

Sm₂O₃ composite PEO solid polymer electrolyte

Peter P. Chu^{*}, M. Jaipal Reddy

Department of Chemistry, National Central University, Chung-Li 32054, Taiwan

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Abstract

A novel lithium composite solid polymer electrolyte based on a polymer, poly(ethylene oxide) (PEO), and a rare earth oxide, Sm₂O₃, is reported. The incorporation of lithium salt and samarium oxide to PEO shows a dramatic modification of surface morphology. Scanning electron microscopy (SEM) shows that at a low Sm₂O₃ content, the polymer film displays smooth morphology. This indicates that satisfactory interaction takes place between the oxides and the polymer in the presence of the salt. Differential scanning calorimetry (DSC) results corroborate the SEM micrographs, where the crystallinity decreases further to 10% when compared with a pure PEO/Li salt polymer electrolyte. ⁷Li magic angle spinning (MAS) NMR spectra suggest two major lithium species attributed to the Li⁺ ions associated with amorphous PEO and Sm₂O₃. The conductivity in the composite electrolyte is one order of magnitude higher compared with pure PEO/Li electrolyte. The oxide–salt complex functions as cross-linking centres for the PEO segments and establishes additional pathways to conduct ions through the filler surface, thus complements ion movement. The ionic conductivity decreases, with increasing content of Sm₂O₃ to over 10 wt.% where an aggregated Sm₂O₃:Li-rich domain is identified.

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Keywords: Composite polymer electrolyte; Ionic conductivity; Differential scanning calorimetry (DSC); ⁷Li MAS NMR; Samarium oxide; Polyethylene oxide

1. Introduction

The pioneering work of Wright and co-workers [1,2] motivated research on solid polymer electrolytes three decades ago and later Armand et al. [3] realized these materials have potential application in batteries with high specific energy and other ionic devices. Solid polymer electrolytes are advantageous in terms of shape, geometry, mechanical strength, and the potential for strong electrodelectrolyte contact. The disadvantage that precludes their usage in high-energy power sources and other devices is the relatively low ionic conductivity at ambient temperature compared with ‘wet’ or ‘gel’ analogues. Increasing the ionic salt concentration in the polymer does not overcome the low ion conductivity limitation. In general, a higher salt content favours reduction of the crystalline fraction of polymer but causes high ion-pairing interaction, which leads to salt aggregation [4–7].

Not only does the ‘salting-out’ effect reduce the crystallinity of the polymer, but it also reduces the mobile ions that are available for conductivity. To overcome this drawback

and to enhance ionic conductivity, numerous modifications have been proposed, such as incorporation of inorganic oxides, ceramic powders, cross-linking, blending with different polymers, and plasticizers [8–24]. In addition to improving the ionic conductivity, it is also necessary to preserve the mechanical strength and stability of the electrodelectrolyte interface.

To obtain stable polymer electrolytes for rechargeable lithium batteries, nano-sized oxide materials, such as TiO₂, SiO₂, Al₂O₃, ZrO₂, fumed silica and ceramic powders have been dispersed in ion-conducting polymer matrices to obtain nano-composite polymer electrolytes [25–27]. These composite electrolytes exhibit enhanced mechanical strength, higher ionic conductivity and better anodelectrolyte interfacial contact. The inorganic solid oxide filler prevents local reorganization of chains in poly(ethylene oxide) (PEO) and leads to a polymer electrolyte with a high degree of disorder, which thus favours high ion transport. In PEO, cations are coordinated with the oxygen atoms of the polyether chain. The mechanism that drives the ion conduction is ion mobility (i.e. movement) in which the motion of the polymer chain plays a significant role. A detailed understanding of the transport mechanism is difficult but enhancement of conductivity, mechanical strength, and interfacial stability is

^{*} Corresponding author. Tel.: +886-34258631; fax: +886-34227664.
E-mail address: pjchu@cc.ncu.edu.tw (P.P. Chu).

obtainable in the presence of fillers, plasticizers, etc. in polymer electrolytes. Various researchers have interpreted the role of the filler in terms of Lewis acid–base model interaction [28–30]. According to this model, ceramic surface groups provide physical cross-linking centres for the PEO segments and for the anions, and thus reduce the tendency for polymer reorganization. The structural modification establishes additional conducting pathways on the filler surface.

In the present study, rare earth oxide (Sm_2O_3) is incorporated as a filler in a matrix of PEO/ LiClO_4 solid polymer electrolyte. This composite polymer electrolyte system displays an interesting enhancement of ion conductivity and a remarkable change in surface morphology, which is thought to be associated with the properties of the rare earth oxide, and has not been reported in the literature.

2. Experimental

Composite polymer electrolytes based on a rare earth oxide have been prepared by using poly(ethylene oxide) (PEO) [$M_w = 2 \times 10^5$, Aldrich] and LiClO_4 salt in a (90:10) ratio (O:Li = 21:1) and blending with various weight percentages of samarium oxide (Sm_2O_3 , Fluka). The materials were used as received. Initially, the PEO polymer was dissolved in methanol, and then appropriate amounts of LiClO_4 and samarium oxide (Sm_2O_3) were added at 2 h intervals and stirred for 24 h. Finally, the homogeneous mixtures were poured into Teflon dishes, evaporated slowly at 30 °C, and dried in vacuum. Further drying was carried out in a dry box and the mixtures were stored under a nitrogen atmosphere to remove all the traces of solvent until a constant weight was achieved.

The surface morphology of these composite electrolytes was examined by means of scanning electron microscopy (SEM) using a Hitachi [Model 3500N] instrument and gold-sputtered coated films. Differential scanning calorimetry (DSC) studies were performed using a Perkin-Elmer (DSC 7 series) system at a heating rate of 5 °C min^{-1} . Sample weights were maintained in the range 7–8 mg, and all experiments were conducted under a nitrogen flow. Solid-state ^7Li magic angle spinning (MAS) NMR spectra were recorded at room temperature on a Bruker DSX-300 spectrometer, which operated at a resonance frequency of 116.6 MHz for the ^7Li nucleus. A spinning speed of 2 kHz was employed, which was sufficient to remove the small shift anisotropy side bands to avoid major complications.

The ionic conductivity of the electrolyte films was investigated using a cell which consisted of two blocking stainless-steel electrodes with the sample sandwiched in between. Impedance spectroscopy was used to determine the ionic conductivity of the polymer composite films. Measurements were carried out over the frequency range 1 MHz to 10 Hz, with the help of a frequency analyzer Autolab/Pgstat 30

electrochemical instrument. Measurements were made over the temperature range 293–373 K; the system was thermally equilibrated at each selected temperature for 20–30 min. The bulk resistance (R_b) was determined with equivalent circuit analysis software. The conductivity values (σ) were calculated from the equation $\sigma = (1/R_b)(t/A)$, where t is the thickness and A the area of the sample.

3. Results and discussion

3.1. SEM micrographs

Electron micrographs of pure PEO and PEO/ LiClO_4 with Sm_2O_3 films are displayed in Fig. 1. The micrograph for pure PEO shows a rough surface which has several crystalline domains. On blending with lithium salt, the surface morphology of PEO is changed severely. For example, Fig. 1(b) shows a dramatic improvement of surface morphology from rough to smooth. The smooth morphology is closely related to the reduction of PEO crystallinity in presence of the salt. The incorporation of samarium oxide in PEO/ LiClO_4 further improves the smooth morphology, with the development of streaks (Fig. 1(c)) and reduction of crystallinity. In the absence of the salt, separate polymer and oxide phase can be easily identified, which indicates the lack of a driving force for miscibility. Therefore, the salt must drive the inter-phase interaction between oxide and PEO. The fact that salt is acting as the compatibilizer is reasonable, since the ion is capable of forming Lewis acid–base interactions with both the inorganic solid oxide surface groups as well as with ether oxygen of the PEO chain. The mechanical properties are improved due to physical cross-linking by inter-phase interaction between the polymer PEO and filler phases, phase separation occurs, however, when samarium oxide content increases further, at which stage large Sm_2O_3 –Li-rich domains are grown (see Fig. 1(d)). The oxide aggregation is dispersed homogeneously in the films. Even when aggregation begins to take place, the mechanical properties still sustained.

3.2. Differential scanning calorimetry

Differential scanning calorimetric (DSC) thermograms of PEO and PEO/ LiClO_4 with various amounts of samarium oxide are displayed in Fig. 2. The curves indicate a reduction of PEO crystallinity, but complete depression of ΔH_f is not identified. The relative percentage of crystallinity (χ) has been calculated by taking pure PEO as 100% crystalline and using the equation $\chi = \Delta H_f / \Delta H_f^0$ (the melting temperature and heat of fusion (ΔH_f^0) of PEO is 67 °C and 162 J g^{-1} , respectively). The calculated relative crystallinity (χ) and melting temperature (T_m) are summarized in Table 1. Both SEM and DSC studies indicate that PEO crystallinity is deteriorated by the lithium salt and further by the addition of samarium oxide. The melting temperature (T_m) is reduced

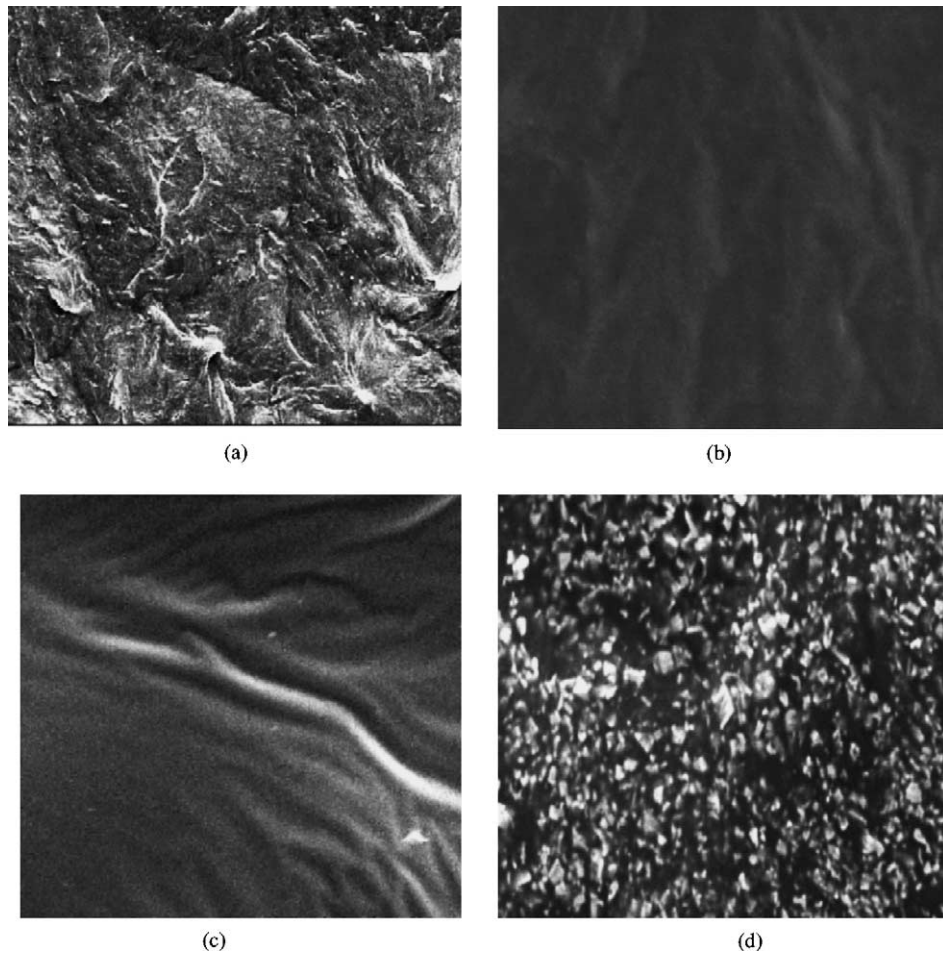


Fig. 1. Electron micrographs (1000 \times) of (a) pure PEO; (b) PEO/Li (90/10); (c) 10 wt.% Sm₂O₃; (d) 12 wt.% Sm₂O₃ in PEO/Li (90/10) polymer electrolyte.

from 67 to 58 °C. The decrease of crystallinity is mild, viz. 10%, on dispersing the samarium oxide. The effect is much less pronounced than when using the salt alone. Ribeiro et al. [31] have noticed a similar decrease in the degree of

crystallinity on adding a ceramic powder, LiAl₅O₈, to PEO and lithium salt.

3.3. ⁷Li MAS NMR spectroscopy

The co-ordination structure of lithium species has been investigated by solid-state ⁷Li MAS NMR spectroscopy. The ⁷Li MAS NMR spectra of the PEO:Li/Sm₂O₃ system is shown in Fig. 3. The NMR spectra of the Sm₂O₃ to PEO/Li

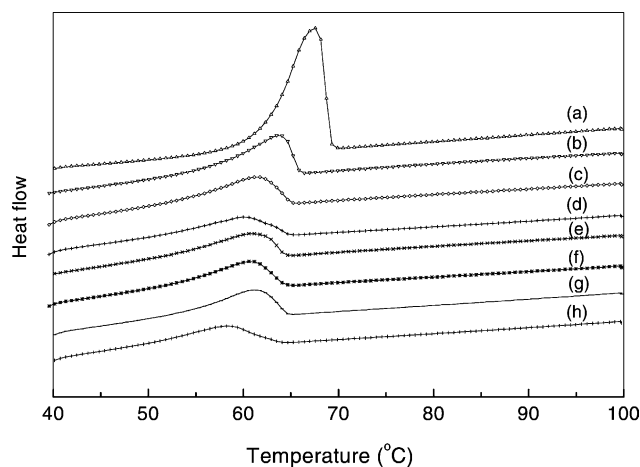


Fig. 2. Differential scanning calorimetric curves of (a) pure PEO; (b) PEO/LiClO₄ (90/10); (c) 5 wt.%; (d) 8 wt.%; (e) 10 wt.%; (f) 12 wt.%; (g) 15 wt.%; (h) 20 wt.% Sm₂O₃ in PEO/LiClO₄ (90/10) electrolyte.

Table 1
Crystallinity (χ) and melting temperature (T_m) of PEO:LiClO₄/Sm₂O₃ composite polymer electrolyte

Sm ₂ O ₃ (wt.%)	Sm:Li ratio	Melting temperature, T_m (°C)	Crystallinity, χ (%)
0	–	63.59	49.7
5	0.82	61.15	44.2
8	1.05	59.82	41.2
10	1.64	60.17	41.4
12	1.97	60.52	42.9
15	2.46	60.94	41.5
20	3.27	57.98	37.6

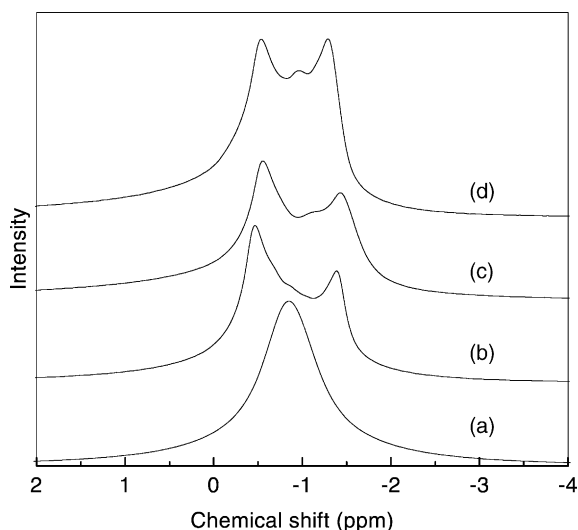


Fig. 3. ${}^7\text{Li}$ MAS NMR spectra of (a) 0 wt.%; (b) 5 wt.%; (c) 10 wt.%; (d) 15 wt.% Sm_2O_3 in PEO/LiClO₄ (90/10) electrolyte.

(Fig. 3(b–d)) compared with the spectra of PEO/Li (Fig. 3(a)) shows the emergence of a satellite peak (i.e. shoulder), which shifts and broadens with increasing Sm_2O_3 content. At the highest content of Sm_2O_3 (15 wt.%), the ${}^7\text{Li}$ peak shows the most upfield shift and two satellite peaks can be identified clearly (Fig. 3(d)). The development of the new satellite shoulder peak indicates the coordination (i.e. interaction) of Li^+ cations with Sm_2O_3 oxide. Therefore, lithium ions exist in two environments in the composite polymer electrolyte system, namely: (i) within the matrix of amorphous PEO and (ii) coordinated with oxygen atoms on the surface of Sm_2O_3 . Further analysis of ${}^7\text{Li}$ NMR measurements is in progress. The NMR results corroborate well with those from SEM and DSC studies, which show a decrease in the long-range order structure by physical cross-linking of polymer PEO moieties and oxide filler in presence of lithium cations in the PEO/LiClO₄ electrolyte by incorporation of Sm_2O_3 . According to Wiezorek et al. [32,33], the Lewis acid of the added oxide filler competes with the Lewis acid character of the lithium cations to form new complexes with the PEO chains. Thus, the filler oxide serves as cross-linking centres for the PEO chains. Such character lowers the tendency for polymer reorganization and promotes an overall mechanically-stable structure. The structure modification can also provide new pathways for Li^+ ions conduction on the filler surface; which is important for enhancing the ion transport.

3.4. Impedance spectroscopy

The ionic conductivity of the composite solid polymer electrolyte (PEO:Li/ Sm_2O_3) system has been derived from complex impedance plots. The bulk resistance (R_b) is determined from the frequency response equivalent circuit with an error below 1%. The complex impedance (CI) plots of different compositions at room temperature are presented in

Table 2
Conductivity and activation energies of PEO:LiClO₄/ Sm_2O_3 composite solid polymer electrolyte system

Sm_2O_3 (wt.%)	Conductivity at 293 K (S cm^{-1})	E_a (eV)	
		Region I	Region II
0	4.54×10^{-6}	0.34	0.19
5	1.08×10^{-5}	0.27	0.18
8	1.86×10^{-5}	0.24	0.18
10	4.45×10^{-5}	0.21	0.17
12	3.22×10^{-5}	0.23	0.18
15	2.86×10^{-5}	0.21	0.19

Fig. 4(A). The bulk resistance decreases with increasing samarium oxide content up to 10 wt.%, but increases again upon further uptake of the oxide (at and above 12 wt.%). The isothermal ion conductivity at room temperature is depicted in Fig. 4(B) and the conductivity data are summarized in Table 2. The conductivity increases with samarium oxide content and reaches a maximum value at 10 wt.%. When the samarium is in excess of 12 wt.%, the conductivity is retarded, but is still greater than that of pure PEO/LiClO₄ solid polymer electrolyte.

Croce et al. [30] have noticed that the conductivity in a composite polymer electrolyte is not a linear function of the filler content. At low oxide contents, the dilution effect is efficiently compensated by the specific interactions of the ceramic surface (as supported by the smooth morphology seen in SEM). This is not, however, the cause of the progressive enhancement in ion conductivity. The filler provides cross-linking centres for the PEO segments, this lowers the tendency for polymer reorganization and promotes a modification of the overall structure. Such a structure modification enhances the mechanical properties and establishes additional pathways to conduct ions at the surface of the ceramics, which thus complements the movement of the ions. On the other hand, the fraction of the oxide–salt complex increases at high filler contents. When the dilution effect predominates, the miscibility with PEO reduces as the oxide begins to aggregate. The separated phase consumes the mobile lithium ions in the oxide aggregate phase, and reduces the physical cross-linking; which has been previously identified as being responsible for the enhancement of ion conductivity. The net result is an optimized ion conductivity at 10 wt.% Sm_2O_3 . Other researchers [34–36] have reported a similar effect on the conductivity with inorganic and ceramic materials as fillers in solid polymer electrolytes. Nevertheless, no clear explanation of this optimization has been advanced.

The comparison of morphology with conductivity suggests that interaction between Sm_2O_3 and PEO in the presence of an ionic salt at an appropriate compositional ratio delivers a more favourable ion conductivity than that in a pure PEO/Li solid polymer electrolyte. The temperature dependence of the conductivity of PEO/Li with samarium is shown in Fig. 5. A sharp increase is noticed at the melting temperature (T_m)

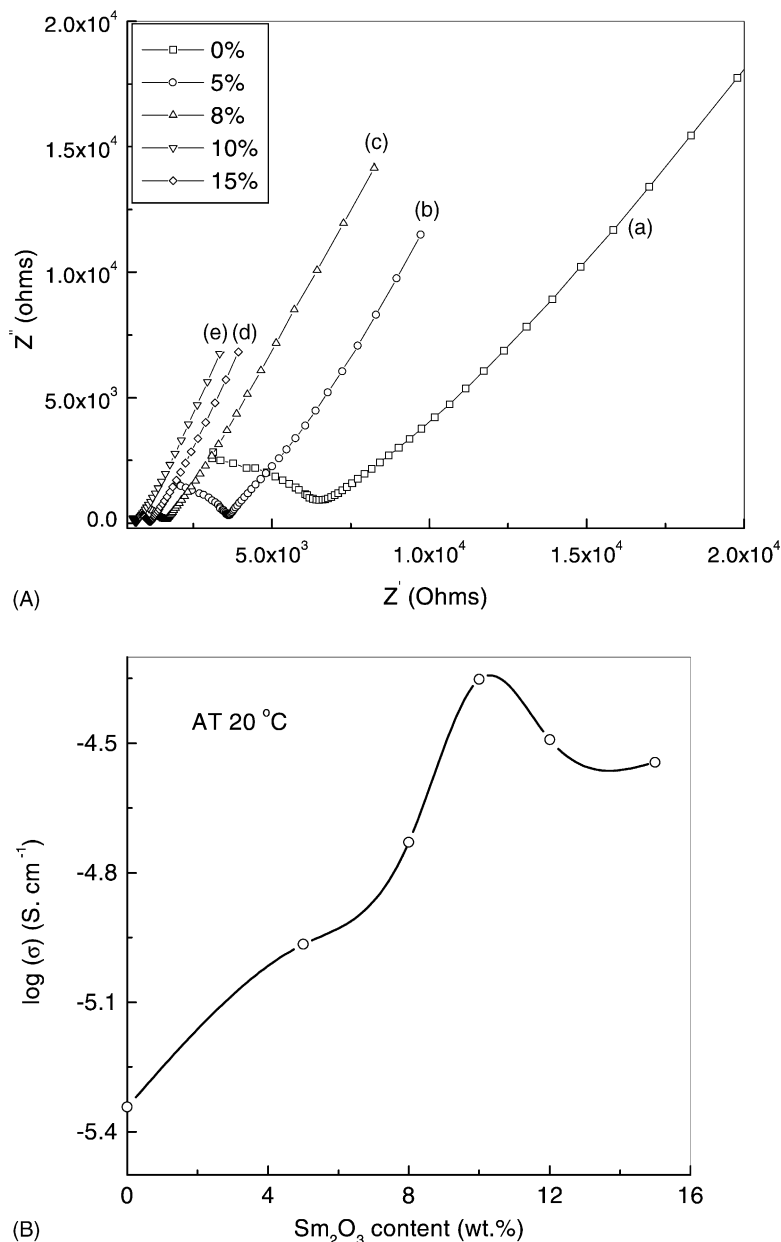


Fig. 4. (A) Complex impedance plots of (a) 0 wt.%; (b) 5 wt.%; (c) 8 wt.%; (d) 10 wt.%; (e) 15 wt.% Sm_2O_3 composite polymer electrolyte system at 20 °C. (B) Dependent of conductivity on Sm_2O_3 content in composite polymer electrolyte system at 20 °C.

of PEO, which is due to an increase in the amorphous domain, as reported in previous studies [7,24,35–39]. In $\log(\sigma)$ versus $1000/T$ plots, the linear variation below and above T_m follows an Arrhenius-type thermally activated process. In both regions, the conductivity relationship can be expressed as: $\sigma = \sigma_0 \exp(-E_a/kT)$, where σ_0 is the pre-exponential factor, E_a the activation energy, and k the Boltzman constant.

The activation energies of the PEO:Li/ Sm_2O_3 composite polymer electrolytes are evaluated by linear fitting in the two regions of Fig. 5, and the results are summarized in Table 2. The activation energies (E_a) determined from the low-temperature region I are higher than those obtained from the high-temperature region II. Most noteworthy is the fact

that the activation energies (E_a) are all smaller in electrolytes doped with Sm_2O_3 . This indicates a difference in ion-conducting behaviour. The overall scenario suggests that an additional conducting mechanism is established upon addition of Sm_2O_3 to the solid polymer electrolyte, which is clearly apparent from NMR studies where two different environments are identified for lithium species. This is contrast to that of the pure solid polymer electrolyte where only polymer moieties play the role. The two lithium species can follow two different conducting paths. The basic ion movement is achieved by random walking through amorphous PEO. A new and additional conduction path is established by lithium-ion hopping in a sequential manner

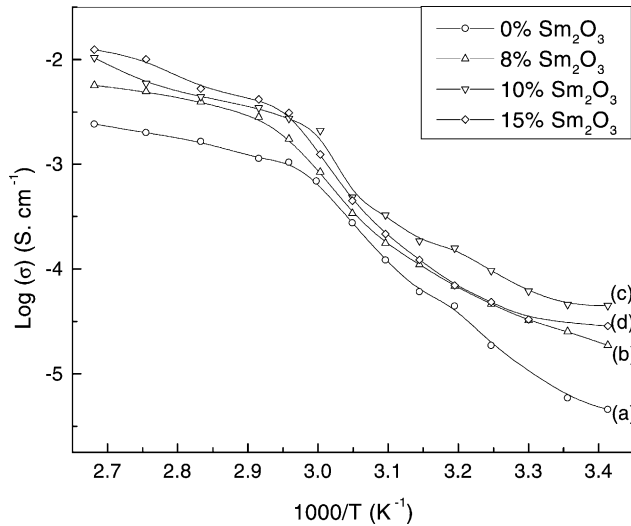


Fig. 5. Temperature dependence of conductivity of (a) 0 wt.%; (b) 8 wt.%; (c) 10 wt.%; (d) 15 wt.% Sm_2O_3 in PEO/ LiClO_4 polymer electrolyte system.

on the surface of the oxide. In this case, charge transport is likely to be achieved by replacing a nearby vacancy on the oxide surface that has a lower activation energy. The presence of an additional conducting channel in the composite polymer electrolyte studied here delivers favourable low-temperature conductivity compared with electrolytes without the oxide and exhibits a lower activation energy in both the high and the low-temperature regions.

Best et al. [40] have discussed nano-composite electrolytes in terms of electrostatic interactions where Li^+ cations will experience a relatively stable potential environment at the filler surface, which will be of the same order as that at

the polymer. Then the lithium ions will be free to move by segmental motion and activated hopping, with a potential barrier which is lowered by the filler. Jayathilaka et al. [41] have proposed that, during migration, the Li^+ cations form weaker transient bonds with the oxygen atoms on the surface of the filler grains, similar to the co-ordinated transient links that they form with the ether oxygen of PEO. This provides extra sites for the cationic transport process, where the bonds between Li^+ ions and the oxygen atoms in the filler surface groups are also subjected to breaking and making as on ether oxygen in PEO polymer.

The conductivity of the Sm_2O_3 composite solid polymer electrolyte follows different curves upon heating and cooling. The conductivities of two polymer electrolyte films containing 5 and 12 wt.% of Sm_2O_3 are shown in Fig. 6. While heating, the conductivity follows the typical behaviour for a polymer electrolyte. Close examination of the data suggest, however, that the nature of the subsequent cooling scan is quite different since the conductivity remains consistently higher than that during the heating. This trend is similar to that observed in previous studies of nano-composite polymer electrolytes, such as TiO_2 , SiO_2 , Al_2O_3 and ceramic-based systems [39]. It is remarkable that favourable transport behaviour is an inherent feature of the composite polymer electrolyte. The possibility that the difference in conductivity is due to a reduced crystallization rate of PEO in the presence of the filler is inconsistent with the fact that a break occurs between 35 and 45 °C near T_c , when cooling the sample. A more plausible explanation of this behaviour is that, once the composite electrolytes are annealed at a temperature higher than the PEO melting transition (i.e. above T_m), the oxide filler is allowed to interact with a more amorphous PEO segment and prevents the local PEO chain

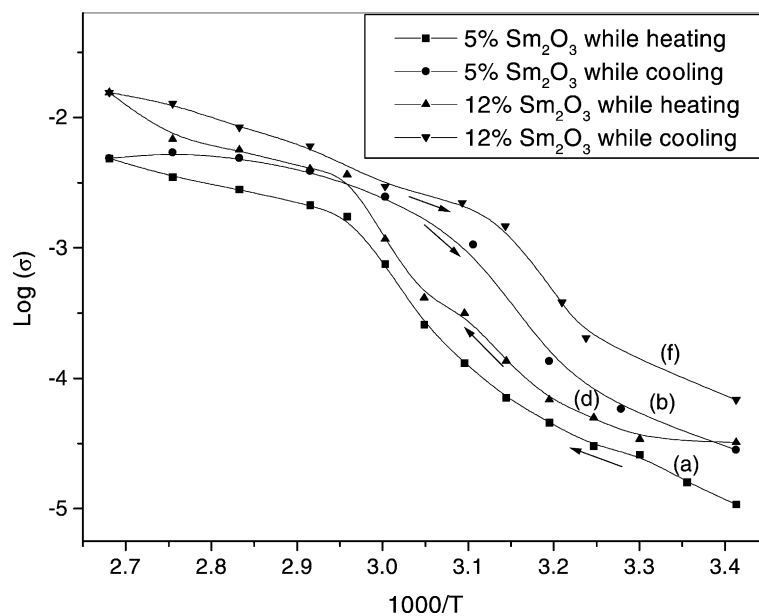


Fig. 6. Temperature dependence of conductivity while (a) heating and (b) cooling for 5 wt.% Sm_2O_3 , and while (c) heating and (d) cooling for 12 wt.% Sm_2O_3 in PEO/ LiClO_4 polymer electrolyte system.

reorganization when cooling. The disordered structure modification is frozen at ambient temperature and displays a high degree of ion conductivity. When the conductivity measurement was repeated 2 days later at room temperature, the ion conductivity remained high and did not revert to its original value prior to the initial heating. The result is again in agreement with the previous finding that physical cross-linking injects an additional conduction mechanism. By increasing such a structure fraction, both the mechanical properties and the ion conduction are improved, simultaneously.

4. Conclusions

Samarium oxide serves as a filler to enhance the ion conductivity and mechanical properties of the PEO/LiClO₄ solid polymer system. The increased conductivity is found to be one order higher, and the optimum value is found at 10 wt.% Sm₂O₃. The deterioration in ionic conductivity at higher oxide contents is attributed to the development of an oxide:Li aggregation phase. Even in the case of aggregation when Sm₂O₃ exceeds 12 wt.%, the mechanical properties are sustained. The overall scenario suggests the presence of an additional conducting mechanism in samarium oxide composite polymer electrolyte compared with that in the solid polymer electrolyte where only polymer chains play a role. As the electrolyte and Sm₂O₃ filler are physically cross-linked, the enhancement of conductivity originates from a synergetic effect of the three components that establishes and additional conduction path in the oxide:Li complex.

Acknowledgements

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