermogravimetric studies were prepared in an identical manner, transferred to open platinum crucibles and analyzed using a Rheometric Scientific TG1000 thermobalance operating under a flowing argon atmosphere. A heating rate of 10 °C.min⁻¹ was used with all samples.

Electrochemical stability. Evaluation of the electrochemical stability window of electrolyte compositions was carried out under dry argon 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 subsequently 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%, 10 mm diameter, 1mm thick) on a stainless steel current collector. A thin-film sample of electrolyte was placed over the counter electrode and the cell assembly was

completed by locating and supporting the microelectrode in the centre of the electrolyte 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 carried out at room temperature within a Faraday cage located inside the measurement glovebox.

3. Results and discussion

3.1. Conductivity

The ionic conductivity in polymer electrolytes is assumed to occur by Lewis acid-base interactions between the cations and the polymer solvent. It is also generally accepted that the ionic conduction occurs mainly in the amorphous component of polymer electrolytes above their glass transition temperature, T_g , with the chain segment mobility playing a critical role in the conductivity mechanism [12]. A strategy which has been developed by many authors for enhancing ion mobility, and consequently the conductivity, is based on the use of a completely amorphous polymer with low values of glass transition temperature. The terpolymer used in the present SPEs combines not only the amorphous properties of the epichlorohydrin but also the solvating behaviour of the ethylene oxide and allyl glycidyl ether segments.

The conductivity-temperature plots for $\text{p(EEO-AGE)LiClO}_4(\text{wt}\%)$ and $\text{p(EEO-AGE)LiTFSI}(\text{wt}\%)$ electrolyte systems are represented in Figure 1 a) and b), respectively. In both electrolyte systems the ionic conductivity varies continuously with temperature and no sudden changes in conductivity, attributable to the fusion of the crystalline phase of oxyethylene segments, were detected. The ionic conductivity was studied as a function of salt concentration. In the $\text{p(EEO-AGE)LiClO}_4(\text{wt}\%)$ electrolyte system (Figure 1a)) the composition with the highest conductivity is recorded for the $\text{p(EEO-AGE)LiClO}_4(\text{wt}\%)$ electrolyte which reaches $4.2 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$ at 55°C , a similar value to that reported for

a system based on a structurally-related terpolymer [13]. The temperature variation of conductivity for the p(EEO-AGE)LiTFSI(wt%) electrolyte system illustrated in Figure 1 b) confirms that the ionic conductivity reaches $8.71 \times 10^{-5} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ at 70°C at a composition with wt% close to 1.

The resulting conductivity isotherms for these solid polymer electrolytes are represented in Figure 2. This figure shows that increasing the guest salt concentration in the lithium perchlorate-based electrolyte system increases the ionic conductivity to a maximum at a composition close to wt%, probably as a result of an increase in the number of charge carriers. Further increase of guest salt concentration results in reduction of conductivity, explained by an increase in transient ionic crosslinks in the system, causing a decrease in chain segment mobility. It has also been suggested that at high salt content formation of ion aggregates will contribute to a decrease in conductivity [9]. In the P(EEO-AGE)LiTFSI(wt%) electrolyte system very large amounts of guest salt can be dissolved in the host polymer without phase separation, a situation that has already been reported for a previous salt/host polymer system [14].

3.2. Thermal Analysis

Figures 3 a) and b) represent the DSC curves for the p(EEO-AGE)LiClO₄(wt%) and p(EEO-AGE)LiTFSI(wt%) electrolyte systems, respectively, and confirm that the electrolytes characterized are completely amorphous. No fusion of regions of oxyethylene chain segments of uncomplexed polymer, or polymer-salt complexes, is apparent in any of the electrolytes studied and no other thermal events are observed below temperatures of about 240°C in the case of the perchlorate-based electrolyte and 274°C in the p(EEO-AGE)LiTFSI(wt%) electrolyte system. The absence of crystallinity in samples of both networks was expected from conductivity measurements. It should be noted that this result is not in agreement with a previously reported study [13]. In this latter case the authors concluded that a polymer-salt complex was formed at high compositions of guest salt (low values of n), giving rise to a melting peak at close to 100°C. The observation of a weight

loss over the same temperature range suggests that this feature might be associated with the presence of adsorbed water or residual solvent in the sample. In contrast, in the present study no existence of a thermal event, nor of weight loss, over the referred temperature range was observed. This difference in behaviour may arise as a consequence of the application of more thorough initial drying procedures used with the salt and polymer components, more efficient removal of casting solvent residues and preservation of the dry state of the electrolytes by elimination of exposure to the environment.

As may be confirmed by reference to Figure 4, the p(EEO-AGE)LiTFSI(wt%) electrolyte system shows a higher thermal stability (293°C) than the perchlorate electrolyte system, which suffers a strongly exothermic process the intensity of which is dependent on the amount of salt present in the sample.

The glass transition temperatures measured for both electrolytes systems are also illustrated in Figure 4. It is clear that the value of T_g is proportional to the salt concentration in the electrolytes. The T_g of solvent-free polymer is close to -48°C and as the value of n is decreased, from low salt content compositions to salt-rich electrolytes, the T_g of the electrolyte increases. This behaviour has been interpreted as a consequence of a reduction in segmental motion caused by an increase in intramolecular and intermolecular coordinations between Li^+ cations and the oxygen atoms in the polymer chain [9]. The results are similar to those obtained by other authors with poly(epichlorohydrin-co-ethylene oxide) and a structurally-related terpolymer as polymer hosts [13, 11]. In the electrolyte system based on lithium perchlorate two T_g 's are observed in samples with higher salt content. This suggests that high concentration of this guest salt may induce phase segregation, an observation consistent with previous studies reported for a blend of poly(ethylene oxide) and epichlorohydrin doped with lithium perchlorate [11].

3.3. Electrochemical stability

The electrochemical stability of an electrolyte during oxidation and reduction cycles is one of the essential parameters for practical use both in energy storage systems and in electrochromic devices. A comparative study of the electrochemical stability of the electrolyte systems was carried out using microelectrode cyclic voltammetry over the potential range from 0V to 7V. Figure 5 shows the cyclic voltammogram of p(EEO-AGE) LiClO₄(wt%) and p(EEO-AGE)LiTFSI(wt%) compositions at room temperature. Both systems show a broad stability window (around 5V versus Li/Li⁺), which confirms that these electrolytes may be applicable in energy storage and electrochromic devices.

4. Conclusion

In this study amorphous, flexible solid polymer electrolytes prepared from the terpolymer of epichlorohydrin with ethylene oxide and allyl glycidyl ether, containing lithium perchlorate and lithium bis(trifluoromethanesulfonyl)imide were found to demonstrate good mechanical and thermal properties. The host polymer used in this study has a relatively complex structure that contributes to a reduction in the tendency of the oxyethylene copolymer segment to crystallize. Both of the other copolymers present in the terpolymer contain oxygen atoms that may contribute to guest salt solvation and ion transport. Although intuitively one would not expect identical behaviour from each of these three different sites, at the present time there is not sufficient information available to support a more precise conclusion regarding the distribution of guest ions between the copolymer segments and further comment must await the results of future spectroscopic characterization of these electrolytes.

In general thin films of solvent-free electrolytes have encouraging conductivity behaviour and good electrochemical stability. As expected the LiTFSI based-electrolyte system showed higher ionic conductivity and thermal stability than the perchlorate system, which makes the LiTFSI salt globally a better choice for application in electrochemical devices.

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Figure 1. Variation of conductivity with $1/T$ of lithium p(EEO-AGE)-based electrolytes: a) p(EEO-AGE)_nLiClO₄ and b) p(EEO-AGE)_nLiTFSI.

Figure 2. Conductivity isotherms of the $p(\text{EEO-AGE})_n\text{LiClO}_4$ and $p(\text{EEO-AGE})_n\text{LiTFSI}$ electrolytes systems (at 65°C – square; at 45°C – up triangle and at 30°C – diamond).

Figures 3 a) and b). Thermal analysis of the $p(\text{EEO-AGE})_n\text{LiClO}_4$ and $p(\text{EEO-AGE})_n\text{LiTFSI}$ electrolyte systems, respectively.

Figure 4. Extrapolated onset of glass transition and degradation temperatures of p(EEO-AGE)-based electrolytes: oval rod – $p(\text{EEO-AGE})_n\text{LiTFSI}$, rectangular rod – $p(\text{EEO-AGE})_n\text{LiClO}_4$.

Figure 5. Voltammogram of $p(EEO-AGE)_5LiClO_4$ and $p(EEO-AGE)_{12}LiTFSI$ electrolytes at a $25\mu m$ diameter gold microelectrode vs. Li/Li^+ . Initial sweep direction is anodic and sweep rate is $100 mVs^{-1}$.