Interactions and transport properties of ionic liquid and hydroxyapatite nano-filler based sodium ion conducting gel polymer electrolyte.

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ABSTRACT

Sodium ion-conducting nanocomposite gel polymer electrolytes (NCGPEs) based on poly (vinylidene fluride-co-hexafluoropropylene) (PVdF-HFP) are presented in this study. Nano sized hydroxyapatite (HAp) filler was used as the active filler and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIMTf) ionic liquid (IL) was used as an additive. The ion/filler-polymer interactions due to dispersion of nano-filler were examined by FTIR spectroscopy. FTIR results showed that considerable changes in CF_3 and SO_3 asymmetric/symmetric vibrational modes of both polymer and IL after addition of HAp nano-filler. Among the samples investigated, addition of 7 wt.% HAp showed the maximum ionic conductivity with the value of 1.7 mS cm^{-1} at room temperature. The XRD spectra showed increasing amorphous nature of the GPEs after addition of nano-filler. The results obtained in the present study have shown that the presence of IL and addition of nano-fillers physico-chemical properties of PVdF-HFP based gel polymer electrolyte (GPE) membranes can be optimized.

1. INTRODUCTION

Rechargeable lithium batteries (RLBs) are more popular now a days due to their high energy density. However, the availability of global lithium resources and its cost have been faced severe problems for the production of energy storage devices. Therefore, finding new battery technologies is an urgent matter. The high abundance and low price of sodium metal show better substitute to lithium. Thus, sodium ion batteries make them an attractive energy storage system and a potential alternative to lithium ion batteries [1–3]. Among different parts of a battery, more attention has been paid for electrolytes since it plays a key role in transporting ions between electrodes and controls overall energy density.

In the last few years, polymer-based electrolytes have shown their potential as an alternative to the conventional liquid electrolytes in energy storage devices [4,5]. Due to the various advantages such as no internal shorting, absence of leakage and non-combustible reaction at the electrode surfaces, they have more attraction over liquid electrolytes [6–8]. Among polymer electrolytes, gel polymer electrolytes (GPEs) have been found to be of great importance because of their inimitable property of combining the characteristics of both solid and liquid electrolytes [4,9]. In general, in a gel polymer electrolyte, a large amount of liquid electrolyte is immobilized in the

solid porous network of polymer chains and liquid-like ion transport takes place through the channels provided by the solid porous matrix of the polymer. The solution cast is the most common method of preparing gel polymer electrolytes in which polymer and liquid electrolytes are dissolved in a common solvent [10,11].

In order to enhance the physical properties of porous polymer electrolytes, dispersion of micro- and nanosized ceramic fillers has been attempted. Conventionally, ceramic fillers are dispersed in polymer electrolytes to improve mechanical, thermal, and electrochemical properties [12–14]. In the case of porous polymer electrolytes, these fillers may fill the pores of the polymer membrane and increases the pore density and connectivity to provide new conducting paths to ions. In the present work, nanocomposite gel polymer electrolyte (NCGPE) based on ionic liquid (IL) and hydroxyapatite (HAp) nanofiller dispersed into PVdF-HFP:NaTf membrane was prepared by solution casting technique. Various structural, morphological and electrochemical studies were performed in order to investigate the effect of nanofiller on the porous polymer:salt:IL membranes.

2. METHODOLOGY

2.1 Preparation of polymer electrolyte

Poly (vinylidinefluoride-co-hexafluoropropyline) (PVdF-HFP), average molecular weight ~400,000), IL, 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIMTf), sodium triflate (NaTf) and hydroxyapatite (HAp) nanopowder (<200 nm particle size) were procured from Sigma Aldrich. The PVdF-HFP, NaTf and HAp were vacuum dried at 90 °C for about 12 h prior to use. The gel polymer electrolyte membranes were prepared using solution casting technique (see Table 1).

2.2 Sample characterization

FTIR spectra of NCGPE membranes with different HAp concentrations have been obtained in the wave length range 500-4000 cm^{-1} using a Bruker Alpha Fourier-transform infrared (FTIR) spectrometer.

The transport properties of samples i.e. ionic conductivities were measured using the computer interfaced impedance analyzer (Solartron SI 1260) over the frequency range 1Hz – 100 KHz.

X-ray diffraction spectra were collected in order to determine the structure and crystallinity of the electrolyte samples and also raw materials. Here Rigaku Ultma 4 X-ray diffractometer was used in an angle range (2θ) of 5 to 90°, at room temperature.

Table 1. Polymer,salt, IL and nanofiller content of prepared samples

Sample Code	PVdF-HFP (wt%)	NaTf (wt%)	BMIMTf (wt%)	HAp (wt%)
M0	23	11	66	00
M4	20	09	64	07
M6	19	08	63	10
M9	16	04	60	20

3. RESULTS AND DISCUSSIONS

3.1 FTIR spectroscopy

FTIR spectroscopic analysis was conducted in order to investigate the ion/filler-polymer interactions and possible conformational changers in the host polymer due to the dispersion of HAp nanofiller. FTIR spectra of the pure hydroxyapatite and the NCGPE films with different HAp content (0-20 wt.%) are given in Fig. 1. The spectra of NCGPEs with HAp are almost similar to that of GPE without filler except two regions i.e. wavenumbers from 500-700 cm^{-1} and 900-1150 cm^{-1}. The closer inspection of pure samples and NCGPEs of those regions can observe that vibrational bands have slightly change and also appearance of new bands.
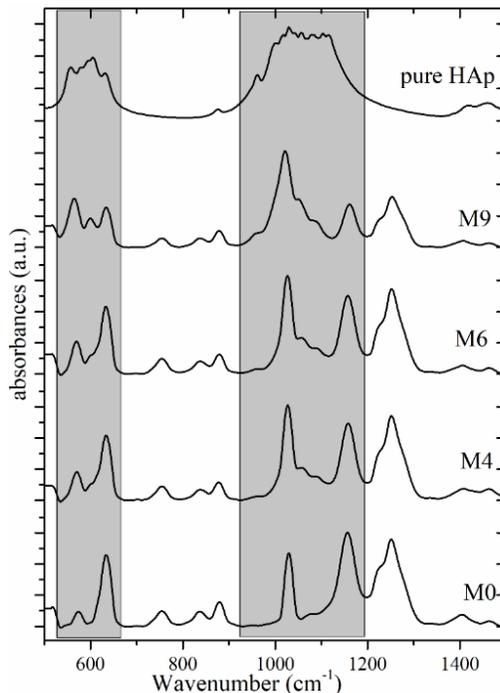
Fig. 1 FTIR spectra of the pure hydroxyapatite and the NCGPE films with different HAp content (0-20 wt.%)

In the GPE without filler (M0), bands are found at 574 and 1073 cm^{-1} are belongs to the CF_3 vibrations of pure IL and pure polymer. In addition, a band found at 1031 cm^{-1} are represented SO_3 vibrational bands of salt [15,16]. Those vibrational bands have indicated minor changes in the GPE with nanofillers. These vibrational changers in the GPE spectra (Fig. 2-c), specially CF_3 at 573 cm^{-1} is a sign of interactions between HAp nanoparticles with IL anion. This band has shifted to the lower wave numbers when HAp percentage is increased (Fig. 2-c). This is a clear indication about the structural change of electrolyte system and that leads to change ion mobility in the system.

Especially, band at 1073 cm^{-1} representing CF_3 vibrations of pure polymer have down shifted to the range of 1050-1059 cm^{-1} (Fig. 2-d). This change of PVdF-HFP is a clear indication about the structural change and lead to increase the polymer chain flexibility when HAp percentage increased.

In addition, SO_3 anion vibrational modes of salt have also changed with the addition of HAp (Fig. 2-d). This may lead to form more free Na-ions of NCGPE system resulting high ion conduction with the addition of HAp. The effect of the addition of HAp nanofiller in the structural changers of NCGPEs can be further studied after analyzing the vibrational modes of PO^{4-} anion of HAp (Fig. 2- a, b). Those vibrational bands can be found at 599, 954 and 1089 cm^{-1} in the nanocomposite GPE membranes (M4, M6 and M9). These significant changers and new interactions clearly indicate the substantial modifications of electrolyte system due to dispersion of HAp.
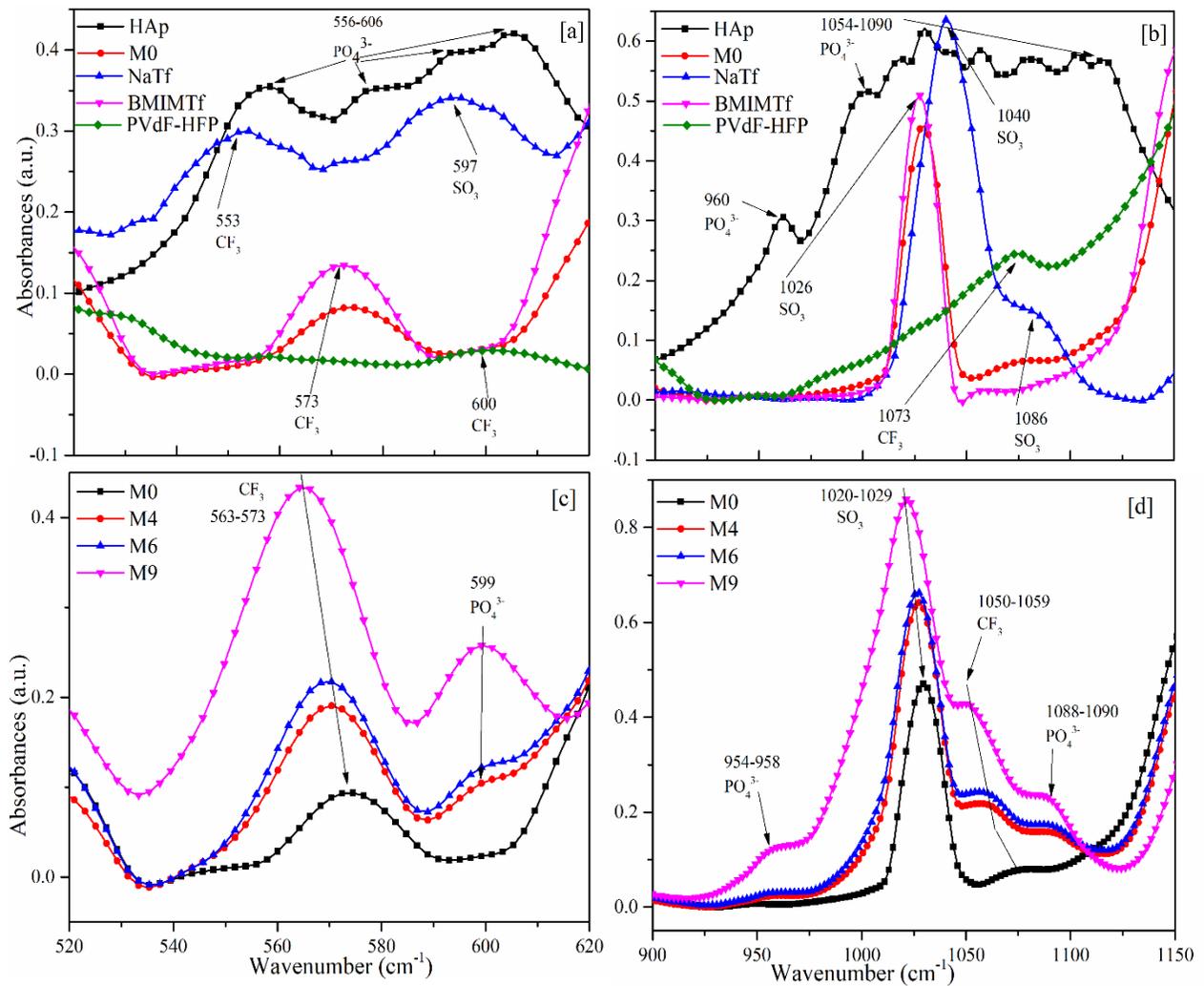
Fig.2. FTIR spectra of pure samples (a) wavenumber range 520-630 cm^{-1} (b) wavenumber range 925-1125 cm^{-1}, FTIR spectra of NCGPE with different wt% of HAp, (c) wavenumber range 520-630 cm^{-1} (d) wavenumber range 925-1125 cm^{-1}.

3.2 Ionic conductivity

The ionic conductivity of NCGPE membranes with different concentrations of HAp (7,10 and 20 wt.%) was measured in three different temperatures (room temperature, 40 ^{o}C, 60 ^{o}C). In order to confirm Na^+ ion conduction in the NCGPE films, complex impedance spectroscopy studies were performed on symmetrical SS|gel nano composite|SS cell. In cell, the gel film was in contact with a stainless steel (SS), a blocking electrode. Fig. 3 shows the comparative complex impedance plots recorded at three different temperatures. The impedance response of the cell with SS electrode shows the steep rising behaviour of an imaginary impedance in the low-frequency range, indicating the ion blocking nature of the SS electrodes (Fig.3). These observations comfirms Na^+ ion conduction in the NCGPEs.

According to the Fig. 4, it may be noted that the optimized Na^+ nanocomposite gel polymer electrolyte (i.e., with 7 wt.% HAp content) exhibits ionic conductivity of the order of $\sim 1.7 \times 10^{-3}$ Scm^{-1} at 27 ^{o}C and 3.07×10^{-3} Scm^{-1} at 60 ^{o}C, showing promise for potential application in Na-batteries over a substantially wider temperature range. Also the ionic conductivity behavior of this study is very similar to ceramic filler added other polymer electrolyte systems [17–20]. It is found that as the temperature increases, the conductivity also increases for all the compositions. As the temperature increases, the polymer expands easily and the associated free volume change takes place. Thus, ions solvated molecules or polymer segments move into the free volume. The increase in free volume leads to the increase in ion mobility and segmental mobility of the polymer electrolytes [21] . Another factor that, HAp nanofiller react with the polymer chains and these interactions lead to the reduction in the crystallinity of the polymer host. This effect could be the reason for the enhanced ionic conductivity after addition of HAp nano particles.
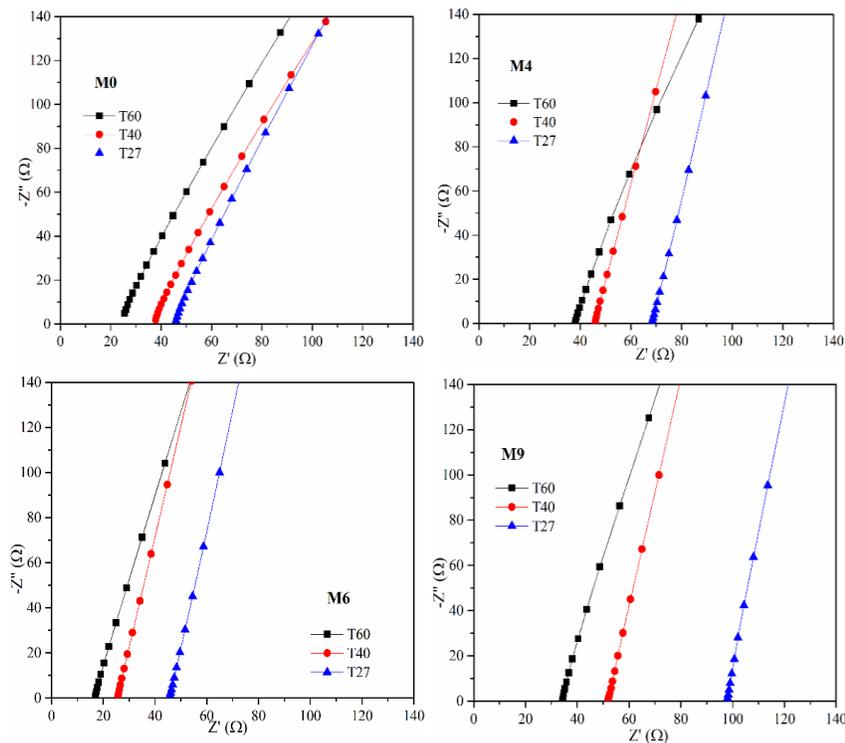
Fig.3 Nyquist plots of nanocomposite gel polymer electrolytes at different HAp nano particle loading of three different temperatures.

It is an evident that HAp nanofiller here act as a solid plasticizer and has changed the structure of polymer:salt:IL mixture observed in FTIR results, leading to enhance the ion transport properties. This structural change has mainly occurred due to the enhancement of the total amorphous phase content (see XRD results) that facilitate better environment to high ion transport [19,20]. However, the decreases in the ionic conductivity with high amount of filler content may be attributed to the formation of new ion pairs and ion clusters due to re-association of free ions with HAp nano-particles.

The temperature dependent ionic conductivity plots for the samples of gel polymer electrolyte nanocomposite films are shown in Fig.5. The non-linearity of the plots indicates that the ionic conduction seems to follows the Vogel–Tammen–Fulcher (VTF) relation which describes the transport of ions in a viscous matrix [20].

This suggests that addition of HAp nanoparticles in the polymer matrix better facilitates the migration of ions. Intercalation of polymer with HAp nanoparticles impede polymer crystallization, resulting in enhanced amorphicity of the polymer. The lowering of activation energy for Na+ ion transport upon addition of nanoparticles in the present case seems to be consistent with the increased amorphous nature of the polymer electrolytes that facilitates faster Na+ ion motion in the polymer network. The increased amorphous nature also provides larger free volume in the polymer electrolyte system as the temperature increases.

An interesting effect occurs at temperature range where at about 40 °C the conductivity of filler free polymer electrolyte (Fig.5 – M0) decays abruptly, which is associated to the fact that at this temperature the polymer softens and the consistency of the film is lost. In the case of, filler added samples (M4, M6, M9) have not indicate immediate drop as filler free GPEs, that indicates the nanocomposite gel polymer electrolytes are much stable. This is attributed due to the fact that HAp fillers limit the fluidity of the polymer and thereby increase the mechanical strength of the polymer electrolytes making them suitable materials for operation in wide range of temperatures [22].
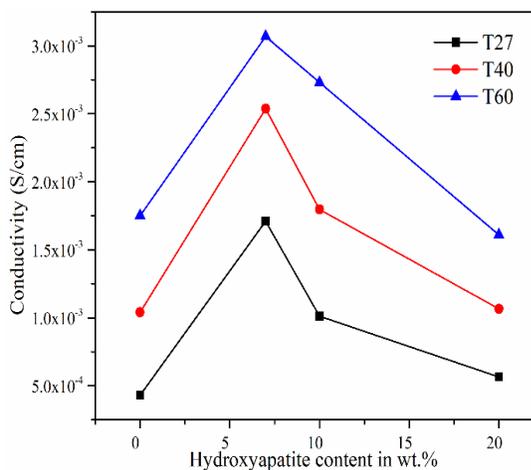
Fig. 4. Variation of ionic conductivity of NCGPEs as a function of HAp nano-filler.
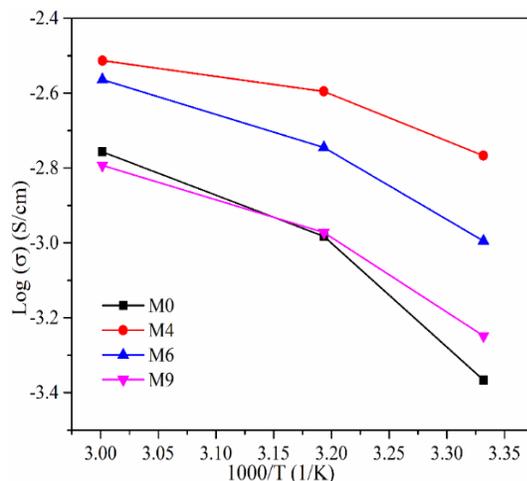
Fig. 5. The temperature dependent ionic conductivity plots of NCGPEs.

3.3 XRD spectroscopy

The XRD patterns of NCGPE membranes with different percentages of HAp nanoparticle are shown in Fig. 6. The XRD pattern of the PVdF-HFP membrane shows the typical characteristics of a semi-crystalline microstructure, i.e. the co-existence of mixed crystalline and amorphous regions with predominant peaks at 2θ values of 14.6, 17, 20, 26.6, and 38 [16]. It is obvious that the ceramic nano-particles are more crystalline and similar nature can be observed for HAp also.

It can be clearly seen that higher the filler content, the NCGPEs show more crystalline nature (M9) and when the filler content is decreased up to considerable level amorphous properties has increased. Here, The XRD spectra of the NCGPEs that include less filler content (M4) mainly indicate intense sharp peak between 10 and 30°. This peak has changed as less intense broader one when nanoparticle increased up to 7 wt.% (M4). This sample has been showed the highest ionic conductivity. It indicates that there is an optimum filler amount that can be controlled the crystallinity of NCGPE because semi-crystalline nature of PVdF-HFP will also predominant with high polymer content. However, results of this study clearly showed that transport properties i.e. ionic conductivity is directly affected by the crystallinity of the NCGPEs.
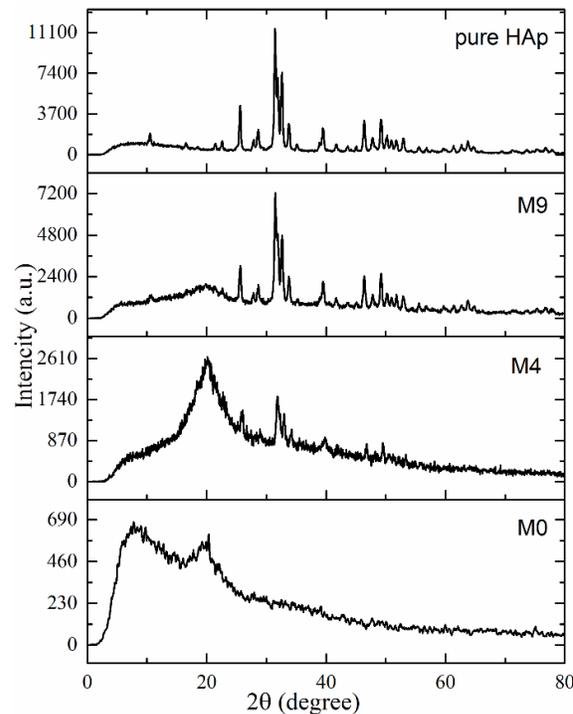
Fig. 6. XRD spectra of nanocomposite gel polymer electrolyte containing different amounts of hydroxyapatite nanoparticles

4. CONCLUSION

In this study, nanocomposite gel polymer electrolytes (NCGPEs) were prepared by solution casting technique after addition of hydroxyapatite (HAp) nanoparticles. The structure and ion interaction properties of the membranes have been investigated using FTIR, XRD and AC impedance spectroscopy. FTIR results showed that HAp nanoparticles have been interacted with electrolyte system leading to formation of new structure. Further, XRD data indicated that increase the amorphous phase content of NCGPEs after addition of HAp in low percentage level. All these changers are clear evidences for the role played by the filler to enhance the ionic conductivity of polymer:salt:IL membranes. NCGPE (i.e., with 7 wt.% HAp content) exhibits ionic conductivity of the order of $\sim 1.7 \times 10^{-3}$ Scm^{-1} at 27 $^{\circ}$C and 3.07×10^{-3} Scm^{-1} at 60 $^{\circ}$C, showing promise for potential application in Na-batteries over a substantially wider temperature range.

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