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Correlation of Ion-Ion Interaction with Electrical Conductivity in Solid State Polymeric Separator for Energy Storage Applications

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Abstract. In the present study, we report innovative study on the prepared high quality solid state free standing thin polymeric separator. In prepared free standing polymeric separator, polymer (PEO) has been used as host matrix; appropriate bulky anion salt ($LiPF_6$) as conducting species and Nano ceramic filler ($BaTiO_3$) is used to enrich the mechanical and thermal stability of separator used for the device applications. The Fourier Transform Infra-Red (FTIR) result has been analysed properly of the prepared materials to look the microscopic interaction among polymer-ion, ion-ion and polymer-ion-clay interaction. Electrical conductivity results has been recorded using the impedance spectroscopy results which gives the estimated value of the order of ~10^{-3} Scm^{-1} of the nano ceramic doped polymeric separator which is desirable for energy storage application. A fine correlation has been established between the obtained results by this two analysis.

INTRODUCTION

The advancement of polymeric frameworks with high ionic conductivity is one of the fundamental targets in polymer research for their potential applications in energy storage/conversion devices such as high energy lithium ion battery, supercapacitors and fuel cells. Lithium ion polymer batteries have preferences, because of their high ionic conductivity, high energy density, dissolvable free conduction, leak proof, wide electrochemical potential windows, ease in procedure capacity and light weight. For the most part, ionic conduction in polymer electrolytes is commanded by the indistinct elastomeric stage. The reported literature reveals that it is very difficult to achieve all the desirable properties for device applications in a single material system. The properties preliminary desired for energy device applications are; material should have very high ionic conductivity (10^{-3} –10^{-4} S cm^{-1}), stability towards electrode at the interface and dimensional stability for design flexibility. As a consequence the practical realization of a light weight high energy density device comprising of all solid components still remains a challenge. Slow ion dynamics in heterogeneous PNC films, poor mobility of polymer chain at room temperature, high internal resistance (internal friction, ion pairing i.e. concentration polarization, polymer viscosity, charge immobilization) are the primary factors responsible for low ambient ionic conductivity in conventional solvent free solid polymeric ionic conductors. This difficulty has prompted us to investigate the relaxation behavior in such systems. Since, temperature plays a crucial role in controlling ion dynamics, polymer chain motion, flexibility of the composite matrix etc., it became necessary to probe the correlation of microscopic interaction and electrical conductivity of polymer nanocomposites having heterogeneous composition. Winters gill and Fontanilla, studied low-frequency dielectric parameters of polyethylene oxide (PEO) and polypropylene oxide based polymer electrolytes [1]. Bulky anion lithium hexafluorophosphate ($LiPF_6$) is the most common lithium salt employed in lithium-ion batteries because it offers good electrolyte conductivities and film forming. However, the ionic conductivity of PEO–lithium

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salts (LiX) electrolytes at ambient temperature (10^{-7}–10^{-6} Scm−1) is not high enough for most practical applications. In order to over- come this problem, consistent research efforts have been devoted to improve the ionic conductivity in PEO–LiX (X=ClO_4,CF_3,SO_3, BF_4, PF_6 etc.) composite polymer electrolytes [2]. However, plasticizers tend to decrease the mechanical strength of the electrolytes, particularly at a high degree of plasticization. Alternatively, inorganic fillers are used to improve the electrochemical and mechanical properties. The fillers affect the PEO dipole orientation by their ability to align dipole moments, while the thermal history determines the flexibility of the polymer chains for ion migration. They generally improve the transport properties, the resistance to crystallization and the stability of the electrode/electrolyte interface. The conductivity enhancement depends on the filler type and size [3]. In 1999, the addition of carbon to improve the conductivity and stability of polymer electrolytes was proposed by Appetecchi and Passerini. However, the room temperature conductivities for various weight percent of carbon are within the range of 10^{-6} S cm^{-1}.

Present Paper reports a very high electrical conductivity (~10^{-3} Scm^{-1}) of polymer nanocomposite films consisting of PEO+ $LiPF_6$+wt. % $BaTio_3$. The polymer-ion and ion-ion interaction has been studied by fourier transform infrared (FTIR) results. A good correlation has been established in electrical conductivity and enhanced fraction of free anion which results the fraction of cations.

MATERIAL AND EXPERIMENTAL WORK

Materials

Poly (ethyl oxide) (PEO) as purchased from sigma Aldrich with average molecular weight of 600,000 and was used without further purification. Dissolved in acetonitrile, (<130nm) were also purchased from sigma Aldrich, and salt $LiPf_6$

Preparation of Polymer Electrolyte

Free-standing polymer clay nanocomposite (PNCE) films wereprepared using high purity (AR grade) poly (ethylene oxide) (PEO) from Aldrich (USA), salt ($LiPF_6$) from (M/s Across Organics) and $BaTiO_3$ supplied by the Clay Minerals Society (USA). T. PCNE films were prepared by a solution-casting technique with differentweight ratios of modified $BaTiO_3$ clay. The host polymer (PEO) and salt ($LiPF_6$) were dissolved in acetonitrile at a constant ratio of ether oxygen to lithium ion (O/Li) ∼17:1. The polymer–salt solution was stirredfor8hfollowedbythe addition of $BaTiO_3$ clay. Subsequently, this viscous composite fluid was cast into a polypropylene dish and the solventwas allowed to evaporate slowly. The resulting free-standing clay based polymer nanocomposite (PNCE) filmshave the general formula PEO+$LiPF_6$ +wt. % $BaTio_3$) where x varies from 0 (pure polymer–salt complex, PS) to 20wt. % with respect to the host polymer (w/w) [8].

Characterization Techniques

FTIR spectroscopy was used to study the interactions between constituents of polymer and filler interactions. Such interactions should be manifested through FTIR spectra as frequency shift, band intensity changes, splitting of bands and alterations of band shapes. The work was carried out using FTIR Bruker Tensor-27 in the range from 4000-400 cm-1 in transmission mode. Impedance spectroscopy is carried out by ch instrument 760. For this sample is placed between two electrodes

RESULTS AND DISCUSSIONS

Fourier transform infrared (FTIR) analysis

Fourier transform infrared (FTIR) spectroscopy has been used to probe the possibility of interaction among the composite components at the microscopic level [5]. The FTIR spectrum of PNC films based on PEO+ $LiPF_6$+wt. % $BaTio_3$ with different oregano clay concentrations (0, 5, 10, 15 and 20) in the wavenumber region (400–4000 cm^{-1}). The characteristic absorption peak observed in the spectral pattern at the wavenumbers 840,957,1107,1294,1340,1481, 1645,1982, and 2640 cm^{-1} are attributed to $\gamma(CH_2)_s$,$\gamma(CH_2)_a$,$\gamma(COC)_S$,$(CH_2)_s$, $w(CH_2)$,$\delta(CH_2)_s$,C=O and assemtric C-H stretching respectively . The detailed assignment of the experimentally observed FTIR bands and effect of clay on changes in their

TABLE 1 Band Assignment of free standing PNC films comprising of $(PEO)_{17}LiPF_6$+xwt%$BaTiO_3$

X=00	X=05	X=10	X=15	X=20	ASSIGNMENT
840	841	837	842	837	γ(CH2)s+γ(COC)s
957	955	980	983	952	γ(CH2)a+(COC)a
1107	1097	1033	1098	1092	γ(COC)s
1294	1252	1273	1277	1251	(CH2)s
1340	1362	1387	1357	1362	W(CH2)a
1481	1461	1462	1477	1473	δ(CH2)s
1645	1649	1650	1647	1654	C=O
2672	2833	2764	2886	2890	AssemtryC-H stretching

The typical vibrational modes of PF6- anion have been observed at 847 cm^{-1}. They are attributed to the deformation and stretching modes of PF6-, respectively. The (PF6-) band for pure polymer salt (PS) complex appearing at 847 cm^{-1} exhibits significant asymmetry. This asymmetric profile keeps on changing with change in the clay concentration in the composite phase. This asymmetry in the anion stretching vibrational mode is an outcome of the degeneracy arising out of more than one contribution possibly due to the presence of free anion and ion pairs. In order to be sure for this possibility the (PF_6^-) band (847 cm^{-1}) has been deconvoluted using Voigt profile with a commercial software peak fit [6]. The deconvoluted pattern composed of two distinct contributions appearing at 843 and 862 cm^{-1}. The peak appearing at 837cm^{-1} has been attributed to spectroscopically free anions anions and peak appearing at 848 cm^{-1} has been attributed to presence of ion pairs in the solid polymer clay matrix. The presence of two distinct degenerate FTIR band in the experimental spectrum of m_3 (PF_6^-) provides anunambiguous evidences of strong ion–ion interaction in the PS and PNC films. It appears that even at a very low clay concentration, the fraction of free anion and hence free cation available in the PNC matrix appears to be more when the data is compared with that of pure polymer salt (PS) complex provides a clear picture of enhancement in the available free charge carrier (Li^+ ions) on immediate addition of clay (5wt. %) into the polymer salt complex matrix. The fraction of free anion and hence fraction of free cations for various clay concentration. A comparison indicates relatively higher fraction of free charge carriers at 15wt. % clay concentration. Beyond this, the free anion these results clearly suggest convincing evidence for clay assisted ion dissociation effect in the polymer nanocomposite films. This feasibility due to stronger clay–ion interaction seems logical in view of the dipolar characteristics of $BaTiO_3$ clay. The variation in free anion fraction with clay concentration is expected to have a direct impact on electrical transport. Suchfraction gets reduced; however, the available free charge carrier is still more in the composite film in comparison to that of the pure polymer salt.

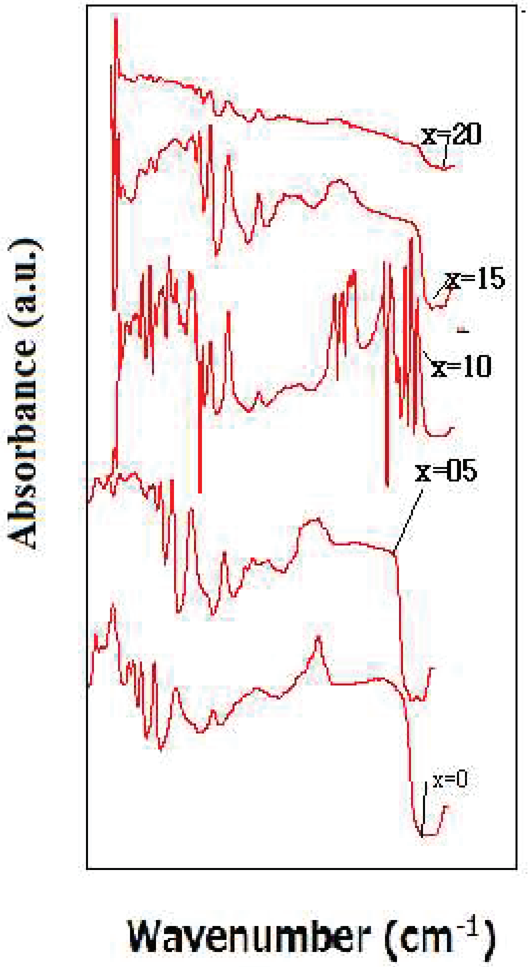

FIGURE 1 FTIR spectrum of free standing PNC films comprising of $(PEO)_{17}LiPF_6$+xwt%$BaTiO_3$

TABLE 2: Estimation of Fraction of free anion and ion pair of $(PEO)_{17}LiPF_6$+xwt%$BaTiO_3$films

Wt.% of $BaTio_3$	Free ion position	%Area	Ion pair position	% Area	Correlation Coefficient
00	936	30	954	69	0.99692588
05	940	48	957	51	0.98261451
10	949	29	971	70	0.96728110
15	928	56	951	43	0..99353079
20	946	49	959	50	0.98967508

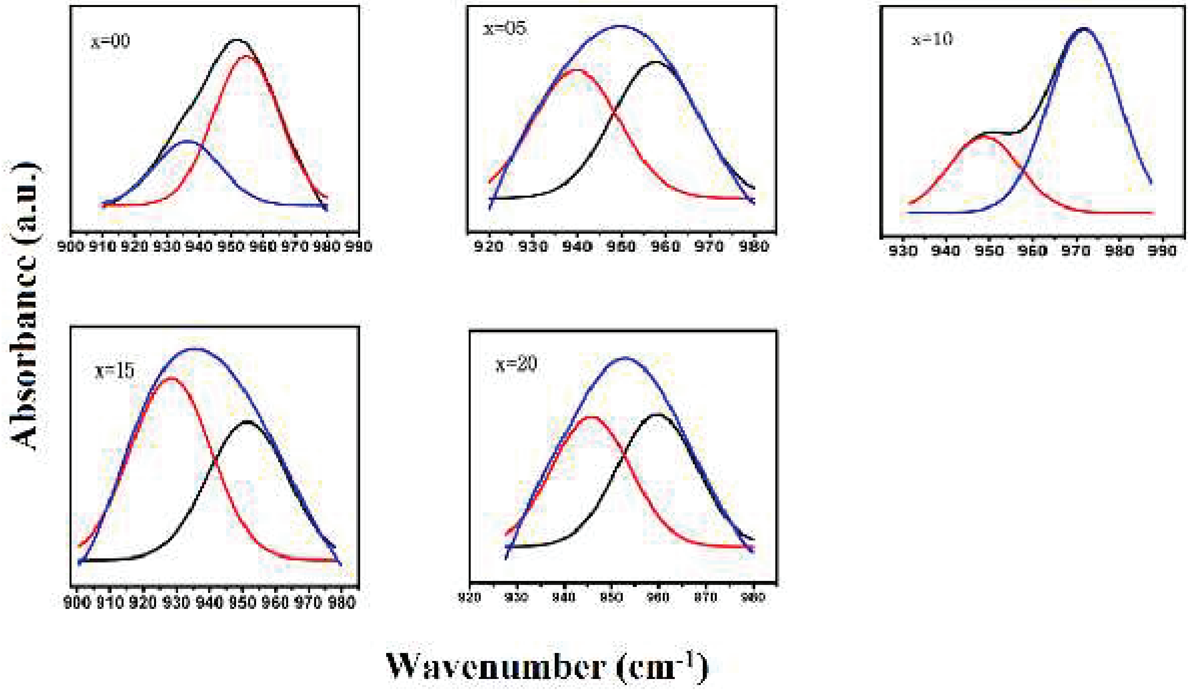

FIGURE 2: The deconvolution pattern of hexafluorophosphate anion of $(PEO)_{17}LiPF_6$+ xwt%$BaTiO_3$

Electrical Conductivity Studies

Electrical conductivity of polymer electrolyte is calculated by the equation $\sigma = (T/R_b) \times A$. The highest electrical conductivity has been achieved at 11.4×10^{-2} Scm^{-1} for 15 wt. % of $BaTio_3$. It is seen that the electrical conductivity is decreased beyond 15wt. % of $BaTiO_3$. It is may be due to decrease in the number of charge carriers which lower the segmental motion of the polymer chain.

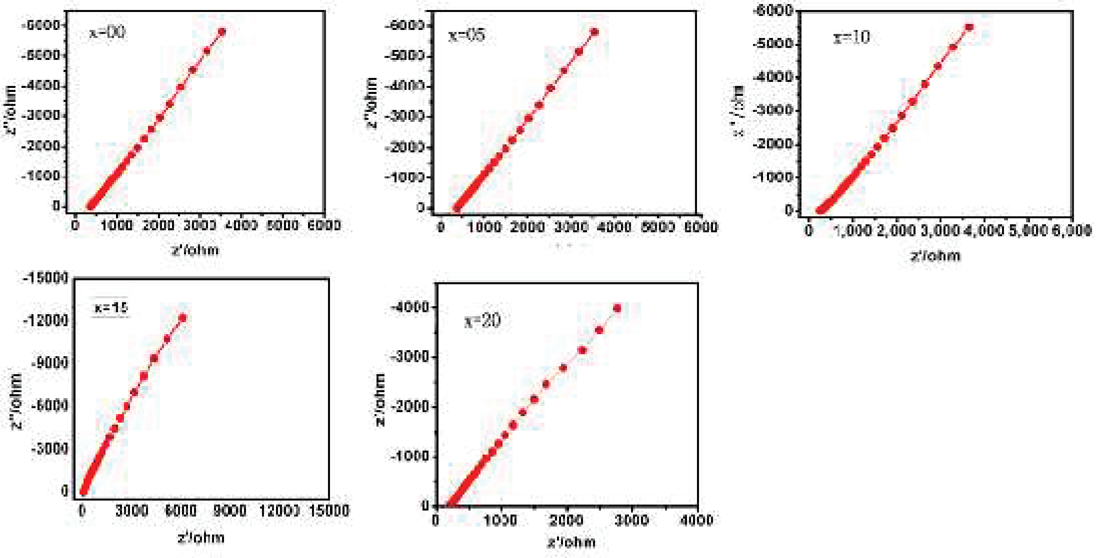

FIGURE 3: Nyquist plot of prepared PNC films comprising of $(PEO)_{17}LiPF_6$+ xwt%$BaTiO_3$

For better understanding the electrical conductivity of the prepared materials has been recorded in the table3.

Polymer Electrolyte	Nano Filler(x wt.% of $BaTio_3$)	Conductivity(s/cm^{-1})
PEO+$LiPf_6$	0	492.8×10^{-4}
PEO+$LiPf_6$	5	528×10^{-4}
PEO+$LiPf_6$	10	674×10^{-4}
PEO+$LiPf_6$	15	114×10^{-3}
PEO+$LiPf_6$	20	110×10^{-3}

CONCLUSION

PEO-based polymer electrolyte systems with various weight percent's of $LiPF_6$ have been synthesized using solution castingtechnique. The system with 15 wt. % $BaTiO_3$ exhibits a maximum conductivity of 10^{-3} Scm^{-1}at room temperature. The temperature dependence of ionic conductivity of the electrolytes obeys the VTF relationship. At the molecular level, FTIR studies provide strong evidence that there is a specific interaction between PEO, $LiPF_6$ and $BaTiO_3$. The change in peak intensity, shape and position confirms the complexation process of PEO–$LiPF_6$–$BaTiO_3$ systems.

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