Correlation of Microscopic Interaction with Electrical Conductivity in Polymer Separator of Energy Storage Devices

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Abstract In the present report solid polymer nanocomposite (PNCs) comprising of $(PEO)_{14}$ + $NaClO_4$ + wt% $BaTiO_3$ has been prepared by solution casting method. Important characterization like: FTIR (Fourier Transform Infrared Spectroscopy), and conductivity have been performed for the applicability of the prepared materials in device application. The highest conductivity of the prepared polymer nanocomposite materials has been estimated 1×10^{-4} Scm^{-1} for 15 wt% of $BaTiO_3$. A very fine correlation has been built among polymer-ion, ion-ion and polymer ion interaction with obtained conductivity results.

1 Historical Background and Introduction

Solid State Ionics, a big research of in the branch of Materials Science and it manages the solid materials which have quick particle transport. The ionic conductivity of these solids is high when contrasted with that of liquid electrolytes. Subsequently, they can be conceivably utilized as incredible interchanges of liquid/aqueous electrolytes to create solid state electrochemical gadgets viz. batteries [1]. The exploration in the field of Solid State Ionics envelops examinations of physical and concoction conduct of the solids with quick particle development inside of the mass and additionally their mechanical perspectives. These materials typically called as 'Solid Electrolytes' and have degree to build up all-solid-state electrochemical gadgets for e.g., Batteries, power modules, super capacitors, electro chromic shows, sensors photograph electrochemical sunlight based cells (PESCs) [2]. Ionic ally directing solid polymeric movies have been used in numerous

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enerplogy related divisions like high vitality thickness solid polymer batteries, PEM energy components, and super capacitors, and so forth. Such applications require an alluring conductivity esteem 10^{-3} Scm^{-1} at room temperature. With a specific end goal to accomplish this conductivity esteem, an extensive assortment of particle directing material frameworks, for example, solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs), and composite polymer electrolytes (CPEs), and so forth have been arranged and assessed. On the other hand, the vast majority of the frameworks have shown conductivity much lower than the alluring worth for gadget application under encompassing conditions. In any case, various confinements came to be recognized later, when assessed for their suitability in gadget application. The essential variable forcing extreme restriction on their relevance are (i) low encompassing ionic conduction, (ii) focus polarization, and (iii) poor strength (warm, mechanical, synthetic and electrochemical, and so forth properties). Another purpose behind lower ionic conduction is concentration polarization whose origin lies in ion association effect because of the presence of both cations and anions in the host polymer matrix [3]. The advancement of polymeric framework with high ionic conductivity is one of the principal focuses in polymer research. This is a result of their potential applications in solid state batteries. Polymer batteries have inclinations, for instance, high ionic conductivity, high energy densities, dissolvable free conduction, leak proof, wide electrochemical dependability windows, ease in technique limit and light weight. Generally, ionic conduction in polymer electrolytes is told by the unclear elastomeric stage. Polymers having the dipole moment aligned parallel to the chain shape show a dielectric relaxation because of the end's variance to-end vector of the chains. The investigation of dielectric relaxation in solid polymer electrolytes is an intense methodology for acquiring data with respect to the qualities of ionic and atomic collaborations. The dielectric parameters connected with relaxation procedures are of specific centrality in particle leading polymers where the dielectric steady assumes a principal part, which demonstrates the capacity of a polymer material to dissolve into salts [4]. The frequency-dependent conductivity and dielectric relaxation are both sensitive to the motion of charged species and dipoles of the polymer electrolytes. Winters gill and Fontanilla, studied low-frequency dielectric parameters of polyethylene oxide (PEO) and polypropylene oxide based polymer electrolytes. The high molecular weight poly (ethylene oxide) (PEO)-based composite polymer electrolytes are emerging as the best candidates to be used as polymer matrix because of their solvation power, complexion ability and ion transport mechanism directly connected with the alkaline salt (Li^+). $\mathrm{LiPF_6}$ 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 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 [5]. A common approach is to add low molecular weight plasticizers to the polymer electrolyte system. The plasticizers impart salt-solvating power and high ion mobility to the polymer electrolytes. 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 [6]. 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. 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} Scm^{-1}. Formation of intercalated polymer nanocomposite (PNC) is considered an effective approach where ion pair formation [7]. Solid state polymer nanocomposite films deals under the area of solid state ionic devices. Solid state ionic devices are a multidisciplinary branch of science. Firstly polymer were considered to be insulator, after the discovery of ionic conductivity phenomenon in solid state has started first by Peter Wright and Michel Armand who had introduced the first newly branch of solid ionic conductors in the 1970s. These studies showed that liquid electrolyte has higher ionic conductivity compared to other electrolyte systems. This ionic liquid has several disadvantages such as leakage problem; gas formation during operation can be difficulty in handling for portable applications, which has great resulted in increasing studies conducted on solid polymer electrolyte and its potential for applications in solid batteries, electro chromic windows, sensors, fuel cell, and others. Presently, science and technology is very advanced and provide the comfort for human being [8]. With the advancement in science and technology, the demand for fuel and energy is increasing, but on the other hand power sources like fossil fuel and other power sources are very limited. Therefore we have to be mindful about new power sources like energy storable devices i.e., battery. It is a replacement of the fossil fuel. Technology has made our life luxurious and gazettes like mobiles, calculator, tabs, and paper screen are in full use. But all of them required a power source like battery, fuel cell, and capacitors. So power sources having high capacity are desirable. Many researchers are working in this direction to enhance the properties (storage capacity, life cycles) of power sources like battery, fuel cell and super capacitor. There can be no hesitation if we can say that the demand of electricity will increase in future and humans completely depend on it. In present day's batteries offer a high energy which makes life easier and handier, so use of batteries will likewise increase. Enormous use of fossil fuels leads to the greenhouse effect and environment degradation and one need to aware about these harmful effects. We have to follow technological development that uses limited energy resources more efficiently and reduces the burden on the environment. Fossil fuels are the lifeline for vehicles including surface transport and other utilities [9]. To increase the conductivity of the materials, we coat it with the thin film of carbon. It increases the cycling and safety of the battery and helps to prevent internal corrosion of the electrodes and electrolyte. The thin film provides more surface area for the intercalation of ions or electrons and increases the charging and discharging rate of battery.

2 Experimental Work

2.1 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, (<130 nm) were also purchased from sigma Aldrich, and salt $NaClo_4$.

2.2 Preparation of Polymer Electrolyte

Free standing polymer clay nanocomposite (PNCE) films were prepared using high purity (AR grade) poly (ethylene oxide) (PEO) from Aldrich (USA), salt ($NaClo_4$) 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 different weight ratios of modified $BaTiO_3$ clay. The host polymer (PEO) and salt ($NaClO_4$) were dissolved in acetonitrile at a constant ratio of ether oxygen to lithium ion (O/Na) $\sim$14:1 [10]. The polymer–salt solution was stirred for 8 h followed by the addition of $BaTiO_3$ clay. Subsequently, this viscous composite fluid was cast into a polypropylene dish and the solvent was allowed to evaporate slowly. The resulting free-standing clay based polymer nanocomposite (PNCE) films have the general formula PEO+$NaClO_4$ +wt% $BaTio_3$) where x varies from 0 (pure polymer–salt complex, (PS) to 20 wt% with respect to the host polymer (w/w) [11].

3 Experimental Technique

3.1 FTIR Spectroscopy

Fourier transform infrared spectroscopy (FTIR) Bruker Tensor-27 was used in the range from 4000 to 500 cm^{-1} in transmission mode. FTIR relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule [12]. The frequency range are measured as wave numbers typically over the range 4000–400 cm^{-1}. In FTIR the background emission spectrum of the IR source is first recorded, followed by the emission spectrum of the IR source with the sample in place. The ratio of the sample spectrum to the background spectrum is directly related to the sample's absorption spectrum. The resultant absorption spectrum from the bond natural vibration frequencies indicates the presence of various chemical bonds and functional groups present in the sample. FTIR is particularly useful for identification of organic molecular groups and compounds due to the range of functional groups, side chains and cross-links involved, all of which will have characteristic vibrational frequencies in the infra-red range was used to study the interactions between constituents of polymer and filler interactions [13]. 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 to 400 cm^{-1} in transmission mode. Impedance spectroscopy is carried out by ch instrument 760. For this sample is placed between two electrodes.

3.2 Impedance/Dielectric Analysis

Complex impedance spectroscopy(CIS) is a most important tool used mostly used in characterize the microstructure and electrical property. It can be analysis of the a.c response of a system to sinusoidal perturbation and calculation of impedance resistance for an ac circuit as a function of frequency. This spectroscopy is also very effective to study properties of intragranular and interfacial regions and their interrelations, their temperature and frequency dependent phenomena in order to separate the individual contributions from the total impedance and their interfaces with electronically conducting electrode [14, 15]. Also, it enables us to calculate the relaxation frequency, which is an intrinsic property of the sample, independent of its geometrical factors. Apart from these it also helps us to find

(i) a.c and d.c conductivity
(ii) Dielectric constant
(iii) Dielectric loss (tan δ) the frequency dependence of various impedance parameters of a material can be described via the complex permittivity (ε^*), complex impedance (Z^*), complex admittance (Y^*), complex electric modulus (M^*) and dielectric loss or dissipation factor (tan δ). They are in turn related to each other as follows:

$$\textit{Complex Impedance}:\ \mathrm{Z}(\omega) = \mathrm{Z}' - \iota\, \mathrm{Z}'' = \mathrm{Rs} - \mathrm{j}/\omega\, C_s$$
$$\textit{Complex Admittance}:\ Y(\omega) = Y' + jY'' = \frac{1}{Rp} + j\omega Cp = G(\omega) + jB(\omega)$$
$$\textit{Complex Modulus}:\ M(\omega) = \frac{1}{\varepsilon(\omega)} = M' + jM'' = j\omega C_o Z(\omega)$$
$$\textit{Dielectric Constant}:\ \varepsilon(\omega) = \varepsilon' - j\varepsilon''$$
$$\textit{Loss Tangent}:\ \tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{M''}{M'} = -\frac{Z'}{Z''} = \frac{Y'}{Y''}$$
$$\textit{Complex Resistivity}:\ \rho(\omega) = \rho' - j\rho'' = Z \times \left(\frac{C_o}{\varepsilon_o}\right)$$
$$\textit{Complex Conductivity}:\ \sigma(\omega) = \sigma' - j\sigma'' = Y \times \left(\frac{\varepsilon_o}{C_o}\right)$$

where square root of C_o Is vacuum capacitance of the cell, G is conductance and B is susceptance, now the subscripts s and p for series parallel combination of the circuits elements, respectively. Out of these parameters, the impedance and admittance plane representation provide useful information when various within the cell have different relaxation time as in the case of the solid electrolytes cells.

4 Result and Discussion

In this chapter effect of adding $BaTio_3$ with varying weight percent from nano filler on polymer have been discussed in this chapter (nanocomposite where x = 0, 1, 2, 5, 7, 10, 15, 20 and have been done from various characterizing techniques. Results obtained from FTIR, impedance spectrometer, in this chapter.

4.1 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. The FTIR spectrum of PNC films based on PEO + $NaClO_4$ + wt% $BaTio_3$ with different oregano clay concentrations (0, 1, 2, 5, 7, 10, 15 and 20) in the wavenumber region (400–4000 cm^{-1}). The characteristic absorption peak observed in the spectral pattern at the wavenumber 630, 957, 1107, 1294, 1340, 1481, 1645, 1982, and 2640 cm^{-1} are attributed to ClO_4, $\gamma(CH_2)_a$, $\gamma(CH_2)_a$, $\gamma(COC)_S$, $(CH_2)_s$, $w(CH_2)$, $\delta(CH_2)_s$, 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. It appears that even at a very low filler 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 (Na^+ ions) on immediate addition of filler (5 wt%) into the polymer salt complex matrix. The fraction of free anion and hence fraction of free cations for various filler concentration. A comparison indicates relatively higher fraction of free charge carriers at 15 wt% filler concentration. Beyond this, the free anion these results clearly suggest convincing evidence for filler assisted ion dissociation effect in the polymer nanocomposite films [16–17]. This feasibility due to stronger filler ion interaction seems logical in view of the dipolar characteristics of $BaTiO_3$ filler. The variation in free anion fraction with filler concentration is expected to have a direct impact on electrical transport. Such fraction gets reduced however, the available free charge carrier is still more in the composite film in comparison to that of the pure polymer salt (Fig. 1 and 2, Table 1).

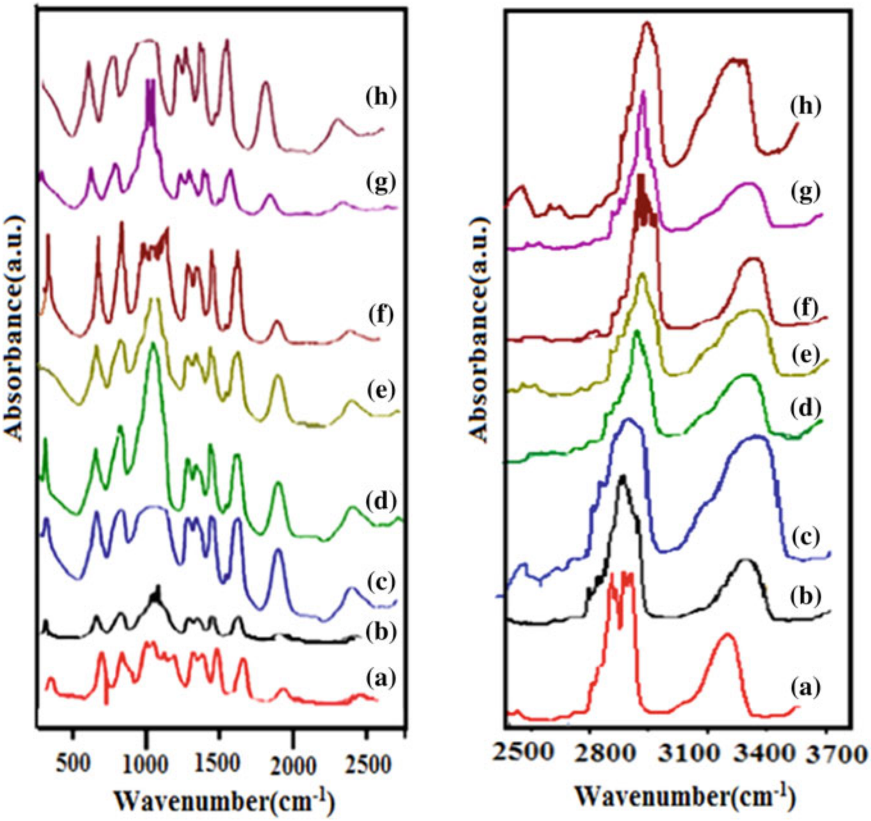

Fig. 1 FTIR spectrum for polymer electrolyte films $(PEO)_{14}NaClO_4 + x\ wt\%\ BaTiO_3$ (x = 0, 1, 2, 5, 7, 10, 15, 20)

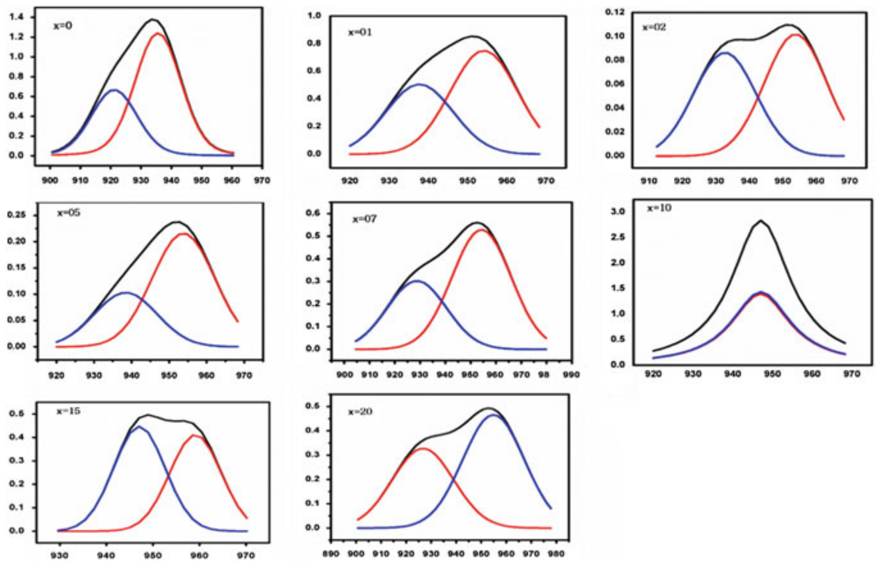

Fig. 2 deconvolution pattern of ClO_4^- in *$(PEO)_{14}NaClO_4$ + x wt% $BaTiO_3$* (x = 0, 1, 2, 5, 7, 10, 15, 20)

Table 1 Band Assignment of free standing PNC films comprising of $(PEO)_{14}NaClO_4$ + x wt% $BaTiO_3$

wt% of $BaTio_3$	Free ion position	% Area	Ion pair position	% Area	Correlation coefficient
00	921	30	953	69	0.99692588
01	938	40	953	59	0.98261451
02	932	45	954	54	0.92931351
05	928	32	951	67	0.95760567
07	929	36	953	63	0.97196511
10	931	22	946	77	0.92962323
15	931	31	954	68	0.98141858
20	935	41	958	58	0.95905313

5 Conductivity

PEO-based polymer electrolyte systems with various weight percent's of $NaClo_4$ have been synthesized using solution casting technique. The system with 15 wt% $Batio_3$ exhibits a maximum conductivity of 10^{-4} Scm^{-1} at room temperature. The temperature dependence of ionic conductivity of the electrolytes obeys the VTF relationship [18]. At the molecular level, FTIR studies provide strong evidence that

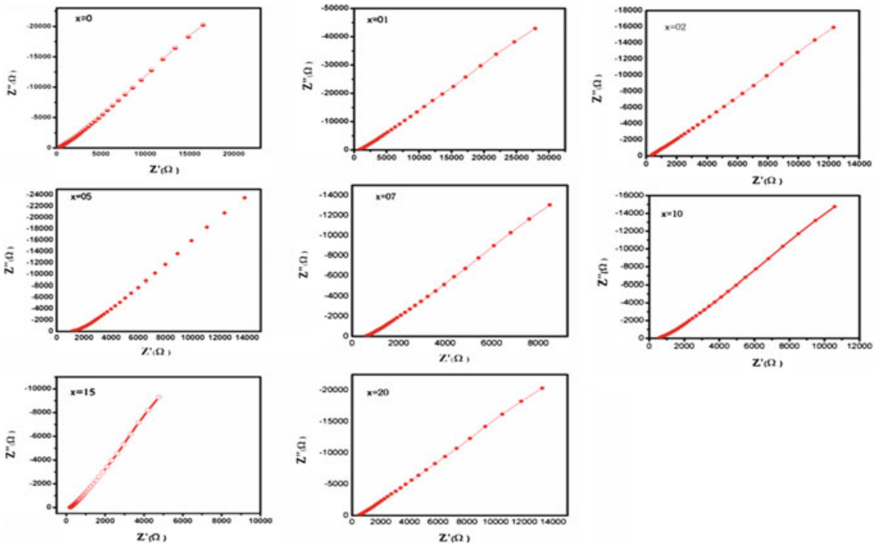

Fig. 3 Impedance plot at room temperature of $(PEO)_{14}NaClO_4$ + *wt% BaTiO₃* (x = 0, 1, 2, 5, 7, 10, 15, 20)

Table 2 Conductivity values of SPEs based on PEO-$NaClO_4$ + $BaTiO_3$

Polymer electrolyte	Nano filler (x wt% of $BaTio_3$)	Conductivity (s/cm^{-1})
PEO + $NaClO_4$	0	5.7×10^{-6}
PEO + $NaClO_4$	1	7.2×10^{-6}
PEO + $NaClO_4$	2	1.2×10^{-5}
PEO + $NaClO_4$	5	6.5×10^{-6}
PEO + $NaClO_4$	7	1.2×10^{-5}
PEO + $NaClO_4$	10	1.2×10^{-5}
PEO + $NaClO_4$	15	1×10^{-4}
PEO + $NaClO_4$	20	3×10^{-5}

there is a specific interaction between PEO, $NaClo_4$ and $BaTio_3$. The change in peak intensity, shape and position confirms the complexation process of PEO+ $NaClo_4$ + $BaTiO_3$ systems [19–21] (Fig. 3 and Table 2).

6 Conclusions

PEO-based polymer electrolyte systems with various weight percent's of $NaClO_4$ have been synthesized using solution casting technique. The system with 15 wt% $Batio_3$ exhibits a maximum conductivity of 10^{-4} 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, $NaClO_4$ and $BaTio_3$. The change in peak intensity, shape and position confirms the complexion process of PEO–$NaClO_4$–$BaTiO_3$ systems.

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