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Effect of Nano filler on PEO based polymer electrolytes for energy storage devices applications

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ABSTRACT

Ionically conducting solid polymer films have been utilized in many energy related sectors like high energy density solid polymer batteries, PEM fuel cells, and super capacitors, etc.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 ($NaClO_4$) 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-filler interaction. Electrical conductivity results has been recorded using the impedance spectroscopy results which gives the estimated value of the order of ~10^{-4} Scm^{-1} of the nano ceramic doped polymeric separator which is desirable for energy storage application. A fine correlation has been established between the electrical conductivity and FTIR results analysis.

Keywords: Impedance Spectroscopy, Electrical Conductivity, Capacity

INTRODUCTION

Presently, science and technology is very advanced and provide comfort for human being. With the advancement in science and technology, the demand for fuel and energy is increasing, but on 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. rechargeable battery, supercapacitor, fuel cell etc.[1] 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 should be no hesitation if we say that the demand of electricity will increase in future and humans completely depend on it.[2] 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 which in turns about aware of 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.[3] However, they are exhaustible. The resources (Burning of petrol) are polluting the environment. So, there is need to search new energy sources having high energy density, high efficiency which can replace fossil fuels. Battery is the one of most power source that is being used for a long across the globe. This power source makes the technology so advanced as a result we live in an electronic world. A Battery is an electrochemical cell in which cathode and anode are connected with each other by a conducting material for the conduction of electrons and ions takes place through the external circuit and electrolyte respectively.[4] The mechanism of the battery working remain same in previous time as well as present time, only change comes in the materials which is used to make electrode and electrolyte. Every battery have all most same design as they are composed of three components i.e. cathode, electrolyte and anode. Cathode is a positive electrode which is associated with reductive chemical reaction and liberates lithium-ions which

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is intercalated with layered anode which is made up of graphite all this happen in charging process.[5] During discharging process, electrons and ions intercalate with cathode which is generally made up of lithium. Anode is a negative electrode which accepts the Lithium-ions from the cathode. During discharge process, it released the electrons into the external circuit. The anode contains more negative potential. Electrolyte is a material in which movement of ions (conductive) takes place from cathode to anode and vice versa.[6] It is related to ionic conductivity. It means when we use highly conducting electrolyte, ionic conductivity of battery should increase. Inside a battery the conduction of ions takes place through electrolyte from anode to cathode, it happens when charging process takes place. In the discharging time, the Lithium-ions start moving from anode to cathode and simultaneously, electrons start moving spontaneously from anode to cathode.[7] Then electric energy is produced due to the flow of electrons and due to this phenomena, external device like cell phone, watches start working. In 1991, first Li-ion battery (Nishi, Li-ion secondary battery) was introduced by Sony Corporation. The high capacity and long life of this battery makes this battery highly successful in market and now it is used frequently all over world. Now days, Li-ion battery is used to drive the vehicles for public use. The Li-ion batteries are much popular although they have some problems which should be improved i.e. poor cycle performance is one of them.[8-9] In daily life, we use Li-ion batteries in our cell phones and we see that the storage capacity of batteries start reducing with the every charge of battery.

In the present study, we prepared the polymer electrolyte films through standard solution cast technique. The prepared films characterized through, Impedance and FTIR spectroscopy. From impedance spectroscopy, the estimated value of electrical conductivity is of the order of 10^{-4} Scm^{-1}. The FTIR spectroscopy probes the polymer-ion, ion-ion interaction which is well corroborated by the impedance spectroscopy results.

EXPERIMENTAL METHODOLOGY

Free-standing polymer nanocomposite (PNC) films were prepared using poly ethylene oxide (PEO; M.W. 6×10^5; Sigma Aldrich) as the host polymer, sodium salt ($NaClO_4$; Sigma Aldrich) as conducting species and nano filler $BaTiO_3$(Sigma Aldrich) used for enriching the properties of polymer nano composites. The host polymer (PEO) and salt ($NaClO_4$) were dissolved in acetonitrile at a constant ratio of ether oxygen to lithium ion (O/Na) ~14:1.[10] The polymer–salt solution was stirred for 8h followed by the addition of $BaTiO_3$nano filler. Subsequently, this viscous composite fluid was cast into a polypropylene dishes and slides and the solvent was allowed to evaporate slowly. The resulting free-standing filler based polymer nanocomposite (PNCE) films have the general formula PEO+$NaClO_4$+wt. % $BaTiO_3$, where x varies from 0 to 20wt. % with respect to the host polymer (w/w).[11]

Fourier transform infrared spectroscopy (FTIR) (model: Bruker Tensor-27) was used in the range from 4000-400 cm^{-1} in absorbance mode. This absorption corresponds specifically to the bonds present in the molecule.[12-13] Impedance spectroscopy has been carried out by the electrochemical analyzer (model: CHI-760). The impedance spectroscopy measurement of the sample SS//PNC//SS has been performed in the frequency range from 10 Hz to 1MHz.

RESULT AND DISCUSSIONS

In the present study, the prepared polymer nanocomposite films have been characterized via FTIRand Impedance spectroscopy.

Fourier transforms 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 represents in the table 1 of PNC films based on PEO+ $NaClO_4$+xwt. % $BaTiO_3$ (x= 0,1, 2,5,7, 10, 15 and 20) in the wavenumber region (400–4000 cm^{-1}) has been characterized for the detailed analysis.[14]

Table 1. FTIR band assignment of polymer nanocomposite films based on $PEO)_{14}$ $NaClO_4$+x wt. % $BaTiO_3$ filler film

x=0	x=1	x=2	x=5	x=7	x=10	x=15	x=20	Assignment
623	618	635	628	618	635	635	650	$\nu(ClO_4^-)$
841	856	839	851	856	856	823	839	$\gamma(CH_2)_a$ +$\nu(C0C)_S$
941	950	965	943	965	956	950	965	$\gamma(CH_2)_S$ +$\nu(COC)_a$
1141	1092	1107	1101	1107	1107	1107	1124	$\nu(COC)_S$
1259	1233	1265	1250	1233	1248	1248	1265	$\tau(CH_2)_s$
1359	1345	1345	1342	1345	1345	1345	1328	$w(CH_2)_s$
1475	1454	1469	1472	1469	1469	1486	1469	δ $(CH_2)_s$
1627	1643	1660	1640	1628	1643	1660	1643	ν (C=O)
1961	1975	1958	1983	1958	1958	1975	1975	ν (C=C)
2828	2889	2874	2889	2889	2874	2889	2889	$\nu(CH_2)$
3564	3552	3553	3557	3552	3552	3552	3569	ν (O-H)

Out of large number of characteristic absorption peak observed in the spectral pattern at the wavenumber 623, 941, 1141, 1259, 1359, 1475, 1627, 1961 and 2828 cm^{-1} are attributed to ClO_4^-, $\gamma(CH_2)_S$, $\gamma(CH_2)_a$,$\gamma(COC)_S$,$(CH_2)s$,$w(CH_2)$,$\delta(CH_2)_s$,$\nu(C=O)$ and asymmetricC-Hstretching respectively. 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 nano filler (5 wt.%) into the polymer salt complex film. The fraction of free anion and hence fraction of free cations for various filler concentration are reported somewhere else.[15-18]

Polymer-Ion Filler Interaction

The effect of nanofiller on addition in polymer salt matrixhas resulted in substantial changes in the profile of FTIR spectrum of polymer (PEO) host indicatedby clay concentration dependence of the spectralchanges recorded in the wavenumber region 1200-1300 cm^{-1} attributed to CH_2 twisting, mode of the host polymer (PEO) exhibits significant modification (Figure 1).

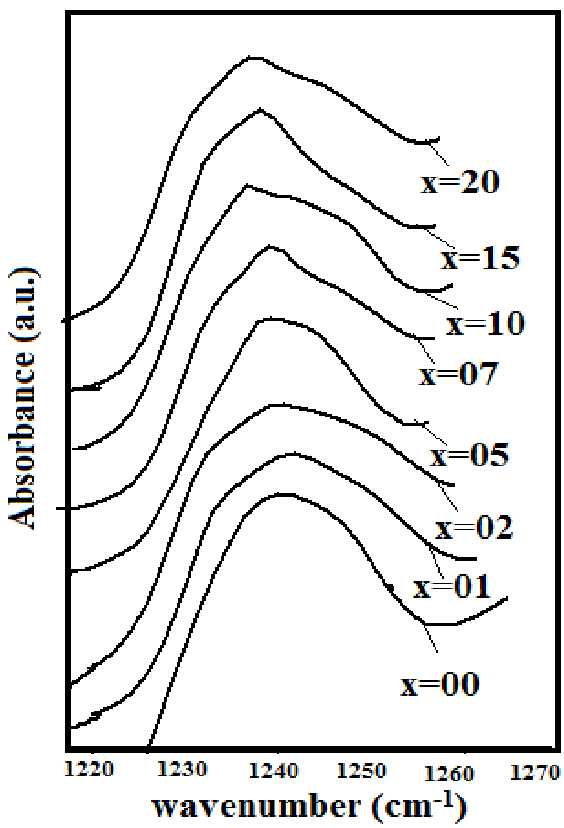

Figure 1. Changes in band profile of twisting mode of CH_2 in $(PEO)_{14}$ $NaClO_4$+xwt%$BaTiO_3$ filler films.

The splitting and marked asymmetryof the FTIR band in this region may be the effectof strong interaction between nanofiller and host polymer resulting into complex vibrational mode. Toobserve if such a change is the effect of vibration of the (CH_2) vibration of the host polymer, we have contrasted/selected the band patternin the region of interest. The selected spectrum clearly shows the modulation of bands observed at 1260 cm^{-1} for PNC film with nano filler concentration. This assignment seems logical on comparing the selected pattern with that of host matrix and PS complex films.

Electrical Conductivity Analysis

PEO-based polymer electrolyte systems with various weight percent's of nano filler concentration of $BaTiO_3$ have been synthesized and characterized via impedance spectroscopy. The impedance spectroscopy measurement was performed in the limited frequency range (10 Hz to 1 MHz). Fig 2 shows the electrical conductivity results with respect to the nanofiller concentrations. In the inset of Figure 1 the Nyquist plot is shown as a representative of the impedance pattern. The inset pattern of impedance spectroscopy for the PS films shows a small semicircle at higher frequency followed by a steep spike at low frequency region.[19-25]

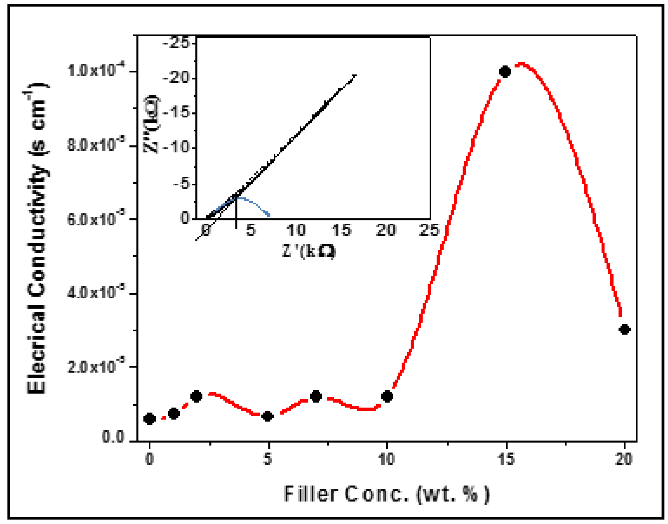

Figure 2. The spectrum of dc conductivity with respect to filler conc. Comprising of $(PEO)_{14}$-$NaClO_4$+xwt.%$BaTiO_3$ filler, Impedance spectroscopy pattern of PS complex film (Inset)

The high frequency small semicircular arc is attributed to the transport of charge carriers inside the bulk materials and comprising of the materials electrical components, resistance and capacitance are in parallel combination. The low frequency spike is attributed to the electrode double layer capacitor formation at electrode electrolyte interface.[26] The estimation of electrical conductivity from the impedance results are followed by the formula electrical conductivity $\sigma_{dc} = \frac{1}{R_b}\frac{\ell}{A}$ where, R_b is the bulk resistance, ℓ is the thickness of the plastic separator films and A is the contact area of the electrode. Figure 2 shows two maxima in the variation of electrical conductivity w.r.t. nano filler concentration which may be attributed to the presence of two types of charge carriers in the materials sample.

CONCLUSIONS

A PEO-based polymer electrolyte system with various weight percent's of nanofiller concentration has been prepared via standard solution cast technique. The prepared nanocomposite films have been characterized through FTIR and Impedance spectroscopy analysis. The FTIR spectroscopy analysis has proven microscopic interaction among the different composite components present in the materials sample. Electrical conductivity analysis from impedance spectroscopy results the maximum value of electrical conductivity has been estimated at x=15wt.% nanofiller concentrations which support FTIR results.

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