Structural, electrical and electrochemical studies of sodium ion conducting blend polymer electrolytes

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ARTICLE INFO

ABSTRACT

In the present study sodium ion conducting polymer blend electrolytes has been prepared using poly (vinylidene fluoride – hexafluoro – propylene) (PVdF-HFP), poly (methyl methacrylate) (PMMA), and sodium thiocyanate (NaSCN) salt by solution-cast technique. The highest ionic conductivity of the optimized blend polymer electrolyte system [PVdF(HFP)-PMMA (4:1)] (20 wt%)-[NaSCN (1 M)] (80 wt%) has been found to be 4.54×10^{-2} S cm^{-1} at room temperature. The temperature dependence conductivity plot shows the Arrhenius behaviour and its activation energy calculated from the plot were found to be 0.13 eV. The structural and morphological studies of polymer blend electrolyte were investigated by XRD, SEM and FTIR spectroscopy. Complex formation between polymer and salt has been confirmed by these studies. The thermal properties of optimized electrolyte system were examined by differential scanning calorimetry (DSC) techniques. The ionic transport number was calculated using d.c polarization techniques and was found to be 0.92, which shows that electrolyte system is predominantly ionic in nature. The electrochemical potential window of optimized polymer blend electrolyte was tested and observed to be ~2.8 V.

1. Introduction

The studies on polymer electrolytes are quite interesting to physicists, chemists and engineers because of their fundamental physical properties and potential application in various electrochemical devices such as batteries, fuel cells, supercapacitors, sensors and display devices [1–4]. These materials have various advantages over the liquid electrolytes, such as; corrosion, self-discharge, bulky design, miniaturization etc. They exist in crystalline and amorphous phases. The existence of amorphous phase and lower values of glass transition temperature are responsible for ion conduction in such systems. Various approaches have been adopted for synthesis of new polymer electrolytes exhibiting higher ionic conductivity at ambient temperature such as polymer blends [5–7], copolymers [8], comb branch polymer [9], cross linked networks [10,11], addition of plasticizer [12,13], addition of ceramic filler [14–16], use of a larger anion of dopant salt (acid) etc [17,18]. Out of the abovesaid techniques, polymer blending is one of the most promising and feasible ways to improve the ionic conductivity, flexibility and mechanical strength of the polymeric systems. According to this methods, when two or more polymers are mixed together and give rise to a homogeneous mixture, miscible or compatible blend is formed in which one polymer is adopted to absorb the electrolytes active species while another remains as an un-dissolved inert second phase, providing toughness to the polymer electrolytes films [12,19]. PVdF-HFP has been chosen as a host polymer in the present studies because of its appealing properties. It has high dielectric constant (ε_r) of 8·4 and existing in both the phases, amorphous and crystalline. Amorphous phase enhances higher ionic conduction in the system; meanwhile crystalline phase provides strong mechanical support to the polymer electrolytes [20–22]. In order to improve the ionic conductivity, poly(methyl methacrylate) (PMMA) has been used because it has a good amorphous and compatible nature. It is also known that PMMA gels were found to have better interfacial prop-

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erties for electrode and provides good mechanical properties with another polymer [19]. Sodium ion conducting polymer electrolytes have potential to be used as an electrolyte materials in electrochemical devices particularly batteries. Sodium metal may be considered as an alternative to lithium as a negative electrode (anode) for the fabrication of sodium-batteries because of its low cost, nontoxicity, low atomic mass (23.0) and high electrochemical reduction potential (−2.71 V vs. SHE) [15,23,24]. The proper combination of low mass and high voltage leads the possibility of employing sodium as an anode material in a rechargeable battery of high specific energy [15]. Combining all of the abovesaid properties of polymers and salt, we have chosen PVdF(HFP)-PMMA-NaSCN) based blend system for our present investigations. Further, Optimized polymer blend electrolytes has been characterized using various techniques, namely, X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transformed infra-red (FTIR), Differential scanning calorimetric (DSC), ionic conductivity, ionic transference number measurement and electrochemical potential window in present investigation.

2. Experimental details

2.1. Preparation of polymer blend electrolytes

The polymer blend electrolytes PVdF(HFP)-PMMA-NaSCN are prepared by using standard "solution cast" techniques. Polymers, poly(vinylidenefluoride-co-hexafluoropropylene), PVdF(HFP) with an average molecular weight of 4,00,000 (Aldrich), poly(methylmethacrylate), PMMA with an average molecular weight of 1,30,000 (Aldrich), inorganic salt, Sodium thiocyanate, NaSCN (Loba Chemie) has been used without further purification. N-N dimethyl formamide, DMF (Merck) has been used as a solvent. First of all the polymers (PVdF-HFP and PMMA) in different weight ratios were dissolved in a common solvent, DMF to get polymer-blend. Secondly, liquid electrolytes were prepared by dissolving suitable amount of dopant salt in a common solvent, DMF separately. Thereafter, the mixture of polymer-blend and liquid electrolytes in suitable amounts were mixed together and stirred continuously with a magnetic stirrer for 8 h at a temperature of 60 °C until homogenous solutions were obtained. Finally, the solutions were poured into glass petri dishes and left to dry at room temperature for about 35–40 days to form a free standing film (~200–300 μm thick). The films were kept in desiccators for further drying and to avoid any atmospheric contamination.

2.2. Instrumentation

The structural, thermal, electrical and electrochemical characterization of polymer blend electrolytes PVdF(HFP)-PMMA-NaSCN) has been performed with the help of different instruments techniques. X-ray diffraction (XRD) patterns of the synthesized films were recorded using Bruker D8 (Advance) diffractometer with Cu-K$_\alpha$ radiation over the Bragg angle (2θ) range of 10-60°. The scan rate was fixed at 5° min^{-1}. The surface morphology of the polymer blend electrolyte was studied with the help of scanning electron microscope (JEOL JXA − 8100 EPMA). Fourier transform infrared (FTIR) spectra of the polymeric systems were recorded using Bruker vertex 70 spectrophotometer. The thermal analysis of the blend systems were carried out using differential scanning calorimetry (DSC) with the help of Mettler Toledo DSC 822E from −70 to 175 °C at a heating rate of 10 °C min^{-1} in presence of nitrogen atmosphere. The electrical conductivity of polymer blend electrolytes were measured by means of an ac impedance spectroscopic techniques with the help of LCR Hi-Tester (HIOKI-3522-50, Japan) over the frequency range of

100 kHz to 1 Hz with a signal level of 10 mV. The samples were cut into a proper size and sandwiched between two stainless steel electrodes for taking the conductivity measurements. The ionic transport number and electrochemical stability of the polymer blend system were carried out by CHI 608C, CH Instruments, USA.

3. Results & discussion

3.1. Structural and morphological studies

Fig. 1(a–e) shows the X-ray diffraction (XRD) spectra of (a) Pure NaSCN (b) Pure PVdF(HFP) Film (c) Pure PMMA Film (d) PVdF (HFP)-PMMA (4:1) film (e) [PVdF(HFP)-PMMA (4:1)] (20 wt%)-[NaSCN (1 M)] (80 wt%) based polymer blend electrolytes respectively.

It can be seen from Fig. 1(a) that pure NaSCN salt have a sharp intense peaks at an angle of 2θ = 13.34°, 26.77°, 27.81°, 30.24°, 38.33°, 41.16°, 43.99°, 59.3° and 59.23°, which shows the crystalline nature of ionic salts. Fig. 1(b) shows three broad peaks appearing at 17.0°, 25.14° and 40.4° for the PMMA film which confirms its complete amorphous nature. Further two separate peaks found at 2θ = 20.16° and 38.21° for the PVdF(HFP) film is an indication of its semi-crystalline nature as shown in Fig. 1(c). Fig. 1(d) shows that the crystallinity as well as intensity of the host polymer PVdF(HFP) gets decreased by the addition of PMMA in the polymer-blend complex. This indicates that the two polymers PVdF(HFP) and PMMA have good compatibility with each other. Finally Fig. 1(e) shows the absence of almost all the corresponding peaks of NaSCN salt in the polymer blend complex. It gives the clear indication of complete dissolution of salt in the polymer complex and it does not contain any separate phase in the complex system. The various parameters such as scherrer length (l), d-spacing, relative peak intensity of pure salt, polymers, polymer blend and polymer blend electrolytes has been calculated from XRD plot and tabulated in Table 1. From the table, it can be seen that the lowest value of scherrer lengths of polymer blend electrolyte is achieved which conforms its amorphous behaviour.
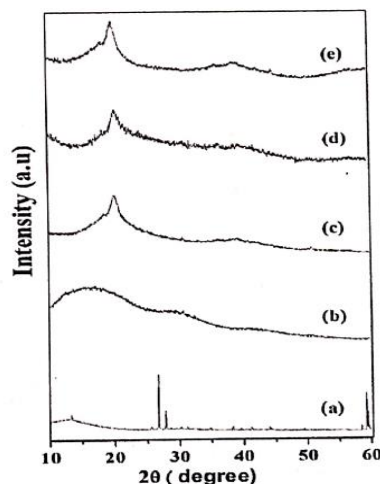

Fig. 1. X-ray diffraction (XRD) spectra of (a) Pure NaSCN, (b) pure PMMA film, (c) pure PVdF(HFP) Film, (d) PVdF(HFP)-PMMA (4:1) film, (e) [PVdF(HFP)-PMMA (4:1)] (20 wt%)-[NaSCN (1 M)] (80 wt%).

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Table 1
X-ray diffraction data of NaSCN based polymer blend electrolytes.

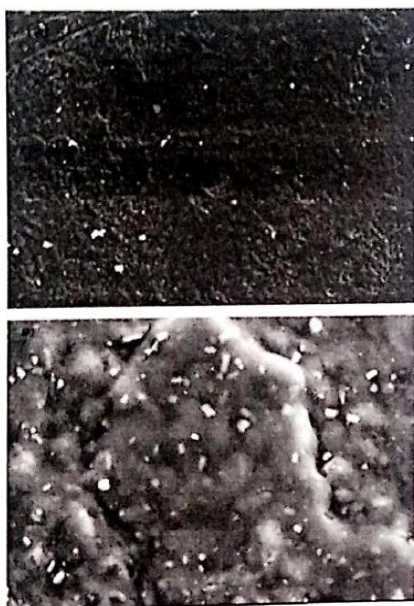| Sample	2θ (deg)	θ	d (Å)	l (Å)	Intensity
Pure NaSCN	26.77	13.38	2.48	12.95	100
Pure PVdF(HFP) Film	20.16	10.08	4.4	0.17	100
Pure PMMA Film	17.05	8.52	5.2	0.095	100
PVdF(HFP)-PMMA (4:1)	20.4	10.20	4.35	0.11	100
[PVdF(HFP)-PMMA (4:1)](20 wt%)-[NaSCN(1 M)](80 wt%)	20.16	10.08	4.4	0.11	100

Fig. 2. SEM images of (a) PVdF(HFP)-PMMA (4:1) film, (b) [PVdF(HFP)-PMMA (4:1)] (20 wt%)-[NaSCN (1 M)] (80 wt%) film.
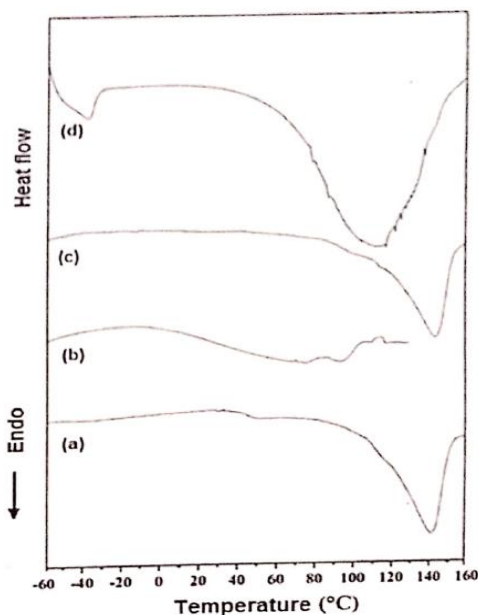

Fig. 3. FTIR Spectra of (a) pure NaSCN, (b) pure PVdF(HFP) film, (c) pure PMMA film, (d) PVdF(HFP)-PMMA (4:1) film, (e) [PVdF(HFP)-PMMA (80:20)] (20 wt%)-[NaSCN (1 M)] (80 wt%) film.

Fig. 2 shows the morphology of PVdF(HFP) – PMMA (4:1) blend film and [PVdF(HFP)-PMMA (4:1)] (20 wt%) – [NaSCN (1.0 M)] (80 wt%) polymer blend electrolytes as examined by scanning electron microscope.

It is clear that the PVdF(HFP)-PMMA blend film contains a porous texture having small pore size at the microscopic level and having highly interconnected networks as can be seen from Fig. 2 (a). Further, Fig. 2(b) shows the uniformly distributed pores which is responsible for better ionic conductivity in the [PVdF(HFP)-PMMA (4:1)] (20 wt%) – [NaSCN (1 M)] (80 wt%) polymer blend electrolyte system.

FTIR is a convenient tool to provide information about a chain structure of the polymer and their interactions with a different functional groups present in it.

Fig. 3 shows the FTIR spectra of NaSCN based polymer blend electrolyte systems. Fig. 3(b) shows the FTIR spectra of pure PVdF(HFP) polymer film. It contains several peaks at wave numbers of 435, 481, 601, 772, 879, 1177 and 1404 cm^{-1} which corresponds to the presence of vinylidene groups [20,25,26]. The presence of 435 and 481 cm^{-1} peak in both the spectra are assigned to the wagging and bending vibration of $-CF_2$, the peak at wave number 946, 772 and 601 cm^{-1} represents the crystalline

phase of PVdF(HFP) polymer [27]. The vibration peaks at 1177 and 1404 cm^{-1} represents the scissoring and stretching vibration of -CF_2 group. Similarly the peaks appear at 879 and 772 cm^{-1} indicates -C-F- stretching and out of plane C–H bending of vinylidene groups respectively. The symmetric and asymmetric stretching vibration of CH_2 molecules is observed at wave number 3022 and 2979 cm^{-1} respectively. Fig. 3(c) shows the spectra of pure PMMA polymer. The vibration bands observed at 751, 998 and 1180 cm^{-1} corresponds to rocking, wagging and twisting modes of $-CH_2$ in PMMA polymer and similarly vibration peaks appear at 844 and 1821 cm^{-1} is meant for C-O-C stretching and C=O stretching vibrations respectively [19]. broad vibration peak at 2948 cm^{-1} is because of the symmetric stretching mode of C–H molecules of PMMA. Fig. 3(e) shows the FTIR spectra of NaSCN based polymer blend electrolyte. By the addition of liquid electrolytes in polymer blends, a new peak is observed at 2065 cm^{-1}, which indicates that thiocyanate (SCN$^-$) is strongly interacting with the polymer blend. Further the vibration peaks of polymer blend observed at 481, 751, 837, 879, 1180, 1404 and 1795 cm^{-1} are shifted to 511, 749, 839, 878, 1199, 1416 and 1782 cm^{-1} respectively in the polymer blend electrolytes. The increasing or

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decreasing intensity pattern and shifting of vibrations frequency peak of pure PVdF(HFP) and PMMA polymer shows the strong interaction of two polymers and salts in a polymer blend electrolyte system. Table 2 shows some of the important peaks and vibration band of NaSCN based polymer blend electrolytes.

3.2. Thermal properties

Differential scanning calorimetry (DSC) is one of the most important techniques for thermal characterization of any polymeric materials. It helps in predicting the glass transition temperature, melting temperature and thermal stability of a material. Fig. 4 shows the DSC thermogram of NaSCN based polymer blend electrolytes. It can be seen from Fig. 4(a) clearly shows that the endothermic peak of pure PVdF(HFP) polymer is observed at 141 °C, which corresponds to the melting point of the polymer. Fig. 4(c) shows the melting temperature of polymer blend is shifted to ~142 °C, which further indicates the formation of entirely new high melting complexes. In Fig. 4(d) the broadening of endothermic peak is also observed, which indicates the possible complex formation of NaSCN based polymer blend electrolyte systems at a microscopic level. Apart from that, an additional endothermic peak is also observed at − 40 °C and is mainly attributed to the glass transition temperature of PVdF(HFP) and another peak observed at 107 °C, which is indicate to decreased crystallinity of polymer matrix in the polymeric system and leads to the improve in the segmental motion of the polymeric chain and therefore enhances the ionic conductivity of polymer blend electrolytes. Further, it is also observed the melting temperature of 141 °C of pure polymer PVdF(HFP), reduces to about 124 °C by the addition of guest polymer PMMA and salt NaSCN in host polymer PVdF(HFP). Finally, the thermal stability of the polymer blend system is observed in the range of − 37 °C to 107 °C.

3.3. Electrical characterization

3.3.1. Electrical conductivity of liquid electrolytes

In order to synthesize polymer blend electrolyte, first of all we have to synthesize and optimize liquid electrolyte. Fig. 5 NaSCN-DMF shows the variation of electrical conductivity of liquid electrolyte with respect to different molar concentration of salt. The conductivity of pure DMF is found to be ~10^{-5} S cm^{-1}. From the figure it can be seen for the liquid electrolytes, that initially the electrical conductivity increases sharply by three orders of magnitude by increasing the salt concentration upto 1.0 M concentration of each salts (NaSCN) and after that it attains a saturation level
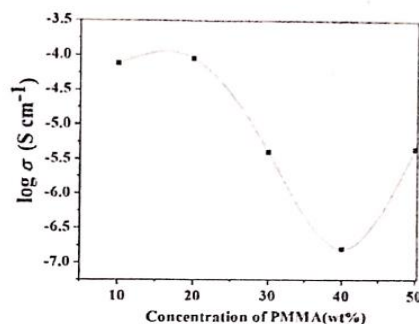

Fig. 4. DSC curves of (a) pure PVdF(HFP), (b) pure PMMA, (c) PVdF(HFP)–PMMA (4:1) film, (d) [PVdF(HFP)-PMMA (80:20)] (20 wt%)-[NaSCN (1 M)] (80 wt%) film.
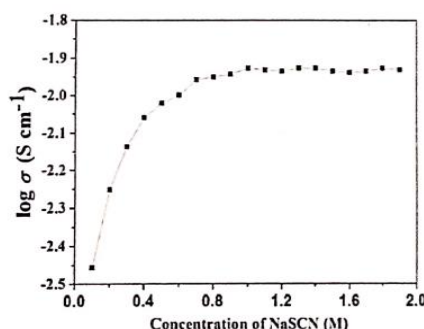

Fig. 5. Variation of electrical conductivity (σ) of liquid electrolytes (a) NaSCN-DMF as a function of varying salt concentration NaSCN respectively.

where the conductivity remains constant upto 2.0 M concentration of salts. By addition of salts beyond 2.0 M concentration, the electrical conductivity either remains constant or starts decreasing. This behaviour of liquid electrolytes can be understood in terms of ion-dissociation processes. Initially, when the salt concentration increases, the number of free mobile ions also increases which favours the enhancement in the electrical conductivity. At higher salt concentration ion-aggregation takes place due to the presence of a large number of ions and is mainly responsible for limiting the conductivity of electrolyte systems [28].

The maximum conductivity of liquid electrolyte for NaSCN-DMF system is observed to be $\sigma_{NaSCN} = 1.1 \times 10^{-2}$ S cm^{-1} at 1.0 M salt concentration of salts. Hence this concentration of liquid electrolyte has been further chosen for the synthesis of their respective polymer blend electrolytes.

3.3.2. Ionic conductivity of polymer blend electrolytes

Fig. 6 shows the electrical conductivity pattern of polymer blend, PVdF(HFP)-PMMA as a function of different weight percent of PMMA. It is observed from the plot that by increasing the PMMA concentration, initially the conductivity increases and reaches its maximum value ~8.9×10^{-5} S cm^{-1} at 20 wt% of PMMA concentration, thereafter it goes on decreasing and film is also not stable after that. XRD and DSC studies also witnessed the proper miscibility and complex formation of polymer blend at 4:1 ratio. Finally, polymer blend of PVdF(HFP)-PMMA (80:20) ratio has been chosen

Table 2
Assignment of important FTIR bands of PVdF(HFP)-PMMA-NaSCN polymer blend electrolytes.

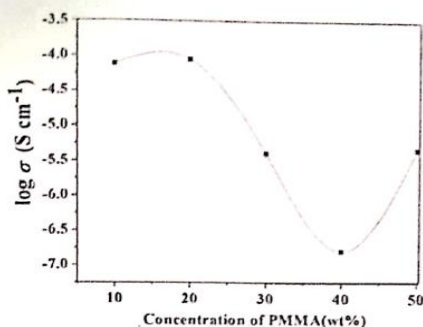|	IR Bands (cm^{-1})	Assignments
PVdF(HFP)	511	Bending vibration of -CF$_2$
	601	α-Phase
	772	Out of plane C–H bending
	946	α-Phase
	878	–C–F– stretching
	1416	Scissoring vib. –CF$_2$
	2813	Asymmetric stretch of C–H
	2933	Symmetric stretch of C–H
PMMA	749	Rocking of CH$_2$
	837	Bending vib. C–O–C
	989	Wagging vib. CH$_2$
	1073	Stretching vib. CH$_2$
	1391	twisting mode of CH$_2$
	1731	Asymmetric stretching C–O
	1782	stretching mode of C=O
SCN$^-$	2065	Stretching vib. S–C≡N

Fig. 6. Ionic conductivity of polymer blend PVdF(HFP)-PMMA as a function of PMMA (wt %).

as an optimized composition for the synthesis of polymer blend electrolytes.

Fig. 7 shows the variation of ionic conductivity of (a) PVdF (HFP)-PMMA-NaSCN polymer blend electrolytes. It can be seen from the plot that [PVdF(HFP) (80 wt%)-PMMA (20 wt %)] (20 wt%)-[NaSCN] (1.0 M)] (80 wt%) composition of polymer blend electrolytes having free-standing film exhibits maximum room temperature conductivity of about 4.54×10^{-2} S cm^{-1} for NaSCN based polymer blend systems. The maximum conductivity is due to the proper PVdF(HFP)-PMMA polymer blend formation and salt interaction that has already been confirmed by XRD spectra as well. The higher conductivity in polymer electrolyte system could be attributed to the higher amorphicity due to the steric hindrance. Higher amorphicity provides mobile Na$^+$ ion more free volume giving rise to higher conductivity of the electrolyte system. Addition of polymer blend in liquid electrolytes increases the conductivity up to 20 wt% and after that the conductivity falls-down. The low concentration of polymer blend provides the availability of more free ions due to the dissociation of ion aggregates. At lower blend concentration, viscosity is very small and hence it supports the conductivity processes. But at higher concentration of polymer blend, conductivity decreases due to higher viscosity and lower value of mobility.

3.4. Temperature dependence conductivity

One of the most important properties of polymeric system is its temperature dependence behaviour, as it provides information about their suitability in different electrochemical devices, which needs to be operated over wide ranges of temperature varying from freezing point to about 100 °C or even more for its practical applications. Fig. 8 shows temperature dependence ionic conductivity pattern of NaSCN based polymer blend electrolyte systems. From the plot it is evident that as the temperature increases the ionic conductivity also increases for both the complex systems. The increase in conductivity with temperature may be due to the decrease in viscosity and hence increased chain flexibility [29]. The conductivity pattern shows almost Arrhenius behaviour up to 70 °C which can be expressed as $\sigma = \sigma_0 \exp(-E_a/kT)$, where σ_0 is the pre-exponential factor, E_a the activation energy and T the absolute temperature in Kelvin scale. The activation energy is found to be of the order of 0.13 eV, which has been calculated by fitting the curve in lower temperature region up to 70 °C. Fig. 8. Temperature dependence ionic conductivity of (a) [PVdF (HFP)-PMMA (80:20)] (20 wt%)-[NaSCN (1 M)] (80 wt%) polymer blend electrolytes.

The variation in ionic conductivity with temperature is explained in terms of segmental motion that results in an increasing free volume of the sample and hence the motion of ionic charges. The amorphous nature of polymer blend provides free volume of the system upon increasing the temperature. Thus the segmental motion either permits the ions from one site to another or provides the pathway for ions to move. This inter-chain or intra-chain ion movements are responsible for high ionic conductivity in the polymeric systems.

3.5. Electrochemical studies

3.5.1. Electrochemical potential window

Electrochemical potential window is also referred as the electrochemical stability of polymeric system. It is one of the most important parameters, which provides information about the working voltage range of any electrochemical devices. In the present studies, the potential window of polymer blend electrolyte systems has been measured using linear sweep cyclic voltammetry techniques by sandwiching the electrolyte material in between two stainless steel (SS) blocking electrodes. Fig. 9 shows the linear sweep cyclic voltammograms of polymer blend electrolytes [PVdF (HFP)-PMMA (4:1)](20 wt%)-[NaSCN] (80 wt%) at a scan rate of
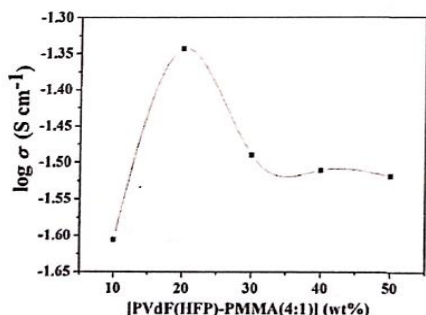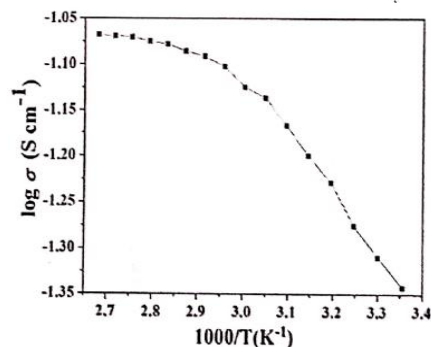

Fig. 7. Variation of ionic conductivity of blend polymer electrolyte (a) PVdF(HFP)-PMMA-NaSCN as a function of different weight percent of [PVdF(HFP)-PMMA] (4:1) polymer blend concentration.

Fig. 8. Temperature dependence ionic conductivity of (a) [PVdF(HFP)-PMMA (80:20)] (20 wt%)-[NaSCN (1 M)] (80 wt%) polymer blend electrolytes.
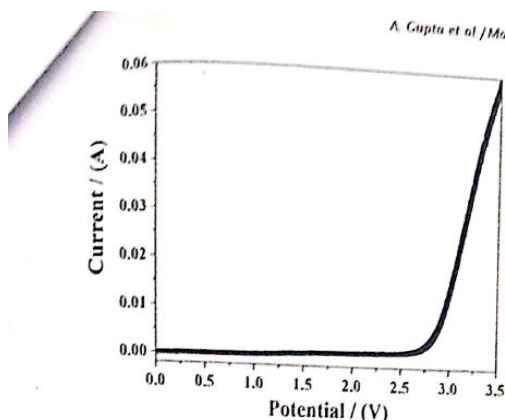
Fig. 9. Linear sweep cyclic votammetry curves of polymer blend electrolytes with scan rate of 5 mV s⁻¹ for a cells, (a) SS|[PVdF(HFP)-PMMA (80:20)] (20 wt%)-[NaSCN] (80 wt%) |SS recorded at room temperature.

$5 \, mV \, sec^{-1}$. The observed I-V characteristics are the combined effect of anodic and cathodic responses for the two electrodes configuration. It can be seen from figure the polymer blend electrolytes under present studies that the values of current goes on increasing gradually with increase in the applied voltage across the cells upto a certain voltage and after that point, current increases abruptly.

The voltage corresponding to abrupt increase in current value is called as "Electrochemical Potential Window or Working Voltage". The abrupt increase in current takes place due to the decomposition of the electrolytes. It provides information about the level of voltage up to which the electrolyte material is safe to use. In a present studies the NaSCN based polymer blend electrolyte shows the working potential window of ~2.8 V, which basically defines the range of potential upto which it can safely be used in any electrochemical devices.

3.5.2. Ionic transport number measurement

Ionic transport number measurement is one of the most important techniques to know the ionic and electronic conductivity contribution separately in the overall electrical conductivity of any materials. In the present studies, polarization method has been used for the measurement of ionic transport number for the poly-
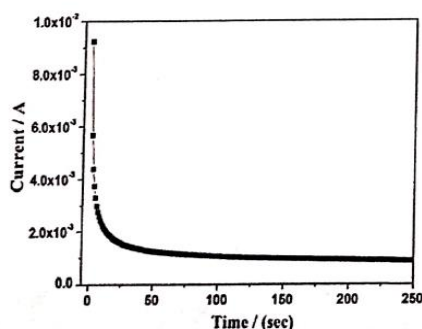

Fig. 10. Polarisation current as a function of time of polymer blend electrolytes of cell SS|[PVdF(HFP)-PMMA (80:20)] (20 wt%)- [NaSCN] (80 wt%) |SS at room temperature.

mer blend electrolytes. Fig. 10 shows the plot of polarization current as a function of time for NaSCN based polymer blend electrolytes.

The voltage applied across the cell is 1.0 V, which is within the potential window range of both the blend electrolytes. The ionic transport number has been calculated 0.92 of polymer blend electrolytes. The values of ionic transport number shows that the charge transport in the polymer blend electrolytes is predominantly ionic in nature of polymer blend electrolyte system.

4. Conclusion

A novel sodium ion based polymer blend electrolytes based on PVdF(HFP)-PMMA-NaSCN has been prepared and characterized. Different types of structural, thermal, electrical and electrochemical studies have been performed and following conclusions have been drawn.

- XRD and FTIR studies reveal the complex formation of NaSCN based polymer blend electrolytes at a molecular level.
- The surface morphology and topography image has been obtained from scanning electron microscopy studies for the polymer blend electrolyte system, which shows the porous texture and hence supports the electrical conductivity through its polymeric network.
- Thermal stability of the polymer blend electrolyte system has been performed using differential scanning calorimetry techniques, which shows that they are quite stable in a wider temperature range varying from −30 to 107 °C.
- 1.0 M concentration of NaSCN salt in DMF is found to be the optimized concentration for making liquid electrolytes having conductivity of the order of $\sim 10^{-2} \, S \, cm^{-1}$ which has been further used for the preparation of polymer blend electrolytes.
- The optimized composition of polymer blend, PVdF(HFP)-PMMA (4:1), shows the maximum conductivity of the order of $10^{-5} \, S \, cm^{-1}$ that has been used further for the preparation of polymer blend electrolytes.
- 20 wt% of polymer blend, PVdF(HFP)-PMMA (4:1) is sufficient for the synthesis of NaSCN based polymer blend electrolytes having electrical conductivity of the order of $10^{-2} \, S \, cm^{-1}$ at room temperature with acceptable mechanical strength.
- The ionic transport number and electrochemical window of NaSCN based polymer blend electrolyte has been found to be 0.92 and 2.8 V respectively.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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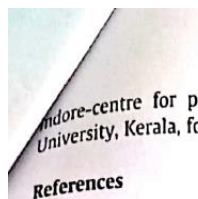Distt. Anuppur (M.P.)

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A. Gupta et al./Materials Today: Proceedings 34 (2021) 780–786

Indore-centre for providing the XRD facility and STIC, Cochin University, Kerala, for DSC measurement.

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