

Inhibited crystallization and its effect on conductivity in a nano-sized Fe oxide composite PEO solid electrolyte

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Abstract

Crystallinity and conductivity results for a new nanocomposite PEO:LiClO₄ with nano-sized Fe₃O₄ particles are presented in this paper. The DSC measurements have shown a decrease in the degree of crystallinity of PEO by the inclusion of LiClO₄ salt and further decrease with the addition of Fe₃O₄ nanoparticles. The nano-sized Fe₃O₄ surface has a Lewis acidic group capable of interaction with Lewis base centers of the polymer PEO chain in the nanocomposite electrolyte, resulting in decrease in PEO crystallinity and enhancement of miscibility in the presence of LiClO₄ salt. Annealed at 125 °C of the PEO:LiClO₄ electrolyte shows melting endotherm at 175 °C, but this endotherm is absent with the incorporation of nano-sized Fe oxide particles.

This electrolyte system has a one and a half order of magnitude higher ionic conductivity compared to a standard PEO:LiClO₄ electrolyte. Optimized conductivity is found at a 10 wt.% Fe₃O₄ composition while above this concentration, the conductivity is decreased due to aggregation of a Fe₃O₄:Li rich phase.

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1. Introduction

In recent years, substantial interest has been devoted to nanocomposite polymeric materials because of their superior properties such as ionic conductivity and mechanical stability over pure polymer electrolytes [1–3]. The basic method of composite polymer electrolyte formation is the dispersion of inorganic oxides like TiO₂, Al₂O₃, etc., into a polymer–salt electrolyte solid matrix. A commonly accepted formation mechanism between the inorganic–polymer composite electrolyte is the complex formation through Lewis acid–base reactions [4–6]. According to this model, inorganic surface groups provide cross-linking centers for the PEO segments. This particular linkage reduces the polymer reorganization tendency and establishes the structural modifications of the host polymer matrix. Additionally, the filler surface groups of the inorganic solid oxide forms ion–filler complexes. The major conduction path still originates

from the amorphous polymer region, but additional ion transport is established from the ion–filler complexes through sequential replacement of ions to adjacent “holes” on the inorganic oxide surface [7].

In the case of composite polymer electrolytes, the ‘best’ distribution of the mobile ions are in the vicinity of available amorphous region or ‘structurally disordered region in PEO’ and on the available sites of the Fe₃O₄ oxide surface. Due to the enhancement of structural disorder, the mobility of the ions is much higher. At the same time, new dynamic phenomena are observed on the filler surface. The mobile ions are no longer independent of either PEO or Fe₃O₄, and the order and directions of their transport are largely determined by their interactions. The ionic transport within amorphous PEO and also on the filler surface seems to be of the same order. The Li⁺ ions environment on the filler surface is a salient feature in enhancing the ion conductivity. Apart from the basic ion transport via random walking through an amorphous PEO, a second conduction path is established on the surface of nano-Fe₃O₄ where the charge transport is likely achieved by replacing the nearby vacancy (“hole”) hopping in a sequential manner. The conductivity caused by the

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ionic hopping processes is now found to increase with filler content, where filler content prevented crystallization of the polymer PEO. The hopping rate is high, if the material is of short-range order (i.e. amorphous fraction), but much lower, if it has a long-range ordered structure.

Interactions in nanocomposite electrolytes can be accounted for by electrostatic models [8], where Li^+ cations will experience a relatively stable potential landscape at the filler surface, which will be same order as that in the polymer. Then the lithium ions will be free to move by segmental motion and activated hopping, with a potential barrier, which has been lowered by the filler. In the migration process, 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 they form with the ether oxygens of PEO [9]. This stipulates additional sites for the cationic transport process, where the bonds between the Li^+ ions and the oxygen in the filler surface groups are also subjected to breaking and making.

The purpose of the current study is to examine the crystallinity and conductivity in a nanocomposite electrolyte of PEO: LiClO_4 by the inclusion of nano- Fe_3O_4 particles. The nanoparticles have a large surface area [10].

2. Experimental

The synthesis of the Fe_3O_4 nanoparticles is by a chemical coprecipitation method [11,12]. Deoxygenated distilled water was used in the synthesis process. The solutions of ferric chloride hexahydrate $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and ferrous chloride tetrahydrate $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were prepared as a source of iron with a molar ratio of 2:1 by dissolving the respective chemicals in deoxygenated water under vigorous stirring. A solution of sodium hydroxide, NaOH 1 M, was slowly injected with vigorous stirring in order to obtain a pH value of 9. This reaction proceeded under the protection of N_2 gas throughout the preparation process to avoid possible oxygen contamination. The black precipitate was isolated in a magnetic field, and the supernatant was removed from the precipitate by decantation. After washing the precipitate several times, 0.01 M HCl was added to neutralize the anionic charge on the nanoparticle surfaces. Cationic colloidal particles were separated by centrifugation. The crystal structure and phase purity of the Fe_3O_4 nanoparticles were checked by powder X-ray diffraction. The average particle size (~ 13 nm), shape, and morphology were examined using transmission electron micrograph (TEM) and is shown in Fig. 1.

Nanocomposite polymer electrolyte films have been prepared by the blending of poly (ethylene oxide) (PEO) (MW: 2×10^5 , Aldrich), dried LiClO_4 salt and Fe_3O_4 in appropriate amounts. Initially, the polymer PEO was dissolved in tetrahydrofuran (THF) followed by the addition of appropriate amounts of LiClO_4 and Fe_3O_4 in 2 h intervals and stirred for 24 h at 60°C . The homogeneous mixtures were poured into Teflon dishes and evaporated slowly at 40°C and dried in vacuum. Further drying was achieved in a dry-box under argon atmosphere to remove traces of solvent completely.

The surface morphology of these composite electrolytes has been studied by Scanning electron microscopy (SEM) using an

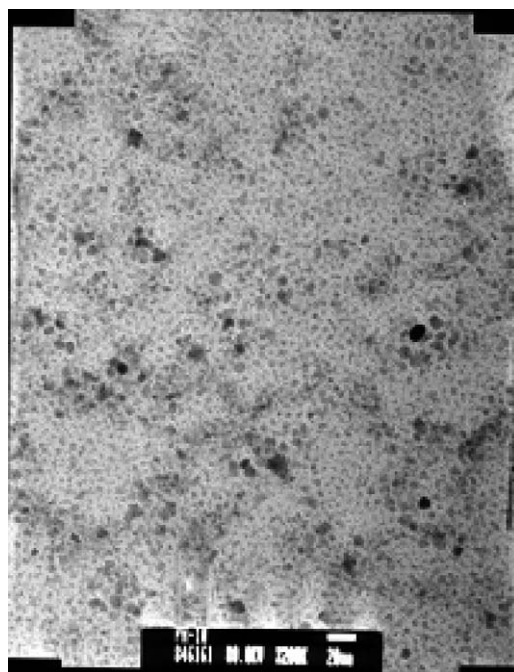


Fig. 1. Transmission electron micrograph of Fe_3O_4 nanoparticles.

Hitachi (Model 3500N) instrument. Samples were coated with thin gold films using sputtering. Differential scanning calorimetry (DSC) studies were performed using a Perkin-Elmer (DSC 7 series) system at a heating rate of 5°C min^{-1} . The sample weights were maintained in the range of 5–6 mg and all experiments were carried out under nitrogen.

Impedance spectroscopy was used to measure the ionic conductivity of these composite films. Measurements were carried out over the frequency range of 1 MHz to 10 Hz, with the help of a frequency analyzer AUTOLAB/PGSTAT 30 (potential/galvanostat) electrochemical instrument. These measurements were made over the temperature range 298–373 K, and the system was thermally equilibrated at each selected temperature for 20 min. The bulk resistance (R_b) was determined from the equivalent circuit analysis by using frequency response analyzer (FRA) software. The conductivity values (σ) have been calculated from the equation $\sigma = (1/R_b)(t/A)$, where t is the thickness and A is the area of the sample.

3. Results

The electrolyte surface morphology could be modulated by both ionic salt and oxide particles [7,13–15]. The surface morphology of pure PEO and Fe_3O_4 blend PEO: LiClO_4 electrolyte films are shown in Fig. 2. The appearance of a rough surface in the SEM micrograph of pure PEO suggests several crystalline domains. The PEO surface morphology changes severely when LiClO_4 and nano- Fe_3O_4 are incorporated. Fig. 2(b)–(d) shows the development of the surface morphology from rough to smooth with increasing the nano- Fe_3O_4 concentration in PEO: LiClO_4 . The surface morphology at a 5 wt.% Fe_3O_4 in PEO is homogeneously dispersed nano-oxide particles along with a smooth matrix of the composite film (see Fig. 2(c)), which sug-

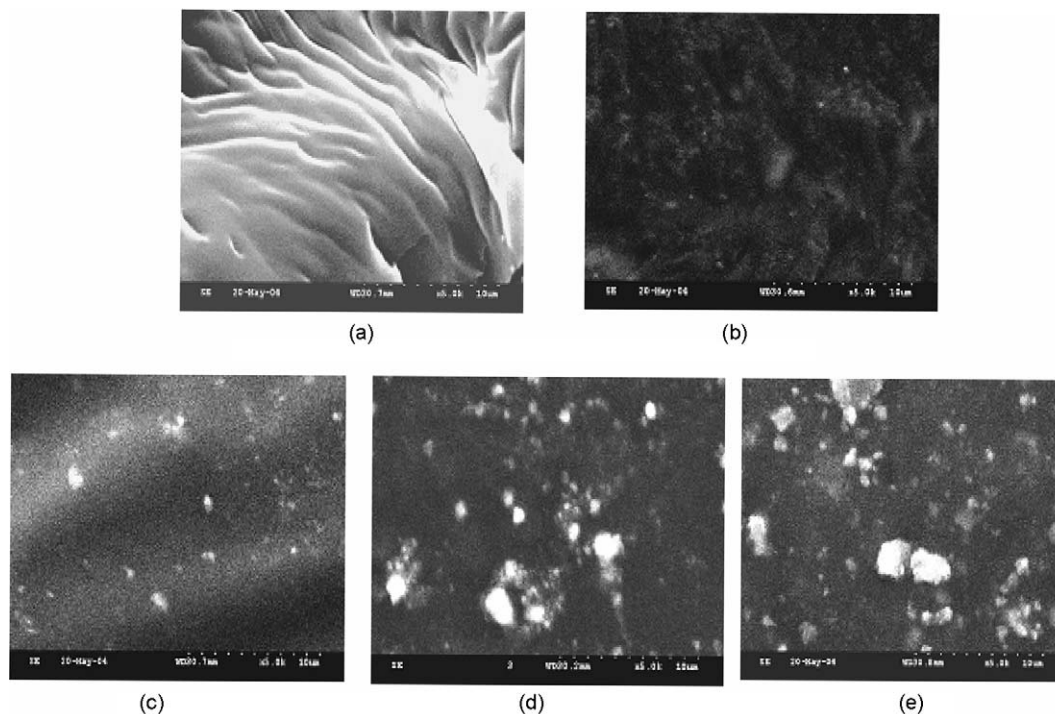


Fig. 2. SEM pictures (5000 \times) of: (a) pure PEO; (b) PEO:LiClO₄ (EO/Li ratio: 20/1); (c) 5 wt.%; (d) 10 wt.%; (e) 15 wt.% of Fe₃O₄ in PEO:LiClO₄ (EO/Li ratio: 20/1) polymer electrolyte.

gests satisfactory miscibility between the three moieties. The smooth morphology is closely related to the reduction of PEO crystallinity due to cross-linking with cations of both lithium salt and nano-Fe₃O₄. At higher contents of nano-Fe₃O₄ (i.e. above 10 wt.%) in PEO:LiClO₄ electrolyte is found to have a rough surface with an inhomogeneous composite matrix along with development of aggregated phases. The aggregated phase may correspond to nano-Fe₃O₄ with lithium ions.

Fig. 3 shows the DSC endotherm heating traces of the Fe₃O₄ nanocomposite PEO:LiClO₄ polymer electrolyte system. From Fig. 3, the melting endotherm of PEO is broadened and the melting temperature has been decreased by the inclusion of LiClO₄ salt in PEO. The broadening of the melting endotherm is apparent along with decrease in the heat of fusion (ΔH_f) by inclusion of nano-Fe₃O₄ in PEO:LiClO₄ electrolyte matrix. The

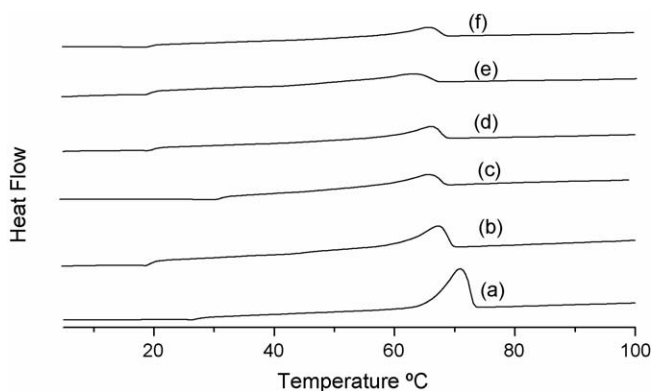


Fig. 3. DSC heating traces of: (a) pure PEO; (b) PEO:LiClO₄; (c) 5 wt.%; (d) 8 wt.%; (e) 10 wt.%; (f) 15 wt.% of Fe₃O₄ in PEO:LiClO₄ electrolyte films.

crystallization curves of pure PEO and nanocomposite Fe electrolyte films are shown in Fig. 4. The crystallization exotherms in these composite films are shifted towards lower temperatures and broaden with increasing Fe₃O₄ content in the PEO:LiClO₄ solid electrolyte matrix. The occurrence of T_c is lower than the T_m , which is a typical characteristic for macromolecular materials.

Changes in relative crystallinity (χ) in the composite electrolyte films have been calculated by assuming pure PEO being 100% in the equation $\chi = \Delta H_f / \Delta H_f^\circ$ (where ΔH_f° is the heat of fusion of pure PEO and ΔH_f is related to PEO complex) [7,13,16]. The crystallinity and crystallization temperature (T_c) with the function of Fe₃O₄ content in PEO:LiClO₄ are shown in Fig. 5. From the figure it is seen that χ and T_c decrease with Fe filler content up to 10 wt.% and further increase of Fe₃O₄ content

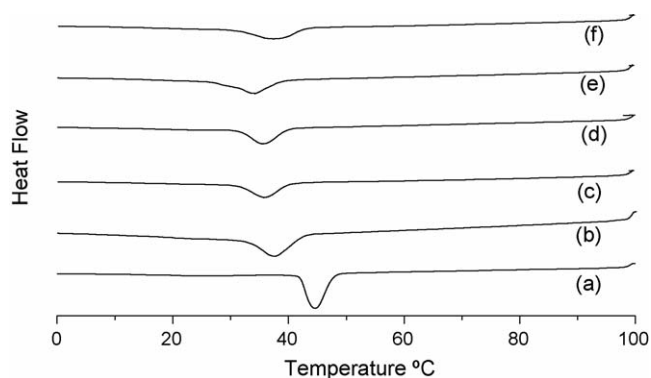


Fig. 4. DSC cooling traces of: (a) pure PEO; (b) PEO:LiClO₄; (c) 5 wt.%; (d) 8 wt.%; (e) 10 wt.%; (f) 15 wt.% of Fe₃O₄ in PEO:LiClO₄ electrolyte films.

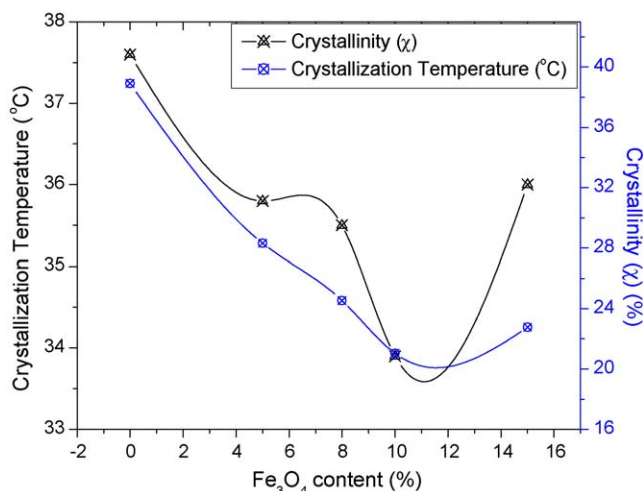


Fig. 5. Crystallinity and crystallization temperatures of Fe₃O₄ nanocomposite PEO:LiClO₄ polymer electrolyte system.

in PEO:LiClO₄ raised χ and T_c . The reduction in crystallinity in the nanocomposite electrolyte is due to Lewis acid–base interaction between the three moieties of PEO, LiClO₄ and Fe₃O₄, which is strong enough to effectively inhibit PEO crystallization. The slight rise in χ and T_c at above 10 wt.% of Fe₃O₄ in PEO:LiClO₄ may be due to larger aggregated phases of Fe:Li rich domains. This suggests the development of an aggregated phase, which is consistent with the results in the SEM photographs of the nanocomposite electrolyte at higher Fe₃O₄ contents in PEO:LiClO₄ solid matrix.

The DSC traces of the Fe nanocomposite PEO:LiClO₄ polymer complexed films after an annealing treatment at 125 °C for extensive period of 12 h are shown in Fig. 6. A new endotherm is apparent after annealing the PEO:LiClO₄ electrolyte, which occurred at 175 °C. Earlier studies confirm that high temperature melting peaks can be identified after an annealing treatment of PEO electrolyte systems [17,18]. The apparent endotherm corresponds to a stable PEO:Li salt complex. Although the melting

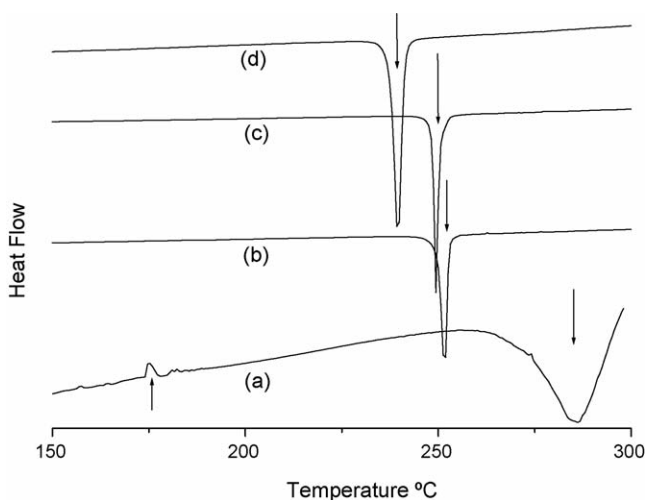


Fig. 6. DSC heating traces of annealed samples at 125 °C: (a) PEO:LiClO₄; (b) 5 wt.%; (c) 10 wt.%; (d) 15 wt.% of Fe₃O₄ in PEO:LiClO₄ electrolyte films.

occurs over a wide temperature range, and the heat of fusion is small, it is nevertheless strong evidence that such a stable complex can be formed between the PEO with a smaller cation such as lithium. This stable crystal complex phase implies either lower enthalpy or higher entropy compared to melting endotherm, which was found at lower temperature of the PEO complexed films. This stable complexed crystal peak is absent in the nano-Fe₃O₄ composite PEO electrolyte films, which suggests that the nano-Fe oxide prevented formation of additional crystallization of the PEO:Li stable complex. In the DSC thermal measurement with elevated temperature a broad crystallization exothermic (T_{ce}) peak in annealed pure PEO:LiClO₄ polymer electrolyte at 284 °C is apparent. The crystallization exotherm (T_{ce}) of PEO:LiClO₄ with Fe₃O₄ nanocomposite are shown in Fig. 7. The exotherm observed corresponds to PEO:Li crystallization in the melted liquid phase. This occurs over a wide temperature range window, and the heat of fusion is higher. Nevertheless, it is evidence that such PEO:Li crystalline complexes of long-range order can be formed between PEO with lithium in the melt phase. This polymer PEO–Li crystal complex phase implies either a higher enthalpy or lower entropy compared to the crystallization endotherm usually found at lower temperature of PEO complexed films while cooling (see Fig. 4). This crystallization complex peak is shifted towards lower temperatures with a smaller window in the nano-Fe₃O₄ nanocomposite PEO:LiClO₄ electrolyte films (see Figs. 6 and 7). The Lewis acidic character of the nano-Fe oxide interacts with Li ions, which decreases the crystallization exothermic temperature (T_{ce}) in nanocomposite electrolyte films. The increase of Fe₃O₄ concentration in the PEO:LiClO₄ complex decreases the crystallization exothermic temperature (T_{ce}). A reason for the decrease in T_{ce} may be due to the nano-oxide Fe particles which compete with the PEO polymer chain to form Fe:Li rich domains even at elevated temperatures in the melt phase.

The isothermal ionic conductivity is a function of the nano-Fe₃O₄ in composite PEO:LiClO₄ solid polymer electrolyte is shown in Fig. 8 at ambient temperature. The ion conductivity increases with the Fe₃O₄ oxide content and an optimum value

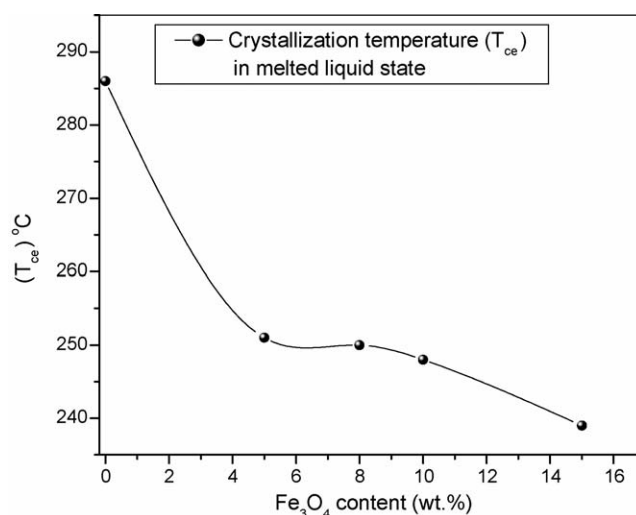


Fig. 7. Crystallization exothermic temperature (T_{ce}) of annealed samples.

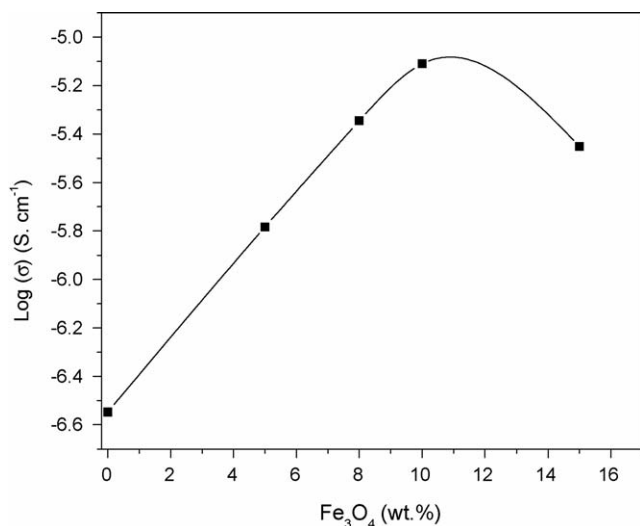


Fig. 8. Isothermal conductivity of Fe₃O₄ nanocomposite PEO:LiClO₄ polymer electrolyte system.

is found at 10 wt.% of Fe₃O₄ with one and a half order enhancement over a PEO:LiClO₄ solid polymer electrolyte. In the case of 15 wt.% Fe₃O₄, the conductivity is degraded but still is one order larger than that of a pure PEO:LiClO₄ solid electrolyte. As shown by SEM and DSC studies, the organic–inorganic miscibility is better at inter-medium compositions and higher fraction of amorphous phase, but above 10 wt.% Fe₃O₄ concentration there occurs aggregation of larger Fe–lithium rich domains. The conductivity enhancement in this PEO:LiClO₄ with Fe₃O₄ nanocomposite can be attributed to an increase in the amorphous fraction. In composite polymer electrolytes the conductivity is not a linear function of the filler concentration [5,19–25]. At a low content level of Fe₃O₄ content in PEO:LiClO₄, a dilution effect causes specific interactions with the Fe₃O₄ surface, which promotes fast ion transport, and overall affect enhances the amorphous fraction and consequently the increase in ionic conductivity. The dilution effect may predominate at a high Fe₃O₄ content in PEO:LiClO₄ electrolyte, and the conductivity decays.

The effect of temperature (T) on the conductivity (σ) of the Fe₃O₄ nanocomposite PEO:LiClO₄ system is shown in Fig. 9. The conductivity was found to be larger in the nanocomposite PEO:LiClO₄ electrolyte compared to pure PEO:LiClO₄ electrolyte in the studied temperature range. A sharp increase occurs at the PEO melting temperature (T_m). This is due to an increase in the amorphous domain, which is a typical characteristic of PEO electrolytes [19,26–28]. The $\log(\sigma) - 1000/T$ plots could be explained by different models in polymer electrolytes. A PEO:LiClO₄ electrolyte follows an Arrhenius-type thermally activated process below and above T_m . In this nanocomposite electrolyte of Fe₃O₄ in the PEO:LiClO₄ system follows VTF-type and Arrhenius-type thermally activated process in region-II and region-I, respectively at lower content of Fe₃O₄ and also at 15 wt.%. But at 10 wt.% Fe₃O₄ oxide content in PEO:LiClO₄ electrolyte follows the VTF-type thermally activated process in the studied temperature range, which is the best composition in this PEO:LiClO₄ with Fe₃O₄ nanocomposite polymer

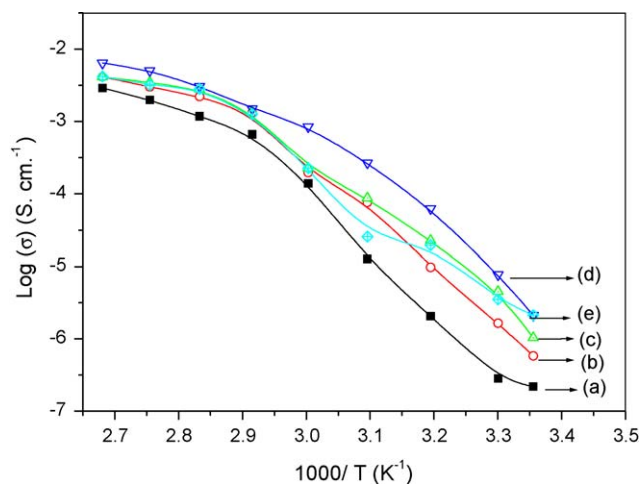


Fig. 9. Variable temperature ion conductivity of: (a) PEO:LiClO₄; (b) 5 wt.%; (c) 8 wt.%; (d) 10 wt.%; (e) 15 wt.% of Fe₃O₄ in PEO:LiClO₄ electrolyte films.

electrolyte system. Further work is in progress to study the transport mechanism and the causes of increase in ionic conductivity in this PEO:LiClO₄ with Fe₃O₄ nanocomposite polymer electrolyte system.

4. Discussion

The SEM, and DSC observations of nanocomposite Fe₃O₄:PEO complex in presence of lithium salt show good interactions between the three components of PEO, LiClO₄, and Fe₃O₄, where the presence of these interactions inhibited crystallization and a produced a pronounced disordered structure (i.e. amorphous). The nano-Fe₃O₄ surface has a Lewis acidic group capable of interaction with Lewis base centers of the polymer PEO. Thus, this nano-Fe₃O₄ oxide not only act as a source of physical cross-linking centers for the PEO chains, it could also facilitate salt dissociation. These interactions are responsible for reduction of PEO crystallinity, stable structure and favorable ion conductivity to the PEO:LiClO₄ with Fe₃O₄ nanocomposite electrolyte. According to Wiczczonek and co-workers [29,30] and our earlier results [7,13,14] it was demonstrated that the Lewis acid of the added oxide filler would compete with the Lewis acid character of the lithium cations to form new complexes with the PEO chains. Wong et al. [31] reported that the interactions of the polymer and cation with surface oxygen atoms occur in the silicate layer. Thus, the Fe₃O₄ oxide acts as cross-linking centers for the PEO chains. Such behavior lowers the PEO reorganization tendency and promoted an overall mechanically stable structure.

The prime factor for understanding the observed correlations in this PEO:LiClO₄ with Fe₃O₄ nanocomposite polymer electrolyte system is the interaction of each Li ion with its dynamic environment. In local equilibrium, each Li ion is surrounded by an arrangement of its neighbours on the surface of Fe₃O₄ and also Li ion along with the PEO chains. In the Li ion conduction process, its neighbours may suitably rearrange in the course of their own hopping motion. At high temperatures, the rearrangement of the neighbours is a fast process. Therefore, the

probability for the Li ion hop to be successful is high. The connectivity of a 'target site' (i.e., hole) is of prime importance for the ion transport dynamics on the Fe_3O_4 nanooxide surface in this PEO: LiClO_4 with Fe_3O_4 nanocomposite electrolyte. If the target site does not provide access to further sites, then the ion has to return for geometrical reasons. At higher concentrations of Fe_3O_4 in PEO: LiClO_4 nanocomposite electrolytes the Li ions may get trapped in the Fe:Li rich aggregated phases and act as small dipoles. Again, it is important to realise that these dipoles interact with each other in the aggregated phases of Fe_3O_4 with Lithium ions. As a result, there is a loss in ionic motion effect, which retards ionic conductivity at higher concentrations of Fe_3O_4 in the current nanocomposite of Fe_3O_4 included PEO: LiClO_4 polymer electrolyte system. Further, a ^7Li -NMR spectroscopy study is in progress to exploit the Li ion environment and its conduction mechanism process in this Fe_3O_4 in PEO: LiClO_4 nanocomposite polymer electrolyte system.

5. Conclusions

The cross-linking through Lewis acid–base interactions in a nanocomposite electrolyte between three moieties of PEO, LiClO_4 and Fe_3O_4 were strong enough to effectively inhibit PEO crystallization. A stable and strong complex was developed at 175°C after annealing at 125°C of PEO: LiClO_4 electrolyte. This stable complex was absent in nano-Fe composite PEO electrolyte films.

The Lewis acidic character of the nano-Fe oxide interacts with Li ions, which decreases the crystallization exothermic temperature (T_{ce}) in the melt phase at elevated temperature. The increase of Fe_3O_4 concentration in PEO: LiClO_4 complex decreases the crystallization exothermic (T_{ce}) peak further and with a smaller window.

The ion conductivity increases with the Fe_3O_4 oxide content and optimum value is found at 10 wt.% Fe_3O_4 with a one and a half order enhancement over a PEO: LiClO_4 solid polymer electrolyte. In the case of 15 wt.% Fe_3O_4 , the conductivity is degraded but was still one order larger than that of a pure PEO: LiClO_4 solid electrolyte. At higher concentration of Fe_3O_4 in PEO: LiClO_4 electrolyte, the Li ions get trapped in the Fe:Li rich aggregated phase and act as small dipoles. The dipoles interact with each other in aggregated phase and a loss in ionic motion occurs, which retards ionic conductivity at higher concentrations of Fe_3O_4 in this nanocomposite of PEO: LiClO_4 polymer electrolyte system.

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