Ionic conductivities of hybrid inorganic sulfide–polyether electrolytes

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Abstract

Hybrid polymers combining P₂S₄ moieties with oligoether spacers have been prepared, and the conductivities and glass transition temperatures of their solutions of lithium salts have been examined. The materials are highly viscous but mostly not rubbery. A high ambient temperature conductivity of 10⁻³⁹ S cm⁻¹ was obtained with LiTFSI dissolved in the sulfide–PEO matrix. The decoupling of Li⁺ motion from the polymer segmental motion is demonstrated, suggesting that, in certain cases, the transport number for Li⁺ ion in the sulfide–PEO matrix will be much higher than in a typical PEO-based salt-in-polymer system.

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1. Introduction

Ionically conducting polymer electrolytes have been extensively studied for developing lithium rechargeable batteries with high reliability and safety, which would be achieved by using solid electrolytes to replace the liquid electrolytes commonly in use [1–3]. Polymer electrolytes explored for these purposes are generally complexes of a lithium salt such as LiClO₄ with a high-molecular-weight polymer such as polyethylene oxide (PEO) [4]. The simple PEO–Li salt complexes exhibit low conductivities of order 10⁻⁷ S cm⁻¹ at room temperature. This conductivity has been improved by synthesizing comb-type polymers with polyether side chains and using salts such as lithium bis(trifluoromethanesulfonylelimide (LiTFSI) [5]. Such electrolytes obtain high ambient conductivity of 10⁻⁴ S cm⁻¹, but higher levels are needed for applications to ambient temperature batteries.

In most polymer electrolytes, ion motion is dependent on the segmental motion of polymer chains [6,7]. This strong coupling of the salt cation to the polymer is a major problem with “salt-in-polymer” solid electrolyte since it promotes low cation transport numbers. Low cation transport numbers lead to severe concentration gradients during cell operation, causing premature failure [8].

By contrast, inorganic sulfide glasses such as Li₂S–SiS₂ and Li₂S–P₂S₅ systems are known to be single ion conductors [9–13]. These glasses exhibit high Li⁺ ion conductivity, up to 10⁻³ S cm⁻¹, at room temperature. The sulfide anionic species are bound into the glass network, and are essentially immobile (hence the conduction process is described as “decoupled” from the structural relaxation process [6]). This lends a major advantage to superionic glass electrolytes.

Unfortunately, glassy materials have inherent brittleness and this property prevents close and persistent electrolyte–electrode contact. In order to endow glassy electrolytes with mechanical flexibility, glass–polymer composite materials have previously been prepared from intimate mixtures of sulfide-based glasses and branched PEO polymers with high-molecular-weight [14,15]. The composite films obtained are indeed flexible, but their conductivities prove to be considerably below those of the glasses alone.

An alternative strategy for obtaining flexible electrolytes with high single cationic conductivity, which has been exploited in the present work, is to prepare polymeric electrolytes in which blocks of the superionic glass structure are incorporated as an integral part of the polymer structure. These may be thought of as molecular level hybrid inorganic sulfide-polymer electrolytes,
or simply “hybrid” electrolytes. By moving \( T_g \) below ambient these polymeric hybrid materials could, in principle, have both a rubbery compliance and high ambient temperature conductivity [7], while maintaining the decoupled conduction mechanism of sulfide superionic glasses [16].

In the present study, hybrid polymers incorporating \( \text{PS}_m \) and \( (\text{CH}_2-\text{CH}_2-\text{O})_n \) (i.e. PEO) segments have been prepared by reacting a mixture of phosphorus penta-sulfide \( (\text{P}_2\text{S}_3) \) and an –OH terminated oligoether of variable length. The ionic conductivities and glass transition temperatures of two distinct types of electrolyte based on the product are examined. In one, the hybrid molecular polymer serves as a solvent for the dissociating salt LiTFSI \( (\text{LiN(\text{SO}_2\text{CF}_3)}_2) \) so is merely a variant of the salt-in-polymer solid polymer electrolyte. In the second, which is closer to our initial concept, lithium sulfide \( (\text{Li}_2\text{S}) \) is reacted with the \( \text{PS}_m \) moieties of the polymer to form an acid–base product analogous to that in the thiosulfide superionic glasses. In this latter case single ion conductivity can be expected. The effects of varying oligoether spacer lengths and proportions relative to \( \text{P}_2\text{S}_3 \) in the hybrids are also investigated. Of particular interest will be the extent to which this type of polymer can promote decoupling of \( \text{Li}^+ \) motion from the polymer segmental motion.

2. Experimental

2.1. Preparation of hybrid electrolytes

Reagent-grade \( \text{Li}_2\text{S}, \text{P}_2\text{S}_3 \), ethylene glycol dimethyl ether (DME), diethylene glycol (DEG), poly(ethylene glycol) (PEG) with molecular weights of 200, 400 and 600 were all purchased from Aldrich or Alfa and used as received. LiTFSI donated by 3M corporation was also used as received. Hybrid materials based on sulfide network combined with oligoether spacer units were synthesized from the reaction between \( \text{P}_2\text{S}_3 \) and one of oligoethers such as DEG and PEGs. Mole ratios of \([\text{oligoether}] / [\text{P}_2\text{S}_3] = 3/4, 1/2, \) and 1/4 were selected. The reaction was carried out in a refluxing DME solution coupled to a NaOH gas scrubber until no more \( \text{H}_2\text{S} \) gas was produced by the condensation process. Solvent DME was then largely removed from the solution using a rotovapor and the residual viscous liquids were dried in a vacuum oven at 100 °C for 2 days. The products were highly viscous liquids. The presumed structure of the hybrid materials is shown in Scheme 1.

The \( n \) value in this structure refers to the repeating oxyethylene units and oligoether spacers with different lengths. Spacers based on DEG, PEG200, PEG400, and PEG600, respectively, correspond to \( n = 2, 5, 9, \) and 14. The \( m \) value in the structure refers to repeating sulfide units and the mole ratios of [oligoether]/[\( \text{P}_2\text{S}_3 \)] = 3/4, 1/2, and 1/4, respectively, correspond to \( m = 1.67, 3, \) and 7.

Initially it was expected that high and decoupled conductivity would be obtained by reacting the \( \text{PS}_m \) groups in the above polymer with \( \text{Li}_2\text{S} \) to produce a PEO-linked polyanion. However, the solubility of \( \text{Li}_2\text{S} \) proved unexpectedly low, probably for the reasons discussed below. As an alternative route to obtain ion-conducting electrolytes, lithium salts were dissolved in the hybrid thiosulfide–polyether polymer, in which they prove extremely soluble. LiTFSI powder was dissolved directly into the polymer by heating to around 100 °C in sealed vials. Alternatively, \( \text{Li}_2\text{S} \) and the hybrid polymer were reacted in a refluxing DME solution until homogeneous solutions were obtained. The solvent was then removed by careful heating followed by slow vacuum evaporation. The final products with LiTFSI or \( \text{Li}_2\text{S} \) were either very viscous clear liquids or translucent rubbery solids, depending on the hybrid composition. Lithium ion concentrations are defined using the ratio \([\text{Li}] / ([\text{P}]+[\text{O}])\), which quantifies the number of lithium ions per repeating unit of the hybrid shown in Scheme 1.

2.2. Measurements

Electrical conductivities were measured by an ac impedance method using a HP 4192 impedance analyzer. For liquid samples, a homemade dip-type cell with two parallel platinum disks [7] was used. For rubbery samples a sandwich type cell in which a film of electrolyte, of known thickness was compressed between opposing rods of aluminum or stainless steel, was employed. The conductivities were determined during slow cooling from 100 to –30 °C in the frequency range 5 Hz to 1 MHz.

To determine the glass transition temperatures \( (T_g) \) of the hybrid materials, simple differential thermal analysis (DTA) measurements were carried. After quenching to the temperature of liquid nitrogen, samples were heated up to room temperature at a heating rate of approximately 20 K min\(^{-1}\).

3. Results

3.1. Hybrid polymers with LiTFSI as dissolved salt

Firstly, the effect of the oligoether spacer lengths in the hybrids on the conductivities of their solutions with
LiTFSI is examined. Fig. 1 shows an Arrhenius plot of the electrical conductivities for the case \( m = 1.67 \) with different spacers (i.e. different \( n \) values). In this case, the lithium ion concentration, defined by the quantity \( [\text{Li}] / ([\text{P}] + [\text{O}]) \), is fixed to 0.06. All these electrolytes are highly viscous liquids.

The conductivities exhibit in all cases the super-Arrhenius behavior typical of most glass-forming liquids above their \( T_g \). The conductivities increase with an increase in \( n \) value from 2 to 9, i.e. with increasing PEO spacer length. Beyond \( n = 9 \) the effect saturates. Fig. 2 shows the effect of \( n \) value on (i) the isothermal conductivities, obtained from Fig. 1, and (ii) the \( T_g \) values for the hybrids both with and without LiTFSI. The conductivities at 100 °C are monotonically increased by increase in \( n \) value, while those at 75, 50, and 25 °C are maximized at the composition with \( n = 9 \). The highest ambient temperature conductivity, \( 10^{-4.7} \text{ S cm}^{-1} \) at 25 °C, is obtained with the hybrid of \( n = 9 \) (for which \( T_g = 47 °C \)). \( T_g \) for hybrids both with and without LiTFSI, increases monotonically with an increase in \( n \) value. The addition of LiTFSI to the hybrid molecular polymer increases \( T_g \) at all compositions.

Next, the effect on their conductivities of the ratios of [oligoether]/[P$_2$S$_5$] in the hybrids, is investigated. Fig. 3 shows the Arrhenius plot for electrical conductivities of hybrid electrolytes \( (n = 9 \text{ and } [\text{Li}] / ([\text{P}] + [\text{O}]) = 0.06 \) with different P$_2$S$_5$ contents (i.e. different \( m \) values). All the electrolytes shown here are again very viscous liquids, although \( T_g \) never rises above \(-45 °C \). Fig. 4 shows the isothermal conductivities obtained from Fig. 3 and \( T_g \) of the hybrids with and without LiTFSI, as a function of \( m \) value. The conductivities at 100 and 75 °C are maximized at the composition with \( m = 3 \), while those at 50 and 25 °C are maximized at the composition with \( m = 7 \). The highest conductivity at 25 °C, \( 10^{-4.2} \text{ S cm}^{-1} \), is obtained in the hybrid with \( m = 7 \) (\( T_g = -65 °C \)). \( T_g \) for hybrid polymers both with and without LiTFSI are monotonically decreased with an increase in \( m \) value.

Finally, the effect of the lithium ion concentration in the hybrids on their conductivities is examined. Fig. 5 shows the temperature dependence of electrical conductivities for hybrid electrolytes \((n = 9 \text{ and } m = 7)\) with different Li content from \( 0.02 \leq [\text{Li}] / ([\text{P}] + [\text{O}]) \leq 0.30 \). The electrolytes obtained are again all viscous liquids for which \( T_g \) is always less than \(-30 °C \). Fig. 6 shows the
isothermal conductivities and $T_g$ values of the hybrids ($n = 9$ and $m = 7$) as a function of Li content.

The conductivity is unexpectedly high at low Li content and remains high until $[\text{Li}] / ([\text{P}] + [\text{O}]) = 0.09$ is exceeded; an unexplained high temperature maximum in the conductivity is found for this composition. $T_g$ increases monotonically with Li content over the whole range.

Addition of LiTFSI to the hybrids raises not only the number of $\text{Li}^+$ carriers but also $T_g$ due to transient crosslinking between PEO chains and $\text{Li}^+$ ions. Increase in $T_g$ reduces the mobility of the polymer segments and, at balance with the effect of increasing charge carrier concentration, the conductivity maximum is observed. Usually this maximum is broader than in the present case [1,2]. The maximum observed at high temperature for $[\text{Li}] / ([\text{P}] + [\text{O}]) = 0.09$ is not seen in the temperature range below 0 °C. The highest conductivities, $10^{-2.6} \text{ S cm}^{-1}$ at 100 °C and $10^{-3.9} \text{ S cm}^{-1}$ at 25 °C, are obtained at the composition $[\text{Li}] / ([\text{P}] + [\text{O}]) = 0.09$ ($T_g = -64 °C$).

## 3.2. Hybrid polyanion by incorporation of Li$_2$S

Fig. 7 shows an Arrhenius plot of the electrical conductivities of electrolyte obtained when Li$_2$S is reacted with hybrid polymer ($n = 9$) with different $m$ values. Open triangles, circles, and squares, respectively, denote the hybrids of $m = 1.67$, 3, and 7 in which the lithium concentration of $[\text{Li}] / ([\text{P}] + [\text{O}]) = 0.02$. The conductivities are maximized at the composition of $m = 3$, which exhibits conductivities of $10^{-4.8} \text{ S cm}^{-1}$ at 100 °C and $10^{-6.0} \text{ S cm}^{-1}$ at 25 °C and $T_g$ of $-54 °C$.

This composition is a very viscous liquid, however, addition of extra Li$_2$S produces a translucent rubbery material. For an Li$_2$S content yielding $([\text{Li}] / ([\text{P}] + [\text{O}]) = 0.06$ (the conductivity is shown by closed circles in Fig. 7), it is seen that this ($m = 3$) hybrid has suffered a decrease in conductivity of about one order of magnitude, to $10^{-5.9} \text{ S cm}^{-1}$ at 100 °C. The $T_g$ value has increased somewhat, to $-47 °C$. The conductivities in these cases show much smaller departures from Arrhenius behavior and it will be seen later that their conductivities are much less dependent on the structure.

## 4. Discussion

Ionic conductivities are determined by a combination of charge carrier concentration and charge carrier mobility, and the latter may be limited by the host relaxation time reflected in $T_g$. In the favorable case of fast ion glasses the mobility is much higher than expected from $T_g$ because of the decoupling phenomenon referred to in Section 1. In either case, decreasing $T_g$ tends to increase conductivity. In the present work we have succeeded in the objective of lowering the $T_g$ of the thiophosphate conducting medium, but the conductivity has not been concomitantly increased.

Although we have obtained a conductivity which is high, $10^{-3.9} \text{ S cm}^{-1}$, at 25 °C by salt-in-polymer
electrolyte standards, these results have only been obtained at the expense of a net decrease in conductivity relative to the values achieved in the glassy solid (10\(^{-3}\) S cm\(^{-1}\) at 25°C). Furthermore the above conductivity has been achieved at the expense of introducing a mobile anion hence of losing the key advantage of uni-cationic conduction. For the case in which single ion conductivity is retained (by incorporating Li\(_2\)S), an original objective, the loss in conductivity has been even more serious—a decrease to 10\(^{-6.0}\) S cm\(^{-1}\), although in this case a rubbery solid, also an original objective, was obtained. What can be responsible for such disappointing results? Since the structural relaxation time at 25°C has been decreased so greatly (by decrease of T\(_g\)) the answer must lie either in a decrease of charge carrier concentration or in the loss of the very favorable decoupling index R\(_g^*\) of the original glass—about which more is said below.

The Li\(_2\)S content in the most conducting case is about 3 mol.\% which is certainly well below that in the original glass. This is no doubt part of the reason for the lower conductivity, since Li\(_2\)S–P\(_2\)S\(_5\) glasses of comparable Li content are also poor conductors [16]. However, it is also clear that the decoupling index has changed in a very unfavorable direction because the conductivity is low despite the fact that T\(_g\) is now well below room temperature.

To discuss decoupling we note that the decoupling index R\(_g\) provides a quantitative measure of the extent to which the fast ion mobility differs from those of the remaining particles, hence of how truly uni-cationic the conductivity process is. Formally, R\(_g\) is the ratio of the structural relaxation time at the microscopic level to the conductivity relaxation time (also at the microscopic level), and R\(_g^*\) is its value at the particular temperature T\(_g\) where the structural relaxation time is about 100 s. Because of this relation we can obtain R\(_g^*\) from a measure of the conductivity for the system at T\(_g\). This can then be used in the approximate relation [17]

\[ \log R_g^* = 14.3 + \log \sigma_{T_0} \]

Due to the limitations of our impedance measurements, the conductivity for the present systems at their T\(_g\) can only be obtained by extrapolation. In view of the curvilinear plots of Fig. 5, the appropriate extrapolation is one using the Vogel–Fulcher–Tamman equation [18] modified for conductivity [19] in the light of the free volume model for diffusivity [20]

\[ \sigma = A T^{1/2} \exp[-B/(T - T_0)] \]  

(1)

where A and B are constants and T\(_0\) is the vanishing mobility temperature. The best-fit parameters of A, B, and T\(_0\) and the calculated \(\sigma_{T_0}\) and R\(_g^*\) values for the hybrids with LiTFSI, are listed in Table 1. For the most conductive sample at ambient temperature (\(n = 9, m = 7, \) and [Li]/([P]+[O]) = 0.09), the value of R\(_g^*\) proves to be 10\(^{1.9}\), and the highest value found is for the nearby composition (\(n = 14, m = 1.67, \) and [Li]/([P]+[O]) = 0.06), for which R\(_g^*\) is 10\(^{2.4}\). This value is more than five orders of magnitude larger than the value of the value 10\(^{-3}\) found for the typical salt-in-polymer electrolyte [21]. However, it is 9 orders of magnitude below the values found for the superionic glasses [17]. It is this loss of cationic mobility that is mainly responsible for the generally disappointing conductivity of our salt-in-hybrid polymer electrolyte relative to those observed for the sulfide glasses [12,13]. We attribute the increased coupling to the presence of the polyether segment oxygens that serve as traps for the Li\(^+\) species.

Much higher R\(_g^*\) values are found for the polyanion hybrid even though the conductivity of this hybrid is lower, as seen in Fig. 7. In this case the conductivity can be measured much closer to T\(_g\) than in the previous case, and quite close bounds can be placed on its extrapolated value at T\(_g\). We show this in Fig. 8 using, as alternative means of extrapolation, both the Arrhenius law extrapolation and the VFT law. The conductivity at T\(_g\) must

Table 1
VFT fitting parameters for the hybrids with LiTFSI

<table>
<thead>
<tr>
<th>n value</th>
<th>m value</th>
<th>[Li]/([P]+[O])</th>
<th>T(_g) (K)</th>
<th>A (K(^{1/2}) S cm(^{-1}))</th>
<th>B (K)</th>
<th>T(_0) (K)</th>
<th>(\log \sigma_{T_0})</th>
<th>log(R_g^*)</th>
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lie between the limits set by the alternative laws, hence in the range \(10^{-8.2} - 10^{-11}\) S cm\(^{-1}\). These values imply decoupling indexes between 10\(^{3.3}\) and 10\(^{6.1}\). Both of these values are larger than the maximum value for the LiTFSI salt-in-hybrid-polymer electrolyte, suggesting that it is indeed possible to make single ion conducting hard rubber polymers in this manner. What has not been achieved yet are the high decoupling ratios of the original superionic glasses. On the positive side, the conductivities obtained are as high as those (10\(^{-6}\) S cm\(^{-1}\) at ambient) achieved in oxide glasses, such as lithium phosphorus oxyxynitride (LiPON) glasses, which have been successfully applied in thin film battery technology [22].

In order to obtain the optimum ionic rubber by this approach it appears that a different combination of superionic conducting blocks and polymer linkers will be needed. The oxygen traps responsible for the poor conductivities of oxide superionic glasses and of the present hard rubber electrolytes must be avoided, and the lithium ion content must be increased. Methods for obtaining these improvements are currently under testing.

5. Conclusions

Novel hybrid electrolytes combining \(P_2S_5\) and an oligoether spacer have been prepared. In this way the \(T_g\) of \(P_2S_5\)-containing ion conducting media has been lowered below ambient, and high ambient temperature conductivities, up to 10\(^{-3.9}\) S cm\(^{-1}\) have been obtained. However, these values have only been obtained by a salt-in-polymer approach using LiTFSI as salt. In a system with truly superionic (single ion conducting) blocks, a conductivity of 10\(^{-6.0}\) S cm\(^{-1}\) at room temperature has been obtained. In each case the decoupling index at \(T_g\), \(R_g^*\), is found to be higher than for the typical salt-in-polymer (super-coupled) electrolytes. The results suggest that a substantial fraction of the Li\(^+\) ions in the hybrids are not limited by polymer segment motion but move in the sulfide matrix. There are reasons to expect that greatly improved versions of these hybrid polymer electrolytes will be realizable by development of this line of research.

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