RESEARCH REVIEW JOURNALS
Volume-03
Issue-08
August-2018

ISSN: 2455-3085 (Online)
RESEARCH REVIEW International Journal of Multidisciplinary
www.rrjournals.com [UGC Listed Journal]

Exploration on ION Transport and Materials Properties of PEO based KNO_3-Salt Complexed Solid Polymer Electrolyte (SPE)

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ARTICLE DETAILS

Article History
Published Online: 07 August 2018

Keywords
Polymer Electrolyte, Films, Salt, Decreased

ABSTRACT

Ion conducting electroactive polymers or polymer electrolytes in thin flexible forms show great technological potentials to fabricate all-solid-state min/micro electrochemical power sources viz. batteries, fuel cells, supercapacitors etc. Pure polymeric materials are known for their poor electrical conductivity and referred to as insulators. However, polymers can be made electroactive i.e. electron, ion and/or mix conducting by complexing / dissolving electronic, ionic and / or both materials. First ion conducting solid polymer was reported in 1973 and subsequently, the first practical battery based on Solid Polymer Electrolyte (SPE) film was demonstrated in 1979 . Since then, wide variety of SPE film materials, involving different mobile ionic species viz. H^+, Ag^+, Li^+, Na^+, K^+, Mg^{2+}, etc., have been investigated. In the synthesis of majority of SPE films, reported in the past, high molecular weight polar polymer viz. poly (ethylene oxide) PEO has been used commonly / extensively as polymeric host matrix. This is due to the fact that PEO possesses relatively higher electrochemical stability as well as an exceptional ability to dissolve wide variety of salts as compare to other polymers. The polar and flexible main chain dissociates the salt and hence, carrier ions are generated. These ions can migrate through the amorphous region of the polymer via interchain / intrachain segmental motion. This paper reflects Investigations on Ion Transport and Materials Properties of PEO based KNO_3 -salt complexed solid polymer electrolyte (SPE) and NANO-composite polymer electrolyte (NCPE) films.

1. Introduction

Ion conducting electroactive polymers or polymer electrolytes in thin flexible forms show great technological potentials to fabricate all-solid-state min/micro electrochemical power sources viz. batteries, fuel cells, supercapacitors etc. Pure polymeric materials are known for their poor electrical conductivity and referred to as insulators. However, polymers can be made electroactive i.e. electron, ion and/or mix conducting by complexing / dissolving electronic, ionic and / or both materials. As mentioned, first ion conducting solid polymer was reported in 1973 and subsequently, the first practical battery based on Solid Polymer Electrolyte (SPE) film was demonstrated in 1979. Since then, wide variety of SPE film materials, involving different mobile ionic species viz. H^+, Ag^+, Li^+, Na^+, K^+, Mg^{2+}, etc., have been investigated. In the synthesis of majority of SPE films, reported in the past, high molecular weight polar polymer viz. poly (ethylene oxide) PEO has been used commonly / extensively as polymeric host matrix. This is due to the fact that PEO possesses relatively higher electrochemical stability as well as an exceptional ability to dissolve wide variety of salts as compare to other polymers. The polar and flexible main chain dissociates the salt and hence, carrier ions are generated. These ions can migrate through the amorphous region of the polymer via interchain / intrachain segmental motion. The degree of amorphousity in the polymer predominantly controls the ion conduction phenomenon in the polymer salt complexes. Larger is the amorphous region in polymeric host, higher would be the ionic conductivity. However, PEO based SPEs often exhibit low ionic conductivity ($\sigma \leq 10^{-4}$ Scm^{-1}) at room temperature, hence, not much useful for practical device applications at ambient temperature. Nevertheless, the room temperature conductivity of SPEs can be significantly increased by fractional dispersal of low dimension (µm or nm) particles of insulating / inert filler materials such as Al_2O_3, SiO_2, TiO_2 etc. in fractional amount. Such systems are known as composite polymer electrolytes in which the enhancement in the conductivity is predominantly due to the increase of amorphous region in PEO as a consequence of the dispersal of the filler particles. When nano-size filler particles are dispersed, they are referred to as Nano-Composite Polymer Electrolytes (NCPEs). Akin to 2–phase inorganic composite electrolytes, NCPEs are also 2 –phase organic composite electrolytes in which SPE acts as I^{st} –phase host matrix and nano-particles of filler material as II^{nd} –phase dispersoid. [12]. The dispersal of nano particles also brings substantial improvements in several other physical properties of NCPE films viz. mechanical stability, intimate electrode / electrolyte contacts as well as enhanced interfacial reactivity during battery application. SPE and / or NCPE films are usually casted by the traditional solution cast method. However, as mentioned in the present study an alternate procedure, referred to as hot-press (extrusion) technique, has been used for casting SPE/NCPE films [13-14]. This technique is recently getting wide acceptability amongst various research groups due to the fact that it is relatively, quicker, inexpensive / cost- effective, completely dry / solution-free procedure as compare to the traditional solution cast method. The present chapter discusses the results of various experimental studies viz. ion transport and materials properties on SPE: (PEO: KNO_3) and NCPE: [70PEO: 30KNO_3] + SiO_2 membranes casted by hot-press technique. The procedure for hot-press casting of SPE and NCPE films has already been discussed in

Chapter II. Based on the salt concentration dependent conductivity measurements, Solid Polymer Electrolyte (SPE) film composition: (70PEO: 30KNO_3), has been found to have highest ionic conductivity (σ ~ 3.98 $\times 10^{-7}$ Scm^{-1}) at room temperature [Agrawal et al 2009]. Using this SPE composition: (70PEO: 30 KNO_3) as I^{+}-phase host matrix, NCPE films have been hot-press casted after dispersing nano-particles (~ 8nm) of SiO_2 as II^{nd} – phase dispersoid. SiO_2-dependent conductivity measurements on different NCPE films revealed further that NCPE film: (70PEO: 30 KNO_3) + 5SiO_2 exhibited highest conductivity at room temperature. This has been referred to as Optimum Conducting Composition (OCC) NCPE film. The ion transport property has been characterized in terms of basic ionic parameters viz. conductivity (σ), mobility (μ), mobile ion concentration (n) and ionic transference number (t_{ion}). These parameters have been determined experimentally using ac/dc techniques. The characterization of morphological, structural, spectroscopic and thermal properties has been done on NCPE OCC film using SEM, XRD, FTIR and DSC techniques respectively.

1.1 ION Transport Property Studies

1.1.1 SALT /DISPERSOID CONCENTRATION DEPENDENCE OF Σ, μ, N IN SPE & NCPE FILMS

The variation of room temperature conductivity as a function of salt concentration in different hot-press casted SPE films has been shown in Fig. 1.1. It can be noted that conductivity increased rapidly with the increase in salt concentration up-to 30 wt. (%). However, on further addition of salt by 40, 50 wt. (%), the conductivity decreased slightly. SPE films beyond 50 wt. (%) appeared brittle and less stable. SPE film: (70PEO: 30 KNO_3) exhibited highest conductivity (σ) ~ 3.98 × 10^{-7} Scm^{-1} at room temperature (27°C). In Fig. 1.1, the initial increase in σ was attributed to the dissociation of KNO_3 salt, resulting thereby into generation of carrier ions. The complexation of the salt in PEO may also results into the increase in amorphous region in polymer which, in turn, may give rise to increased ionic mobility and hence, the increase in ionic conductivity. The decrease in σ (beyond 30 wt. %) may be due to association / aggregation of ions which might have resulted into decrease in the number of mobile ions. This SPE composition: (70PEO: 30 KNO_3) has been selected as I^{st}-phase host for casting Nano-Composite Polymer Electrolyte (NCPE) membranes: [70PEO: 30 KNO_3] + x SiO_2, after dispersing fractional amount (x in wt.%) of SiO_2 nano-particles as II^{nd}-phase, as mentioned. Further, SiO_2-concentration dependent conductivity has been measured at room temperature on different NCPE films and plotted in Fig. 3.2.

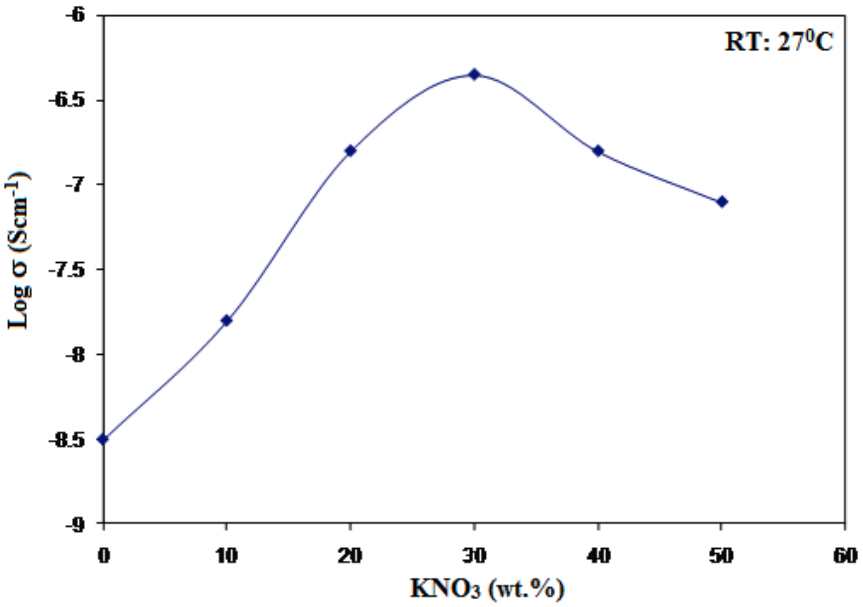

Fig. 1.1 Salt Concentration dependent conductivity variation for hot-press casted SPE films (PEo : KNO_3)

It can be clearly noticed that two σ – maxima [at x = 1 & 5 wt. (%)] appeared in 'log σ – x' plot. The conductivity of NCPE film for x = 5 wt. (%) was relatively higher than that for x = 1 wt. (%). Hence, this NCPE film: (70PEO: 30 KNO_3) + 5SiO_2, with room temperature conductivity (σ) ~1.07 $\times 10^{-6}$ Scm^{-1}, has been referred to as Optimum Conducting Composition (OCC). An enhancement of more than 3-fold in the room temperature conductivity of SPE host has been obtained simply by dispersing SiO_2 nano-particles. Besides this, NCPE OCC film appeared relatively more stable / flexible mechanically. The existence of two conductivity maxima has been noticed for majority of NCPE films reported in the past and explained on the basis of two percolation model, suggested by [15]. According to them, the σ-maxima corresponds two kinds of transport mechanism operative in the system. The first σ – maxima can be related to the usual salt dissociation while the second σ-maxima as well as the conductivity variation around this ratio is related to the well-known 2-phase composite effect and can be explained on the basis of space-charge and / or percolation model [16-20]. The reason for conductivity increase in NCPE OCC film was explored by measuring the ionic mobility (μ) and mobile ion concentration

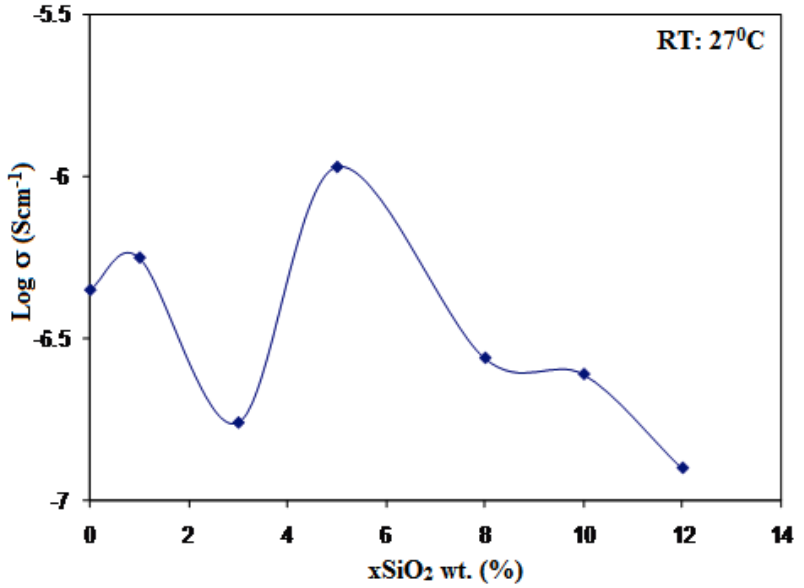

Fig. 1.2 'Log σ-x' plot for hot-press casted NCPE films : (70 PEO : 30 KNO_3) + x SiO_2

(n) In different NCPE films as a function of SiO2 filler concentration. As already mentioned in Chapter 2, 'μ' can be evaluated employing a d.c. polarization Transient Ionic Current (TIC) technique [21-22]. Subsequently, 'n' can be known by substituting μ & σ data in the basic equation: n = σ/ μq. Fig. 3.3 shows 'log μ – x' and 'log n – x' plots for NCPE films: [70PEO: 30 KNO3]: x SiO2. One can clearly notice that these plots look almost akin to 'log σ-x' plot of Fig. 1.2 with maxima appearing for both μ and n at x = 5 wt. (%). Hence, σ-enhancement in NCPE OCC film can be attributed obviously to the increase in both μ & n. It is worth mentioning here once again that the values of μ & n obtained by this method are average values which include the contributions of both kinds of mobile ions (cations + anions).

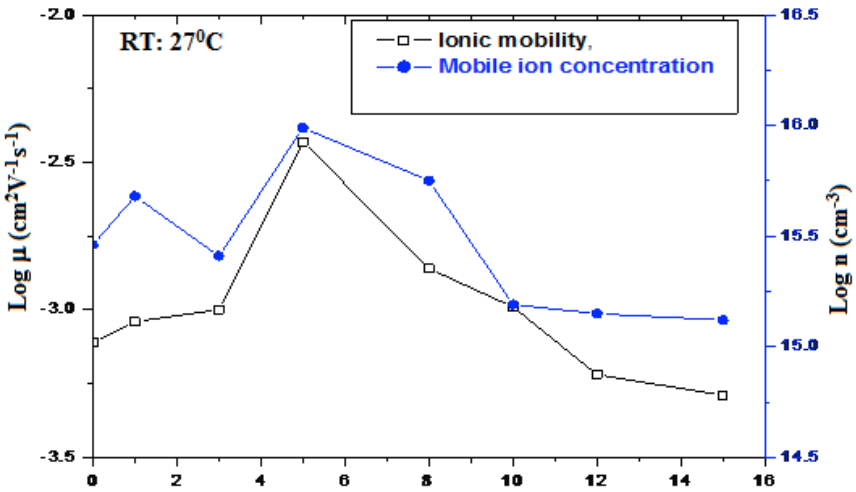

Fig 1.3 'Log μ-x' & 'Log n-x' plots for NCPE films : [(70 PEO : 30 KNO_3) + xSiO_2]

The room temperature values of these ionic parameters: ionic conductivity (σ), ionic mobility (μ) and mobile ion concentration (n) for both SPE film: (70PEO: 30KNO3) and NCPE OCC film: (70PEO: 30KNO_3) + 5SiO_2 are listed in Table 1.1 along with the activation energy (E_a), total ionic transference (t_{ion}) and cationic transference (t+) numbers, to be discussed later.

Table 1.1: Room temperature (27°C) values of some basic ionic parameters viz. ionic conductivity (σ), ionic mobility (μ), mobile ion concentration (n) along with activation energy (E_a), ionic transference (t_{ion}) and cationic transport (t+) numbers.

Film	σ (Scm^{-1})	μ ($cm^2 V^{-1} s^{-1}$)	n (cm^{-3})	t_{ion}	E_a (eV)	t+
Pure PEO	3.2×10^{-9}	-	-	-	-	-

SPE film: (70PEO: 30 KNO_3)	3.98×10^{-7}	1.37×10^{-3}	1.81×10^{15}	0.98	0.34	0.27
NCPE OCC Film: (70PEO: 30 KNO_3) +5 SiO_2	1.07×10^{-6}	2.89×10^{-3}	2.31×10^{15}	0.98	0.31	0.36

1.1.2 TEMPERATURE DEPENDENCE OF Σ, μ, N IN SPE AND NCPE OCC FILMS

Fig. 1.4 shows 'log σ – 1/T' plot for different NCPE films including the filler free Ist – phase SPE host. The conductivity of SPE/NCPE films initially increased linearly with the increase in the temperature followed by a slight upward change in the slope ~ 65-70°C then increased linearly again afterward. The upward jump in σ can be attributed to the well-known semi-crystalline amorphous phase transition of polymer PEO which occurs at temperature (T_m) ~ 65°C. 'Log σ – 1/T' plot below T_m follows Arrhenius type behaviour, hence, can be expressed by equation:

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad \text{..... (3.1)}$$

where σ_0 is the pre-exponential factor and E_a is the activation energy. E_a can be computed by least square linear fitting of the data. E_a values ~ 0.34 and 0.31 eV were obtained for SPE host and NCPE OCC films respectively. Fig. 1.5 shows 'log μ – 1/T' and 'log n – 1/T' plots for NCPE OCC film. It can be noticed that μ remained almost unaltered while n increased with increasing temperature. This is indicative of the fact that as the temperature increased, more carrier ions become available for conduction. Besides determining ionic mobility (μ) by TIC techniques, one can also evaluate the total ionic (cationic + anionic) transport number (t_{ion}) from 'current-time'plot. The results of t_{ion} measurement by dc TIC technique as well as the cationic transference number (t+) by combined ac/dc method are presented below.

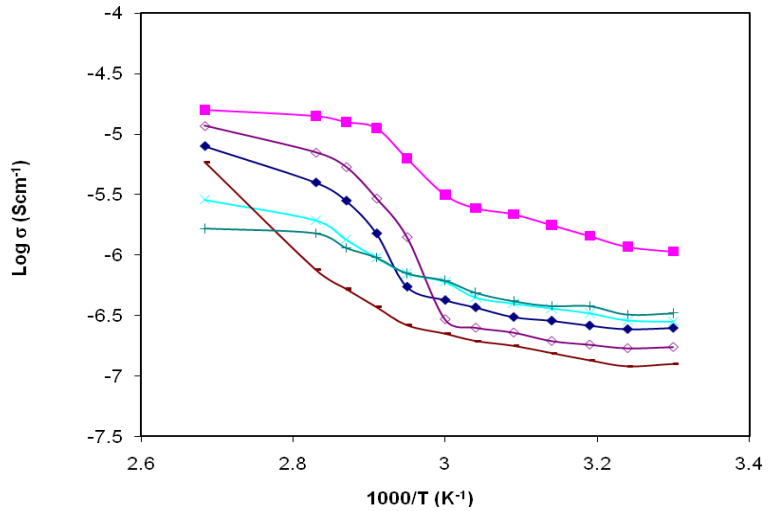

Fig. 1.4: Log σ-1/T plots for different NCPE membranes: (1-x) (70PEO: 30KNO_3) +xSiO_2, x = 0 (♦) (filler free SPE host), x = 1 (-), 3 (◊), 5 (■), 8 (x), 10 (+).

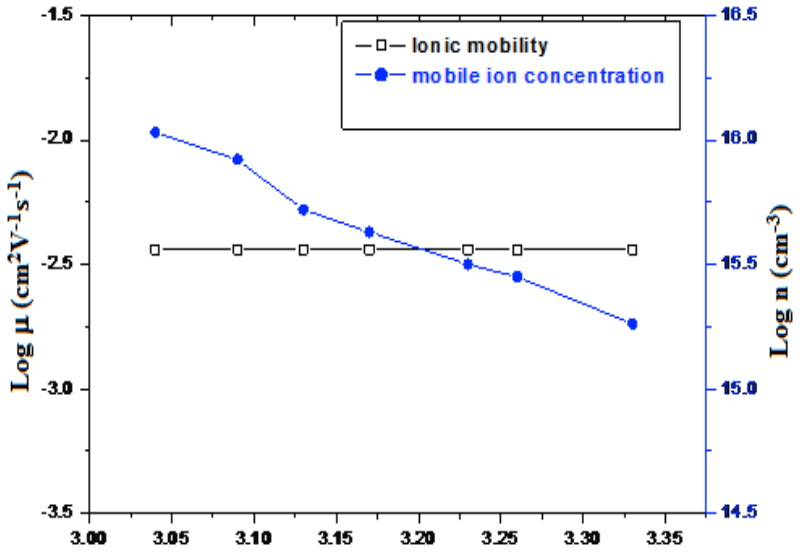

Fig. 1.5: 'Log μ–1/T' (□) & 'log n – 1/T' (•) plots for NCPE OCC film : (70 PEO : 30 KNO_3)+5SiO_2

1.1.2 TOTAL IONIC TRANSFERENCE (T_{ION}) AND CATIONIC TRANSFERENCE (T+) NUMBER MEASUREMENT IN SPE AND NCPE OCC FILMS

Fig. 1.6 shows a typical TIC plot for NCPE OCC film sandwiched between two SS blocking electrodes. The total current approached almost to zero in about 2 hours. This clearly indicated the fact that all the mobile ions (cations + anions), in the electrochemical cell SS // NCPE OCC // SS subjected to an external dc potential, got polarised completely at the respective electrode / electrolyte interfaces. Similar TIC plot was received for SPE film also. From the initial and final current values, t_{ion} ~ 0.98 was obtained for both SPE and NCPE films. Table 1.1 listed t_{ion} value for both SPE and NCPE OCC film. The value of t_{ion} close to unity is indicative of the fact that both SPE and NCPE OCC film materials are predominantly ion conducting. However, the cationic transport number (t+) is a key parameter as regards to the performance of the electrolyte in a battery is concerned. Hence, in order to evaluate K^+ - ion transport number in SPE and NCPE OCC films, a combined ac/dc technique, as suggested by Evans et al [Evans et al 1987] and discussed in Chapter 2, has been used. The polymer electrolyte film, placed between two K-metal electrodes, was subjected to an external fixed dc potential (ΔV) = 0.5 V for 5 hrs. The cell resistance of the film sample was measured before and after polarization using IS technique. The complex impedance (Z'-Z'') plots for the cell before and after polarization are shown in Fig. 1.7. From the two semi-circles (depressed with center below the real axis), the values of cell resistances: R_b and $R_b + R_i$, before and after polarization respectively, have been obtained. The variation of the cell current during polarization was also monitored and shown in Fig. 3.8. This plot provided the value of initial (I_0) and final (I_s) currents. Finally, the cationic (K^+) transference number (t_+) has been evaluated with the help of following equation [Evans et al 1987]:..... (3.2)

$$t_+ = \frac{I_s (\Delta V - R_0 I_0)}{I_0 (\Delta V - R_s I_s)}$$

Substituting the data in the above equation, t+ ~ 0.27 and 0.36 were obtained for the SPE host and NCPE OCC films respectively. It is worth mentioning here that for almost all the polymer electrolyte materials reported so far, the value of exhibited cationic transference number ≤ 0.5.

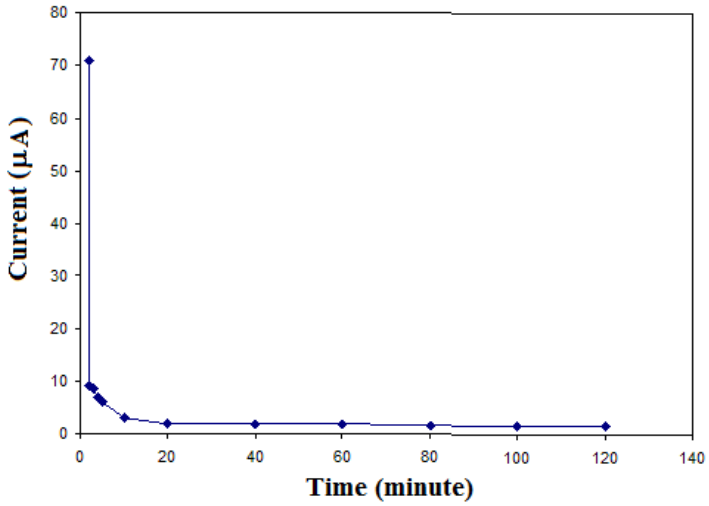

Fig. 1.6 Variation of polarizing current as a function of time in a typical cell : SS//NCPE film//SS

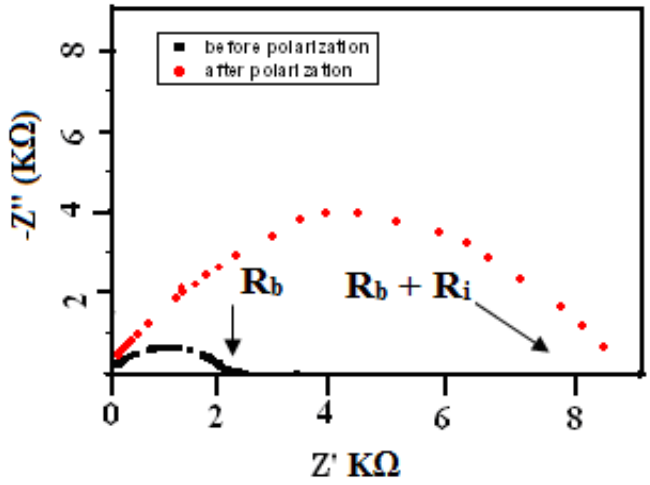

Fig. 1.7: Complex Impedance (Z'-Z'') plots before and after the polarization of the cell K // NCPE OCC film // K

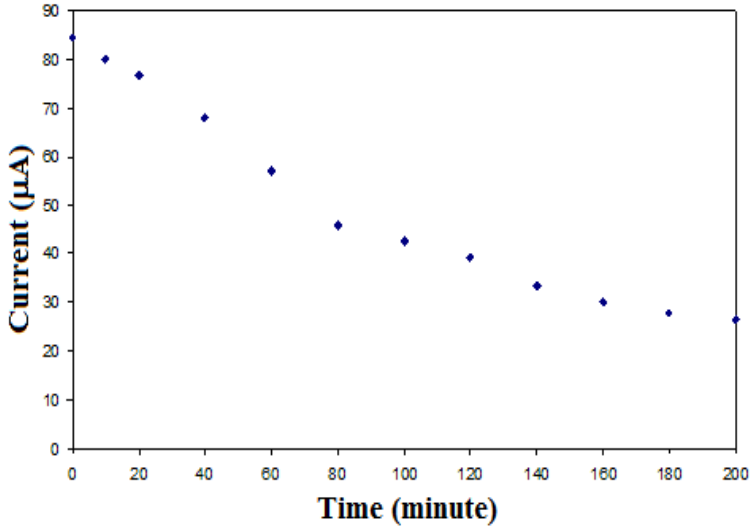

Fig. 1.8: Polarization current versus time plot for the cell: K//NCPE OCC film//K.

1.2

Materials Property Studies

Fig. 1.9 shows SEM micrographs for hot-pressed SPE: (70PEO: 30 KNO_3) and NCPE OCC: (70PEO: 30 KNO_3) + 5 SiO_2 films. The pictures of surface morphology clearly indicated a uniform distribution of salt as well as SiO_2 particles in the respective films. Fig. 1.10 (a-d) illustrates the XRD patterns for films of pure PEO, SPE (I^{st}-phase host) and NCPE OCC as well as polycrystalline powder of KNO_3. On comparing these patterns, one can note obvious changes in the peak patterns. This is a clear indication of the complexation of salt in the polymeric host. Many of the peaks belonging to the salt appeared (although overlapped) in the XRD pattern for SPE & NCPE films. The peaks look slightly displaced with decreased intensity. The positions of two main peaks of PEO remained almost intact even after complexation of salt in PEO (in SPE) and dispersal of SiO_2 (in NCPE). However, the intensity of PEO main peaks has been decreased substantially specially in NCPE film. This is indicative of decrease in degree of crystallinity and / or increase in degree of amorphousity in PEO. FTIR spectroscopic responses for films of pure PEO, SPE (I^{st} – phase) and NCPE OCC are simultaneously shown in Fig. (a-c) for direct comparison. The main spectral features of pure PEO viz. broad absorption bands corresponding to symmetric / anti symmetric stretching modes (C-H) of CH_2 group around 2950-2800 cm^{-1}; broad vibrational bands corresponding to symmetric / anti-symmetric C-O-C stretching modes around 1100-1000 cm^{-1}; gauche (OC-CO) conformation in between 950-800 cm^{-1} etc. are all present in the spectra of SPE & NCPE OCC films. However, slight variations in the shapes can be noticed which may be due to the complexation of salt in the polymer. No substantial changes have been noticed for the presence of SiO_2 filler particles which may probably be due to the fact that dispersal of SiO_2 in the system in small fraction.

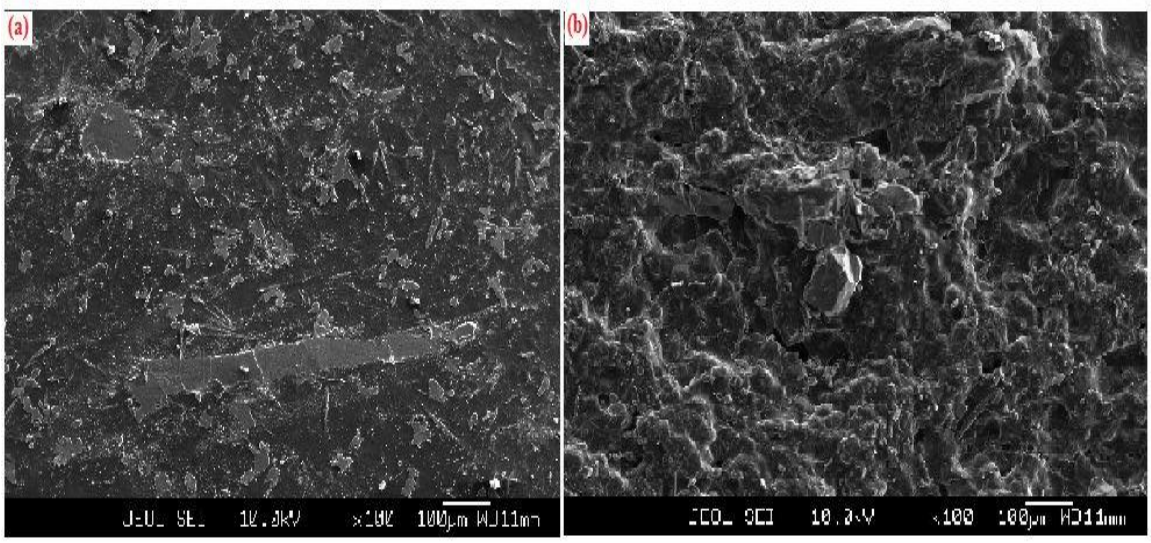

Fig. 1.9: SEM micrographs for (a) SPE: (70PEO: 30 KNO_3) (b) NCPE OCC: (70PEO: 30 KNO_3) + 5 SiO_2

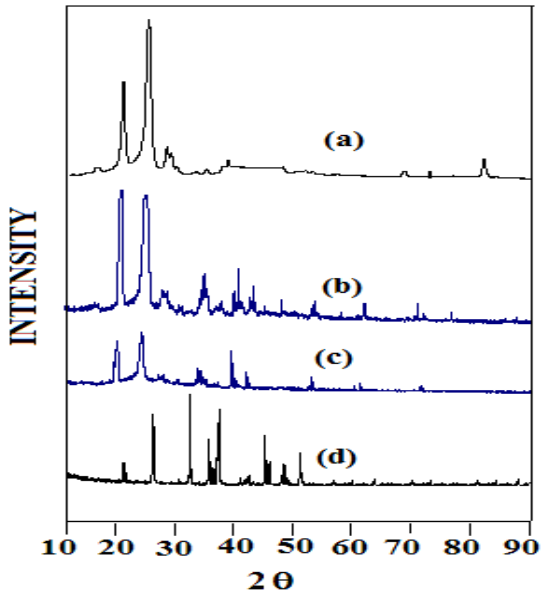

Fig. 1.10: XRD pattern for (a) Pure PEO film, (b) SPE host film: (70PEO: 30KNO_3), (c) NCPE OCC film: (70PEO: 30 KNO_3): 5SiO_2, (d) poly-crystalline powder: KNO_3.

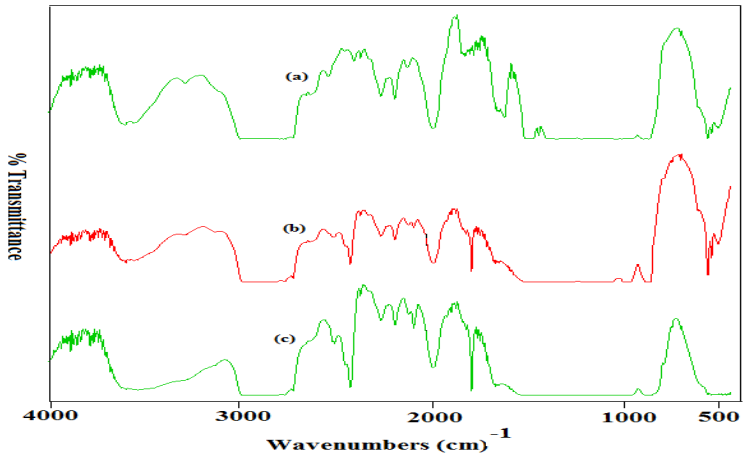

Fig. 1.11: FTIR spectrographs for: (a) Pure PEO film, (b) SPE host film: (70PEO:30KNO_3), (c) NCPE OCC film: (70PEO: 30KNO_3) + 5 % SiO_2

The thermal analysis was also done on SPE and NCPE OCC films. Fig. 1.12 shows DSC thermograms for films of pure PEO, SPE (I^{st}– phase host) and NCPE OCC. The dominant endothermic peak ~ 65-70°C, belonging to the semi-crystalline – amorphous phase transition temperature (T_m) of PEO, is clearly visible in all DSC thermograms. However, slight shifts in the peak position could be noticed which may be due to complexation of salt KNO_3 in the polymer PEO.

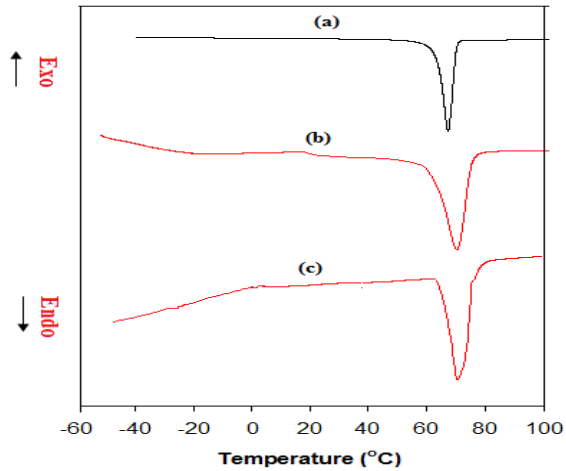

Fig. 1.12: DSC thermograms for: (a) pure PEO film, (b) SPE host film: (70PEO:30KNO_3), (c) NCPE OCC film: (70PEO: 30KNO_3) + 5 % SiO_2.

1.3 Conclusion

A new NCPE film: (70PEO: 30 KNO_3) +5SiO_2 has been synthesized by hot-press technique. The hot-press procedure for film casting is a least expensive/solvent free/dry technique and can be preferred over the traditional solution cast method. Fractional dispersal of nano-SiO_2 in to SPE host: (70PEO: 30 KNO_3) enhanced the room temperature conductivity by more than 3-fold. The complexation of salt in polymer to form solid polymer electrolyte has been confirmed by SEM, XRD, FTIR and DSC studies. The total ionic transport number measurement indicated that both SPE and NCPE film materials are predominantly ion conducting medium with the possibility of both cations and anions motion. The cation (K^+) transport number (t+) was measured separately using combined ac/dc technique and has been found to be t+ ~ 0.36 (NCPE) and 0.27 (SPE). Such a low value of cationic transport has been reported for almost all the polymer electrolytes investigated so far. Attempts are being made to increase the value of t+, most relevant as for as the battery performance is concerned.

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