

Role of functional nano-sized inorganic fillers in poly(ethylene) oxide-based polymer electrolytes

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Abstract

The enhancement of the electrochemical properties of poly(ethylene) oxide (PEO)–lithium salt composite electrolytes has been reported for many years, but the mechanism is still not fully understood. Therefore, this study focuses on the reason why the ionic conductivity is increased when inorganic fillers are added to the composite electrolyte. A maximum ionic conductivity is obtained by adding a nano-sized inorganic filler and by post-heat treatment. The conductivity reaches $2.3 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. The nano-sized SiO_2 particles appear to play two roles, namely, the simultaneous arrangement of dipoles in the composite electrolytes and interruption of the crystallization of PEO. The PEO and the inorganic filler generally tend to orient their dipoles to minimize their total energy, so that PEO chains are forced to rotate and orient in a direction parallel to the applied electric field. Thermal treatment increases the amorphous phase of PEO such that subsequent segmental motion of the PEO chain follows, while nano-sized SiO_2 prevents the recrystallization of PEO after heat treatment. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Composite electrolyte; Nano-sized filler; Poly(ethylene) oxide; Solid-state electrochemical device; Silica; Lithium battery

1. Introduction

Poly(ethylene) oxide (PEO) complexes with alkali salts are promising electrolytes for application in solid-state electrochemical devices [1]. The dielectric properties of fillers and thermal treatment are major determinants for enhancing the ionic conductivity of PEO:Li salt composite electrolytes. The fillers affect the PEO dipole orientation by their ability to align dipole moments, while the thermal history determines the flexibility of the polymer chains for Li ion migration.

The addition of inorganic fillers, such as glasses, alumina, silica or other ceramics, to the polymer–lithium salt systems generally improves the transport properties, the resistance to crystallization, and the stability of the electrodelectrolyte interface [2–4]. Whereas the latter two effects are always observed, the conductivity enhancement depends on the filler used, its particle size and also on its particle size [5]. In particular, it has been shown [6] that the effect becomes significant when particles smaller than $10 \mu\text{m}$ are used. The increase in the conductivity of PEO on the addition of fillers has been attributed to an enlargement of the amorphous phase in the polymer matrix [7,8]. From a microscopic point of

view, it has been suggested that ionic transport may benefit from the existence of a space-charge layer at the polymer–filler interface. Croce et al. [9] have developed models to explain the enhanced ionic transport properties in polymer–inorganic composite electrolytes in which acid, normal and basic surface-functional groups are attached on nano-sized fillers. Kumar et al. [10] have advanced a theory which is based on the dielectric properties of the filler and the thermal history of the polymer. The mechanism by which the electrochemical properties are enhanced when ceramic fillers are added is still to be determined. To understand this phenomenon, we have focused on the microscopic changes that may take place in composite electrolytes and have related this effect to the enhancement in conductivity.

2. Experimental

The PEO:LiClO₄–SiO₂ composite electrolyte films were prepared by the tape casting technique using reagent grade poly(ethylene) oxide (Aldrich, $M_v = 400,000$), lithium perchlorate (Aldrich), and nano-sized fumed silica (Degussa-Huls, R805). Poly(ethylene) oxide and lithium perchlorate were dried before the solvation in a vacuum oven for 12 h at 50 and 150 °C, respectively. It is crucial that fumed and nano-sized silicon dioxide (SiO₂, Degussa-Huls, R805),

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which has particles of ~ 12 nm in size and two surface groups of silanol (Si-OH) and octyl ($\text{Si-C}_8\text{H}_{17}$), should be introduced to prevent crystallization of the PEO: LiClO_4 complex, since it has a low density and a large surface area compared with other oxides such as TiO_2 , ZnO_2 , and BaTiO_3 . Acetonitrile was added to the mixed PEO and LiClO_4 to form a slurry. A homogeneously dispersed emulsion of SiO_2 and the solvent was also formed separately. Two types of slurry were mechanically mixed to dissolve the organic and inorganic materials in the solvents, and to achieve a homogenous mixture. After mixing was complete, the homogenous slurry was then transferred to a Teflon plate and the solvent was removed in air at room temperature for 5 h. Tape casting was performed with a doctor blade to yield a uniform film with an average thickness of ~ 100 μm . The tape was then dried at 50 and 25 $^\circ\text{C}$ in an evacuated chamber for 24 h. The final composite electrolyte film was obtained after being kept for over 72 h in a glove box filled with an inert gas. Sandwich-type cells of configuration SUS/composite electrolyte/SUS (SUS: stainless steel plate), were fabricated in the glove box and then sealed with a vacuum packer (HENKELMAN, 200A) to prevent moisture permeation. All specimens, held between blocking electrodes, were subjected to heat treatment at 90 $^\circ\text{C}$ for 24 h, cooled down slowly to room temperature, and then contained in a sealed heating mantle which guaranteed a uniform temperature atmosphere before impedance measurements. Measurements of ionic conductivity were performed at 5 mV in the frequency range 1 Hz to 100 kHz using an ac impedance analyzer (EG&G, M6310, M398 software). A differential scanning calorimeter (DSC2010, TA instrument) was used to measure the glass transition and crystallization temperatures of the composite electrolyte films in the temperature range -70 to 100 $^\circ\text{C}$ at a scanning rate of 10 $^\circ\text{C}$ per min, and from 100 to 0 $^\circ\text{C}$ at a scanning rate of 5 $^\circ\text{C}$ per min. All specimens were put in aluminum pans and punched in a dry box before measurement. The infrared absorption spectrum

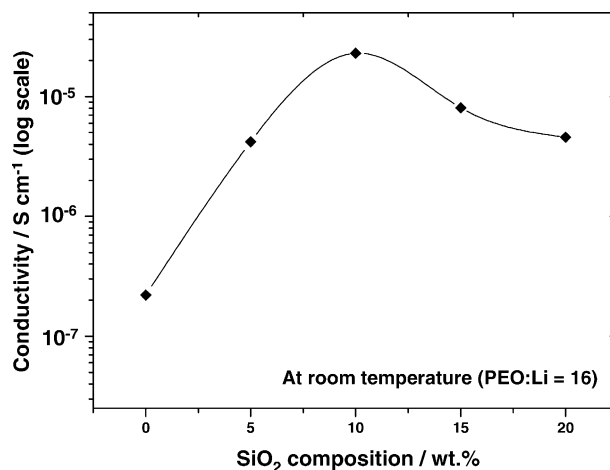


Fig. 1. Variations of ionic conductivity with nano-sized SiO_2 concentration.

was characterized by the rotation and orientation of polymer chains in the spectrum range of 400–4000 cm^{-1} using a Fourier Transform-Infrared Spectroscop (Bomem DA 8). For that measurement, the mixed slurry was cast on a silicon wafer and dried via the same steps used in the preparation of electrolyte films.

3. Results and discussion

3.1. Ionic conductivity

Previous studies have shown [2–4] that the conductivity is enhanced by two to three orders up at room temperature when nano-sized ceramic fillers are added to a polymer–lithium salt complex. The dependence of ionic conductivity on the concentration of nano-sized SiO_2 is shown in Fig. 1 for a PEO:Li ratio of 16. The data show that the ionic conductivity of filler-inserted electrolyte has a maximum

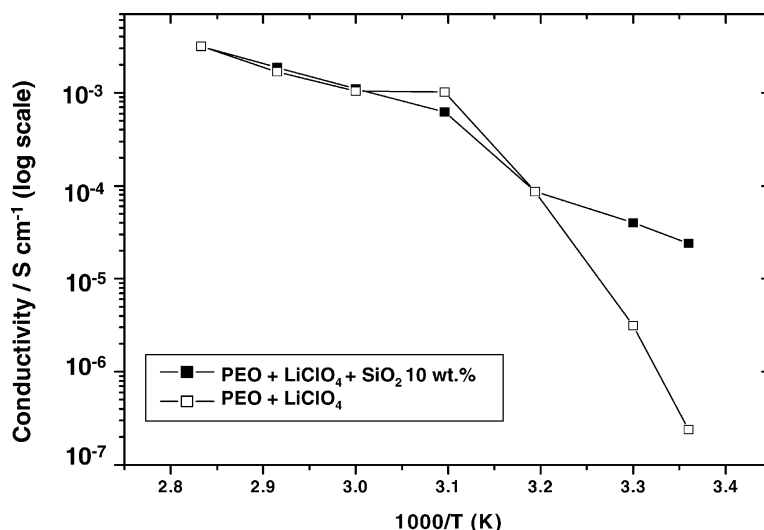


Fig. 2. Temperature of dependence of ionic conductivity.

value of $2.3 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C when SiO_2 is added at about 10 wt.%. In general, the ionic conductivity of polymer solid electrolytes increases with temperature due to the higher segmental motion of polymer chains in the amorphous phase. Under these conditions, the filler's role in assisting lithium ion conduction is insignificant, as shown in Fig. 2 for temperatures above 50°C . For this reason, the present study focuses on the role and the enhancement mechanism of nano-sized fillers at room temperature from two points of view, namely, dielectric properties and the degree of crystallization:

$$\sigma = \sum_i F|Z_i|C_i\mu_i. \quad (1)$$

The conductivity of a solid-state electrolyte has many determinants, such as carrier concentration (C_i), mobility (μ_i) and so on [11], as depicted in Eq. (1). The enhancement in ionic conductivity when adding a high dielectric ceramic filler (TiO_2 , BaTiO_3 , PbTiO_3 , etc.) to a PEO–Li salt complex might be due to the fact that the active dissociation of the Li salt results in an increased concentration of mobile carriers (C_i). This is why many experiments have been performed not only with normal oxides but also with ferroelectric materials [12]. The assumption does not hold well for the present use of SiO_2 , however, as this material has a dielectric constant which is only slightly higher than that of PEO, viz. 3.5–4.2 versus 2.8–3.3.

Consequently, it is considered that the increase of ionic conductivity achieved by adding SiO_2 is mainly related to the mobility, which is represented by μ_i in Eq. (1), which influences the segmental motion in the free volume. Therefore, it is considered that an increase in the mobility would be more effective than the carrier concentration for lithium

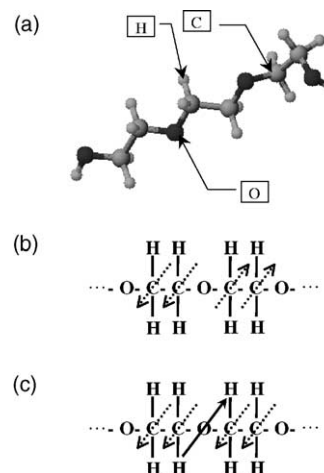


Fig. 3. (a) Poly(ethylene) oxide structure; (b) dipole moments of PEO at stable state; (c) change in dipole moments of PEO when filler is added.

conduction. The similar ionic conductivity at high temperatures (Fig. 2) strongly supports this assumption.

3.2. Dipole moments orientation

The helical structure and dipole moment of the PEO-based electrolyte is shown schematically in Fig. 3a and b, respectively. Kumar et al. [10] presented this concept using a TiO_2 filler. The arrows indicate the dipole moment direction and strength under the different conditions. In the case of the PEO: LiClO_4 electrolyte shown in Fig. 3b, two dipole moments arrange themselves spontaneously in opposite directions to lower their own total energy for sustaining a stable state, which is considered to be reasonable thermodynamically.

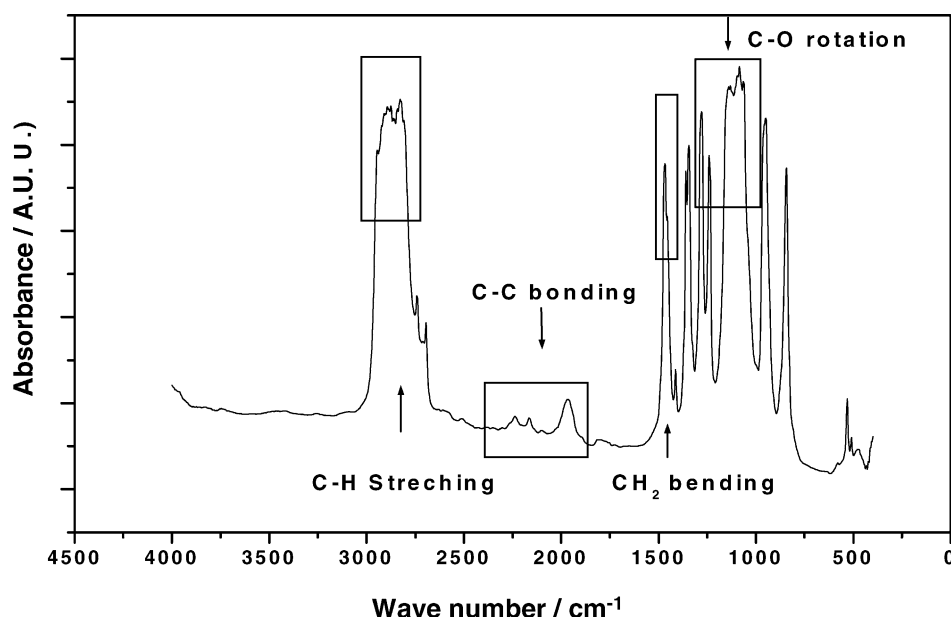


Fig. 4. Fourier transform-infrared spectroscopy of PEO: LiClO_4 film.

Some changes are expected in the dipole moment when fillers are added, which raise the dielectric constant in the system. For example, PEO needs to be modified structurally in order to lessen its total energy when SiO_2 is added to the PEO: LiClO_4 complex. The resulting structure, shown schematically in Fig. 3c, has only dipoles rotating around the C–O bond ($1000\text{--}1300\text{ cm}^{-1}$) partially, but not around the C–C bond and C–H stretching bond ($2850\text{--}3000\text{ cm}^{-1}$), because it has the lowest rotating energy. The FT-IR data shown in Fig. 4 indicate the required energy, in wavenumber (cm^{-1}) units, around each bond C–O rotation can occur at the smallest wavenumber and satisfies the dipole moment arrangement and equilibrium.

If PEO experiences structural modification, it may be placed in an unstable state compared with filler-free electrolytes and some overall structural changes will follow in other bonds. The infrared absorbance spectra of PEO containing Li salt and 10 wt.% SiO_2 are presented in Fig. 5. In the wavenumber range of $3300\text{--}3700\text{ cm}^{-1}$ (Fig. 5A), the broad absorption peaks corresponding to the O–H bond appear in PEO solutions with added Li salt or SiO_2 . The O–H bond originates from the $\text{LiClO}_4\cdot 3\text{H}_2\text{O}$ complex which is formed as the result of the reaction of lithium perchlorate with moisture in the atmosphere. For the specimen that contains SiO_2 only, however, it is considered that the O–H bond comes from one of the functional groups that

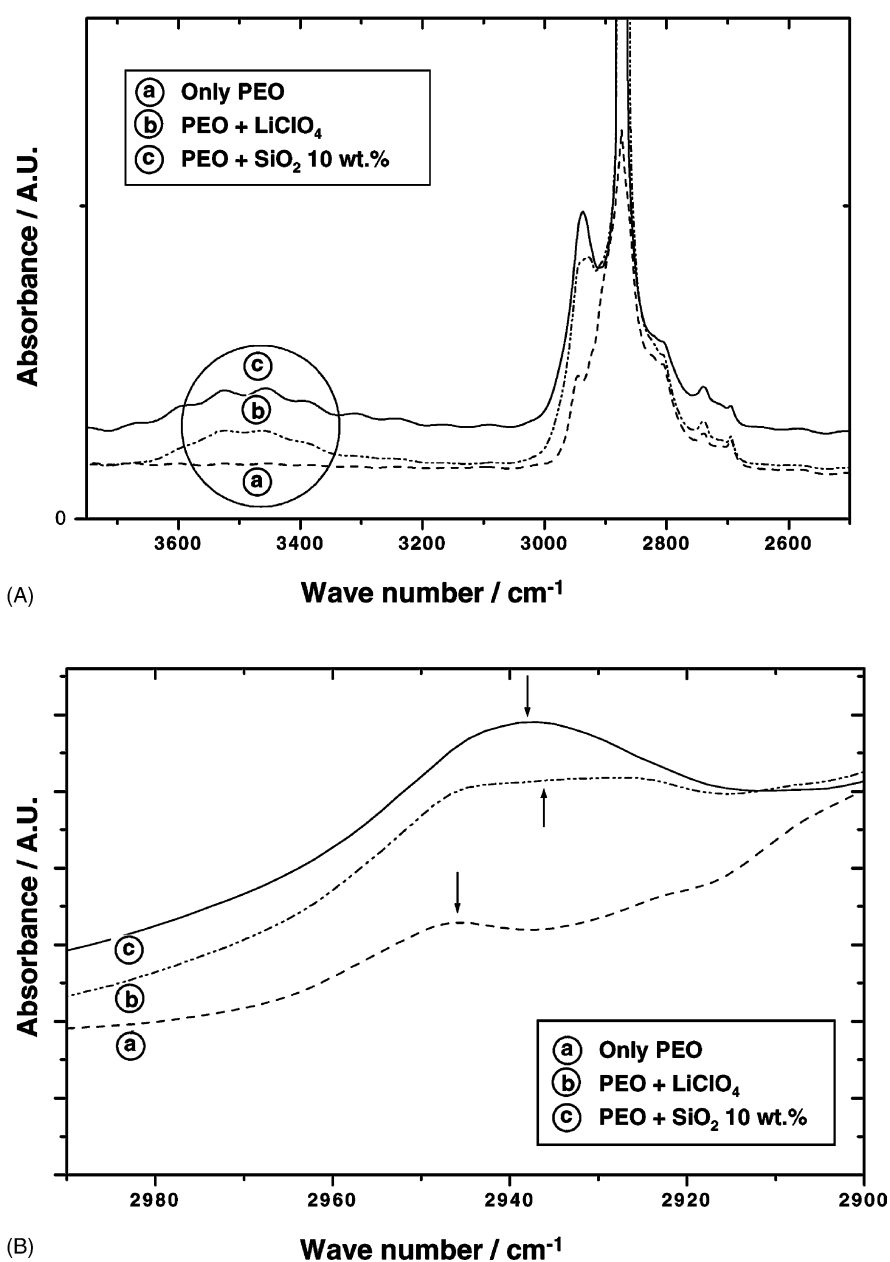


Fig. 5. (A) Absorbance energy range $3700\text{--}3200\text{ cm}^{-1}$ of (a) PEO, (b) PEO: LiClO_4 , (c) PEO: SiO_2 . (B) Shift in C–H stretching energy.

are attached on the surface of SiO_2 particles. Because Si–OH vibration yields peaks in the range $3200\text{--}3750\text{ cm}^{-1}$, which overlap partially with OH vibration, more broad and irregular absorbance peaks are observed.

The C–H bond also undergoes some variations (C–H stretching motion) which result in the band spreading in the range $2850\text{--}3000\text{ cm}^{-1}$ (see Fig. 5A). Not only the maximum values of the peaks but also their boundaries are shifted to the lower frequency side on the addition of SiO_2 to the PEO-based electrolyte. This means that C–H stretching is more restricted when the helical structure of the PEO chains is modified through C–O bond rotation to decrease its own energy, and is stabilized via the addition of dielectric SiO_2 filler to minimize the total dipole moments. This trend will be stronger near filler particles that are added non-uniformly and will be anisotropic with respect to dipole moment direction. Therefore, the distance between the hydrogen atom and the carbon atom will be changed. As a result, the C–H stretching motion is restricted, as shown in Fig. 5. In this wavenumber range, the shifted broad peaks found in the PEO: LiClO_4 film originate from the complex formation between PEO and ClO_4^- anions.

Because the SiO_2 filler has a dielectric constant that is slightly higher than that of PEO, it contributes to the conduction of lithium ions by providing an inner driving force in addition to the external driving force of the applied electric field. It can therefore be concluded that the composite electrolyte, which contains the inorganic filler, is more sensitive to external electric fields and is more efficient for the conduction of lithium ions.

In brief, this behaviour would make dipole moments more changeable and polarized under an electric field of the electric charge and discharge processes. Therefore, the changeable dipole momentum acts as one type of vibration

and can give some activation energy and more chance for ion conduction, which accordingly results in the increase of ionic conductivity.

3.3. Crystallinity

Thermal analysis using differential scanning calorimeter (DSC) was performed in order to observe the change in transition temperature that is caused by the addition of the nano-sized SiO_2 particles for the glass and crystalline phase transformations. In general, a low glass transition temperature indicates the existence of a greater amount of amorphous phase such that the segmental motion of migrating lithium ions is more activated. The effect of SiO_2 filler on the glass transition temperature (T_g) is shown in Fig. 6. The value of T_g is increased markedly by LiClO_4 , i.e. from around -65 to $-36\text{ }^\circ\text{C}$, via the so-called “salt effect”. This effect is in agreement with the FT-IR data shown in Fig. 5 which is due to the formation of a complex between PEO and ClO_4^- anions, as stated above. The value of T_g is lowered by the addition of SiO_2 filler.

It is thought that the nano-sized SiO_2 dispersed emulsion can penetrate the space between the PEO chains and, consequently, homogeneously dispersed SiO_2 filler in the matrix prevents or retards crystallization of PEO due to its large surface area. Considering the ionic conductivity enhancement shown in Fig. 1, it can be assumed that the segmental motion of PEO for lithium ion conduction is activated as a result of the increased amount of the amorphous phase and the expanded width of the PEO chains.

The effect of filler on crystallization temperature has been reported by Appetecchi et al. [13], namely, the crystallization temperature, T_c , disappears after a few days. If T_g represents the degree of segmental motion within polymer

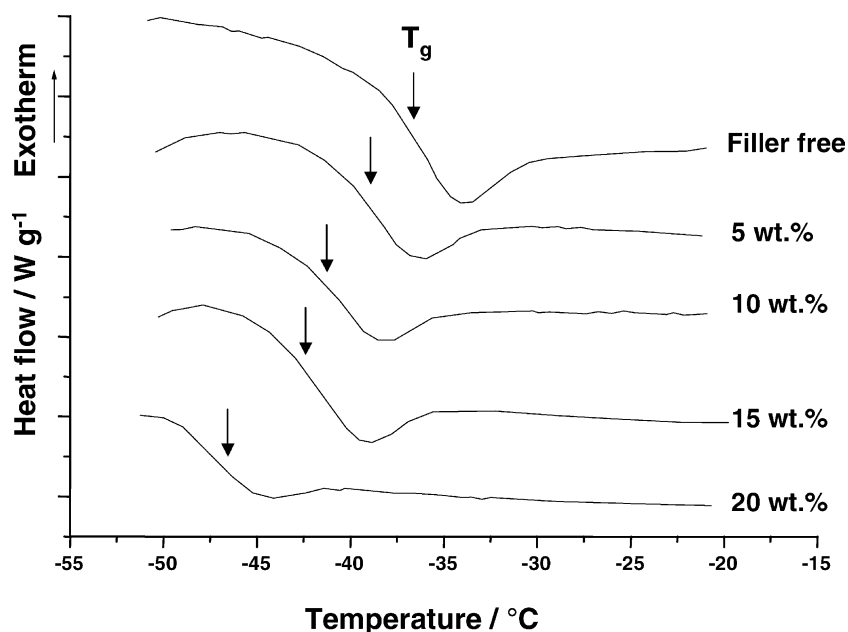


Fig. 6. Change in glass transition temperature, T_g , with SiO_2 addition to PEO: LiClO_4 complex.

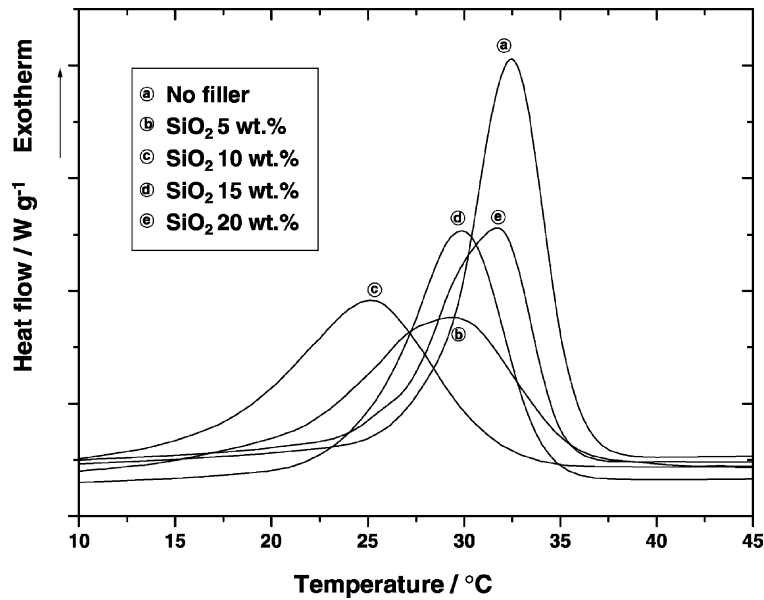


Fig. 7. Change in crystallization temperature, T_c , with SiO_2 addition to PEO: LiClO_4 complex: (a) filler free; (b) 5 wt.%; (c) 10 wt.%; (d) 15 wt.%; (e) 20 wt.%.

chains, T_c provides an index of the thermal stability of the amorphous state.

In the present study, the T_c of the composite electrolytes decreases as SiO_2 is added up to a level of 10 wt.%, as shown in Fig. 7. At greater amounts, however, the value of T_c increases again. The observed range of T_c , viz. 25–35 °C, over which the value is dependent on the filler amount differs from that the reported values around 50–70 °C [13]. As the calorimeter differential scanning started from 100 °C, all the specimens were in the amorphous state at the beginning of measurement. The lower T_c values mean that the temperature range over which they can exist stably in an amorphous state

becomes wider. The PEO: LiClO_4 electrolyte (see (a) in Fig. 7) started to crystallize around 32 °C which led to relatively poor ionic conductivity. In the case of the composite electrolyte with 10 wt.% SiO_2 filler (see (c) in Fig. 7), the amorphous state could be maintained even at 25.1 °C, i.e. at a temperature which is much lower than that of the filler-free system. This indicates an enhancement of the thermal stability of the amorphous phase. Consequently, the ionic conductivity is increased for the nano-sized SiO_2 filler added composite electrolytes at room temperature, as mentioned above.

The relationships between T_g , T_c and ionic conductivity are represented in Fig. 8. The rise of T_c with SiO_2 additions

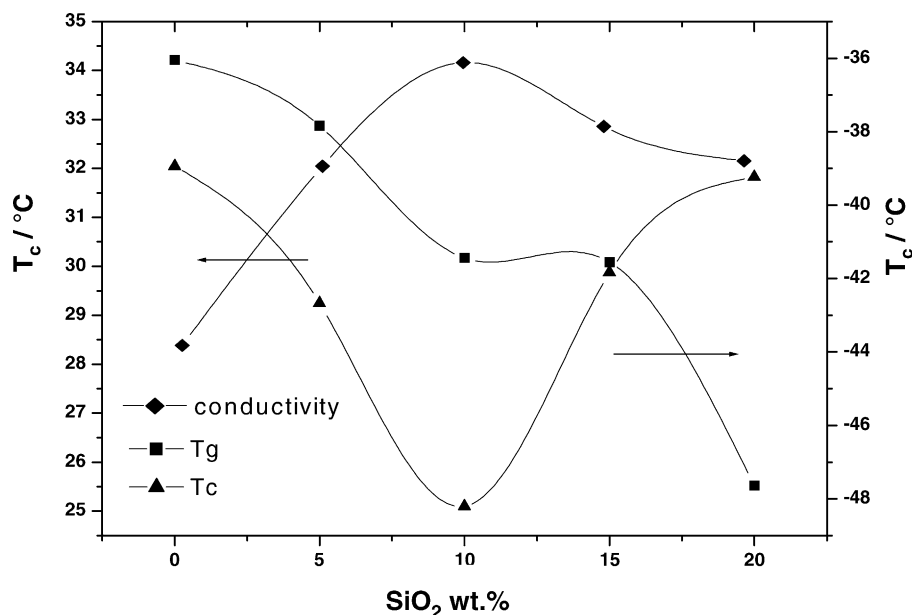


Fig. 8. Relationships between T_g , T_c and ionic conductivity.

over 10 wt.% may be explained by the assumption that the filler acts as a crystallization site, or causes a molecular interaction between polymer chains which leads to lower mobility.

4. Summary and conclusions

An increase in the ionic conductivity from 10^{-7} – 10^{-8} S cm⁻¹ to 2.3×10^{-5} S cm⁻¹ at room temperature is obtained through the addition of nano-sized SiO₂ filler to a PEO:LiClO₄ composite electrolyte. The enhancement in ionic conductivity can be explained by several causes such as lithium ion mobility, and the structural modification and amorphous phase stability of PEO. From the results achieved, it is proposed that the organic and inorganic hybrid electrolyte may be a new promising candidate for all-solid lithium rechargeable batteries.

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