

## Synthesis of Hot-pressed Solid Polymer Electrolytes: (1-x) PEO: x NaBr

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**Abstract:** Synthesis of a new  $\text{Na}^+$  ion conducting hot-pressed Solid Polymer Electrolytes (SPE): (1-x) PEO: x NaBr, where  $0 < x < 50$  in wt. %, has been reported. SPE films have been casted using a hot-press technique in place of the traditional solution cast method. A conductivity enhancement of the two orders of magnitude was achieved in SPE film composition: [70PEO: 30NaBr]. Polymer-salt complexation has been explained with the help of x-ray diffraction (XRD) technique. The  $\text{Na}^+$  ion conduction in the present SPEs have been discussed on the basis of experimental measurements on their ionic conductivity ( $\sigma$ ) and ionic mobility ( $\mu$ ) at room temperature.

**Keywords:** Solid polymer electrolytes, ionic conductivity, hot-press technique, XRD.

### 1. Introduction

Poly(ethylene oxide) PEO based solid polymer electrolytes (SPEs), complexed with variety of ionizable alkali metal salts show tremendous promises specially in thin film battery technology<sup>1,2</sup>. The main materials advantages of the solid polymer electrolytes are their good mechanical processibility, ease of fabrication in the thin flexible film forms which make them as appropriate choices in fabricating all-solid-state thin film

electrochemical devices viz. mini/ micro batteries of desirable shapes/ sizes. Moreover, SPEs provide very good electrode/ electrolyte contacts. Ion conduction in polymers was reported for the first time in 1973 and the first practical SPE battery based on 'Poly (ethylene oxide) (PEO) -Li<sup>+</sup>-ion salt complex' was demonstrated in 1979<sup>3,4</sup>. Since then, a large number of solid polymer electrolytes (SPEs) have been reported<sup>5-7</sup>. SPE films are prepared, in general, by a traditional solution-cast method. However, recently a novel hot-press technique has been developed for casting SPE films. Hot-press technique has several procedural conveniences viz. solution free/ dry, least expensive, quicker procedure etc. than those of solution-cast method<sup>8-11</sup>. The main advantage of using sodium metal ion is its availability in abundance at a cheaper cost than lithium and more softness of the material makes it easier to achieve good contact with electrode and electrolyte in the solid state devices viz. polymeric batteries fabrication.

In the present investigation, we report the synthesis of hot-pressed solid polymer electrolytes (SPEs): (1-x) PEO: x NaBr. Materials characterization was done with the help of XRD studies. The ion transport property studies on SPE films has been done with the help of conductivity ( $\sigma$ ) and ionic mobility ( $\mu$ ) measurements at room temperature.

## 2. Experimental

Solid Polymer Electrolytes (SPEs): (1-x) PEO: x NaBr, where  $0 < x < 50$  wt. %, were synthesized by using the precursor chemicals: poly (ethylene oxide) PEO ( $10^5$  Mw, Aldrich, USA) and NaBr (purity > 98%, Merck, India). The dry powders of NaBr, as complexing salts and poly(ethylene oxide) PEO, as polymeric host, in different wt.% ratios were ground thoroughly at room temperature for about ~1 h in an agate pestle and mortar. The physically mixed PEO-salt mixtures of different compositions were heated separately close to the melting point of PEO (~70 °C) for ~30 min with mixing continuing. This resulted in a hot/ soft slurry of polymer complexed with the salt. The slurry so obtained was then pressed between two SS-cold blocks at  $\sim 1.25 \text{ ton cm}^{-2}$  which gave rise to a uniform thin membrane of thickness  $\sim 0.015 \text{ cm}$ . Polymer-salt complexation and materials characterization were done with the help of XRD patterns using Shimadzu X-ray diffractometer at Cu-K $\alpha$  radiation. The ionic conductivity ( $\sigma$ ) measurements were carried out by the equation:  $[\sigma = l / (R_b \cdot A)]$ , where  $R_b$  is the bulk resistance,  $l$  is the thickness and  $A$  is the cross sectional area of the polymeric sample material. The bulk resistance  $R_b$  was determined on different polymeric films using an LCR- bridge (model: HIOKI 3520- 01,

Japan). The ionic mobility was determined with the help of well-known equation:  $[\mu = d^2 / (V \cdot \tau)]$ , where  $d$  is the thickness of SPE films,  $V$  is the applied external d.c. potential and  $\tau$  is the time of flight. The time of flight ( $\tau$ ) was determined directly employing dc polarization Transient Ionic Current (TIC) technique using an x-y-t recorder (model: Graphtec WX 2300-1L, Japan)<sup>12</sup>.

### 3. Results and Discussion

Figure 1 shows the room temperature conductivity ( $\sigma$ ) variations for the hot-pressed SPE films: (1-x) PEO: x NaBr,  $0 < x < 50$  wt. %. The conductivity increased when the ionic salt NaBr concentration increased initially from 0 to 30 wt. % and then decreased on further addition of salts. The conductivity maxima appeared at  $x = 30$  i.e. the composition: [70 PEO: 30 NaBr] with  $\sigma \sim 7.58 \times 10^{-7} \text{ Scm}^{-1}$ . This highest conducting composition has been referred to as Optimum Conducting Composition (OCC). SPE films beyond 50 wt. % salt concentration appeared, unstable and brittle. A conductivity increase of more than two orders of magnitude was obtained in SPE OCC from that of the pure PEO ( $\sigma \sim 3.2 \times 10^{-9} \text{ Scm}^{-1}$ ). The increase in conductivity is due to the increase in degree of amorphousity and/ or increase in ionic mobility ( $\mu$ ), which can be explained by the various models

3-5.

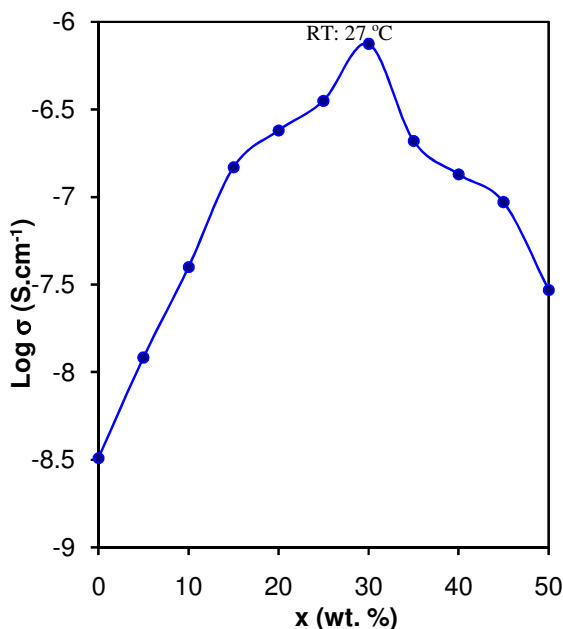


Figure 1. 'Log □ – x' plot of hot-pressed SPEs: (1-x) PEO: x NaBr.

To explain the conductivity enhancement in the present SPE OCC, the ionic mobility ( $\mu$ ) and mobile ion concentration ( $n$ ) studies have been done with the help of d.c. polarization Transient Ionic Current (TIC) technique, as mentioned in experimental section. Fig. 2 shows 'log  $\mu$ -x' and 'log  $n$ -x' plots for SPEs: (1-x) PEO: x NaBr. One can clearly notice the existence of maxima for both  $\mu$  &  $n$  at  $x = 30$  wt. % observed. This explains the fact that the overall increase in conductivity of SPE OCC has been due to increase in both  $\mu$  &  $n$ .

Figure 3 shows the XRD patterns of pure PEO, pure NaBr and SPE OCC: [70PEO:30NaBr]. It can be clearly seen from the figure that characteristics peaks of pure PEO appeared between  $2\theta = 15$ - $30^\circ$  is decreases after the addition of salt NaBr. Some of the peaks of pure PEO became relatively less-prominent/ feeble after salt complexation. This is usually attributed to the increase in the degree of amorphicity and confirmation of polymer-salt complexation.

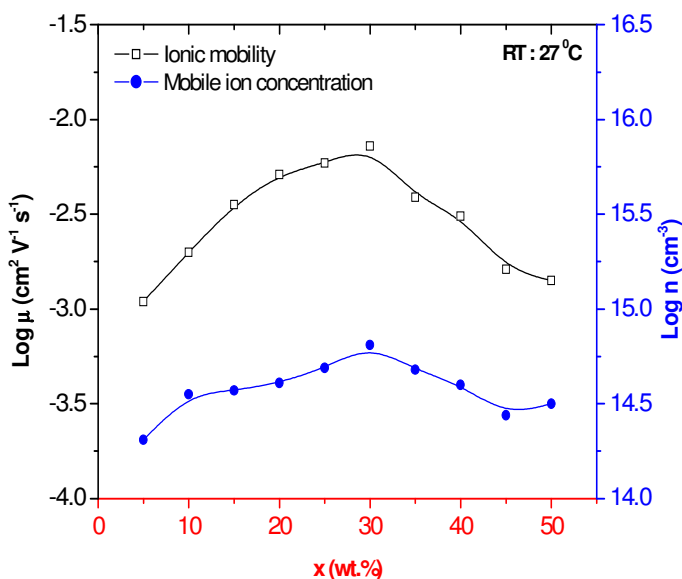


Figure 2. 'Log  $\mu$ -x' and 'log  $n$ -x' plots of hot-pressed SPEs: (1-x) PEO: x NaBr.

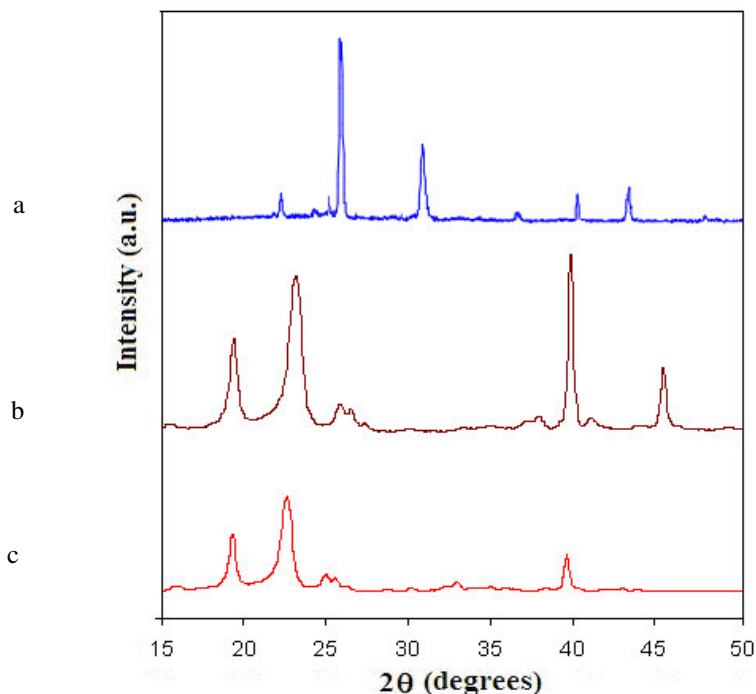


Figure 3. XRD patterns: (a) pure NaBr, (b) pure PEO and (c) SPE OCC: [70 PEO: 30 NaBr].

Figure 4 shows ‘ $\log \sigma - 1/T$ ’ plot for the SPE OCC [70 PEO: 30 NaBr]. The conductivity increased almost linearly with temperature up to  $\sim 65$ - $70$   $^{\circ}\text{C}$  at which an upward jump in conductivity was observed. The jump in conductivity at this temperature corresponds to semi-crystalline to amorphous phase transition temperature ( $T_m$ ) of PEO. The linear portion of ‘ $\log \sigma - 1/T$ ’ plots below  $T_m$  can be expressed by following Arrhenius type equation:

$$\log \sigma(T) = 3.19 \times 10^{-1} \exp (-0.33/kT) \quad [\text{Scm}^{-1}]$$

where 0.33 (eV) is the activation energy ( $E_a$ ) computed by least square linear fitting of the data. The low ‘ $E_a$ ’ in the present SPE OCC is indicative of relatively easier ion migration and this can be potentially used as electrolyte for electrochemical device applications.

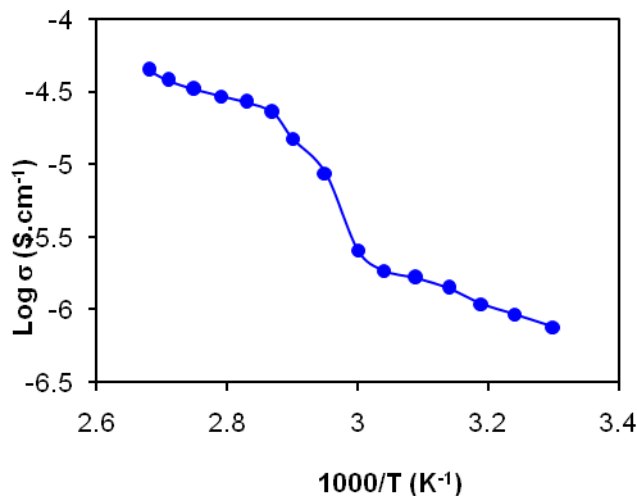


Figure 4. ‘Log  $\sigma$  –  $1/T$ ’ plot for SPE OCC: [70 PEO: 30 NaBr].

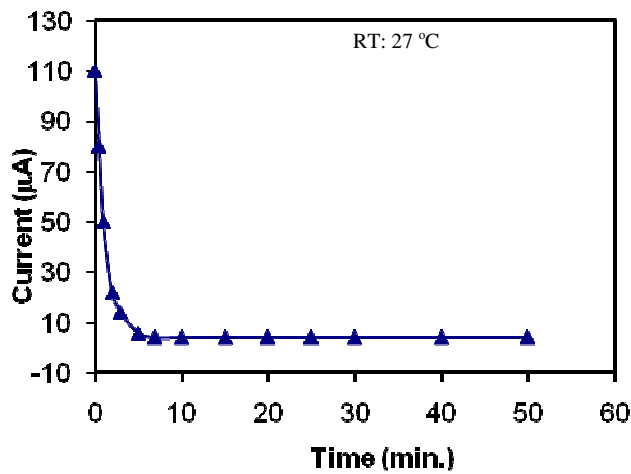


Figure 5: ‘Current vs time’ plot for SPE OCC: [70 PEO: 30NaBr].

The ionic transference number ( $t_{ion}$ ), a direct quantitative measure of extent of ionic contribution to the total conductivity, was also determined for SPE OCC film using TIC ‘current – time’ plot and obtained  $t_{ion} \sim 0.95$ , as shown in Fig. 5. This clearly indicated that SPE OCC film material is purely an ion conducting system and hence, can be appropriately employed as electrolyte to fabricate thin film electrochemical devices viz. batteries.

The major ion conducting species in this SPE OCC are yet to be identified, as both cations & anions may be mobile. However, cations:  $\text{Na}^+$ -ions, being relatively smaller in size than anion  $\text{Br}^-$ , are expected to be the main transporting ionic species in this SPE material.

### 3. CONCLUSION

A new hot-pressed solid polymer electrolyte: [70PEO: 30NaBr], has been synthesized. Materials characterizations have been done by using XRD technique. Ionic conductivity enhancements have been studied using  $\mu$  and  $n$  measurements. The ionic transference number measurement indicated that SPE film material is a pure ion conducting system with cation  $\text{Na}^+$ -ions as the principal charge carriers. The low activation energy for SPE OCC indicative of relatively easier ion transport in the newly synthesized system and hence can be Potentially Used For Electrochemical Device Applications.

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