Morphology and Transport Properties of Polyethylene Oxide (PEO)-based Nanocomposite Polymer Electrolytes

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Authors' contributions

This work was carried out in collaboration between all authors. Authors TOA, POA and AI designed the study. Author TOA wrote the protocol and wrote the first draft while, authors TOA and AM carried out the experimental work and analyses. Authors TOA and AM managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Magnesium Oxide (MgO) Nanoparticles (Nps) synthesized by microwave-assisted coprecipitation method was added as a nanoscale filler together with sodium thiocyanate (NaSCN) into poly (ethylene oxide) (PEO) to form PEO-MgO/NaSCN Nanocomposite Polymer Electrolytes (NCPEs). The MgO Nps were characterized by Scanning Electron Microscopy (SEM). The effect of the incorporation of MgO Nps and dispersion of NaSCN on the morphology and transport properties of Nanocomposite Polymer Electrolytes (NCPEs) were studied employing Fourier Transform Infra-Red (FTIR) Spectroscopy, Optical Microscopy (OM) and ionic conductivity measurement. The FTIR spectroscopy confirmed the existence of strong interfacial interaction between PEO and MgO Nps as the pristine polymer matrix are uniformly interspersed with MgO Nps showing strong absorption bands for the polymer and the MgO NPs. The optical microscopy results showed that the microstructural evolution of pristine PEO polymer is as a result of incorporation and intercalation of MgO Nps and NaSCN proton donor respectively. The temperature dependence of ionic conductivity of the NCPEs seems to follow an Arrhenius-type, thermally activated process with activation energies reducing

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with increase in nanosized filler content. This can be attributed to the smooth transport of Na$^+$ along several crystalline grains and amorphous grain boundaries.

Keywords: Poly (ethylene oxide); polymer nanocomposite electrolyte; sodium ion transport; microwave synthesis; Mgo nanoparticles; structural modification; Ionic conductivity.

1. INTRODUCTION

With the huge demand for communication and electronic devices in recent years, there has been significant pursuit to minimize the device size and implement affordable, compact, lightweight, high-capacity, solid-state rechargeable batteries. High ionic conductivity, strong solvating ability with a number of alkali, alkaline and transition metal salts and improved thermal, mechanical and electrochemical properties are desirable characteristics of the extensively studied polyethylene oxide (PEO) based polymer electrolytes. Polyethylene oxide is the most preferred amongst the family of polymers (polypropylene oxide (PPO), polyoxymethylene and polyether) with similar structure because of its semicrystalline nature at room temperature, exceptional property to dissolve high concentration of a wide variety of dopants and fast ionic conduction in its molten state when compounded into solid polymer electrolyte [1-3]. Recently, the resurgence of research interests in the PEO based polymer electrolytes is linked to the fact that at room temperature they suffer poor conductivity due to retardation of ionic transport imposed by their crystalline phases [1]. Furthermore, enormous efforts have been made to modify the structure of these polymer electrolytes in order to increase their electrical conductivity and improve their thermal, mechanical and electrochemical properties at ambient temperature for viable acceptability in electrochemical devices. Despite numerous challenges, considerable research efforts have been made to develop appropriate synthetic techniques (like plasticization, co-polymerization, etc.) for making good polymer electrolytes but creating one universal technique for developing polymer electrolytes is impossible due to the physiochemical differences between each system [4-9].

The earliest works on the incorporation of inorganic fillers into PEO can be traced back to Weston et al., 1982, Stevens et al., 1986 and Skaarup et al., 1988. The conclusions derived from these works were that such addition led to improved conductivity [10-12]. Following these efforts, Plocharski et al., 1988 and Chen 1988 concluded that the incorporation of highly conducting ceramic NASICON and γAl_2O_3 in the systems PEO-NaI-NASICON and PEO-NaSCN-γAl_2O_3 respectively, leading to increased conductivity was probably due to the enlargement of the polymer amorphous phase and not in conformity with the percolation theory and the model of highly conducting ceramic grains [13,14]. Numerous research efforts have been carried out on composite electrolytes using SiO_2, ionic glass and both crystalline and non-crystalline aluminas as the inorganic fillers, which showed improvements in the transport and mechanical properties of the electrolytes (Wieczorek et al.) [15]. They concluded that the increase in the conductivity in comparison with the un-filled electrolytes, was attributed to the enlargement of the total amorphous phase in the polymer matrix and to some not well-understood interactions between the polymer chains and the ceramic particles [16]. In addition to this, other researchers also noted that that the addition of fine ceramic powders reduces the degree of crystallinity of the polymer, and hence enhances the conductivity, by preventing the agglomeration of polymer chains. They concluded that particle size, in addition to the filler content, appeared to be a critical factor. In fact,

enhancements in conductivity were only possible if the particle size was smaller than 10μm [17]. As gathered from the literatures reviewed above, the general view is that the underlying principles of the mixed-phase electrolytes is not yet well understood, but the general acceptable view is tied to the fact that fillers improve the mechanical properties and considerably stabilize the electrode-electrolyte interfaces. This implies that more systematic work is needed before these systems can be optimally designed for practical applications.

Following the aforementioned observations, a considerable number, of inorganic, ceramic and organic additives, has been reported [18]. The recent trend in PEO based polymer electrolytes is the dispersion of miscellaneous nanoparticles such as TiO_2, Al_2O_3, SiO_2, ZnO and MgO leading to Nanocomposite Polymer Electrolytes (NCPEs) [19-23]. Liao et al., (2004) prepared oligo (ethylene oxide) modified LDH and studied the effect of OLDH addition on the morphology and conductivity of PEO/OLDH nanocomposite polymer electrolyte. In their work, they attributed the enhanced ionic conductivity to the ease of transport of Li^+ along intercrystalline amorphous phase brought about by the dispersion nanoscale OLDH layers. Other classes of layered inorganic materials with negative charged surfaces such as Montmorillonite (MMT) and organically modified MMT have been greatly exploited for use in the PEO based nanocomposite polymer electrolyte systems. In these works, PEO/MMT nanocomposite electrolytes (both exfoliated and intercalated forms) exhibited low conductivity at ambient temperature and high conductivity at high temperature. On the other hand, dispersion of OMMT nanosheets favored a formation of PEO-rich amorphous phase leading to enhanced ionic conductivity [24-31]. In addition to these, some works have been reported on the synthesis and characterization of nanocomposite polymer systems with improved electrochemical, thermal, mechanical and chemical behaviour owing to dispersion of nanosized particles [32,33]. In order to explore these aforementioned properties, Kamlesh et al., (2008) studied the effect of SiO_2 nanoparticles and a salt of ammonium thiocyanate on the polyethylene oxide polymer electrolyte with respect to morphology and electrical conductivity and concluded that that ceramic filler SiO_2 was able to decrease the crystalline content and enhanced salt dissociation of x $(PEO:SiO_2):(1-x)NH_4SCN$. The intercalated silica in PEO polymer host also produced a huge interfacial area with better mechanical and thermal property of the solid composite electrolyte [34].

The choice of MgO as a nanosized ceramic filler in this work is attributed to its abundance in the earth crust, high surface area, and enhanced surface reactivity obtainable from its unusual crystal shapes with a high ratio of coordinative unsaturated edge/corner surface sites as well as defect sites that are inherently more reactive towards incoming adsorbents [35]. In addition to this, the presence of numerous atomic and defective sites on the surface of MgO Nps means that easy diffusion paths are available for Na^+ ion transport and this will in turn improve ionic conductivity, thermal stability and mechanical strength. Subsequently, the use of Na^+ salt in this work is to proffer solution to the existing problem of chemical instability of Li^+ salt with the electrodes in the Li-ion batteries as claimed by many researchers [36], and to reduce cost and over dependence on Li salts for solid state rechargeable batteries. Thus, solid state rechargeable batteries based on Na/Na^+-ion salt solid polymer electrolytes are expected to give battery performance capabilities close to those of Li/Li^+- ion solid polymer electrolyte batteries due to the fact that Na^+- ions have ionic size and weight comparable to those of Li^+-ions. In this work, MgO Nanoparticles (Nps) was synthesized employing Microwave-assisted co-precipitation technique and subsequently blended with dissolved Poly-Ethylene Oxide (PEO) employing solution mixing technique. The hybrid x[PEO-MgO]:(1-x)[NaSCN] nanocomposite polymer electrolytes were then

characterized by Fourier Transform Infrared (FTIR) spectroscopy, Optical Microscopy (OP) and conductivity measurement for possible utilization in electrochemical devices.

2. MATERIALS AND METHODS

Poly-Ethylene Oxide – Magnesium oxide – Sodium thiocyanate (PEO-MgO-NaSCN) Nanocomposite Polymer Electrolytes (NCPEs) were produced via a two-stage reaction involving the synthesis of MgO Nanoparticles (Nps) from magnesium acetate tetra hydrate employing microwave-assisted co-precipitation technique and subsequent mixing of MgO Nps and sodium thiocyanate with PEO dissolved in de-ionized water via one-pot reaction.
Starting materials used for synthesis of MgO Nps are magnesium acetate tetra hydrate, glycine (amino acetic acid) and potassium hydroxide. Magnesium acetate tetra hydrate was dissolved in a standard solution of glycine until a clear solution was obtained and subsequently heated under microwave at a maximum frequency of 2450MHz with the corresponding power output of 700Watts for 5 minutes. This was followed by partial neutralization with KOH solutions and precipitation of the desired oxide specie was obtained. The resulting precipitates were filtered using Whattman-12.5cm filter paper and washed several times with distilled water and solutions of ammonia and propanol until the pH of the washing solution is 7.0. The precipitated MgO powder was dried at 200°C in air for 24h. Finally, surface morphology of the synthesized MgO Nps was observed using EVOI MA10 (ZEISS) multipurpose scanning electron microscope operating at 20kV employing secondary electron signals.

Following this, three samples of PEO-MgO-NaSCN Nanocomposite Polymer Electrolytes (NCPEs) containing 10-30% of MgO Nps were produced by solution casting into Petri dishes. The samples were oven dried at temperature lower than the melting point of PEO for 12hrs and subsequently, flat and uniform thin samples were obtained. The samples were analyzed by a FTIR spectrophotometer in transmission mode without KBr. The spectra were recorded in the frequency range 400 to 4000 cm^{-1}, after 25 scans, with resolution of 2cm^{-1}. The positions and intensities of the IR bands were processed with Spectral Analysis software. Surface morphologies of NCPEs were observed using Micro-Capture (Veho-VMS 004) USB microscope employing optical radiation and the images were analyzed using an Imaging software (Image-J). Finally, the samples were characterized for their ionic conductivities and transference numbers from room temperature to 60°C using Four-point probe resistivity measurement system. The variation of current with time for three different compositions i.e. 95[90 PEO: 10 MgO]:5NaSCN, 95[80 PEO:20 MgO]:5NaSCN and 95[70 PEO:30 MgO]:5NaSCN are given in Fig. 4(a-c) respectively. From these plots, the initial current (i_i) and final current (i_f) are evaluated, and total ionic transference number (t_{ion}) was calculated using the relation:

$$t_{ion} = \frac{i_i - i_f}{i_i}$$

3. RESULTS AND DISCUSSION

The image of the MgO Nps together with the corresponding 3D surface topography and agglomerate size distribution obtained using imaging software (Image-J) are given in Fig. 1. The morphology of MgO particles is such that the particles are closely packed together forming agglomerates as well as defective sites with large surface area suitable for bonding with the host matrix. The agglomerate size is in the range of 128±0.02μm, which makes

MgO very transparent and suitable for this research. The images presented in figure 2(a-d) together with the corresponding 3D surface topography and crystalline domain size distribution are the representatives of the microstructural evolution of pristine PEO polymer as a result of incorporation and intercalation MgO Nps and NaSCN proton donor respectively. Microscopic imaging analysis reveals the degree of the MgO dispersion and intercalation in the PEO-MgO/NaSCN Nanocomposite electrolytes. The variation in contrast and appearance of the images may be attributed the lowering of the crystallinity of PEO as a result of the presence of MgO Nanoparticles and the NaSCN proton donor. The micrograph presented in Fig. 2 (a) represent the pristine polyethylene oxide film wherein the spherullitic growths are discernable with uniform contrast. The average size of the crystalline domain appearing in pristine PEO is 157.20±0.04µm. After blending the pristine polymer with MgO and the NaSCN proton donor, the surface topographies of the NCPEs [Figs. 2 (b) to (d)], were modified and no apparent pattern of PEO crystallites is observed under microscope. This can be attributed to the strong nucleating effect of nanoscale MgO Nps dispersion, leading to non observation of the too small spherulitic growths under our experimental condition. It can be seen from Figs. 2 (b) that the contrast variation is mainly due to the differences in the light yield of the pristine polymer and filler atoms. The pristine polymer matrix appear in dark contrast while the filler matrix in lighter contrast. The average size of the crystalline domain in this NCPE containing 10% MgO Nps is 158.86±0.03µm. Several crystalline grains and lots of microcracks occurring at the grain boundaries are discernable in the image presented in Fig. 2 (c). This reflects strong dispersion of MgO Nps in the PEO-MgO/NaSCN containing 20% MgO where a follow up of the crystalline domain size analysis gave average crystalline domain size to be 157.44±0.02µm. Finally, the morphology of the NCPE containing 30% MgO is presented Fig. 2 (d), where the average crystalline domain size is estimated to be 153.81±0.02µm. The much smaller domain size is attributed to the confined size of crystallite imposed by MgO Nps during synthesis.
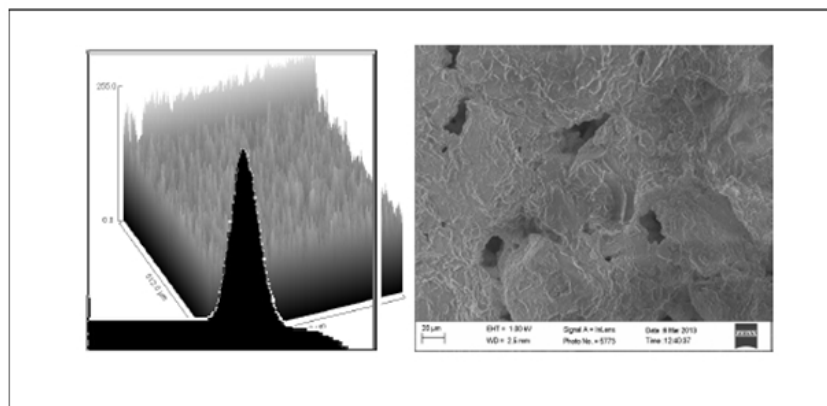

Fig. 1. SEM micrograph, Surface topography and Histogram of particle distribution for MgO Nps.
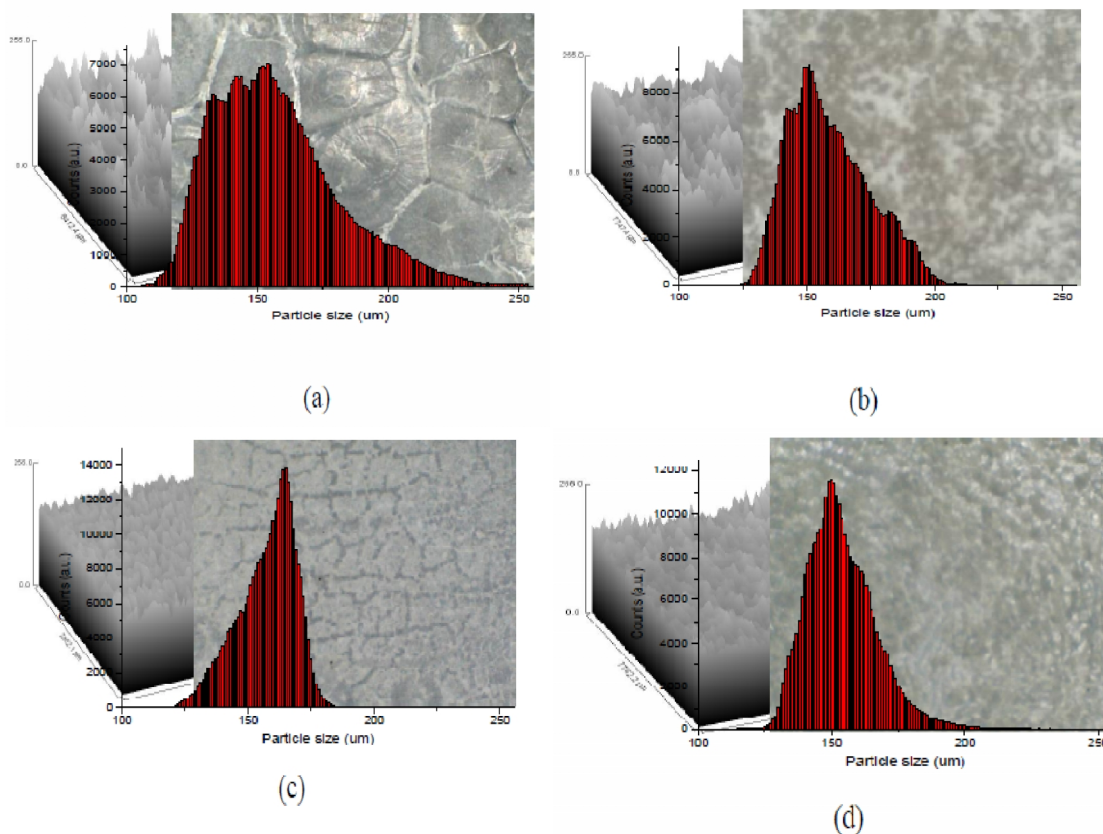
Fig. 2. Optical micrograph, Surface topography and Histogram of particle distribution for (a) Pure PEO film (b) PEO/10% MgO (c) PEO/20% MgO and (d) PEO/30% MgO

The FTIR spectra of the four samples of PEO-MgO-NaSCN nanocomposite polymer electrolytes containing 10-30% of MgO Nps given in Fig. 3.(a)-(d), were recorded periodically to find out if the MgO Nps were embedded in the PEO matrix and chemically bonded to polymer chains. Also, it is an established fact that metallic bonds with hydrogen and oxygen are clearly located in the range below $800cm^{-1}$ up to about 1900 cm^{-1}. In this work, the significant absorptions observed below $800cm^{-1}$ represent metallic bond with oxygen and those above 800 cm^{-1} represent both metallic and metal oxide bonds with hydrogen and hydroxyl groups. The spectra for the NCPE are presented in Fig. 3. (a-d) below. The FTIR spectra display broad bands at 3253.06 cm^{-1}-3992.78 cm^{-1}, which are believed to be associated with the stretching vibrations of hydrogen bonded surface water molecules and hydroxyl groups. It is also noticed that the hydroxyl stretching bands became much broader with increasing MgO content. This strongly supports the idea that a hydrogen bonding can form between either oxygen atoms of PEO and hydroxyl groups of MgO. The asymmetric stretching vibrations occurring in the range 2875.00 cm^{-1}- 2917.43 cm^{-1} represent the characteristic band of phenyl groups due to the C–O–CH$_3$-OH stretching vibrations occurring at 3117.07 cm^{-1}. This OH stretching vibration coexisting with acetates results from the vestige of the amino acetic acid used in the synthesis of MgO Nanoparticles.

The bands occurring at 2235.57 cm^{-1}- 2342.62 cm^{-1} represent the triple carbon bond of the C ≡C stretching vibrations. In addition, the bands at 1078.24 cm^{-1}, 1056.06 cm^{-1} and 1046.42

cm^{-1}are associated with C-OH bending vibrations of the secondary alcohols. The shift to lower frequencies may be attributed to additional bonding of these groups with metallic compounds. The band at 1610.61 cm^{-1} - 1967.46cm^{-1} is associated with both C=O conjugated and non-conjugated stretching vibration implying the existence of carbonyl absorptions. The changes observed in the vibration frequency of vC=O in the NCPEs indicate that the incorporation of the MgO Nanoparticles has great influence on the vibration frequency of vC=O. The bands at 1426.41 cm^{-1} -1460.16 cm^{-1} are associated with the bonding of MgO Nanoparticles with ethylenic groups. The bands at 1340.57cm^{-1} -1363.72 cm^{-1} represent CH$_3$ bending vibration of the phenyl groups. The characteristic band of PEO was observed at 833.28 cm^{-1} - 849.67cm^{-1} due to the C–O–C bending vibration occurring in the range 1266.31 cm^{-1}-1268.24 cm^{-1}.The changes in the C–O–C band in the spectra; suggest that hydrogen bonding is the underlying mechanism in the interaction. In addition, hydrogen bonding has a strong influence on the donor (in our case the –OH of NaSCN) and the absorption maxima of stretching vibration shifts toward higher frequencies. The intercalation of the proton donor (NaSCN) is evident by the bands occurring in the range 2039.79 cm^{-1}-2064.87 cm^{-1} representing the isocyanate groups. The out of plane bending vibrations appearing at 939.36cm^{-1} – 952.87 cm^{-1} are due to slight transformation in the ethylenic groups as a result of oxidation and hydrolysis. Finally, the peak at 2766.01 cm^{-1} is mainly due to residual –OCH$_3$.
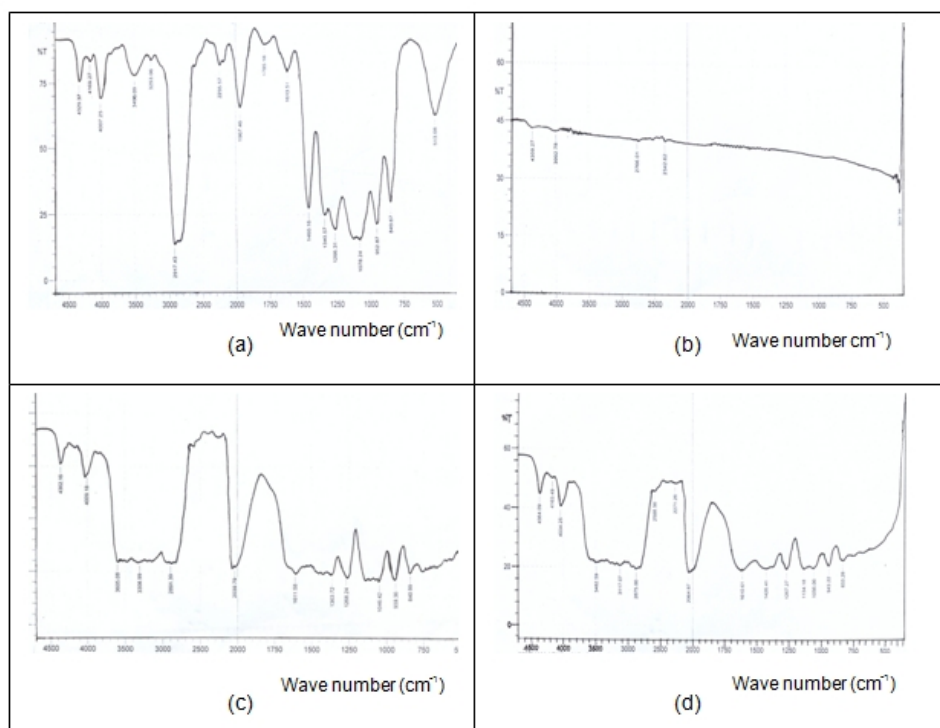

Fig. 3. Fourier Transform Infra red Spectra for (a) Pure PEO film (b) PEO/10% MgO (c) PEO/20% MgO and (d) PEO/30% MgO

In the present study, the likely mobile species are protonic and the total transference number was evaluated from current-time plot in Figs. 4(b-d). The calculated values of t$_{ion}$ for different composite films are 0.92 for the sample containing 30% MgO, 0.90 for the sample containing 20% Mg0 and 0.83 for that containing 10% MgO. From these values, it is obvious that PEO-

MgO-NaSCN nanocomposites polymer electrolytes are essentially ionic materials. The quality of the values is limited due to uncertainty in the measurement of initial current due to quick onset of polarisation. The temperature dependence of the conductivity i.e. $\ln\sigma$ versus $1/T$ plot of 95[90 PEO:10 MgO]:5NaSCN, 95[80 PEO:20 MgO]:5NaSCN and 95[70 PEO:30 MgO]:5NaSCN are shown in Fig. 4(a). The addition of salt NaSCN enhances the conductivity after T_m, in each of the three compositions shown in Fig. 4(a); this may be attributed to phase transition from semicrystalline to amorphous phase. The calculated values for activation energy obtained from the Arrhenius plots and the ionic conductivity at 345K for the NCPEs are given in Table 1. The activation energies for the NCPEs are 6.9×10^{-4}eV, 6.8×10^{-4}eV and 5.9×10^{-4}eV for samples containing 10%, 20% and 30% of MgO Nps respectively. The reduction in activation energy leading to higher conductivity may be due to smoother morphologies of the films upon addition of nanosized fillers.
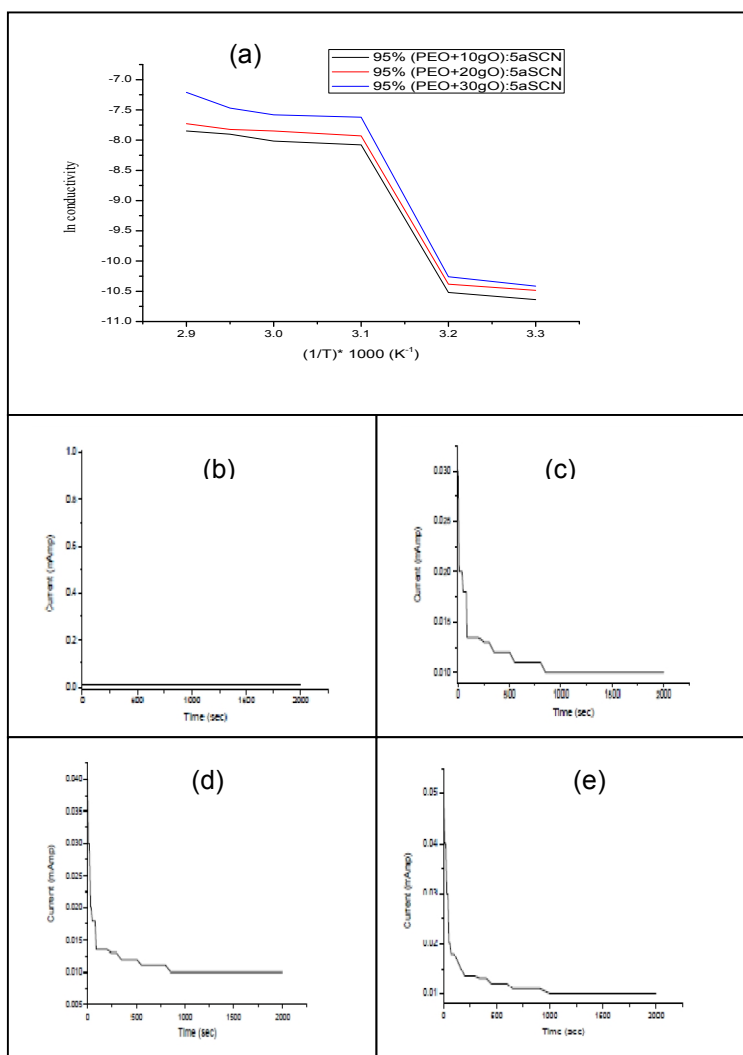

Fig. 4. (a) Variation of conductivity with Temperature for the NCPEs containing 5% NaSCN and Current versus Time curve for (b) Pure PEO film (c) PEO/10% MgO (d) PEO/20% MgO and (f) PEO/30% MgO

Table 1. Transport properties for NCPEs containing 10%, 20% and 30% MgO Nps

Transport properties	10% MgO Nps	20% MgO Nps	30% MgO Nps
Ionic Conductivity (S/cm) at 345K	3.9×10^{-4}	4.4×10^{-4}	7.4×10^{-4}
Transference Number	0.83	0.90	0.92
Activation energy (eV)	6.9×10^{-4}	6.8×10^{-4}	5.9×10^{-4}

4. CONCLUSION

The versatility of Polyethylene Oxide and the multi-functional nature of MgO have been exploited for the development of Polyethylene Oxide (PEO) based Nanocomposite Polymer Electrolytes. The morphological characteristics and transport properties of the developed NCPEs were examined employing SEM, OM, FTIR and dc conductivity. The FTIR spectroscopy revealed that existence of strong interfacial interaction between PEO and MgO NPs as the pristine polymer matrix are uniformly interspersed with MgO NPs showing strong absorption bands for the polymer and the MgO NPs. Thus, the significant absorptions observed below 800cm^{-1} represent metallic bond with oxygen and those above 800 cm^{-1} represent both metallic and metal oxide bonds with hydrogen and hydroxyl groups. Scanning electron microscopy revealed that MgO Nps possess agglomerated crystallites having large surface areas as well as defective sites that favoured easy diffusion of Na+ ions in the NCPEs. Observation with optical microscope also revealed that the crystallinity of the pristine PEO decreases with increase in percentage weight of MgO Nps and addition of ionic donor. Finally, polarisation and conductivity studies confirmed that the transference number and ionic conductivity were found to increase with increase in MgO content (0-30%) of the NCPEs. However, a maximum conductivity of 7.4×10^{-4} S/cm and transference number of 0.92 was observed for sample containing 30 wt% MgO. The temperature dependence of ionic conductivity of the NCPEs seems to follow an Arrhenius-type, thermally activated process with activation energies reducing with increase in nanosized filler content.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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