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REVIEW

Effect of nanoporous alumina filler on conductivity enhancement in $PEO_9(MgClO_4)_2$ polymer electrolyte: a ^{1}H NMR study

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Abstract Ionic conductivity, differential scanning calorimetry (DSC), and ^{1}H nuclear magnetic resonance (NMR) measurements have been performed on $(PEO)_9Mg(ClO_4)_2$ and $(PEO)_9Mg(ClO_4)_2$ + Al_2O_3 (neutral, nanoporous) polymer electrolyte systems. It is observed that the conductivity enhances due to the presence of filler up to 15 wt.% and then decreases. The NMR results are consistent with the idea that the conductivity enhancement is mainly due to the increase in chain mobility and ionic mobility of the solid polymer electrolyte caused by increased amorphocity of the electrolyte due to the presence of filler. DSC results also demonstrate that the fraction of the amorphous phase has increased due to the addition of the filler.

Keywords Polymer electrolyte · Conductivity · Filler · NMR

Introduction

Poly(ethylene)oxide (PEO)-based solid polymer electrolytes have received a considerable attention due to their unique mechanical properties, such as high flexibility in combination with stability and the absence of volatile or toxic compounds compared to other polymer electrolytes. The ability of PEO to dissolve salts of divalent cations and monovalent anions was first demonstrated by Blumberg and coworkers in their original studies of PEO–salt solutions formed with $HgCl_2$ and $CdCl_2$ [1]. James and coworkers [2] reported that PEO forms solutions of Zn, Co, Fe, and Co salts. Magnesium ion conducting solid polymer electrolytes have the advantage of low cost and the cells based on these electrolytes have the possibility of using more stable magnesium metal as an electrode material. Several Mg^{++} ion containing polymer electrolytes have been reported by various groups [3–6].

It has been established that the formation of crystallites in PEO-based systems lowers conductivity at ambient temperature [7, 8]. To overcome this drawback solvating host polymer should be modified to decrease the crystallinity and lower the T_g of the polymer electrolyte, while retaining the solvating properties of the ethylene oxide chain. In order to do this, the use of copolymers, formation of cross-linked networks, the addition of plasticizers, and radiation cross-linking has been used [9, 10]. Alternatively, inert fillers such as Al_2O_3, SiO_2, and TiO_2 have also been used to increase the ionic conductivity in these polymer electrolytes [11, 12]. These systems are generally known as nanocomposite polymer electrolytes. It has been shown that nanosized ceramic powders, when incorporated into the PEO-based electrolytes, can act as solid plasticizers inhibiting crystallization kinetics and promoting the retention of the amorphous phase down to subambient temperatures [12]. These nanocomposite PEO-based polymer electrolytes have shown enhanced ionic conductivity and improved mechanical and thermal stability [12–15]. Although the established view is that the ionic conductivity in PEO-based electrolytes is higher in the amorphous phase above the glass transition temperature of the polymer electrolyte and that crystalline polymer electrolytes are poor ionic conductors, contradictory results have been published recently by Stoeva et al. [16] and Golodnitsky et al. [17].

Polymers have been studied by nuclear magnetic resonance (NMR) which has resulted in valuable information

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about their microstructure, such as the conformation and configuration in copolymers, internal motions and relaxation processes, and the nature of the crystalline and amorphous phases [18]. In this work, we have studied the role of alumina fillers in conductivity mechanism in $(PEO)_9Mg(ClO_4)_2$ polymer electrolyte, with and without alumina filler. The major emphasis of the study is on PEO–Mg salt systems with different weight percentages of Al_2O_3 as filler. $Mg(ClO_4)_2$ salt has been used as the ionic salt to prepare the solid polymer electrolytes. The ionic conductivity, differential scanning calorimetry (DSC), and ^{1}H NMR measurements have been performed on these electrolytes.

Experimental

Sample preparation

PEO (molecular weight, 5×10^6 g mol^{-1}) and Mg $(ClO_4)_2$ were purchased from Aldrich. The nanoporous Al_2O_3 powder (Aldrich) had a pore size 5.8 nm and neutral surface groups. Prior to use, PEO, Mg $(ClO_4)_2$, and Al_2O_3 powder were vacuum dried for 24 h at 40°C, 80°C, and 120°C, respectively. Appropriately weighed quantities of PEO and Mg $(ClO_4)_2$ required for PEO to Mg $(ClO_4)_2$ ratio of 9:1 were dissolved in anhydrous acetonitrile. Al_2O_3 powder was added to the above solution which was magnetically stirred at room temperature for at least 24 h, until a homogenous solution was obtained. The amount of filler added varied from 0 to 18.5 wt.% of the total PEO + Mg $(ClO_4)_2$ weight. The resulting slurry, after stirring, was cast on to a Teflon plate and then left in order to let the solvent slowly evaporate. After vacuum drying for 24 h, homogenous composite polymer electrolyte films of average thickness 100–200 μm were obtained and stored in a vacuum oven.

AC impedance measurements

Complex impedance measurements were made on disc-shaped samples sandwiched between two stainless steel electrodes of 12.72 mm diameter, using a computer controlled Solatron SI 1260 impedance analyzer in the 20 Hz to 10 MHz frequency range. The temperature of the sample was varied from 30°C to 100°C and the measurements were taken at 10°C intervals on heating. The ionic conductivity was derived from the complex impedance data.

DSC measurements

The melting temperature of samples PEO_9Mg $(ClO_4)_2$+ 15 wt.% Al_2O_3 were determined using a Perking Elmer Pyris DSC Instrument. Samples were placed in aluminum DSC pans with a capacity of 40 μl. The measurements were carried out at a heating rate of 10°C/min from −100°C to 20°C using a low temperature cell. A flow of nitrogen gas was maintained over the perforated pan to avoid any contact with atmospheric moisture.

NMR measurements

All NMR experiments were carried out on a Varian Mercury YH 300 spectrometer (300 MHz proton frequency) using PFG Auto 4 probe. NMR measurements were done on solid polymer electrolyte samples prepared as above. ^{1}H NMR spectra were obtained at temperatures between 30°C and 70°C. Spin–spin relaxation time T_2, which directly reflects the degree of mobility of the probing nuclei, was measured using full width at half maximum (FWHM) of the spectra obtained after a 90° pulse of length 25 μs.

Results and discussion

Ionic conductivity

Figure 1 shows ln σ vs. $1/T$ plots obtained from complex impedance spectra of the $PEO_9Mg(ClO_4)_2$ + x wt.% Al_2O_3 system at several Al_2O_3 concentrations on heating from 25°C to 100°C. The data exhibit an enhancement in conductivity due to the presence of the alumina fillers over the entire temperature range studied. As expected, a discontinuity can be seen in curvature of the curve for the filler-free electrolyte around 60°C. This is due to the melting of PEO crystallites in the complex. The larger conductivity

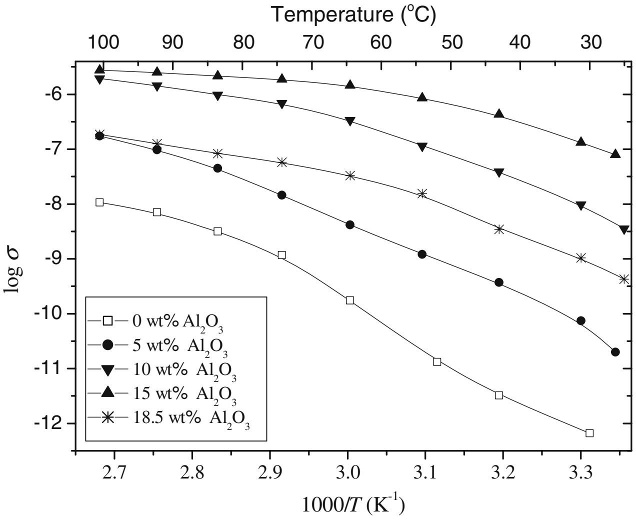

Fig. 1 ln σ vs. $1/T$ curves for $PEO_9Mg(ClO_4)_2$ + x wt.% Al_2O_3 for five compositions: x=0, 5, 10, 15, and 18.5

increase observed below ~50°C is likely to be caused by the conversion of a significant proportion of crystalline polymer into amorphous polymer due to the presence of filler. For the filler-free electrolyte, lower temperatures favor the crystallization of PEO–salt complexes and of unreacted PEO, while the higher temperatures produce a larger fraction of the amorphous phase with higher conductivity. In the crystalline phase, the polymer chains are rigid, and hence, the chain mobility is almost negligible and the conductivity is low. Polymer segments are flexible in the amorphous phase. Ionic motion is facilitated by the flexibility of the polymer chain segments producing a strong coupling between the segmental motion of the polymer and the ionic transport giving rise to a higher conductivity in the amorphous phase.

As depicted in Fig. 1, at each temperature σ increases with increasing Al_2O_3 content up to 15 wt.% and then decreases considerably. All the conductivity plots of the filler incorporated electrolytes exhibit similar curvature expected for an amorphous electrolyte obeying the Vogel–Tamman–Fulcher (VTF) relation. This suggests that the nanocomposite polymer electrolyte has amorphous structure and the ionic transport takes place by the same mechanism as in the amorphous phase of the filler-free electrolyte.

The variation of ionic conductivity of $PEO_9Mg(ClO_4)_2$ + x wt.% Al_2O_3 for five compositions: x=0, 5, 10, 15, and 18.5 is shown in Fig. 2. From these conductivity isotherms, it is clear that, at a given temperature, the conductivity increases with increasing alumina content up to 15 wt.% and then decreases considerably. According to the ideas proposed by several previous workers [12–15], the composite polymer electrolyte system at low filler concentrations may be imagined as a conducting medium where filler grains are randomly and uniformly distributed throughout the volume. The presence of the filler grains could give rise to additional favorable conducting pathways in the vicinity of the surface of the grains. The number of such additional high conducting pathways is expected to increase with increasing filler surface area. At low enough filler concentrations, where the grains are still well separated, these surface interactions can account for the observed conductivity increase with increasing filler concentration. An additional contribution to the observed conductivity enhancement could come from the increased amorphous nature of the polymer electrolyte due to the presence of the filler at low concentrations. As suggested by several previous workers, the presence of a low concentration of alumina fillers appears to favor the retention of the amorphous phase of the electrolyte.

The decrease of conductivity at filler concentrations higher than 15 wt.% is evidently due to the locking effect of the geometric constrictions imposed by the more abundant highly resistive alumina grains. This makes the long-chain polymer chains more “immobilized” giving rise to a restricted segmental motion and a lower conductivity.

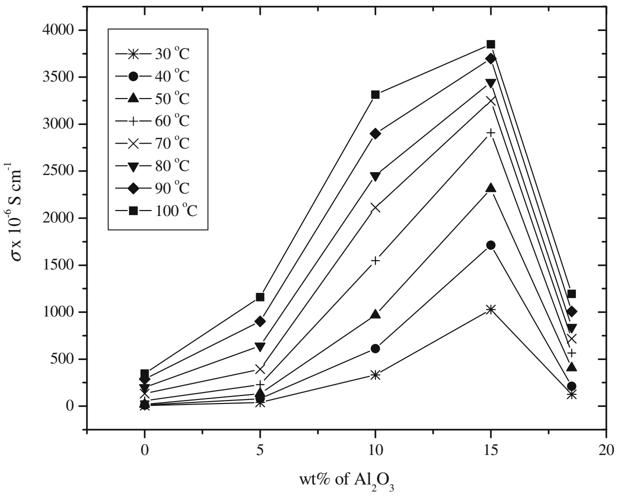

Fig. 2 Ionic conductivity isotherms of $PEO_9Mg(ClO_4)_2$ + x wt.% Al_2O_3 for five compositions: x=0, 5, 10, 15, and 18.5

A maximum value of ionic conductivity for 15 wt.% Al_2O_3 composition imply that the filler has increased also the carrier concentration of lithium ions as suggested by Croce et al. [12, 15]. Increased carrier concentration would also increase the ionic conductivity. Although we have no T_g data for compositions greater than 15 wt.% Al_2O_3, studies on PEO_9:$Cu(CF_3SO_3)_2$ incorporating Al_2O_3 grains have shown that the maximum conductivity composition correspond to the minimum T_g composition [19, 20].

DSC results

DSC thermograms for the samples $PEO_9Mg(ClO_4)_2$ and $PEO_9Mg(ClO_4)_2$+15 wt.% of Al_2O_3 are shown in Fig. 3. According to Fig. 3, apparent phase transitions have been observed at −50.2°C and −58.4°C, respectively, for $PEO_9Mg(ClO_4)_2$ and $PEO_9Mg(ClO_4)_2$+15 wt.% of Al_2O_3. This indicates that the addition of the filler has reduced the glass transition temperature of the polymer and increased the more conducting amorphous phase.

^{1}H NMR

^{1}H NMR measurements of samples $PEO_9Mg(ClO_4)_2$ and $PEO_9Mg(ClO_4)_2$ + x wt.% Al_2O_3, x=0,5, 10, 15, and 18.5 were taken on heating from 30°C to 70°C. The variation of full width at half maximum with temperature is shown in Fig. 4.

In solids, randomly oriented magnetic dipoles create magnetic fields called local magnetic fields. These magnetic fields vary from site to site within the lattice and increase the distribution of resonance frequency and line width. In liquids, magnetic field is homogeneous and gives sharp

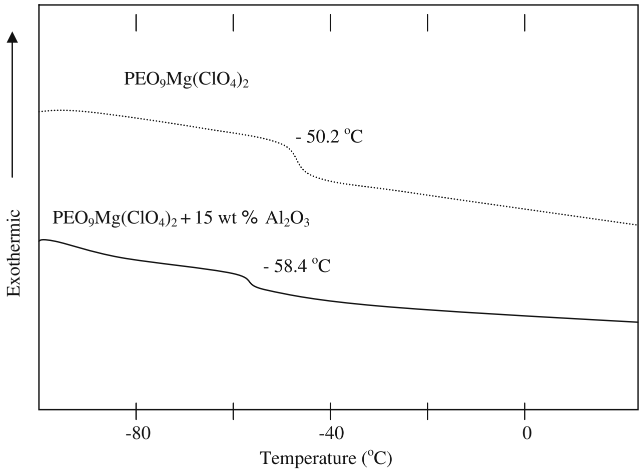

Fig. 3 DSC thermograms for $PEO_9Mg(ClO_4)_2$+15 wt.% Al_2O_3 on heating at a rate of 10°C/min in the temperature range, −100°C to 20°C

peaks due to small variation in the energy levels. According to Fig. 4, FWHM decreases with increasing temperature, i.e., NMR peaks get narrower indicating that the solid properties of the polymer electrolyte decrease due to decrease in crystalline phase and increase in the amorphous phase. These curves correlate well with ln σ vs. $1/T$ curves depicted in Fig. 1, suggesting that the conductivity increase due to increase in temperature as well as due to presence of filler comes mostly from the increased amorphous phase in the material.

The spin–spin relaxation time T_2 is inversely proportional to FWHM. Higher T_2 value in general reflects a higher mobility of the probing species. In this work, the probing nuclei are protons (^1H) bound to the polymer chain. Therefore, any change in the mobility of ^1H directly indicates a similar change in the mobility of the polymer chains. As it can be extracted from Fig. 4, T_2 increases with weight percent of Al_2O_3 up to 15 wt.% and then decreases, indicating that the highest polymer segmental mobility in the polymer electrolyte is observed at 15 wt.% of Al_2O_3. In order to fulfil the aim of this work, it is sufficient to investigate the trend of T_2. However, precise values of spin–spin relaxation time can be obtained by using other NMR methods [21].

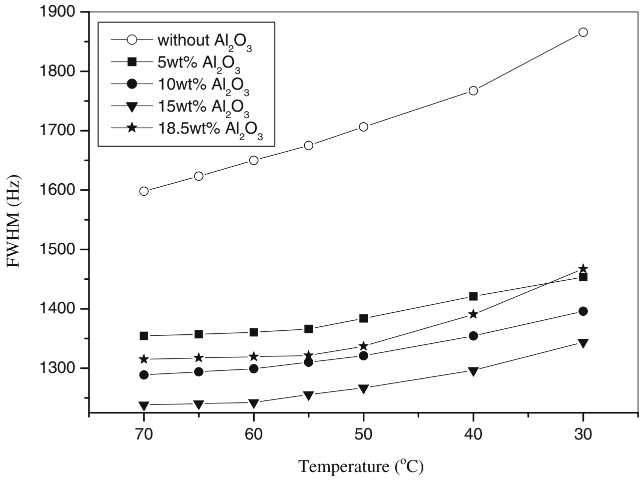

Fig. 4 Variation of FWHM with temperature for the samples $PEO_9Mg(ClO_4)_2$ + x wt.% Al_2O_3 for five compositions: x=0, 5, 10, 15, and 18.5

T_2 depends on the motion of the nuclei in the polymer electrolyte. Increase in temperature of the polymer melt increases the mobility of polymer segments due to increased amorphocity and hence increases T_2. A similar effect is caused by the presence of alumina filler up to 15 wt.%. Beyond this alumina composition, T_2 decreases as the high concentration of filler material restricts polymer segmental motion, as described earlier.

The results from the ^1H NMR measurements on the polymer electrolyte are consistent with the results of the DSC and conductivity measurements and suggest that the ionic conductivity increases due to the presence of the alumina filler up to 15 wt.% composition mainly due to the increased amorphous phase. Beyond this filler concentration, the conductivity drops, possibly due to restrictions imposed on chain segmental mobility by the presence of higher concentration of filler material.

The above interpretation, however, cannot explain fully the conductivity enhancement due to the filler observed in the amorphous phase in the electrolyte at temperatures above the PEO crystallite melting temperature of ~60°C, because the electrolyte is already in the amorphous state at these temperatures. As suggested by previous workers, surface interactions, most likely through the formation of Lewis acid–base type transient bonding of migrating ionic species with O and OH surface groups on filler grains, could possibly be responsible for this conductivity enhancement [12–14, 20]. The presence of filler grains could give rise to additional transient sites for ionic migration, in addition to promoting an amorphous phase that allows polymer chains more dynamic, thus providing favorable conducting pathways for migrating species. This can contribute to the ionic conductivity enhancement in the amorphous phase.

Several PEO-based polymer electrolytes incorporating nanosize fillers such as Al_2O_3, SiO_2, and TiO_2 have demonstrated convincingly that the conductivity enhancement is due to one or more of the following processes:

(a) The availability of additional transient hopping sites at O and off surface groups on alumina through Lewis acid–base type of bonding
(b) The increase in carrier concentration due to the presence of the filler

(c) The increase of the fraction of the high conducting amorphous phase caused by the filler at low filler concentration

In the present system, it appears that all those three mechanisms contribute to the observed conductivity enhancement as evident by ionic conductivity, DSC, and NMR data.

Conclusions

For the $PEO_9Mg(ClO_4)_2$, according to the DSC results, the exothermic peak shifts from −50.2°C to −58.4°C indicating that the glass transition temperature of the polymer electrolyte has decreased by addition of Al_2O_3. This indicates that due to the presence of Al_2O_3, the amorphocity of the material has increased.

The ^{1}H NMR spin–spin relaxation time T_2 has increased up to 15 wt.% of Al_2O_3 and then decreased. This is attributed to increase in the segmental mobility of the polymer chains, due to increase of the amorphocity. As the mobility of the chain segments within amorphous phase is higher than that in the crystalline phase, these provide additional experimental evidences for the enhancement of ionic conductivity associated with the increased amorphous phase of the polymer electrolyte due to addition of filler. At higher filler concentrations, physical constrictions restrict chain mobility resulting in a decrease in T_2 and hence a decrease in conductivity.

Additional major contributions to ionic conducting enhancement due to the filler, at temperatures above ~60°C, where the electrolyte is already in its amorphous phase, is likely to come also from possible Lewis acid–base type transient bonding between migrating ionic species and O and OH surface groups on alumina grains and also from an increase in carrier concentration caused by the presence of filler grains.

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