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Effect of TiO_2 nano-filler and EC plasticizer on electrical and thermal properties of poly(ethylene oxide) (PEO) based solid polymer electrolytes

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ABSTRACT

Ionic conductivity of poly(ethylene oxide)–lithium trifluoromethanesulfonate ($LiCF_3SO_3$ or LiTf) based polymer electrolyte has been increased by incorporating TiO_2 nano-filler. Incorporation of 10 wt.% TiO_2 exhibited the highest conductivity enhancement with a value of 4.9×10^{-5} S cm^{-1} at 30 °C. A further enhancement in conductivity to a value of 1.6×10^{-4} S cm^{-1} at 30°C has been obtained by the incorporation of 50 wt.% ethylene carbonate (EC) plasticizer. Both additives cause a reduction of the PEO crystalline phase content and an increased segmental flexibility leading to conductivity enhancement.

1. Introduction

Research and development of lithium ion conducting solid electrolytes has received a great deal of attention in the last two decades due to the growing demand for lithium ion batteries in applications ranging from portable electronic devices such as mobile phones, cameras, computers and electro-optical devices to hybrid electric vehicles [1–3]. Among various approaches followed in order to improve the capacity, cyclability and long term stability of lithium ion rechargeable batteries particularly for high energy density applications, lithium polymer batteries have drawn much attention due to their many advantages such as the absence of electrolyte leakage, light weight, flexible geometry, ease of roll–roll fabrication and improved safety [1].

High molecular weight poly(ethylene oxide) (PEO) based polymer electrolytes containing lithium salts are of particular interest because of their easy formation of complexes with lithium salts and high mobility of charge carriers [3–5]. A large number of research papers have been published on PEO–LiX (X = ClO_4^-, $CF_3SO_3^-$, BF_4^-, PF_6^- and so on) [3,6–10] polymer–salt complexes investigating their electrical, thermal and optical properties. However, a major drawback of these PEO–LiX electrolyte membranes for practical applications is that they tend to crystallize at ambient temperatures resulting low ionic conductivity [4,5,11,12]. Local relaxation and segmental motion of the polymer chain allow Li^+ ion transport which can occur only in the amorphous state. On the other hand, a room temperature ionic conductivity value of 10^{-4} S cm^{-1} or above is required for practical applications of these membranes in lithium ion batteries [13].

Generally two methods have been adopted to enhance the room temperature ionic conductivity of PEO based polymer–salt complexes; one is the incorporation of nano-sized ceramic fillers such as TiO_2, SiO_2, ZrO_2 and Al_2O_3 in the polymer matrix and the other is the incorporation of plasticizers such as ethylene carbonate (EC), propylene carbonate (PC) and polyethylene glycol (PEG). Plasticization is one of the traditional ways of reducing crystallinity and increasing the amorphous phase content of polymer electrolytes. These plasticizers can improve the room-temperature ionic conductivity of PEO–LiX complexes, but the mechanical properties and the potential stability of these polymer films will deteriorate with the addition of plasticizers [4]. On the other hand, as first reported by Weston and Steele in 1982, and subsequently by many other groups, nano-sized ceramic fillers such as SiO_2, TiO_2 and Al_2O_3 can enhance the ionic conductivity while retaining the mechanical properties of these polymer electrolyte membranes [4,6,8,12,14,17]. Polymer electrolytes incorporated with these nano-sized ceramic fillers are usually known as nano-composite polymer electrolytes.

Among the nano-sized ceramic fillers studied in the past, TiO_2 was found to be the best candidate to increase the ionic-conductivity. Chung et al. [10] studied the effects of TiO_2, Al_2O_3 and SiO_2 in PEO–

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$LiClO_4$ polymer electrolyte and identified TiO_2 as the filler with greatest enhancement in ionic conductivity due to the weakened interactions between the polymer chain and the Li^+ ions. Scrosati et al. [9] have also studied the same PEO–$LiClO_4$ complexes with TiO_2 and Al_2O_3 ceramic fillers and reported that TiO_2 was the best filler exhibiting greatest enhancement in ionic conductivity. To the best of our knowledge, there are no reports available in the literature on the ionic conductivity enhancement of PEO–$LiCF_3SO_3$ (commonly denoted as PEO–LiTf) polymer electrolyte due to the incorporation of nano-sized TiO_2 ceramic filler or due to the combined effect of both TiO_2 nano-filler and EC plasticizer.

In this work, we have studied the effect of TiO_2 incorporation on thermal and electrical properties of PEO–LiTf polymer electrolyte. The effect on ionic conductivity and thermal properties such as glass transition temperature and crystallite melting temperatures has been systematically studied for the nano-composite electrolyte incorporating different wt.% of TiO_2 (5, 10, 15 and 20). It was found that out of the different compositions studied, the electrolyte with 10 wt.% TiO_2 showed best enhancement in room temperature ionic conductivity. The addition of EC plasticizer to this PEO–LiTf–10 wt.% TiO_2 electrolyte showed a further enhancement in ionic conductivity without deteriorating the mechanical stability.

2. Experimental

Poly(ethylene oxide) (PEO) (molecular weight, 4×10^6) from Polysciences Inc. and $LiCF_3SO_3$ from Aldrich were used as the starting materials to prepare the solid electrolytes. TiO_2 powder from BDH and ethylene carbonate (EC) (purity of 98%) from Aldrich were used as the ceramic filler and the plasticizer, respectively. Prior to use, PEO, $LiCF_3SO_3$ and TiO_2 were vacuum dried for 24 h at 50, 120 and 200 °C respectively. To prepare the $(PEO)_9LiTf + x$ wt.% TiO_2 ($x = 0$, 5, 10, 15 and 20) polymer electrolyte, appropriately weighed quantities of PEO and LiTf required for ether oxygen to lithium ion ratio of 9:1 were dissolved in anhydrous acetonitrile, and subsequently the required amount of TiO_2 nano-filler was added to the mixture which was magnetically stirred at room temperature at least for 24 h, until a homogeneous slurry was obtained. The resulting slurry was cast onto a Teflon plate and kept inside the fume hood for 24 h in order to allow the solvent to slowly evaporate. Then the film was vacuum dried for 24 h at room temperature to completely remove any trace amount of the residual solvent and moisture. This procedure yielded free-standing and visually homogeneous composite polymer electrolyte films with average thickness of 100–200 μm. The same procedure described above was followed to prepare $(PEO)_9LiTf + 10$ wt.% $TiO_2 + 50$ wt.% EC by incorporating the required amount of EC.

Complex impedance measurements were performed on disc shaped samples sandwiched between two spring-loaded stainless steel blocking electrodes of 13 mm diameter, using a computer controlled SI 1260 Schlumberger Impedance/Gain-phase Analyzer in the frequency range from 20 Hz to 10 MHz. The temperature of the sample was varied from 25 to 100 °C and the measurements were taken at approximately 10 °C intervals on heating. The temperature of the sample was measured with a thermocouple kept in thermal contact with the sample. The ionic conductivity was derived from the complex impedance data.

Polymer electrolyte films with weight of 5 to 15 mg were sealed in aluminum pans to perform DSC studies and an empty aluminum pan was used as the reference. Perkin Elmer, Pyris 1 DSC with a heating rate of 10 $°C\ min^{-1}$ from -120 °C to 120 °C in the heating cycle was used to perform the thermal analysis. Glass transition temperature (T_g) and crystallite melting temperature (T_m) were determined from the inflection point and endothermic peak, respectively. During the measurements, sample holders were purged with dry N_2 gas in order to avoid moisture condensation.

3. Results and discussion

The most significant enhancements in ionic conductivity of polymer electrolytes have been achieved through the incorporation of plasticizers or ceramic fillers into the polymer matrix [3,4,9,10,15–19]. The addition of plasticizer in general helps to increase the amorphous phase content of the polymer–salt complexes leading to increased segmental mobility of the polymer chains. However, as described earlier, the incorporation of plasticizer alone would deteriorate the mechanical properties of the polymer electrolyte film while the incorporation of nanosize ceramic fillers was found to improve the mechanical strength of the polymer electrolyte films. Therefore, one of the best ways to increase the ionic conductivity while retaining the mechanical strength is through the addition of both the plasticizer and the ceramic filler together into the polymer matrix.

EC would be a better plasticizer because of its low viscosity compared to other commonly used plasticizers. Among the many plasticizers which were reported to yield conductivity enhancement in polymer electrolytes, propylene carbonate (PC) and ethylene carbonate (EC) appear to be of significant importance. Even though PC (a liquid at room temperature) has a higher dielectric constant compared to EC (solid) and thereby can contribute for greater dissociation of the ionic salt, its higher viscosity would lead to reduced mobility of ions [20]. Therefore, EC would be a better plasticizer if used alone.

Fig. 1 shows the variation of conductivity with inverse temperature for the composite polymer electrolyte system $PEO_9LiTf + x$ wt.% TiO_2 ($x = 0$, 5, 10, 15 and 20) taken on the heating run. Fig. 2 shows the conductivity of isotherms at different compositions of TiO_2. According to these observations, incorporation of TiO_2 has increased the ionic conductivity significantly and 10 wt.% TiO_2 incorporated sample exhibits the maximum enhancement at all measured temperatures. The lowering of T_g and T_m (Fig. 4a and b) due to the addition of TiO_2 agrees with the enhanced conductivity. These data are summarized in Table 1.

According to the literature, TiO_2 has high Lewis-acid character [10] compared to other commonly used ceramic fillers such as Al_2O_3, SiO_2 and ZrO_2. Incorporation of TiO_2 may lead to high transient conducting pathways due to the Lewis acid–base type interactions between the polar surface groups of the filler and the ionic species in the electrolyte, as originally proposed by Wieczorek et al. [21]. Due to these Lewis-acid–base interactions, there would be mainly two important structural modifications taking place at the ceramic surface [22–24]. One effect is the

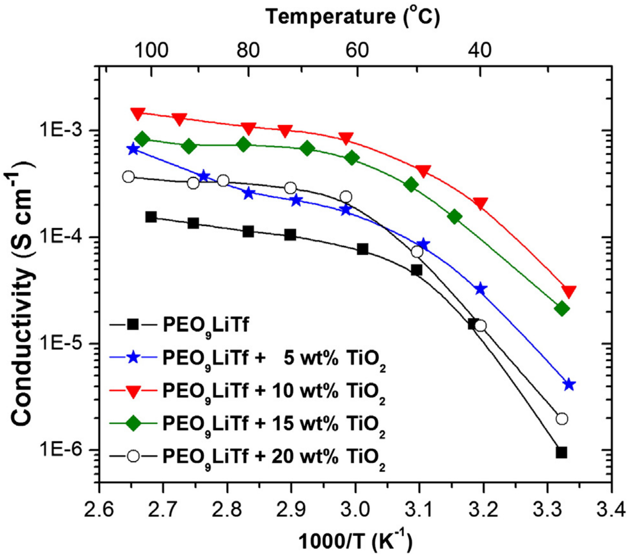

Fig. 1. Variation of conductivity with inverse temperature for composite polymer electrolytes incorporating TiO_2 ceramic powder; $(PEO)_9LiTf + x$ wt.% TiO_2 ($x = 0$, 5, 10, 15 and 20).

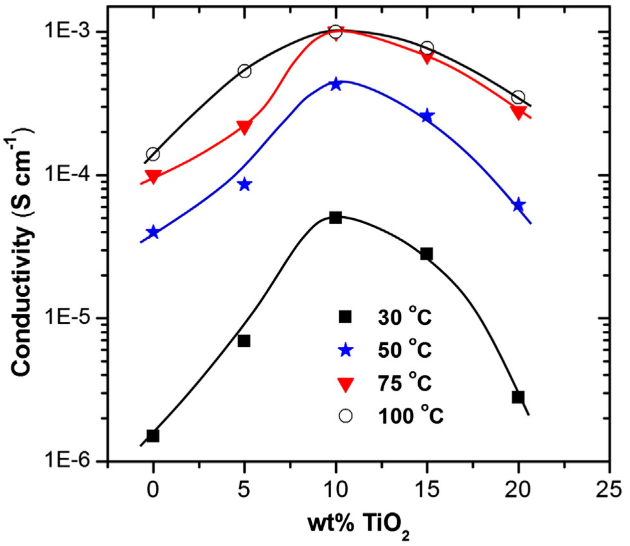

Fig. 2. Conductivity isotherms for different amounts of TiO_2 incorporation in $(PEO)_9LiTf$ + *x* wt.% TiO_2 polymer membranes.

promotion of lithium ion conducting pathways by lowering the PEO reorganization tendency through the cross-linking of PEO segments and anions on the polymer electrolyte. The other effect is the promotion of salt dissociation caused by lowering of ionic coupling because of the Lewis-acid–base interaction with the ionic species. In addition to this effect, TiO_2, due to its higher dielectric constant (435) compared to that of PEO (2.8–3.3), would lead to active dissociation of Li salt resulting in an increased concentration of mobile carriers and thereby the conductivity. This active salt dissociation and the increased lithium ion conducting pathways would lead to enhancement in ionic conductivity in these composite polymer electrolytes.

As can be seen in Fig. 1, conductivity variation of 5 wt.% sample behaves differently compared to other filler-added and filler-free electrolytes, especially the conductivity value increases with a quicker rate at temperatures higher than 80 °C. We believe that this variation would be due to the increased mobility of ions caused by the Lewis-acid interactions and also, there would be no blocking cluster formations at low filler levels. When the TiO_2 content in the composite electrolyte is increased beyond 10 wt.%, the effect of phase separation becomes increasingly dominant, resulting the blocking effect and subsequently an apparent reduction in the measured conductivities.

ln σ vs 1/T plots shown in Figs. 1 and 3 are semi-linear with two different slopes at t < 60 °C and t > 60 °C. The discontinuity in ln σ vs 1/T plots at around 60 °C is due to the melting of PEO crystallites as expected. The trend in activation energy variation also supports the conductivity increase due to the filler effect. As shown in Table 1, decrease in activation energy with the addition of TiO_2 and further decrease with the addition of TiO_2 with EC at temperatures less than 60 °C indicates the increased mobility of ions in the polymer matrix, thereby leading to increased conductivity. At temperatures higher than 60 °C, ln σ vs 1/T plots seem to have almost same slope for all the samples resulting almost equal activation energy values (see Table 1). This nearly equal activation energies for filler-free, filler-added and filler plus EC-added samples at high temperatures (>60 °C) could be due to the increased mobility of mobile ions caused by the temperature raise, independent of the effect of filler or plasticizer.

Table 1

Glass transition temperature (T_g), crystallite melting temperature (T_m), conductivity at 30 °C and activation energy (E_a) for filler-free, 10 wt.% TiO_2 added and 10 wt.% TiO_2 + 50 wt.% EC added solid polymer electrolytes.

Polymer electrolyte	T_g (°C)	T_m (°C)	σ at 30 °C (S cm^{-1})	E_a (<60 °C) (KJ mol^{-1})
PEO_9LiTf	−39	64	1.4×10^{-6}	120.6
PEO_9LiTf + 10 wt.% TiO_2	−46	60	4.9×10^{-5}	78.8
PEO_9LiTf + 10 wt.% TiO_2 + 50 wt.% EC	−50	50	1.6×10^{-4}	57.5

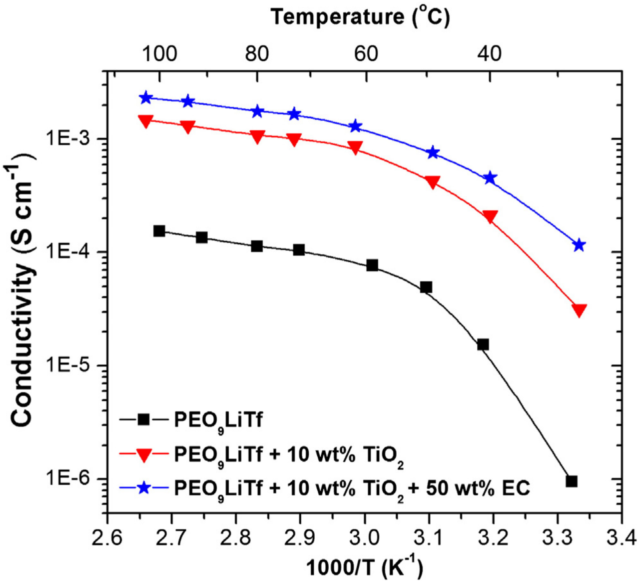

Fig. 3. Variation of conductivity with inverse temperature for filler-free, 10 wt.% TiO_2 added and 10 wt.% TiO_2 + 50 wt.% EC added solid polymer electrolytes.

Fig. 4a and b shows the crystallite melting temperature (T_m) and the glass transition temperature (T_g) for filler-free, filler-incorporated and filler plus EC incorporated electrolyte samples. Table 1 summarizes the values of ionic conductivity (σ), crystallite melting temperature (T_m), glass transition temperature (T_g) and activation energy (E_a) for these three samples. T_g has reduced from −39 °C to −46 °C due to the incorporation of 10 wt.% TiO_2 and to −50 °C due to the incorporation of 50 wt.% EC. This reduction in T_g with TiO_2 and then with EC incorporation suggests increased segmental flexibility of polymer chain and it is in agreement with the observed conductivity enhancement. Reduction in T_g weakens the complexation between Li^+ ion and the ether oxygen atoms in the polymer chain facilitating the migration of Li^+ ions.

An important observation seen in Fig. 4a is the decrease of the shaded area under the endothermic peak with the addition of TiO_2 and EC. As this area represents the amount of crystalline phase present in the composite polymer electrolyte, the drop in this shaded area with the addition of TiO_2 and then with TiO_2 plus EC strongly suggests that the amount of crystalline phase present in the electrolyte goes down with the addition of ceramic filler and then with filler plus plasticizer. Crystallite melting temperature, T_m also decreases from 64 °C to 60 °C due to the incorporation of 10 wt.% TiO_2 exhibiting reduced fraction of crystalline phase present in the electrolyte in agreement with the DSC data shown in Fig. 4a. This also supports the observation of enhanced conductivity due to 10 wt.% TiO_2 incorporation. A further drop in T_m to 50 °C due to the addition of 50 wt.% EC is a strong evidence for the increased fraction of the amorphous phase. It would be important to recall that the T_m for bare PEO is 74 °C [25].

Even though the increased fraction of the amorphous phase, as evidenced from thermal data also contributes to the observed conductivity enhancement, in addition to the two mechanisms described earlier, namely the creation of Lewis-acid–base type transient bonds and higher ionic dissociation, the observation that the conductivity enhancement is observed even in the high temperature amorphous phase (Fig. 1), clearly demonstrate that these two mechanisms prevail at all temperatures.

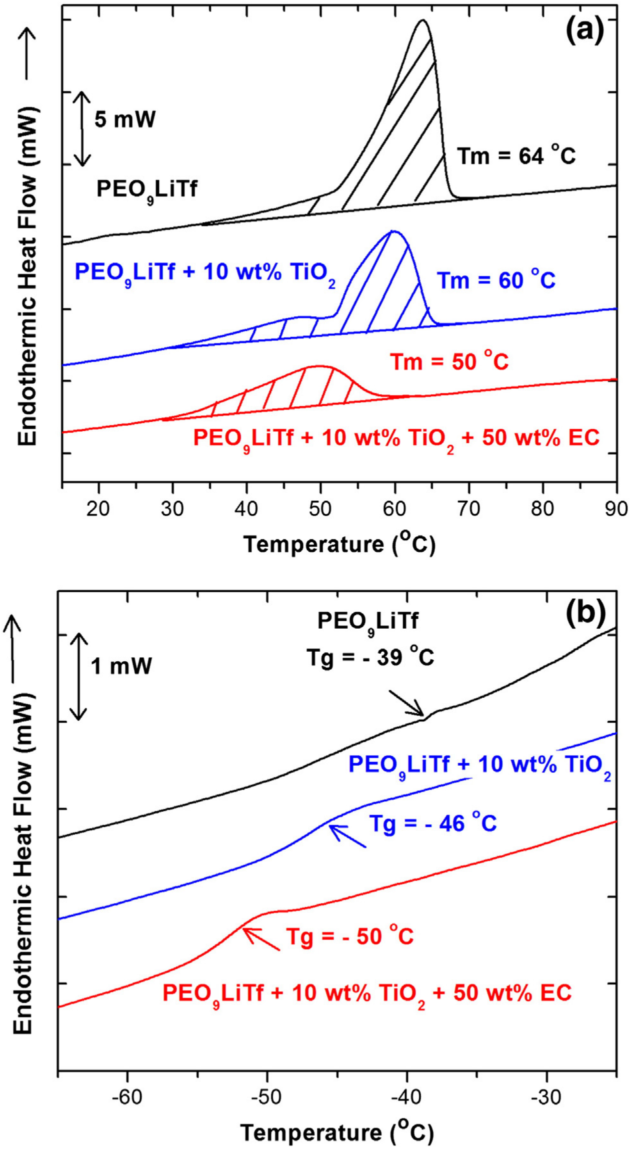

Fig. 4. DSC endotherms taken during the heating run for filler-free, 10 wt.% TiO_2 added and 10 wt.% TiO_2 + 50 wt.% EC added solid polymer electrolytes showing the variation of; (a) Crystallite melting temperature (T_m). (b) Glass transition temperature (T_g).

4. Conclusions

Since TiO_2 has the high Lewis-acid character compared to other commonly used ceramic fillers (such as Al_2O_3, SiO_2 and ZrO_2), incorporation of TiO_2 exhibited the maximum conductivity enhancement with 10 wt.% TiO_2 composition with the highest conductivity value of 4.9×10^{-5} S cm^{-1} at 30 °C, an order of magnitude higher conductivity than the filler free PEO_9LiTf electrolyte. A further enhancement in conductivity up to 1.6×10^{-4} S cm^{-1} at 30 °C without deteriorating the mechanical stability was obtained due to the incorporation of 50 wt.% EC with PEO_9LiTf–10 wt.% TiO_2. Decrease in T_g, T_m and E_a with the addition of TiO_2 and then a further decrease with the addition of TiO_2 + EC strongly support the increased amorphous phase content and increased segmental flexibility causing the conductivity enhancement. TiO_2 nanofiller contributes to the conductivity enhancement through the formation of Lewis acid–base type transient bonding for Li^+ ion hopping, by enhanced ionic dissociation and also by increasing the amorphous phase content, whereas the EC plasticizer evidently participates in the latter two mechanisms.

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