

## Materials Characterization and Ionic Drift Velocity Measurements of Nano Composite Polymer Electrolytes

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### Abstract

*Materials characterization and ionic drift velocity ( $v_d$ ) measurements of PEO-based hot-pressed Nano Composite Polymer Electrolytes (NCPEs):  $(1-x)$  [70PEO:30KBrO<sub>3</sub>]+  $x$  SiO<sub>2</sub>, where  $0 < x < 20$  wt%, are reported. NCPEs have been synthesized by using hot-press method in place of the traditional solution cast method. Materials characterization of the present NCPEs were explained with the help of XRD, TGA studies. The ionic drift velocity measurements of Optimum Conducting Composition (OCC) of the present NCPE have been done with the help of various experimental techniques. The ionic transference numbers ( $t_{ion}$ ) of the NCPE OCC have also been determined at various temperatures.*

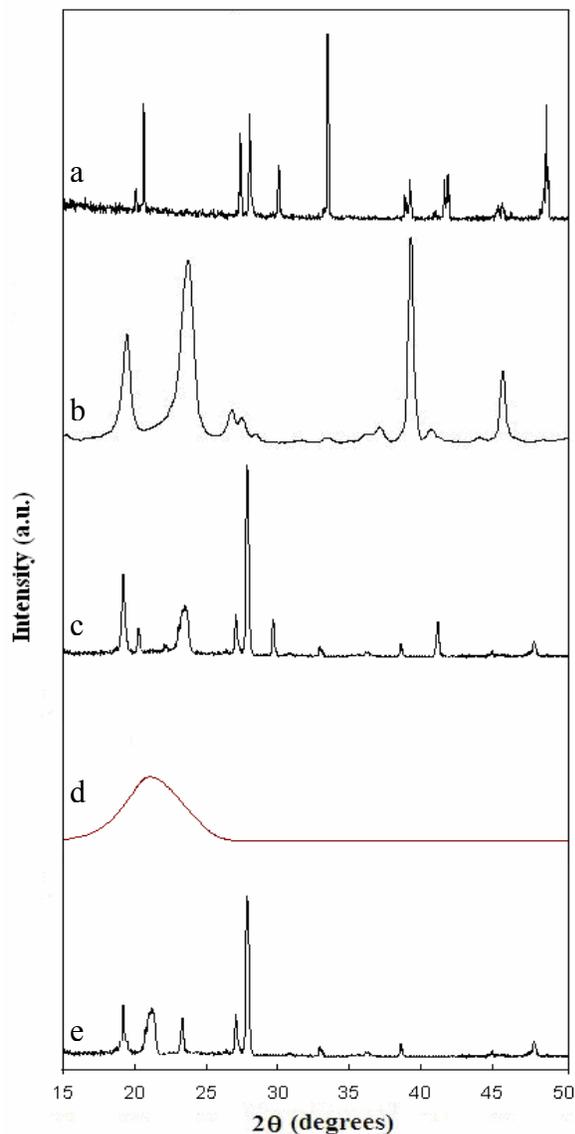
**Keywords:** Nano composite polymer electrolyte, Hot-press technique, XRD, TGA.

### Introduction

Ion conducting nano composite polymer electrolytes (NCPEs) show tremendous technological promises to develop all-solid state electrochemical devices viz. batteries, sensors, fuel cells, super-capacitors, memories, electrochromic displays *etc.* [1-5]. Solid polymer electrolytes (SPEs) show poor conductivity, less flexibility and less mechanical stability [6]. To overcome these difficulties NCPEs have been developed in last 30 years. Among the known polymers, poly (ethylene oxide) PEO-based NCPEs are one of the most promising materials due to their good mechanical and electrochemical properties [7-10]. The size of the filler particles plays a significant role to improve the ionic conductivity, mechanical stability, electrode electrolyte interfacial reactivity of the polymeric

systems. In general, NCPEs have prepared by traditional solution-cast/ sol-gel techniques but these techniques have some drawbacks. Very recently, a hot-press method has been developed in place of the traditional casting method to prepare various ion conducting solid polymer electrolytes (SPEs) and NCPEs [11-14]. The PEO-based NCPEs:  $(1-x)$  [70PEO:30KBrO<sub>3</sub>]+  $x$  SiO<sub>2</sub>, where  $0 < x < 20$  wt%, have been prepared by hot-press method in the previous communication [15].

To understand the formation of ion conducting nano-composite polymer electrolytes and ion conduction in polymer electrolytes, present investigation, reports the materials characterization and ionic drift velocity ( $v_d$ ) studies of NCPEs:  $(1-x)$  [70PEO:30KBrO<sub>3</sub>]+  $x$  SiO<sub>2</sub>, where  $0 < x < 20$  wt.%.



**Figure 1**

**Fig. 1:** XRD patterns: (a)  $\text{KBrO}_3$ , (b) pure PEO, (c) SPE host: (70PEO: 30 $\text{KBrO}_3$ ), (d) nano filler  $\text{SiO}_2$  and (e) NCPE OCC: 95(70PEO: 30 $\text{KBrO}_3$ )+5  $\text{SiO}_2$ .

### Experimental Procedure

The AR grade precursor chemicals: poly (ethylene oxide) PEO ( $10^5$  Mw, Aldrich, USA),  $\text{KBrO}_3$  (purity > 98%, Merck, India) and  $\text{SiO}_2$  (> 99.8%, size ~ 8nm, Sigma, USA) were used for synthesis of hot-pressed NCPEs:  $(1-x)$  [70PEO:30 $\text{KBrO}_3$ ]+  $x$   $\text{SiO}_2$ , where  $0 < x < 20$

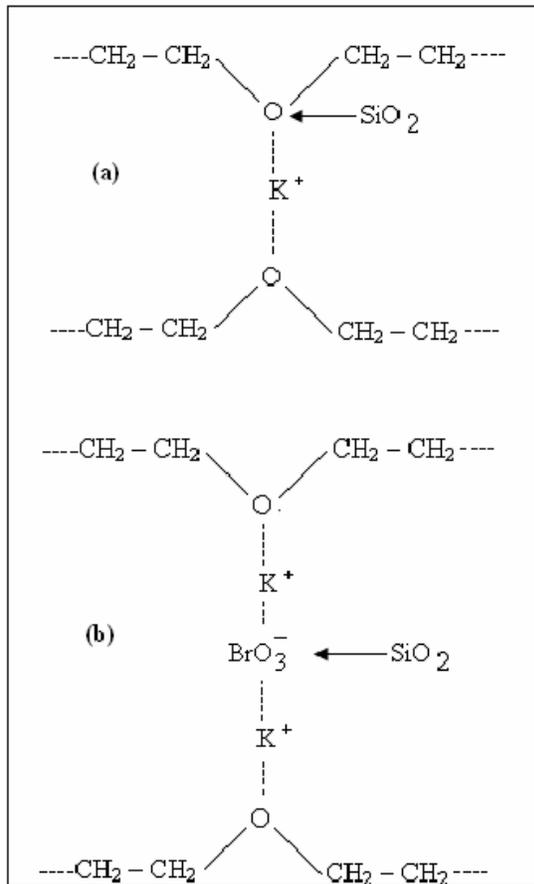
wt%. The details related to hot-press casting method and ionic conductivity ( $\sigma$ ) measurements of the present NCPEs have been given elsewhere [15]. Materials characterization were done with the help of X-ray diffraction (XRD) (model: Shimadzu) and thermogravimetric analysis TGA (model: SDT Universal) techniques. The ionic mobility ( $\mu$ ), mobile ion concentration ( $n$ ), ionic transference number ( $t_{\text{ion}}$ ) and ionic drift velocity ( $v_d$ ) measurements of NCPEs have been carried out using different experimental techniques. The details related to these measurements have been given in elsewhere [16-18].

### Results and discussion

The nano composite polymer electrolytes (NCPEs):  $(1-x)$  [70PEO:30 $\text{KBrO}_3$ ]+  $x$   $\text{SiO}_2$ , where  $0 < x < 20$  wt% have been synthesized using hot-press method and the composition: 95(70PEO: 30 $\text{KBrO}_3$ )+5  $\text{SiO}_2$  with conductivity ( $\sigma \sim 4.36 \times 10^{-7} \text{ S.cm}^{-1}$ ) have been identified as Optimum Conducting Composition (OCC) in our previous communication [15]. XRD is very useful technique to identify the polymer-salt/ nano filler complexation. The XRD patterns of pure PEO,  $\text{KBrO}_3$ , polymer host: (70PEO: 30 $\text{KBrO}_3$ ), nano-filler  $\text{SiO}_2$  and NCPE OCC: 95(70PEO: 30 $\text{KBrO}_3$ )+5  $\text{SiO}_2$ , is shown in Figure1. It is clear from the figure that the some of the peaks of pure PEO became relatively broader as well as less-prominent/ feeble after salt complexation and/ nano-filler  $\text{SiO}_2$  dispersal.

This is usually attributed to the increase in the degree of amorphicity and it is confirmed the formation of NCPEs or polymer-salt complexation. The scanning electron micrograph (SEM) and differential scanning calorimetric (DSC) analysis has also been confirmed the formation of NCPEs, as reported elsewhere [15]. The ionic conductivity enhancement in the present NCPEs can be

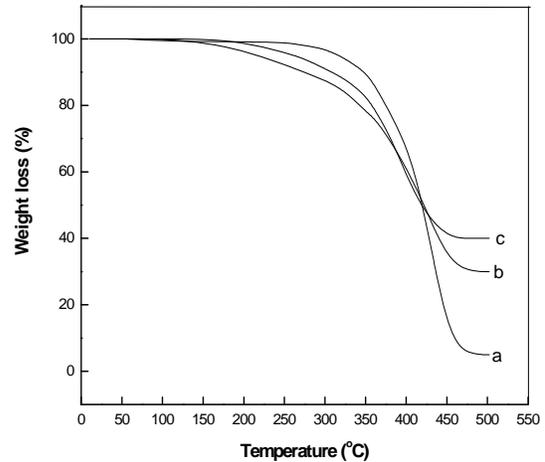
attributed by the two separate percolation thresholds involving two different kinds of mobile species: cation ( $K^+$ ) and anion ( $BrO_3^-$ ). The ionic conductivity enhancement in NCPE is also due to the Lewis acid-base reaction [19,20]. The schematic presentation of two kinds of cross-linking in  $K^+$  ion conducting NCPEs: (a) polymer segments via cation interaction and (b) polymer segments via cation-anion interaction, is shown in Figure 2.



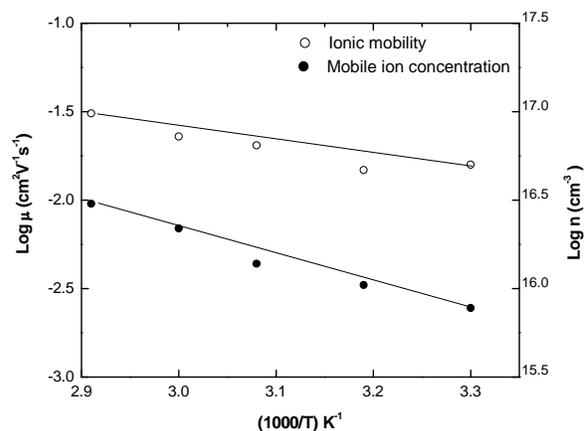
**Fig. 2:** Schematic presentation of two kinds of cross-linking in  $K^+$  ion conducting NCPEs: (a) polymer segments via cation interaction and (b) polymer segments via cation-anion interaction

Figure 3 shows the thermo-gravimetric analysis (TGA) curves pure PEO, SPE host: 95(70PEO: 30KBrO<sub>3</sub>)+5 SiO<sub>2</sub> and NCPE OCC: 95(70PEO: 30KBrO<sub>3</sub>)+5 SiO<sub>2</sub>. It can be clearly observed from the figure that the total weight loss

for pure PEO (~ 95 %) is larger as compared to both SPE host (~ 70 %) and NCPE OCC (~ 60 %). The thermal stability of polymer is improved and degree of amorphicity is also increases by the dispersal of nano-filler SiO<sub>2</sub>.



**Fig. 3:** TGA curves: (a) PEO, (b) SPE host: (70 PEO: 30 KBrO<sub>3</sub>) and (c) NCPE OCC: 95 [70PEO:30KBrO<sub>3</sub>] + 5 SiO<sub>2</sub>.



**Fig. 4:**  $\log \mu - 1/T$  and  $\log n - 1/T$  plots for NCPE OCC: 95 [70PEO:30KBrO<sub>3</sub>] + 5 SiO<sub>2</sub>.

The ionic mobility ( $\mu$ ) and mobile ion concentration ( $n$ ) of the present NCPE OCC: 95(70PEO: 30KBrO<sub>3</sub>)+5 SiO<sub>2</sub> were determined at various temperatures. Figure 4 shows the  $\log \mu - 1/T$  and  $\log n - 1/T$  plots for NCPE OCC: 95 [70PEO:30KBrO<sub>3</sub>] + 5 SiO<sub>2</sub>. It can clearly note

from the figure that ionic mobility ( $\mu$ ) and mobile ion concentration ( $n$ ) increased as the temperature increased. The increase in both  $\mu$  and  $n$  with temperature is probably due to the increase in the preferred conducting pathways as well as the dissociation of more number of  $K^+$  ions from the ionic salts.

The linear portion of these plots can be expressed by the following Arrhenius type behaviors:

$$\begin{aligned} \mu(T) &= 6.01 \times 10 \exp(-0.158/kT) \text{ [cm}^2\text{V}^{-1}\text{s}^{-1}] \quad (1) \\ n(T) &= 8.73 \times 10^{20} \exp(-0.305/kT) \text{ [cm}^{-3}] \end{aligned}$$

where the numerals 0.158 and 0.305 in eV are the energies involved in the two thermally activated processes and can be designated as the energy of migration ( $E_m$ ) and energy of formation ( $E_f$ ) respectively. (-) ve sign appearing in the argument of the exponential terms indicate the increase of the factor on the left hand side of the equation with increasing temperature. The ionic transference number ( $t_{ion}$ ) of the NCPE OCC: 95 [70PEO:30KBrO<sub>3</sub>] + 5 SiO<sub>2</sub> has been evaluated using dc polarization technique at different temperatures, as mentioned in section EXPERIMENTAL. The 'current vs time' plots for NCPE OCC at different temperatures, is shown in Figure 5.

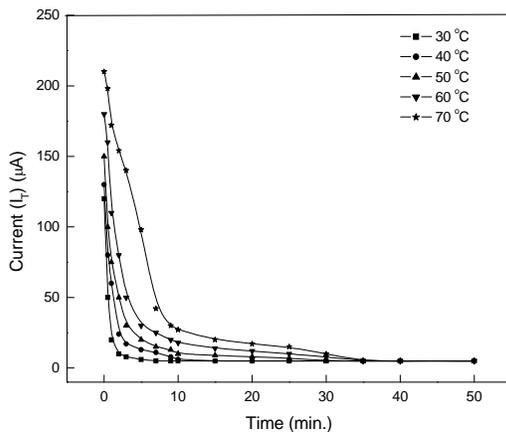


Fig. 5: Current vs time plots for NCPE OCC: 95 [70PEO:30KBrO<sub>3</sub>] + 5 SiO<sub>2</sub> at different temperatures.

$t_{ion} \sim 0.95$  obtained at all the temperatures and it is indicated that the majority of charge carriers ( $\sim 95\%$ ) are cations  $K^+$  and only a very small contribution ( $\sim 5\%$ ) of anion  $KBrO_3^-$ . The time elapsed for total current ( $I_T$ ) to approach a minimum value of the current got prolonged as the polymeric samples temperature increased.

Ionic drift velocity ( $v_d$ ) of NCPE OCC: 95 [70PEO:30KBrO<sub>3</sub>] + 5 SiO<sub>2</sub> have been determined at different temperatures. Figure 6 shows ' $\log v_d - 1/T$ ' plot for NCPE OCC. It can be clear from the figure that the  $v_d$  increased with temperatures and this can also be expressed by following Arrhenius type equation:

$$v_d(T) = 4.48 \times 10^7 \exp(-0.16/kT) \text{ [cm.s}^{-1}] \quad (2)$$

where the numeral 0.16 is the drift energy ( $E_d$ ) in eV.  $v_d$  is directly proportional to  $\mu$  at a fixed external dc electric field, ' $\log v_d - 1/T$ ' and ' $\log \mu - 1/T$ ' variations and the energies:  $E_d$  and  $E_m$ , involved in the two separate thermally activated processes, are almost identical.

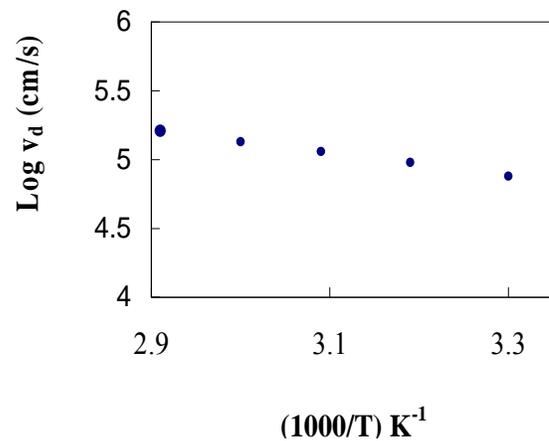
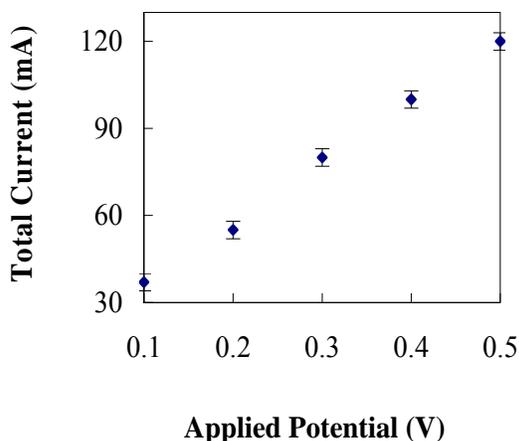


Fig. 6:  $\log v_d - 1/T$  plot for NCPE OCC: 95 [70PEO:30KBrO<sub>3</sub>] + 5 SiO<sub>2</sub>.

To ensure that the peak current ( $I_T$ ) data, used to evaluate  $v_d$ , are genuine i.e. free from the effect of instant polarization charge build-up in NCPE OCC on the application of external dc potential, the current values were instantly measured after

the dc voltages were applied. Figure 7 shows 'current vs voltage' plot for the NCPE OCC: 95 [70PEO:30KBrO<sub>3</sub>] + 5 SiO<sub>2</sub>. The linear (Ohm's-law type) variation of current with voltage clearly indicated the fact that the  $I_T$ -data used for the determination of  $v_d$  were appropriate and almost free from the effects of instant polarization charge build-up in the sample.



**Fig. 7:** ' $I_T$  versus V' plot for NCPE OCC: 95 [70PEO:30KBrO<sub>3</sub>] + 5 SiO<sub>2</sub>.

## Conclusions

Materials characterization and formation of NCPEs have been studied. The ionic drift velocity and corresponding energies have been determined with the help of temperature dependent  $\sigma$ ,  $\mu$ ,  $n$ , and  $I_T$  measurements. The ionic transference number measurements by dc polarization clearly indicated the fact that the present NCPEs are almost pure ion conducting materials with majority of K<sup>+</sup> ions take part in conduction process. Hence, the polymeric electrolyte membranes may prove to the suitable candidates for fabricating all-solid-state devices.

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