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Microscopic Interactions in Nanocomposite Electrolytes

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ABSTRACT: Nanocomposite electrolytes of a fully amorphous trifunctional polyether (3PEG) and poly(methylene ethylene oxide) (PMEO) have been complexed with two lithium salts and nanoparticulate (∼20 nm) fillers of TiO_2 and Al_2O_3. Addition of the fillers to the polymer salt complexes shows a significant change in the conformational modes of both polymers, especially the D-LAM region between 200 and 400 cm^{-1}, indicating a reduced segmental flexibility of the chain. These changes are more pronounced with the use of TiO_2 than Al_2O_3. Incorporation of the nanoparticulate fillers to the electrolytes fails to influence the degree of ion association, suggesting that the number of charge carriers available for conduction in both polymers using both $LiClO_4$ and $LiCF_3SO_3$ is not the source of any conductivity increase. Addition of the fillers, which was seen to increase the conductivity in PEO-based systems, generally lowers the conductivity in the present PMEO systems, while the addition of TiO_2 has little or no effect except in the cases of 3PEG 1.5 and 1.25 mol/kg $LiClO_4$. In this case, 10 wt % TiO_2 provides a conductivity increase of half an order of magnitude at approximately 60 °C. We also report for the first time a Raman spectroscopy investigation into the PEO-based nanocomposite electrolytes. The present results are discussed in terms of the electrostatic interactions involving dielectric properties of the fillers, of special interest being the interactions between the polymer and the fillers and between the ionic species and the fillers, when the effect of crystallization can be ignored.

Introduction

Investigations into solid polymer electrolytes have been motivated due to their potential use in various electrochemical applications, particularly those where a high energy density is required, for example, electric vehicles and portable computers.[1] Batteries based on polymer electrolytes also have the capabilities of outstanding performance in terms of mechanical stability, reliability and safety. A major drawback for these materials, however, is that they suffer from a relatively low ionic conductivity when compared to most liquid or ceramic electrolytes, as well as a low cation transport number.[2]

In a simple approach, the ionic conductivity of an electrolyte system can be described by the relationship

$$\sigma = F\sum_i n_i z_i \mu_i \tag{1}$$

where F is Faraday's constant, n is the number of charge carriers of the ionic species i, z_i is the charge, and μ_i is the mobility of the species. The number of charge carriers available in a polymer electrolyte is determined by the type of salt and the host polymer. As a result of ion association and ion−polymer interactions, which lead to an increased glass transition temperature, a lower than expected conductivity is observed especially at higher salt content.[3]

Binary salt−polymer electrolytes based on poly(ethylene oxide) (PEO) have been thought to be useful in lithium polymer batteries. However, this material is semicrystalline, which inhibits conduction of the lithium ion.[3] The highest conductivity of PEO is found above 65 °C, the melting point of PEO, where segmental motion and local relaxation of the polymer can assist conductivity. To preserve the highly conductive amorphous phase of PEO, plasticising salts and liquids have been commonly added.[3]

Recently, the use of inert nanosized fillers within poly(ethylene oxide)−salt complexes (nanocomposites) have been the subject of much interest due to reports of large increases in conductivity (approximately an order of magnitude at the melting point of PEO), greater cationic transport numbers, and increased electrochemical stability. Part of the conductivity increase was suggested to stem from the decrease in the extent of crystallization in systems such as PEOn:$LiClO_4$ which is brought about by the presence of the nanoparticulate fillers.[4]

To examine the effect of particle size, dielectric constant, surface properties, and Lewis acid−base type effects, other fillers such as $BaTiO_3$, fumed SiO_2, $LiTaO_3$, C_{60}, etc.,[5−8] have been used by other researchers. In all cases, conductivity increases were described above that of the pure polyether−salt systems, suggesting a nonspecific mechanism for the conductivity enhancement. However, the intermolecular interactions in these systems—between the polymer, filler, and salt—are yet to be experimentally examined.

In previous work we reported results on a nanocomposite electrolyte based on a trifunctional amorphous copolymer. The fully amorphous system was chosen in order to separate out the different mechanisms for conductivity enhancement, the primary one being changes caused by crystallinity. This work suggested that the filler may reduce ion association in a polymer−$LiClO_4$ complex, as well as modifying a conformational mode in the electrolyte, thereby resulting in an increase in conductivity.[9]

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Table 1. EO/PO:Li Ratios for Various mol/kg Concentrations Used in the Polymer Electrolytes in This Work

mol/kg	EO:Li[a]	EO/PO:Li	mol/kg	EO:Li[a]	EO/PO:Li
1	23:1	21:1	1.75	13:1	12:1
1.25	18:1	17:1	2	11:1	10.5:1[b]
1.5	15:1	14:1	2.8	8:1	

[a] For PMEO and PEO systems. [b] Solubility limit for lithium salts in 3PEG.

In the present work we describe an extended study of the trifunctional amorphous polyether (3PEG) used in our previous study.[9] Poly(methylene ethylene oxide) (PMEO) is included as an amorphous analogue to the well-studied PEO systems reported by others. The aim of the present investigation is to determine whether there is an effect of the nanoparticulate fillers on the ionic conductivity in amorphous polymer electrolytes where all effects due to crystallinity can be neglected. Differential scanning calorimetry, dielectric and Raman spectroscopy experiments are used to investigate the molecular level effects of the nanofiller.

Experimental Section

The nanocomposite electrolytes were prepared as described earlier.[9] The amorphous polymer materials used here were a polyether triol with molecular weight of 5000 g/mol, with ethylene oxide and propylene oxide units in a 3:1 ratio (3PEG) and poly(methylene ethylene oxide) (PMEO) (Taynet) with a molecular weight of 157 000 g/mol.[10] It was assumed that the mole fraction of methylene groups was so small that the number of ether oxygens per gram was essentially the same as PEO.[10] PEO samples were made using M_W 600 000 from Polysciences. The different polymer samples used in the study are summarized in Table 1.

Two nanosized fillers were used: Degussa P25 TiO_2 (21 nm) and Degussa Al_2O_3 (13 nm). Both powders were dried in a dry argon atmosphere (<2 ppm H_2O) at 250 °C for 24 h prior to dispersion. The amount of the fillers were 10 wt % in all samples, which corresponds to 3 vol % for the TiO_2 and to 5 vol % for the Al_2O_3.

Polymer (PMEO and PEO) and filler along with a required amount of $LiClO_4$ (Aldrich, used as received) were mixed with an excess of acetonitrile (Aldrich, used as received). The samples were cast onto microscope slides and dried under vacuum at 70 °C for 3 days.

Differential scanning calorimetry (DSC) analysis was completed on a Perkin-Elmer DSC-7 operating in the temperature range −110 to 20 °C. The instrument was calibrated using cyclohexane. Measurements were obtained at a scan rate of 20 °C/min, with the T_g determined as the onset of the transition.

Raman spectra were recorded using a Dilor Labram spectrometer, equipped with a confocal microscope (Olympus BX40) with a 50× objective for both sample illumination and collection of scattered light. A He−Ne laser (wavelength 632.8 nm, 7 mW) was used for excitation. For detection of the Raman scattered light, a 1800 lines/mm grating and a Peltier cooled CCD camera (Wright) with a resolution of 2 cm^{-1} were used. All samples were enclosed in an airtight heater stage (Linkam THMS 600) under a constant flow of argon gas in order to avoid moisture absorption. The data were fitted with PeakFit,[11] using a linear background with a Gaussian function for the free ions, ion pairs, and triplets and a Voight function for higher aggregates. The error associated with the fit is dependent on the systematic errors due to the model chosen and on the stochastic errors due to the quality of the data. We estimate the maximum total error to be ±10% for all calculated intensities.

Silver electrodes were applied to the cured 3PEG samples for ac impedance measurements on a Novocontrol broad-band dielectric spectrometer. PMEO samples were measured in a specially designed liquid cell. Experiments were done under a flow of N_2 gas, between 200 and 400 K with a step size of 5 K, a frequency range of $10^{-2}-10^{7}$ Hz, and a sinusoidal signal amplitude of 100 mV.

Table 2. T_gs for Filled and Unfilled 3PEG Electrolytes

sample	unfilled (±2 °C)	TiO_2 (±3 °C)	Al_2O_3 (±3 °C)
3PEG	−64	−64	−64
1 mol/kg $LiClO_4$	−45	−45	−45
1.25 mol/kg $LiClO_4$	−38	−36	−37
1.5 mol/kg $LiClO_4$	−35	−35	−34
1 mol/kg LiTf	−49	−49	−50
1.5 mol/kg LiTf	−47	−48	−40
1.75 mol/kg LiTf	−38	−39	−40

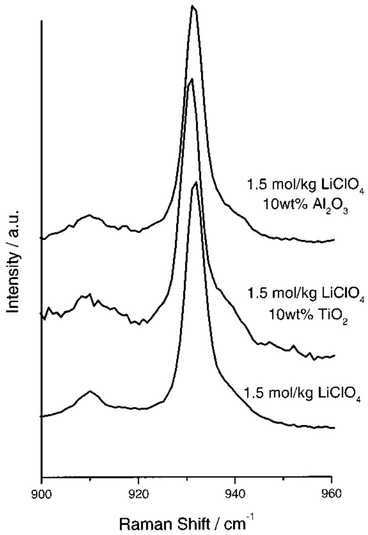

Figure 1. Raman spectra for the cured filled and unfilled 3PEG electrolytes at 25 °C. The symmetric stretching vibration of the ClO_4^- anion centered at 930 wavenumbers is shown.

Results

1. 3PEG. *Differential Scanning Calorimetry.* Subambient DSC measurements of all samples made in this work have been found to be consistent with those previously carried out in our laboratories.[9,12] These results are shown in Table 2. It is important to note that the addition of the filler does not change the shape of the glass transition (T_g), all changes being due to the addition of salt. Repeated DSC measurements on different regions of the original samples showed a small spread in the data due to possible inhomogeneties within the electrolytes. This has been accounted for in the errors in Table 2. As noted in the Experimental Section, only approximately 3 and 5 vol % of TiO_2 and Al_2O_3, respectively, are incorporated in the 3PEG samples. On the basis of this, we would not expect to see changes in the T_g of these systems if the filler is homogeneously dispersed.

Raman Spectroscopy. All Raman spectra were normalized with respect to the 1460 cm^{-1} peak assigned to CH_2 stretch of the polymer backbone. We have examined the 931 cm^{-1} symmetric stretching mode of the ClO_4^- anion, $\nu_s(ClO_4^-)$,[13,14] to determine whether the conductivity increases in the nanocomposite systems are due to an increase in charge carriers. Figure 1 shows that the addition of both the TiO_2 and Al_2O_3 fillers to the samples did not produce any significant decrease in ion pairing at any temperature in these studies.

Lithium triflate has been used in this study as it is spectroscopically easier to observe changes in the extent

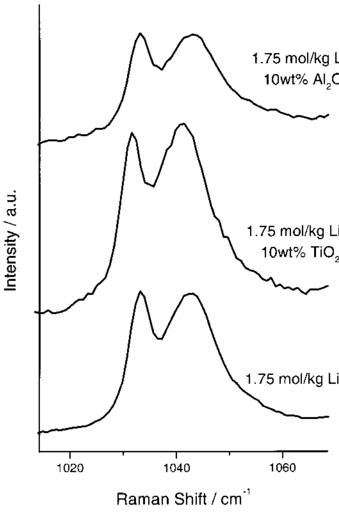

Figure 2. Raman spectra for the cured filled and unfilled 3PEG electrolytes at 25 °C. The symmetric stretching vibration of the $CF_3SO_3^-$ anion centered at 1030 wavenumbers is shown.

of ion pairing of this anion as compared to the perchlorate anion. The symmetric SO_3 stretching mode, $\nu_s(SO_3^-)$, of the $CF_3SO_3^-$ anion can be used to observe free or solvent-separated ions (~1030 cm^{-1}), ion pairs (~1042 cm^{-1}), and higher aggregates (1052 cm^{-1}).[15,16] As shown in Figure 2, we do not observe any significant changes in the ion pairing peak (1042 cm^{-1}) in this work, when using either TiO_2 or Al_2O_3 nanoparticulate fillers.

Figures 1 and 2 also show that the addition of the titanium-based filler to the polymer electrolyte shifts the symmetric stretching vibrations from 1033 to 1030 cm^{-1} for the triflate salt and 932 to 930 cm^{-1} for the perchlorate salt. For both salts, the addition of the Al_2O_3 filler to the two different electrolytes did not influence the peak position. Wendjsö et al. and Perelygin et al. have shown that the positions of the symmetric stretching vibration of the triflate and ClO_4^- anions change when substituting large metal ions.[17,18] The authors suggested this shift to be due to the strong coordination of the metal ion and formation of M^{2+} $CF_3SO_3^-$ pairs and higher complexes. The changes observed in Figures 1 and 2 would suggest that the anion could be weakly coordinated with surface Ti atoms of the Ti-based nanoparticulate filler, due to the small shift in peak positions, but not the alumina-based system.

The polymer conformational modes, observed with Raman spectroscopy, have exhibited distinct changes. Figure 3 shows the effect of TiO_2 and Al_2O_3 on the disorder–longitudinal acoustic mode (D-LAM) of the polymer. This band is highly inhomogeneous, being comprised of a complex group of bands representing the delocalized skeletal bending modes in the polymer chains. The D-LAM bandwidth is determined by the dispersion about the average conformation, and the frequency of the band position is proportional to $1/n^2$, n being the number of skeletal atoms in the section of the backbone involved in the motion. However, it has been shown that the addition of salt can also shift the position of this mode.[19] The intensity of this mode is a measure of the population of LAM-like "breathing" modes of the polymer chain. In previous work, we were unable to ascribe the changes in this mode to either curing or the filler.[9] Here we show that it is the addition of the fillers, especially of TiO_2, and not the curing process that suppresses this mode. Figure 3 shows that the D-LAM mode is localized to the area around 250 cm^{-1} in cured 3PEG. With the addition of the salt, triflate or perchlorate, the intensity decreases and the peak position shifts toward higher wavenumbers. Importantly, on the addition of the nanoparticulate TiO_2 to the pure polymer, this mode is suppressed, suggesting that there is a restricted mobility of the in-phase motions of the polymer chain. The relative intensities of the TiO_2 and the anion peaks, ~400 and ~450 cm^{-1}, respectively, could be influenced by the inhomogeneous nature of the electrolytes, as discussed earlier. Addition of Al_2O_3 to the pure 3PEG and the polymer salt complex does not supress the D-LAM mode to the same extent, suggesting that there is not the same degree of interaction between polymer and nanoparticulate Al_2O_3 filler.

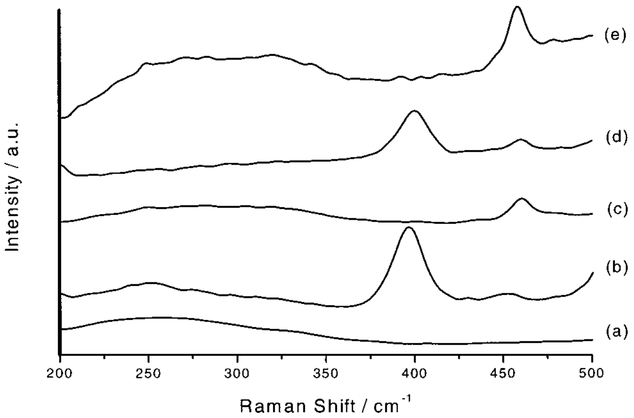

Figure 3. Raman spectra showing the changes in the disordered–longitudinal acoustic mode (D-LAM) for (a) 3PEG, (b) 3PEG 10 wt % TiO_2, (c) 3PEG 1.5 mol/kg $LiClO_4$, (d) 3PEG 1.5 mol/kg $LiClO_4$ 10 wt % TiO_2, and (e) 3PEG 1.5 mol/kg $LiClO_4$ 10 wt % Al_2O_3.

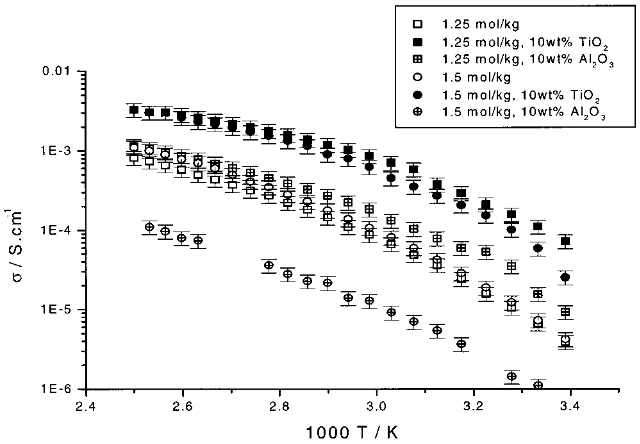

Figure 4. Arrhenius plot for two different salt concentrations of $LiClO_4$ in cured 3PEG.

Conductivity. Figure 4 shows the conductivity of the $LiClO_4$-based 3PEG samples. The unfilled samples show typical $LiClO_4$ behavior in the 3PEG systems, as observed in previous work.[9] The addition of the nanoparticulate fillers produces no change in conductivity in the case of 1 mol/kg salt samples. The 1.25 and 1.5 mol/kg $LiClO_4$ 10 wt % TiO_2 samples show half an order of magnitude increase in the conductivity. A number ($n \geq 3$) of replicate samples have been tested in this study, whose data have been incorporated into the error bars in Figure 4. Figure 5 shows the conductivity data for the 3PEG LiTf system. We note that the fillers only increase the conductivity in the case of the 1.5 and 1.75

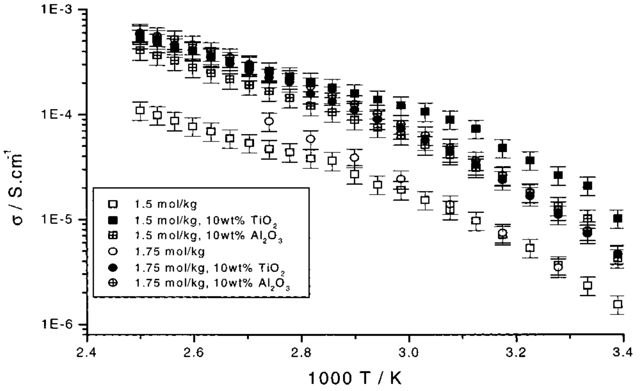

Figure 5. Arrhenius plot for two different salt concentrations of $LiCF_3SO_3$ in cured 3PEG.

Table 3. T_g Data for Filled and Unfilled PMEO Electrolytes

sample	unfilled (±2 °C)	TiO_2 (±2 °C)
PMEO	−65	
1.5 mol/kg $LiClO_4$	−40	−39
2 mol/kg $LiClO_4$	−18	−15
1.75 mol/kg LiTf	−45	−44
2 mol/kg LiTF	−40	−41

mol/kg samples. The 1.0 mol/kg LiTf and 1.0 mol/kg $LiClO_4$ samples (not shown) showed no significant change in conductivity on the addition of the filler.

By comparing the data from Figures 4 and 5, the $LiClO_4$-based systems all have higher conductivity (both the filled and the unfilled samples) compared to the LiTf-based ones. The relative effect of filler is the same, ∼0.5 an order of magnitude increase in conductivity. The addition of filler to the LiTf electrolytes only increases the conductivity to that of the more dissociated, unfilled $LiClO_4$ systems However, as was demonstrated in previous work,[9] the addition of filler to the $LiClO_4$ composites only increased the conductivity of these systems to that of the unfilled Li [bis(trifluoromethansulfonate)amide] systems. This salt is regarded as the most dissociated salt of those currently available.[20]

2. PMEO. *Differential Scanning Calorimetry.* Table 3 shows the T_g for selected samples of PMEO with salt and filler. It is seen that the filled samples have T_gs the same within error as the unfilled samples. The pure PMEO material showed a large heat capacity overshoot at T_g, which was not apparent in the samples which contained TiO_2.

Raman Spectroscopy. Two concentrations of PMEO: $LiClO_4$ have been prepared: 1.5 and 2 mol/kg. Figure 6 shows a band structure similar to the 3PEG systems described above is observed in the salt regions. For the case of LiTf in this polymer, 1.75 and 2 mol/kg concentrations were prepared. Unlike 3PEG, where the LiTf triples and higher aggregates seemed to be restricted and unseen, respectively, here they appear free to form. The addition of the filler to this system did not influence ion association.

The use of PMEO has allowed us to examine in some detail the changes in the conformational modes of the polymer brought about by the addition of filler. Changes in the D-LAM mode of PMEO, in Figure 7(i), are similar to those which have been previously described for 3PEG. Addition of the TiO_2 to the pure polymer acts to suppress the D-LAM motions; however, with increasing temperature, two small peaks become visible. In the PMEO:$LiClO_4$ and the PMEO:LiTf complexes, the D-LAM mode is observable; however, the addition of filler suppresses the mode again.

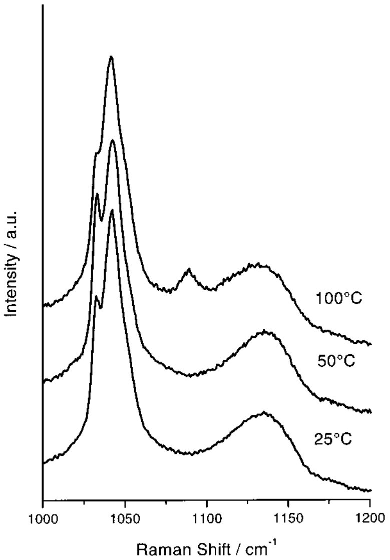

Figure 6. Raman spectra showing the differing band structure of $LiCF_3SO_3$ in PMEO compared to that of $LiCF_3SO_3$ in 3PEG from Figure 2.

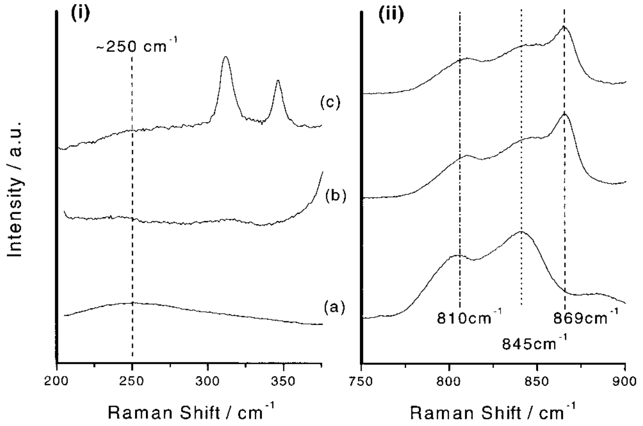

Figure 7. (i) Raman Spectra of the DLAM mode of the PMEO-based electroytes: (a) "pure" PMEO, (b) $PMEO_{11}$:$LiClO_4$, (c) $PMEO_{11}$:$LiClO_4$ 10 wt % TiO_2. (ii) Raman spectra of the PMEO-based electrolytes between 750 and 900 wavenumbers.

In Figure 7(ii), the pure PMEO, PMEO with salt, and the PMEO with filler samples are shown. The region between 800 and 880 cm^{-1} shows a split peak which is a mixture of the conformational modes of the polymer and the CH_2 rocking modes. The peak at ∼805 cm^{-1} has previously been assigned to a symmetric type of CH_2 rocking, $r(CH_2)$, coupled with CH_2 twisting. This peak can also describe a polymer segment of $OCH_2{-}CH_2O$ in the trans conformer. The other peak at ∼845 cm^{-1} has been assigned to C−O stretching and CH_2 rocking. This mode can also describe the polymer segment of $OCH_2{-}CH_2O$ in a gauche conformation.[21] Addition of TiO_2 to PMEO suppresses the intensity of the peak at ∼845 cm^{-1}, suggesting that the polymer motions are being restricted, consistent with the changes in the D-LAM mode which we have interpreted as being a change from a disordered to a restricted structure.

Addition of the lithium salts to PMEO produces a third peak at ∼869 cm^{-1}, which has been assigned as the formation of a polymer:Li interaction in PEO-based

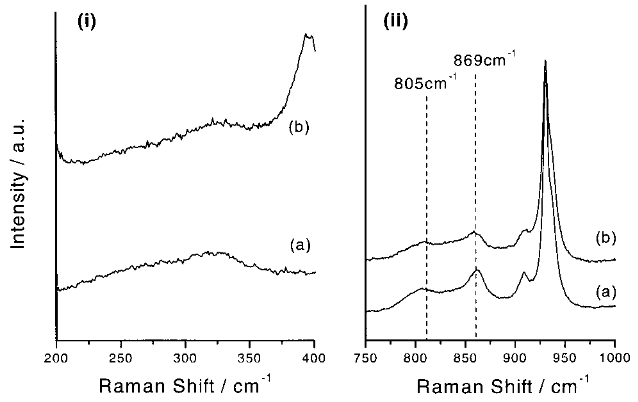

Figure 8. (i) Raman spectra of the DLAM mode of the PEO based electrolytes: (a) PEO_8:$LiClO_4$, (b) PEO_8:$LiClO_4$ 10 wt % TiO_2. (ii) Raman spectra of the PEO based electrolytes between 750 and 900 wavenumbers.

electrolytes, which will be discussed further shortly. The addition of the filler to the polymer electrolyte acts to slightly suppress this mode, perhaps breaking up the interaction between the polymer and the lithium ions or further reducing the symmetry of the polymer electrolyte.

Conductivity. The PMEO and filler samples were found to be too fluid above 50 °C to allow reliable determination of the conductivity. Settling of the filler was frequently observed, causing changing and irreproducible results to be obtained. These data are omitted from the present paper.

3. PEO_8:$LiClO_4$. *Raman Spectroscopy.* To more fully understand the effect of the fillers on the amorphous polymers studied above, the PEO_8:$LiClO_4$ (equivalent to 2.8 mol/kg) electrolyte system has been investigated for comparison. Figure 8 shows the filled and unfilled PEO Raman spectra in the DLAM region ($\sim$300 cm^{-1}) and the 700−1000 cm^{-1} region. In part (i) of this figure, we see that the addition of the filler to the polymer appears to influence the DLAM region by shifting the peak associated with the length of the alkane chain to higher wavenumbers, from 320 to 325 cm^{-1}. This suggests that the polymer chain has been further stiffened by the addition of the filler or in this case that the number of polymer backbone segments that participate in the motion is decreased by interactions with the filler. Also, the softening in the intensity of this peak suggests more disorder being introduced into the polymer backbone.

Figure 8(ii) shows that the filler also influences the strength of the peak at 805 cm^{-1}, previously described in this work, and others, as being due to the symmetrical rocking mode of the $r(CH_2)$ groups.[21] The change in intensity and broadness of this peak can only be attributed to the addition of the high surface area nanoparticulate filler. A more important change to the vibrational signature of the composite electrolyte can be seen in the change of intensity of the peak at 869 cm^{-1}, previously assigned to the vibration of the PEO chain when it is wrapped around the Li ion in a helical conformation. The Li ion has a coordination number of 5[22,23] and interacts therefore with three ether oxygens and up to two anions. The decrease in intensity of this peak would appear to suggest that there are either fewer Li ions occupying this site or there has been a reduction in the symmetry of this site. If in fact the second case is true, this would support the assertion that the increase in conductivity of the PEO complex is due to disordering of the crystalline structure.

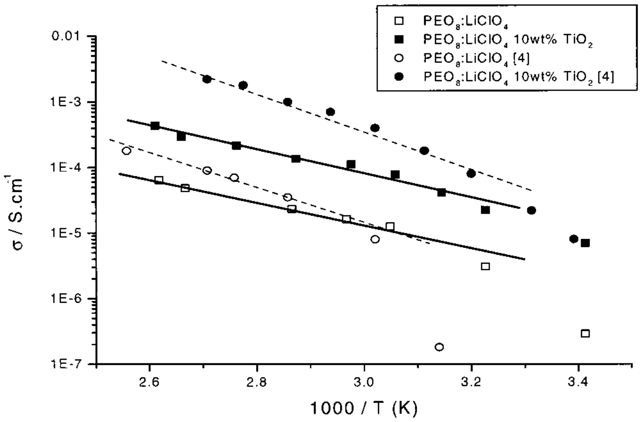

Figure 9. Arrhenius plot for PEO_8:$LiClO_4$ with and without TiO_2. We compare this result to that of Croce et al.[4] Lines on the plot are used to guide the eye (solid lines, this work; dashed lines, Croce et al.[4]).

Conductivity. Attempts to reproduce the conductivity increase seen by Croce et al. and a comparison are shown in Figure 9. We observe an approximately 1 order of magnitude increase in conductivity in the present systems at all temperatures above the melting point. The Croce et al. data show about a 30-fold increase above the melting point. The samples show significantly different slopes (activation energies) on this plot, which is surprising. These differences may arise from differences in sample preparation, origin and batch of TiO_2, cell geometry, and electrolyte type. Nonetheless, a significant increase in conductivity is observed in both cases, and this is the effect of primary interest.

Discussion

The major goal of this investigation was to determine the influence of a ceramic filler upon the ionic conduction in an amorphous electrolyte. From the studies undertaken so far, we note that no significant spectroscopic change in the number of ion pairs can be seen in these systems, suggesting that the fillers may not significantly increase the degree of dissociation of the salts used in these polymers. For cationic transport to increase in these electrolyte systems as suggested by previous authors,[4] the anions must be dissociated from the lithium ion by either the filler or the polymer chains. Tying the anion to a position where it can no longer participate in ion association may help increase cationic conductivity as there may be more such species available for conduction.

In our previous report,[9] the data suggested an interaction between the nanoparticulate TiO_2 and the polymer electrolyte, which was inferred to be TiO_2−ion interactions.[24] However, we find that it is not currently possible to discriminate between the interactions of the anion and the filler from those of the cation and the filler as these interactions may be obscured by other vibrations or may not be visible. A more rigorous examination of transport numbers from electrochemical measurements is required, across a wide compositional range of salt and fillers, before accurate conclusions can be drawn.

The changes in the intensity of the D-LAM region of 3PEG and PMEO due to the influence of the nanoparticulate filler may contribute to understanding changes in the mobility of the polymer, which in turn may be used to understand the influence on conductivity. It has been suggested that changes in this mode could have a twofold effect: first, separation of the polymer chains due to the anion and the filler, which provides a larger pathway for ions to diffuse;[7] second, the addition of the filler reduces order of the polymer chains, by preserving the amorphous phase associated with ionic conductivity, particularly in the case of the high molecular weight PEO studied here. However, in the case of the amorphous polymers, it appears that the opposite is occurring and that, in fact, the polymer chains are going from a disordered to a more ordered state due to the strong polarizing effects of the filler.

Investigation of the D-LAM region in the composites of triflate and Al_2O_3 shows more backbone motions than that in the perchlorate−TiO_2 system, suggesting that the Al_2O_3 filler does not as strongly affect the disorder of the polymer chains, perhaps due to its lower dielectric constant. This may be an explanation for the lower conductivities observed for some of the Al_2O_3-filled samples shown here.

Electrostatic Interactions. To further characterize the influence of the filler on the charge carriers within the electrolyte, we have attempted to estimate the electrostatic interactions between the polymer−salt complex and the fillers (ignoring any filler surface effects which may be present). This has been done by using calculations based upon the work of Lifshitz, using an additivity of dielectric constants approach.[25,26] The composite can be simply modeled by imagining the polymer−salt complex as a point charge, Q, in a medium of dielectric constant ϵ_3 at a distance D from the plane surface of a second medium of dielectric strength ϵ_2. Ignoring quantum mechanical fluctuations of the charge, the interaction energy $W(D)$ can be expressed as if there was an "image" charge of strength $-Q(\epsilon_2 - \epsilon_3)/(\epsilon_2 + \epsilon_3)$ at a distance D on the other side of the boundary.

$$W(D) = \frac{-Q^2}{4(4\pi\epsilon_0\epsilon_3)D}\left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3}\right) \text{ (ref 26)} \qquad (2)$$

where ϵ_0 is the permittivity of a vacuum, ϵ_2 is the dielectric constant of the filler, and ϵ_3 is the dielectric constant of the polymer−salt complex. The potential involved as a function of distance can be examined between the polymer−salt system ($\epsilon_r \approx 15$)[7] and that of the fillers TiO_2 ($\epsilon_r = 435$),[7] Al_2O_3 ($\epsilon_r = 20$),[25] and $BaTiO_3$ ($\epsilon_r \approx 1000$),[7] using eq 2. $BaTiO_3$ was included in this modeling due to the results of Sun et al.,[7] who noted no increase in conductivity above that of TiO_2, when using this ferroelectric filler in the PEO complex. The interaction energy between the point charge and the filler is stronger in TiO_2 and $BaTiO_3$ than in Al_2O_3 due to the relative strength of their dielectric constants. A dielectric constant much higher than that of TiO_2 will have no significant influence on the dynamics of the system, which is consistent with the experimental results of Sun et al.[7]

The strength of this interaction can be placed in perspective by calculating the kinetic energy $3/2kT$ of the cation at 330 K. At this temperature, a significant difference in conductivity is observed for the composites compared to the unfilled system. The TiO_2 filler will have a strong attractive effect, much greater than that of the Al_2O_3 on the cation and the polymer/anion. This attractive effect will occur, for example, between TiO_2 and the free cations up to a distance of 6 Å, where the kinetic energy of this interaction is greater than that between the cation and the polar groups of the polymer electrolyte.

A comparison can be made between these results and the calculated binding energies of the Li cation with 1,2-dimethoxyethane (an analogue of PEO) which is found to be of the order of 268−288 kJ/mol.[27] The latter value is the same order of magnitude as the calculated binding energy of the Li ion at the surface of a high dielectric constant filler. This means that the lithium ion should be able to reside either on the TiO_2 or the polymer chain, providing more sites for conduction. The barrier for cation migration along a polymer chain; i.e., the energy required to move between oxygen binding sites is found to be between 83 and 125 kJ/mol.[28] Up to a distance of 3 Å, the lithium ion may see an even potential between the TiO_2 filler and the ether oxygen sites on the polymer, thus leading to an alternative conduction mechanism which may be of importance for improved conductivity in polymer electrolytes.

From our simple modeling, it can be suggested that there will be a significant polarization in the surrounding area of both fillers, involving the anion and the polymer. Such a strong interaction may indeed lead to a restriction of the polymer chains, as indicated by Raman spectroscopy, in an amorphous material and a possible arrangement of the anions around the surface of the filler.

The cation on the other hand, due to its localized charge, will experience a relatively stable potential landscape, meaning that the potential at the ceramic surface will be of the same order as that at the polymer. The lithium ion will then be free to move by segmental motion and activated hopping, with a barrier which has been lowered by the filler.

Conclusion

DSC, Raman, and impedance spectroscopy studies on 3PEG, PMEO $LiClO_4$, and LiTf complexes and PEO_8:$LiClO_4$ with inorganic fillers have been undertaken as a function of composition and temperature. Addition of the fillers to the 3PEG complexes did not show any significant change in ion association as a function of temperature, as we are unable to discriminate between anion/cation filler and polymer interactions at this time. The lack of change in the shape and onset of T_g on the filled 3PEG polymer electrolytes from the unfilled samples leads us to believe that the conductivity enhancement is not due to T_g. From these data and literature, we show that conformational changes manifested by changes in the DLAM region of the polymer appear to be one source of the conductivity enhancement in the 3PEG-based electrolyte system.

In the PEO_8:$LiClO_4$ system studied here, we noted interesting changes which correlated well with those seen in the amorphous polymer systems. Changes in the DLAM mode and the symmetrical vibrations of the CH_2 groups on the addition of the filler support the hypothesis that the filler preserves the amorphous character of the PEO-based electrolyte. Importantly, the peak at 869 cm^{-1} previously assigned as lithium ions within a helical PEO structure is decreased in intensity upon addition of the TiO_2. In combination with an electrostatic potential, which may influence the ordering−disordering of the polymer complexes examined in this study, this provides one explanation for the increased conductivity exhibited in polymer electrolytes on the addition of nanofillers.

In conclusion, the present investigation shows that the number of ions available for conduction is not the leading cause for the increase in conductivity exhibited in amorphous and semicrystalline host polymers. Instead, we argue that the increase in conductivity is due to the influence of the filler on mobility of both the polymer and the salt as determined from Raman scattering and dielectric spectroscopy experiments and simple modeling using dielectric interactions. In future work we will attempt to further elucidate how the high surface area insulating nanoparticulates influence conductivity through solid-state NMR measurements (ion mobility), changes within the free volume of the polymer using PALS, and closer examination of the impedance spectra for these composite systems.

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