Electrical Conductivity and Ion Transport Number Analysis of Polymer Nanocomposite Films

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Abstract - **Solid state free standing polymer nanocomposite films have been used in numerous vitality related segments like: high energy density solid polymer batteries, PEM fuel cells, super capacitors, etc. Such applications require a desirable conductivity value of the order of ~10^{-3} Scm^{-1} at room temperature. A free standing transparent film of solid state polymer electrolyte based on PEO+ LiPF$_6$ with different compositions of nano sized filler (BaTiO$_3$) in weight percent (x = 0, 1, 2, 5, 10, 15, 20) is synthesized by using standard solution cast technique. Surface morphology of the prepared polymer composition is examined by field emission scanning electron microscopy (FESEM). I-V characteristics of the prepared sample have been characterized for the stability of electrochemical potential window. The transport number analysis of prepared sample has been done to separate out the contribution due to ions and electrons in the electrical conductivity results. The transference number has been estimated and found of the order of ~94%.**
*Keywords:*FTIR,ImpedanceSpectroscopy,Electrical Conductivity

I. INTRODUCTION

Solid State Ionics(SSI) is deal with big research of the branch of Materials Science and it technology with the solid materials which have quick particle transport and arise the different properties with change their electrical , mechanical and so on. 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 SSI 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]., In term of electrical conductivity 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 development of polymeric structure with high ionic conductivity is one of the main centers in polymer research. This is a consequence of their potential applications in strong state batteries. Polymer batteries have inclination, for instance, high ionic conductivity, high energy densities, dissolvable free conduction, leak-proof, wide electrochemical dependability windows, ease in method farthest point and light weight. By and large, ionic conduction in polymer electrolytes is told by the vague elastomeric stage. Polymers having the dipole moment adjusted parallel to the chain shape demonstrate a dielectric relaxation on account of the end's fluctuation to-end vector of the chains. The examination of dielectric relaxation in strong polymer electrolytes is an extraordinary system for getting information as for the characteristics of ionic and nuclear joint efforts. [4] The dielectric parameters associated with relaxation methods are of particular centrality in molecule driving polymers where the dielectric enduring expect a vital part, which shows the limit of a polymer material to break down into salts. The frequency-dependent conductivity and dielectric relaxation are both sensitive to the motion of charged species and dipoles of the polymer electrolytes. 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$^+$). However the lithium salts is one of the best ionic conduction and also used in the most common lithium salt employed in lithium-ion batteries say (LiPF$_6$) because it offers good electrolyte conductivities

and film forming. However, the ionic conductivity of PEO–lithium salts (LiX) electrolyte is of the order of (10^{-7}–10^{-6} Scm^{-1}) is not high enough for most practical applications and neglected ionic conductivity (10^{-8} Scm^{-1}). 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 fundamental point to add low sub-atomic weight plasticizers to the polymer electrolyte framework. The plasticizers give salt-solvating force and high particle versatility to the polymer electrolytes. Be that as it may, one of the greater downside of the plasticizers tend to diminish the mechanical quality of the electrolytes, at a high level of plasticization. Then again, inorganic fillers are utilized to enhance the electrochemical and mechanical properties. The fillers influence the PEO dipole introduction by their capacity to adjust dipole minutes, while the warm history decides the adaptability of the polymer chains for particle relocation [6]. They by and large enhance the vehicle properties, the imperviousness to crystallization and the strength of the cathode/electrolyte interface. The conductivity upgrade relies on upon the filler sort and size. Development of nano dispersed polymer nanocomposite (PNC) is viewed as a powerful approach where ion pair formation can be reduced at optimum level [7]. Numerous scientists are working in this heading to upgrade the properties (stockpiling limit, life cycles) of force sources like battery, energy component and super capacitor. There can be no delay on the off chance that we can say that the interest of power will increment in future and people totally rely on upon it. In present day's batteries offer a high vitality which makes life less demanding and handier, so utilization of batteries will in like manner increment. Huge utilization of fossil energizes prompts the nursery impact and environment debasement and one need to mindful about these hurtful impacts.

The present paper reports, the surface morphology /topography of the prepared nano dispersed polymer nanocomposite film. The electrical conductivity is estimated of the order of 10^{-3} Scm^{-1}. The FESEM is performed to see the surface texture of the prepared films with and without nanofillers. The transport number analysis has also been using d.c polarization technique and the transport number is found to be 0.94.

II.EXPERIMENTAL METHODOLOGY

A. Materials

High purity (AR grade) poly (ethylene oxide) (PEO) from Aldrich (USA) with average molecular weight of 600, 000, Lithium hexafluorophosphate (LiPF$_6$), nanofiller Barium Titanate (BaTio$_3$) purchased from sigma, Aldrich.

B. Preparation of Polymer Electrolyte

Free-standing polymer electrolyte films were prepared by dissolving the host polymer (PEO) in aprotic solvent

(acetonitrile) and stirring continued for 12 hr. The conducting species bulky anion (LiPF$_6$) with stoichiometry ratio (O/Li=17) were dissolved in prepared polymer solution and stirred for 12 hr. The obtained polymer salt complex again doped by nanofiller by wt % (0-20) and again stirred for 13 hr. Subsequently, this viscous composite fluid was cast into a polypropylene dishes and the solvent was allowed to evaporate slowly in vacuum. The resulting free-standing polymer nanocomposite (PNCE) films based on nanofiller concentration (wt/wt) with general formula PEO+LiPF$_6$+ x wt. % BaTio$_3$) where x varies from 0 to 20wt. % with respect to the host polymer (w/w) have been obtained. [11]

C.Characterization Techniques

Impedance spectroscopy

This is carried out by electrochemical analyzer (model No: CHI 760). For this sample is placed between two stainless steel (SS) electrodes.

Ion transport number analysis

The ionic transport number 't$_{ion}$' has been estimated using d.c
Polarization technique at a fixed applied voltage (80 mV) across the sample cell.

FESEM (Field Emission Scanning electron microscope)

Field emission scanning electron microscopy (FESEM) has been characterized to see surface morphology/topography of the prepared nano polymer nanocomposite films.

III.RESULTS AND DISCUSSIONS

Electrical Conductivity

The prepared films have been characterized via ac impedance spectroscopy. The dc bulk resistance obtained by Nyquist plot (reported somewhere else) have been used in calculation of the electrical conductivity of the films by the formula:

$$\sigma_{dc} = \frac{1}{R_b}\frac{\ell}{A}$$, where, R$_b$ is the bulk dc resistance

obtained from the Nyquist plot, ℓ is the thickness of the prepared films and A is the area of the contact electrode. A plot between the electrical conductivity vs nanofiller concentration has been plotted in the Fig 1. From figure1 it is observed that the electrical conductivity is highest (~10^{-3} Scm^{-1}) in the 15 wt. % BaTiO$_3$ among all the prepared PNC films. It may be due to the threshold concentration of the nanofiller in the PS complex films which results the minimization of concentration polarization [15].
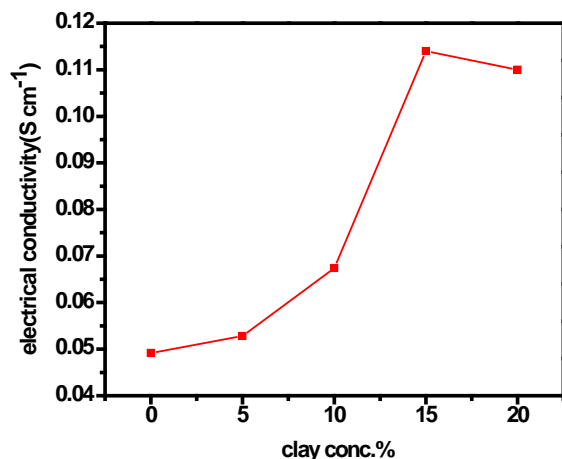
Fig.1: Variation of electrical Conductivity vs. Nano filler conc of the prepared PNC films.

Fig.2.Ion transport of $(PEO)_{17}LiPF_6$ +xwt. % $BaTiO_3$(0,15)at room temperature

Ion Transport Mechanism

The ionic transport number has been measured by using d.c. polarization technique at a fixed applied voltage (10 mV) across the sample cell. The variation in the polarization current as a function of time is shown in Fig. 2. The ionic and electronic contributions in conductivity have been estimated and are given inthe typical variation of polarization current as a function of time for both the PS and PNC films of different filler concentration recorded at ambient temperature. The pattern of variation shows a very high initial total current followed by a sharp drop in its value with the passage of time. The current ultimately attains a saturation value and remains invariant as a function of time. The initial high current is attributed to the contribution from both the ions and the electron in the sample matrix whereas the final saturation current is attributed to the contribution of electronic mobility. It is known as residual electronic current. The transport number analysis of prepared sample has been done to separate out the contribution due to ions and electrons in the electrical conductivity results. The transference number has been estimated and found of the order of 94%.
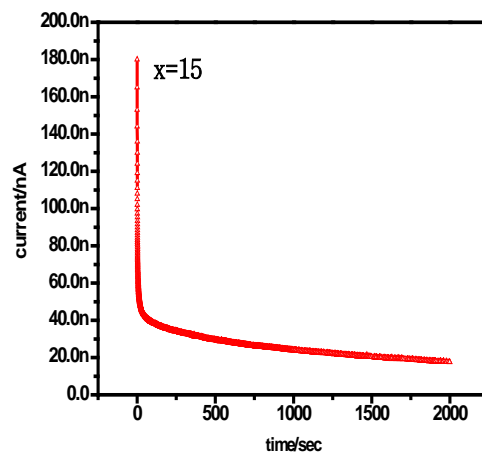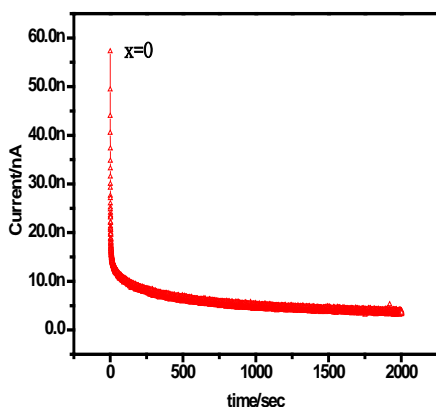

FESEM (field emission scanning electron microscope)

Field emission scanning electron microscopy images of PS complex films and 15 wt. % filler added PNC films are presented in the Fig 3. These micrograph tell that the polymeric crystalline in nature with amphorous boundary. There is no systematic change in surface morphology with polymer to salt ratio and different weight percent of filler, the detailed analysis on the change of surface morphology for PNC film can be elaborate in given below [16]. It can be observed that the surface morphology of PEO and $LiPF_6$ has a uniform surface morphology with some visible and evenly distributed small pores which may be formed during rapid evaporation of solvent under room temp drying.

The morphology structure of thin film were prepared by solution cast technique on addition of $LiPF_6$. It shows that PEO and $LiPF_6$ film contain no clay, a moderately smooth and homogenous morphology was shown. Addition of $BaTiO_3$ polymer modulates the surface microstructure of the films. This can be clearly visible that polymer salt complex indicates the surface scenery due to uneven allotment of crystalline factor primarily amorphous polymer matrix [17]. However the crystalline constituent could be related to PS complex element. The boundary shows the existence of amorphous phase [16].

On further added filler into polymer salt films leading to nanocomposite development appear transform the surface morphology and polymer topography significantly changes and improved homogeneity. Moreover the structure changes is globular like prevailing plate, with accumulation of 15% clay, it's clearly seen that there is reduce in the range of the spherutiles structure and spherutiles happen to distinct with an increase in boundary regions [18]. The quantity of white mark increased, which indicates that the particles are homogenously dispersed by change in surface morphology. The result indicate that surface morphology of PEO and $LiPF_6$, Polymer salt complex with nanofiller surface morphology PNC film shows a marked changes when compared with pure film of PEO-$LiPF_6$[19].
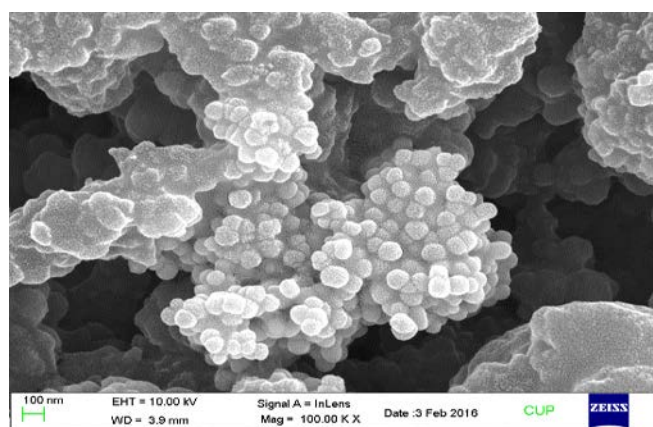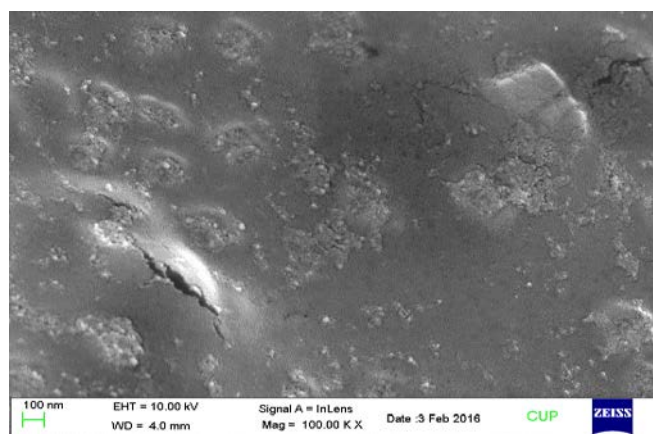
Fig.3. Field emission scanning electron Microscopy of Polymer Nanocomposite Electrolytes with pure $(PEO)_{17}LiPF_6$+wt. %$BaTiO_3$ (x=0, 15).

IV. CONCLUSION

Free standing solid polymer nanocomposite films have been prepared via standard solution cast technique. The system with 15 wt. % $BaTiO_3$ exhibits a maximum electrical conductivity of 10^{-3} Scm^{-1} at room temperature. The transport number analysis of prepared sample has been done and estimated t_{ion}=0.94. The FESEM result indicates that surface morphology of polymer salt complex shows marked changes in addition of nano filler into it.

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