

## **Chapter - 3**

# **Studies on Proton Conducting Nanocomposite Polymer Electrolytes**

## **Studies on Proton Conducting Nanocomposite Polymer Electrolytes**

As described in Chapter 1, ion conducting polymers attracted considerable attention world-wide due to their technological applications as electrolytes in all-solid-state electrochemical devices viz. rechargeable batteries, fuel cells, supercapacitors etc. [MacCallum et al 1987 & 1989; Gray et al 1991 & 1997; Scrosati 1993; Bruce 1995; Murata et al 2000; Agrawal & Pandey 2008]. Particularly, proton (or  $H^+$  ion) conducting polymers are of special interest due to their vast applications in fuel cells, proton batteries, hydrogen and humidity sensors etc. Only a limited number of proton conducting polymer electrolytes are reported, for example, PEO: $NH_4ClO_4$  [Hashmi et al 1990], PEO: $NH_4I+Al_2O_3$  [Chandra et al 1995], PEO-PMA: $H_3PO_4$ -PEGDE [Qiao et al 2002], PVA-PAMPS:PEG [Hamaya et al 2006] etc. Polyethylene oxide (PEO) based polymer-salt complexes are well studied electrolytes. However, these polymer electrolyte membranes, as such, exhibit relatively low ionic conductivity at room temperature as well as poor mechanical integrity; hence, they are of limited use for device applications. Various approaches of structural modifications have been adopted to enhance the electrical, electrochemical and mechanical properties, as discussed in detail in Chapter 1. This includes the dispersion of nano/micro size particles of ceramic fillers such as  $Al_2O_3$ ,  $SiO_2$ ,  $TiO_2$ ,  $MgO$  etc. in polymer-salt complexes. The dispersion of a small fraction of filler particles in the polymer-salt complex not only enhances the ionic conductivity by 1-2 orders of magnitude in general but increases the mechanical integrity and improves the electrode/electrolytes interfacial stability quite substantially.

The ion conducting polymer electrolyte films are usually prepared by solution cast technique. Recently, a novel hot-press (extrusion) technique as an alternate procedure for casting polymer electrolyte membranes has received a wide acceptability [Gray et al 1986; Prosini et al 1998; Appetecchi et al 2000; Capiglia et al 2000; Pandey et al 2008]. This technique promises several advantages over the conventional solution cast method, as already described in Chapter 2.

This chapter reports the ion transport studies on PEO-based ion (proton) conducting nanocomposite polymer electrolyte (NCPE) films PEO:  $NH_4HSO_4$  dispersed with nanosized  $SiO_2$  and prepared by hot-press (extrusion) technique. NCPE films have also been prepared using conventional solution cast method for the comparison of their various properties. A preliminary ion transport studies on the polymer-salt complex (PEO:  $NH_4HSO_4$ ), prepared by the solution cast technique, have been reported by Daniel et al [Daniel et al 1988]. Chandra and coworkers [Maurya et al 1995] carried out the detailed structural and electrical

property studies on this polymer-salt complex using various physical techniques such as optical microscopy, XRD, DTA, IR, transference number, electrical conductivity and mobility measurements. The polymer electrolyte material offers ionic conductivity mainly due to  $H^+$  cations and  $HSO_4^-$  anions. It has been observed that the materials beyond the composition PEO:  $NH_4HSO_4$  (80:20 weight/weight) were glue-like, and hence difficult to handle. The mechanical stability as well as electrical and electrochemical properties have been improved considerably on dispersion of nanosized  $SiO_2$  particles ( $\sim 8$  nm) into polymer electrolyte host (PEO:  $NH_4HSO_4$ ). Two composition of Polymer-salt complexes PEO:  $NH_4HSO_4$  (92:8 w/w) prepared by solution cast method and PEO:  $NH_4HSO_4$  (80:20 w/w) prepared by hot-press (extrusion) as well as solution cast technique have been selected for the dispersion of  $SiO_2$  to prepare nanocomposite polymer electrolyte membranes. A wide variety of experiments have been carried out to characterize the nanocomposite polymer electrolyte and to establish ion transport behavior. The changes in the morphology and structure of the nanocomposite polymer electrolytes due to the dispersion of nanosized  $SiO_2$  and different preparation routes have been studied by Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) studies. Fourier Transform Infra-red (FTIR) spectroscopic studies have been carried out to investigate the effect of  $SiO_2$  dispersion in the polymer-salt complex at the microscopic level. The thermal properties of the NCPE films have been studied by carrying out differential scanning calorimetry (DSC). The electrical conductivity of NCPE membranes, evaluated from complex impedance spectroscopic analysis, has been measured as a function of filler concentration and temperature. Total ionic transport number has been evaluated by d.c polarization technique. The details of various investigations are given in the following sections.

### 3.1 Structural and Thermal Studies

#### 3.1.1 Scanning Electron Microscopy (SEM)

Fig. 3.1 (a-d) shows SEM pictures of filler-free polymer electrolyte PEO:  $NH_4HSO_4$  (92:8 w/w) and nanocomposite film of PEO:  $NH_4HSO_4$  (92:8 w/w) + 3 wt%  $SiO_2$  prepared by solution cast method. Fig. 3.2 (a-d) shows SEM pictures of solution cast and hot-pressed polymer electrolyte films PEO:  $NH_4HSO_4$  (80:20 w/w) + x wt%  $SiO_2$ . The distinct spherulitic texture separated by dark boundaries can be observed in the pure polymer-salt complex (i.e. for  $x = 0$ ) film prepared by solution cast method [Fig. 3.1(a & b) and Fig. 3.2a]. The spherulitic texture is associated with the lamellar structure of crystalline phase, while the dark regions correspond to partial amorphousity of the polymer. A substantial disruption in

the spherulitic texture and hence, in lamellar structure has been observed dispersion of SiO<sub>2</sub> nanoparticles [Fig. 3.1(c & d) and Fig.3.2b]. The micropressed films show no spherulitic texture (Fig 3.2 c and d). This may be attributed to the fact that during the process of film casting by applying sudden pressure at relatively high temperature ~ 80<sup>0</sup>C, the polymer did not find sufficient time to grow a lamellar structure.

### 3.1.2 X-ray Diffraction (XRD) Studies

The X-ray diffraction (XRD) patterns of pure PEO, solution cast filler-free polymer electrolyte PEO:NH<sub>4</sub>H<sub>2</sub>SO<sub>4</sub> (92:8 w/w), nanocomposite film of PEO: NH<sub>4</sub>H<sub>2</sub>SO<sub>4</sub> (92:8 w/w) + 3 wt% SiO<sub>2</sub> and hot-pressed polymer electrolyte films PEO:NH<sub>4</sub>H<sub>2</sub>SO<sub>4</sub> (80:20 w/w) + x wt% SiO<sub>2</sub> (for different x values) are illustrated in Fig. 3.3. After a comparison, it has been observed that all the main peaks of PEO are affected due to the preparation methods and SiO<sub>2</sub> dispersion. Some peaks have become relatively broader/weaker after salt complexation. The comparative “d” values and Scherrer length “P”, associated with two predominant XRD peaks of PEO at 2θ ~ 19<sup>0</sup> and 23<sup>0</sup>, have been calculated for polymer electrolyte membranes PEO: NH<sub>4</sub>H<sub>2</sub>SO<sub>4</sub> (92:8 w/w) + x wt% SiO<sub>2</sub> and PEO: NH<sub>4</sub>H<sub>2</sub>SO<sub>4</sub> (80:20 w/w) + x wt% SiO<sub>2</sub> and listed in Table 3.1(a and b), respectively. Some distinct features noticed in this study are outlined as below:

- (i) The Scherrer length “P”, which is the measure of crystallite size of PEO in this case, has been found to be substantially shortened for the hot pressed PEO:NH<sub>4</sub>H<sub>2</sub>SO<sub>4</sub> (80:20 w/w) + x wt% SiO<sub>2</sub> (x = 0 and 15) materials as compared to that for the solution cast materials. The relatively smaller crystallite sizes were also observed in SEM pictures of the hot press films (Fig. 3.2 c and d). The XRD results support further that during solution cast of the polymer electrolyte films, PEO gets sufficient time to grow the lamellar structures. The presence of spherulite in SEM records confirms this aspect.
- (ii) The dispersion of SiO<sub>2</sub> nanoparticles during both the composite film preparation methods change the crystallite size of PEO substantially (Table 3.1b).
- (iii) ‘d’ values remain almost unaltered, independent of the preparation methods of NCPE films and SiO<sub>2</sub> dispersion (Table 3.1 a & b).
- (iv) XRD patterns, lying in 2θ range ~ 15<sup>0</sup> - 30<sup>0</sup> for SiO<sub>2</sub> dispersed NCPE films (Fig. 3.3c, e and g), appear relatively more intense as compared to undispersed polymer electrolyte films (Fig. 3.3b, d and f). This is indicative of enlargement in the amorphous region of polymer due to SiO<sub>2</sub> dispersion.

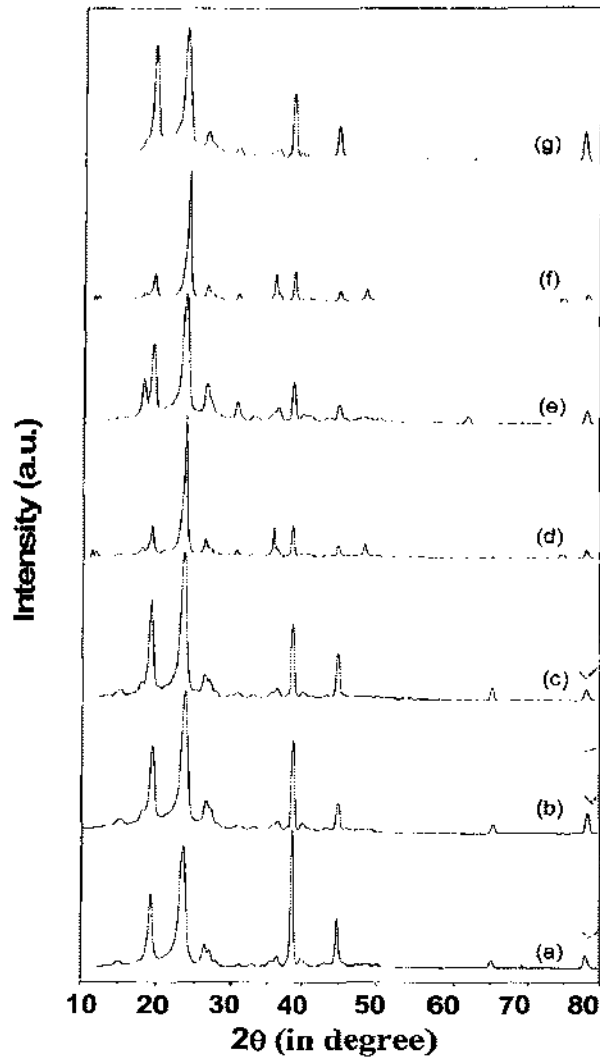


Fig. 3.3: XRD patterns of pure PEO (a), polymer electrolyte films PEO:  $\text{NH}_4\text{HSO}_4$  (92:8 w/w); (b) and PEO:  $\text{NH}_4\text{HSO}_4$  (92:8 w/w)+ 3 wt%  $\text{SiO}_2$  (c); PEO:  $\text{NH}_4\text{HSO}_4$  (80:20 w/w) + x wt. (%)  $\text{SiO}_2$  for x = 0 (d), x = 5 (e) (solution cast); x = 0 (f), x = 15 (g) (hot-press).

Table 3.1a: X-ray diffraction data for two main PEO peaks in the polymer electrolytes films PEO:  $\text{NH}_4\text{HSO}_4$  (92:8 w/w) + x %  $\text{SiO}_2$ .

Preparative Technique	$\text{SiO}_2$ (wt %)	$2\theta$ (degree)	d	$I/I_0$	$l$ (nm)
Solution Cast	0	19.208	4.617	58	11.36
		23.348	3.807	100	8.44
	3	19.212	4.616	66	13.09
		23.379	3.802	100	9.41

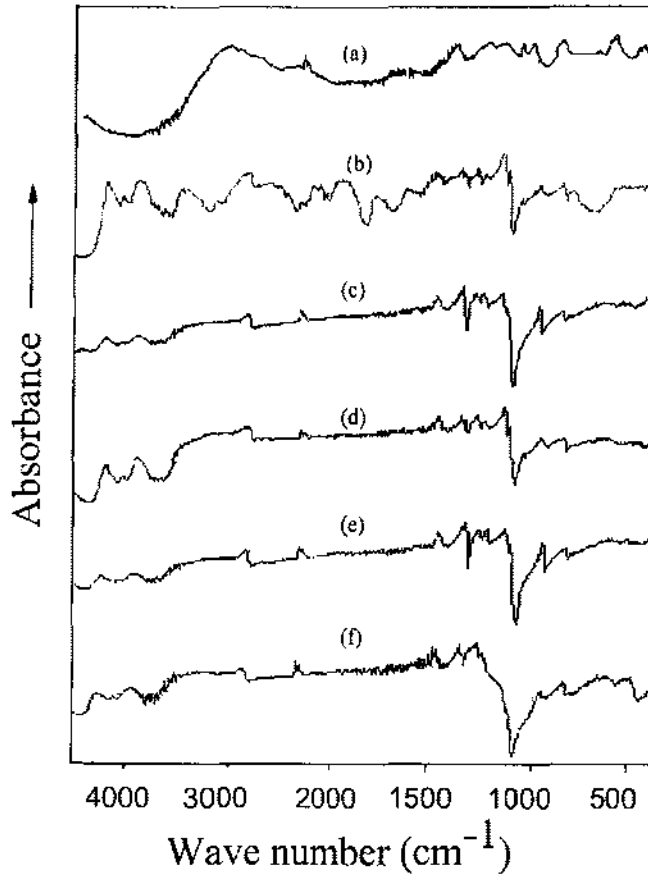
**Table 3.1b:** X-ray diffraction data for two main PEO peaks in the polymer electrolytes films PEO: NH<sub>4</sub>HSO<sub>4</sub> (80:20 w/w) + x % SiO<sub>2</sub>.

Preparative Technique	SiO <sub>2</sub> (wt %)	2θ (degree)	d	I/I <sub>0</sub>	l (nm)
Solution Cast	0	19.222	4.614	25	17.95
		23.661	3.757	100	19.07
	5	19.192	4.621	60	11.95
		23.347	3.807	100	8.53
Hot-press	0	19.820	4.475	30	13.91
		23.960	3.711	100	16.92
	15	19.185	4.623	86	11.82
		23.358	3.805	100	8.58

### 3.1.3 Fourier Transform Infrared (FTIR) Spectroscopic Studies

Fig. 3.4 shows the comparative FTIR spectra for the salt NH<sub>4</sub>HSO<sub>4</sub>, pure PEO, PEO-salt complex and SiO<sub>2</sub> dispersed nanocomposites. Following distinctive features can be extracted from the spectral response:

- (i) The N-H stretching bands of NH<sub>4</sub><sup>+</sup> at ~3160 cm<sup>-1</sup> (ν<sub>3</sub> mode) and ~3020 cm<sup>-1</sup> (ν<sub>1</sub> mode) observed in NH<sub>4</sub>HSO<sub>4</sub> shift towards lower wave number side. The H-N-H bending peak of NH<sub>4</sub><sup>+</sup> vibrations observed at ~1400 cm<sup>-1</sup> for NH<sub>4</sub>HSO<sub>4</sub> also shifts by about 15 cm<sup>-1</sup> towards higher wave number side.
- (ii) A new band at ~1300 cm<sup>-1</sup> is appeared in the spectra of PEO due to the complexation with NH<sub>4</sub>HSO<sub>4</sub>.
- (iii) The bands at ~945 and ~840 cm<sup>-1</sup> of CH<sub>2</sub> belonging to symmetrical and asymmetrical rocking of pure PEO are also present in the PEO-NH<sub>4</sub>HSO<sub>4</sub> complex material. They are related to the 'gauche' conformation of O-[(CH<sub>2</sub>)<sub>2</sub>]-O, suggesting that it has not been changed after complexation with NH<sub>4</sub>HSO<sub>4</sub>. The appearance of new band and shifts in NH<sub>4</sub><sup>+</sup> vibrational bands further suggest the complexation of NH<sub>4</sub>HSO<sub>4</sub> with PEO.
- (iv) No substantial changes in bands of NCPE-spectra occur after SiO<sub>2</sub> dispersion which indicates that the films are in composite phase.



**Fig. 3.4:** FTIR spectra of (a)  $\text{NH}_4\text{HSO}_4$ , (b) pure PEO and polymer electrolyte films PEO:  $\text{NH}_4\text{HSO}_4$  (80:20 w/w) + x wt. (%)  $\text{SiO}_2$  for (c) x = 0, (d) x = 5 (solution cast), (e) x = 0, (f) x = 15 (hot-press).

### 3.1.4 Differential Scanning Calorimetry (DSC)

The differential scanning calorimetric (DSC) studies on polymer electrolyte films PEO: $\text{NH}_4\text{HSO}_4$  (92: 8 w/w) + x wt%  $\text{SiO}_2$ , where x = 0 and 3 (solution cast) and PEO: $\text{NH}_4\text{HSO}_4$  (80: 20 w/w) + x wt%  $\text{SiO}_2$ , where x = 0 and 5 (solution cast) and x = 0 and 15 (hot-press) has been carried out. DSC thermograms, as shown in Fig. 3.5, depict the existence of dominant endothermic peak ~ 58-62 °C which corresponds to semicrystalline-amorphous phase transition and/or melting temperature ( $T_m$ ) of PEO. In addition, two step changes owing to glass transition temperatures,  $T_{g1}$  between -62 to -72 °C and  $T_{g2}$  between -6 to -15 °C has also been observed. Table 3.2 (a and b) lists  $T_m$  and  $T_g$  values for filler free and

nanocomposite polymer electrolyte samples prepared by the two preparation techniques. The dispersion of  $\text{SiO}_2$  nanoparticles in the polymer-salt complex PEO:  $\text{NH}_4\text{HSO}_4$  (80:20 w/w) host matrix substantially influenced  $T_g$ , while  $T_m$  remained almost unchanged. Besides crystalline melting endothermic peak, an additional endothermic broad peak has been observed at  $\sim 85^\circ\text{C}$ . This may be attributed to the amorphous PEO-complex.

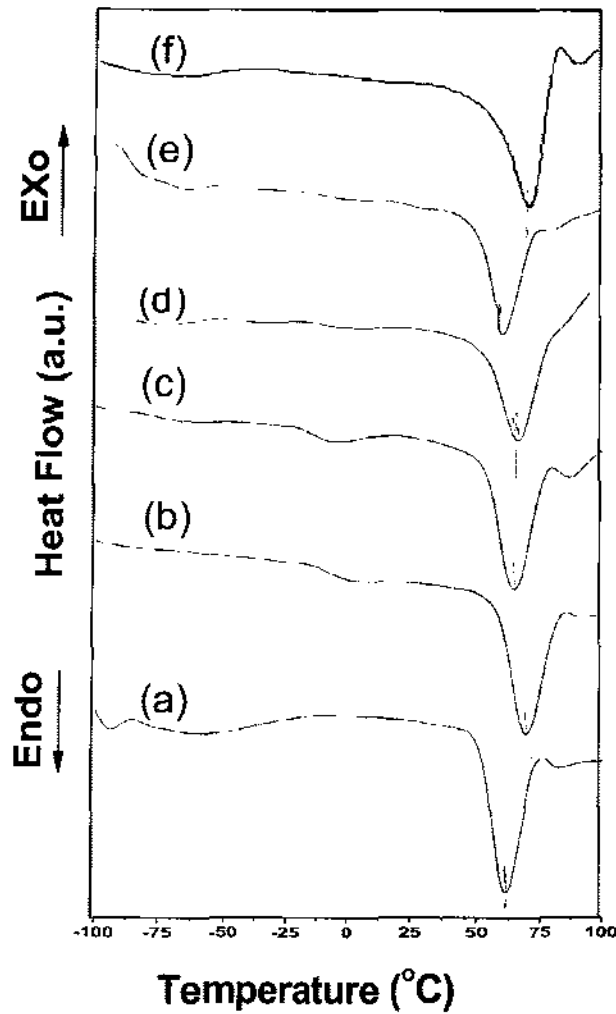


Fig 3.5: DSC thermograms of polymer electrolyte membranes PEO:  $\text{NH}_4\text{HSO}_4$  (92: 8 w/w) + x wt. (%)  $\text{SiO}_2$  for (a) x = 0, (b) x = 3 (solution cast) and PEO:  $\text{NH}_4\text{HSO}_4$  (80:20 w/w) + x wt. (%)  $\text{SiO}_2$  for (c) x = 0, (d) x = 5 (solution cast) ; (e) x = 0, (f) x = 15 (hot-press).



**Table 3.2a:** Glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) of polymer electrolyte films PEO:  $\text{NH}_4\text{HSO}_4$  (92:8 w/w) + x %  $\text{SiO}_2$ .

Preparation Technique	$\text{SiO}_2$ (wt %)	Glass Transition Temperature $T_g$ ( $^{\circ}\text{C}$ )		Melting Temperature $T_m$ ( $^{\circ}\text{C}$ )
		$T_{g1}$	$T_{g2}$	
Solution Cast	0	-66	-14	61
	3	-	-10	60

**Table 3.2b:** Glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) of polymer electrolyte films PEO:  $\text{NH}_4\text{HSO}_4$  (80:20 w/w) + x %  $\text{SiO}_2$ .

Preparation Technique	$\text{SiO}_2$ (wt %)	Glass Transition Temperature $T_g$ ( $^{\circ}\text{C}$ )		Melting Temperature $T_m$ ( $^{\circ}\text{C}$ )
		$T_{g1}$	$T_{g2}$	
Solution Cast	0	-69	-6	62
	5	-65	-4	59
Hot-press	0	-57	-6	58
	15	-55	-3	56

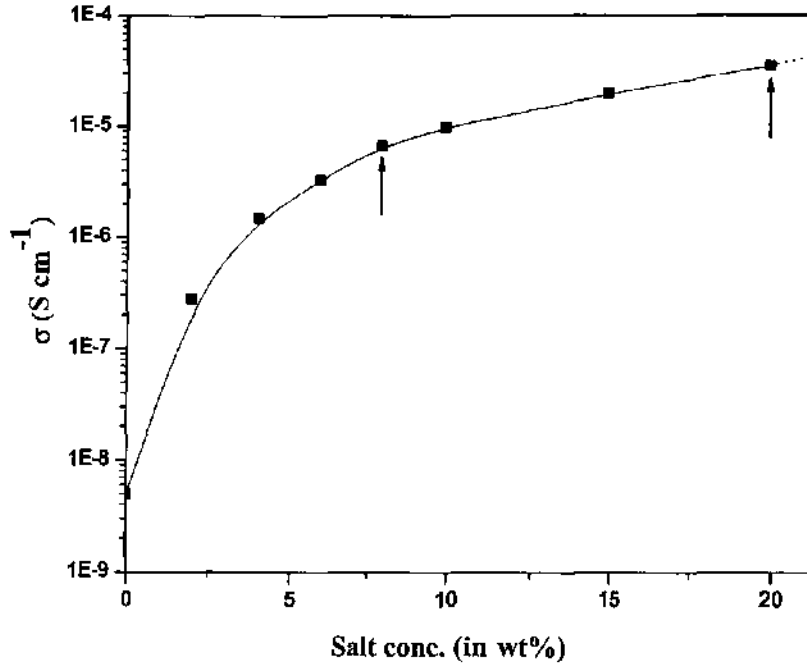
### 3.2 Electrical properties

#### 3.2.1 Electrical Conductivity

##### (a) Conductivity versus composition

Fig. 3.6 shows the variation of room temperature conductivity ( $\sigma$ ) of the polymer electrolyte films PEO: $\text{NH}_4\text{HSO}_4$  of different salt concentrations prepared by solution cast method. The conductivity has initially increased rapidly as the salt content increased upto ~ 5 wt%, thereafter  $\sigma$ -increase has been relatively slow on further addition of the salt. The films beyond 20 wt% salt concentration were found 'glue-like'. The polymer electrolyte film composition PEO: $\text{NH}_4\text{HSO}_4$  (80:20 w/w), although exhibited highest conductivity, was relatively less stable mechanically. The composition PEO: $\text{NH}_4\text{HSO}_4$  (92:8 w/w) was first selected for the dispersion of nanosized  $\text{SiO}_2$  filler particles to prepare nanocomposite using solution cast method. The film composition of PEO: $\text{NH}_4\text{HSO}_4$  (80:20 w/w) was also selected as the polymer electrolyte host for the dispersion of nanosized  $\text{SiO}_2$  filler particles to cast

nanocomposite films adopting two routes (solution cast and hot-press), as mentioned earlier with the aim to improve upon its mechanical stability.



**Fig. 3.6:** Room temperature conductivity as a function of salt concentration in wt (%) for solution cast polymer electrolyte films PEO:  $NH_4HSO_4$ .

The conductivity ( $\sigma$ ) as a function of  $SiO_2$  concentration ( $x$ ) has been measured for NCPE films PEO:  $NH_4HSO_4$  (80:20 w/w) +  $x$  wt%  $SiO_2$  prepared by both the solution cast and hot-press techniques. The ' $\sigma$  vs.  $x$ ' plots, as shown in Fig. 3.7, exhibited a single maxima at  $x = 5$  for solution cast and two maxima at  $x = 5$  and  $x = 15$  for hot-press films. Fig. 3.8 shows  $SiO_2$  concentration dependent conductivity plot for NCPE films PEO: $NH_4HSO_4$  (92:8 w/w) +  $x$   $SiO_2$  prepared by solution cast technique. Two conductivity maxima appeared in  $\sigma$  vs.  $x$  plot at  $x = 3$  and 12 wt%, respectively. Majority of two-phase inorganic composite electrolytes and/or dispersed ionic conductors (DICs) reported so far, exhibit analogous ' $\sigma$  vs  $x$ ' variation [Agrawal and Gupta 1999]. There may be different reasons leading to the ionic conductivity variation in the two-phase composite polymer electrolytes. However, the ion conduction mechanism in these systems can be discussed in the light of various theoretical models based on space-charge double layer effects [Maier 1989, 1994, 1995; Dudney 1989; Agrawal & Gupta 1999]. The increase/decrease in conductivity with increasing filler particle

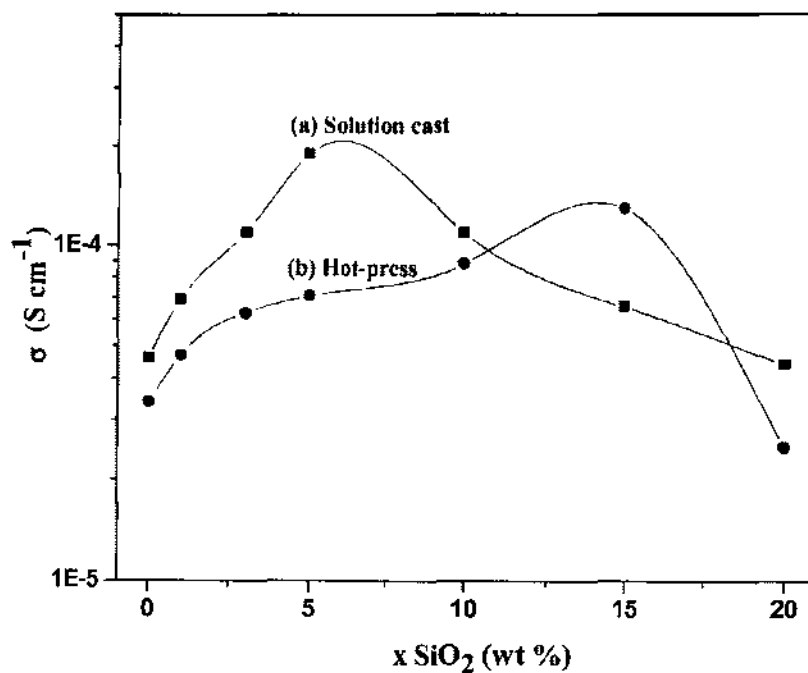


Fig 3.7: Conductivity as a function of filler particle concentration for nanocomposite polymer electrolyte membranes PEO:  $\text{NH}_4\text{HSO}_4$  (80:20 w/w) + x wt. (%)  $\text{SiO}_2$ .

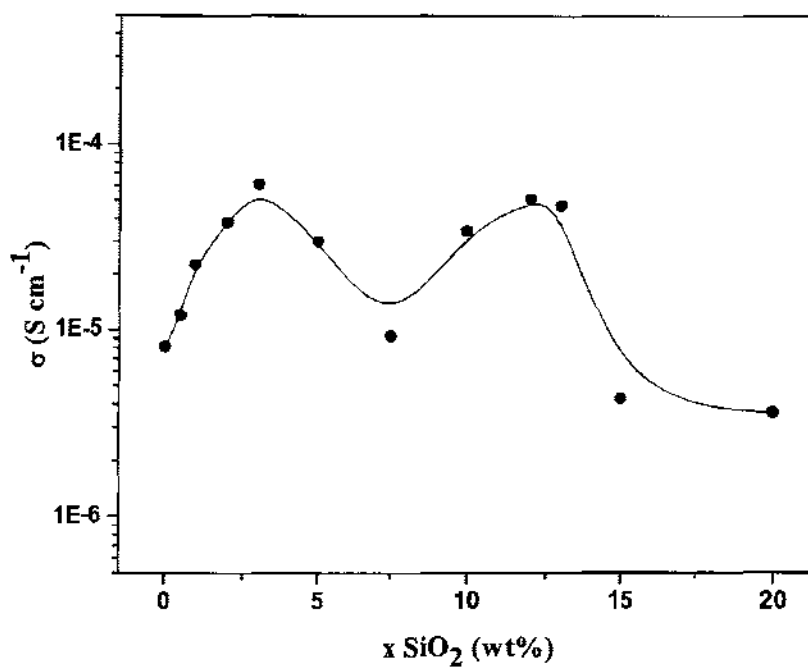


Fig.3.8: Conductivity as a function of filler concentration for nanocomposite polymer electrolyte membranes PEO:  $\text{NH}_4\text{HSO}_4$  (92: 8 w/w) + x wt%  $\text{SiO}_2$  (solution cast).

concentration can be understood in terms of percolation model suggested by Bunde and coworkers [Bunde et al 1985; Roman et al 1986; Roman 1990; Indris et al 2000]. All these models can be conveniently invoked to explain the ion transport phenomenon in composite polymeric (organic) electrolyte systems also. However, due to lack of exact structure-property correlations in polymer electrolyte materials, a complete understanding of conduction mechanisms is still missing. Nonetheless, the mechanistic aspects of ion transport in composite polymer electrolytes can be discussed in the light of a working hypothesis which proposes that the dispersion of submicron size filler particles of large surface area in polymer electrolyte host creates high degree of amorphousity which may also be thought to be due to Lewis acid-base interaction between filler surface states and polymer segments [Wieczorek et al 1995; Przulski et al 1995]. This, in turn, supports enhanced conductivity in terms of increased ionic mobility through amorphous phase [Golodnitsky et al 2002]. Existence of two conductivity maxima in ' $\sigma$  vs  $x$ ' plot for composite polymer electrolytes has also been reported by several workers [Choi et al 1996; Wieczorek et al 1998; Hashmi et al 2000; Singh et al 2002] who proposed two kinds of transport mechanism operative in these systems. The phenomenon can be discussed in the light of percolation model [Bunde et al 1985] and/or the theory proposed by Lakshmi and Chandra [Lakshmi & Chandra 2001] for proton conducting composite polymer electrolyte systems. According to Lakshmi and Chandra, the existence of two maxima in the present proton conducting composite polymer can be attributed to 'two separate percolation thresholds' involving two different kinds of mobile species, cations ( $H^+$  or  $NH_4^+$ ) and anions (possibly  $HSO_4^-$ ). It is well established that in polymer electrolyte networks both cations and anions can move [MacCallum et al 1987 & 1989; Gray et al 1991 & 1997; Scrosati 1993; Bruce 1995]. Nanocomposite films, PEO:  $NH_4HSO_4$  (80:20 w/w) + 5 wt%  $SiO_2$  (solution cast) and PEO:  $NH_4HSO_4$  (80:20 w/w) + 15 wt%  $SiO_2$  (hot-press) exhibited optimum conductivity values  $\sim 2.5 \times 10^{-4} S cm^{-1}$  and  $1.4 \times 10^{-4} S cm^{-1}$  respectively at  $27^\circ C$ , whereas the nanocomposite film PEO: $NH_4HSO_4$  (92:8 w/w) + 3 wt%  $SiO_2$  exhibited optimum room temperature conductivity  $\sim 6.2 \times 10^{-5} S cm^{-1}$ . The conductivity enhancement of approximately an order of magnitude has been achieved in both NCPEs as compared to that of the filler free polymer electrolyte host (Fig. 3.7a ,b and Fig. 3.8). One can obviously note that the conductivity of hot-press casted NCPE film is very close to that of solution casted film. This suggests that hot-press/dry/solvent free procedure of polymer electrolyte film preparation can be preferred over the conventional solution cast method.

(b) Conductivity versus temperature

Fig. 3.9 and Fig. 3.10 show ' $\sigma$  vs  $1/T$ ' plots for the hot-pressed NCPE membranes PEO:  $\text{NH}_4\text{HSO}_4$  (80:20 w/w) + x wt%, where x = 0, 5, 10 and 15 wt. (%) (hot-press) and PEO:  $\text{NH}_4\text{HSO}_4$  (92:8 w/w) + x wt%, where x = 0 and 3 wt. (%) (solution cast). An upward change in the slope could be noticed  $\sim 60^\circ\text{C}$  in all ' $\sigma$  vs  $1/T$ ' plots which corresponds to semicrystalline to amorphous phase transition temperature ( $T_m$ ) of PEO. Such transition is observed also in DSC thermograms (Fig. 3.5). The straight line portion of ' $\sigma$  vs  $1/T$ ' plot below ' $T_m$ ' can be expressed by following general Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad \dots\dots(3.1)$$

where  $\sigma_0$  is the pre-exponential factor,  $E_a$  is the activation energy involved in this thermally activated conductivity process. The values of  $E_a$  have been found to be 0.33, 0.32 and 0.29 eV for  $\text{SiO}_2$  content of 5, 10 and 15 wt.(%), respectively for the hot-press NCPE films (Fig. 3.9) and 0.38 and 0.20 eV for  $\text{SiO}_2$  content of 0 and 3 wt.(%) in solution casted polymer electrolyte, respectively (Fig. 3.10). The values have been computed by least square fitting of straight line portion of different ' $\sigma$  vs  $1/T$ ' plots below  $T_m$ .

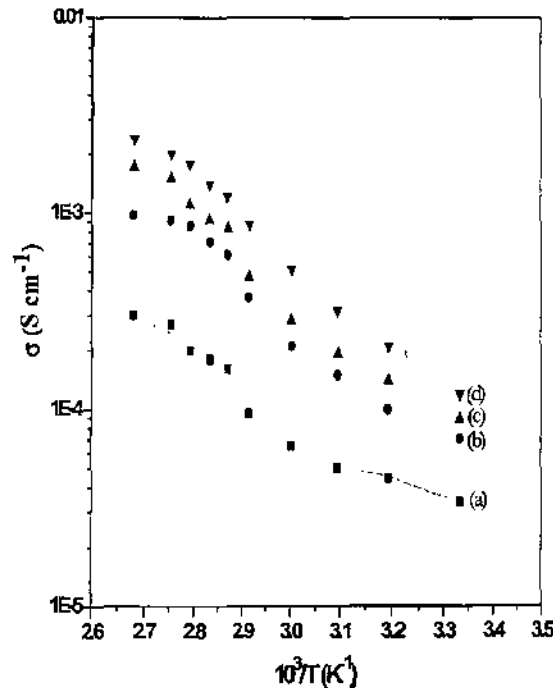


Fig. 3.9:  $\sigma$  vs  $1/T$  plots for hot-pressed nano composite polymer electrolyte membranes: PEO:  $\text{NH}_4\text{HSO}_4$  (80:20 w/w) + x wt. (%)  $\text{SiO}_2$ , x = 0 (a), 5 (b), 10 (c), 15 (d).

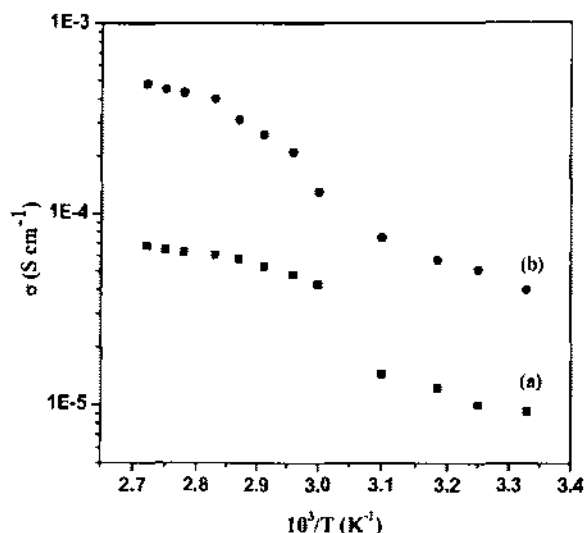


Fig. 3.10:  $\sigma$  vs  $1/T$  plots for solution cast nanocomposite polymer electrolyte membranes PEO:  $\text{NH}_4\text{HSO}_4$  (92:8 w/w) + x wt. (%)  $\text{SiO}_2$ , x = 0 (a), 3 (b).

### 3.2.2 Ionic Transport Number

The total ionic transport number ( $t_{\text{ion}}$ ) of the polymer electrolyte host and NCPE films was determined by polarization method [Wagner & Wagner 1957; Chandra et al 1988], discussed in Chapter 2 (Section 2.2.6.2). A fixed dc potential (1 V) was applied across the cell SS/polymer electrolyte/SS (SS: stainless steel) and the current passing through the cell was recorded as a function of time with the help of x-y-t recorder (Graphtec WX-2300). Fig. 3.11 shows the typical 'current vs time' plot for the NCPE membrane. The values of  $t_{\text{ion}}$  for all the NCPE films have been evaluated using equation (2.17) and found to be  $\sim 0.97$ - $0.98$ . This indicates the fact that the conduction in these composite electrolytes is predominantly ionic and the electronic contribution to the overall electrical conductivity is negligibly small. However, this method fails to tell whether (or which) cation or anion is responsible for the ion transport. To know the cation and anions contribution to the overall conductivity, Tubandt's direct electrolysis technique or coulometry [Chandra et al 1986] are used, generally. Chandra and coworkers [Maurya et al 1995] had measured the cation and anion contribution to the overall conductivity in the polymer-salt complex PEO- $\text{NH}_4\text{HSO}_4$  using the coulometric technique and concluded that in this system cations ( $\text{H}^+$  or  $\text{NH}_4^+$ ) are main charge carriers but anions  $\text{HSO}_4^-$  are also mobile. Due to lack of facilities, this experiment could not be performed in the present nanocomposite polymer electrolyte systems. However,

the cations ( $H^+$  or  $NH_4^+$ ) and anions  $HSO_4^-$  both are expected to be mobile in the nanocomposites.

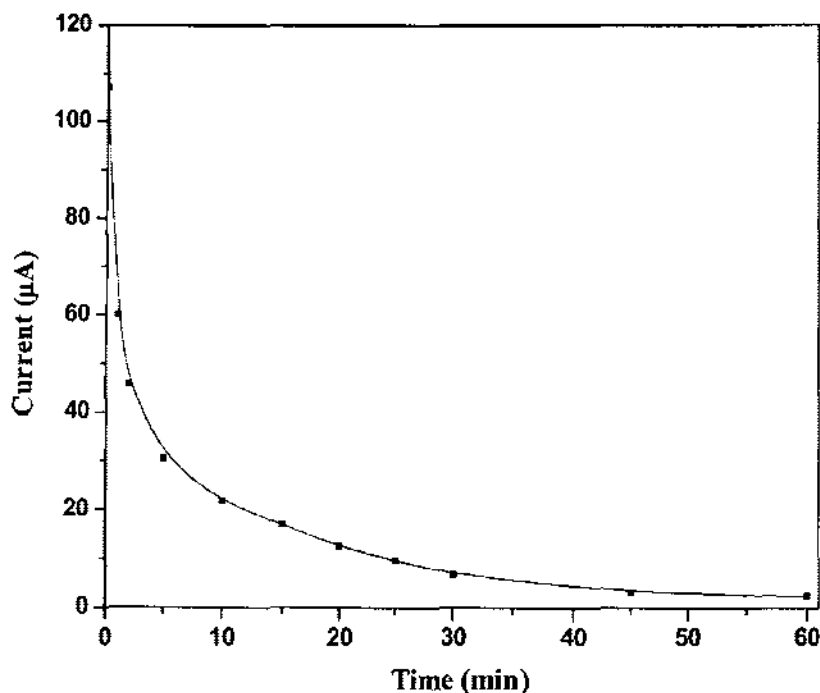


Fig. 3.11: A typical polarization current vs. time plot for the NCPE membrane PEO:  $NH_4HSO_4$  (80:20 w/w) + 10 wt. (%)  $SiO_2$ .

### 3.3 Conclusions

A comparative studies have been carried out on (PEO: $NH_4HSO_4$ ) polymer electrolyte films dispersed with nanosized  $SiO_2$  prepared by a novel hot-press and the conventional solution cast techniques. On the basis of various electrical, thermal and structural studies, following conclusions have been drawn:

- (i) The complexation of the salt in the polymer and formation of nanocomposite polymer electrolyte phase have been confirmed by SEM, XRD, FTIR and DSC studies.
- (ii) The dispersion of nanosized filler particles  $SiO_2$  in the polymer electrolyte hosts PEO:  $NH_4HSO_4$  (80:20 w/w) and PEO:  $NH_4HSO_4$  (92:8 w/w) resulted into conductivity enhancement at room temperature.
- (iii) The conductivity value of hot-press NCPE film is very close to that of solution cast film.

- (iv) The hot-press technique which is a least expensive/solvent-free/dry procedure can be preferred over the solution cast method.
- (v) The temperature dependence of conductivity exhibited Arrhenius type thermally activated behavior both below and above the semicrystalline to amorphous phase transition of PEO.
- (vi) The total ionic transference number has been found to be ~0.97-0.98 which indicates that the charge carriers are predominantly ions (protons) in the newly synthesized polymer electrolyte materials and hence, they can be suitably used for the electrochemical device fabrications.
- (vii) The optimised proton conducting nanocomposite is useful material from the application point of view as electrolyte-cum-separator in devices like proton batteries, hydrogen sensors etc. Using this material, proton batteries has been fabricated and characterized, presented in Chapter 6.

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