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Research Article

SYNTHESIS AND CHARACTERIZATION OF HOT-PRESSED SOLID POLYMER ELECTROLYTES: (1-x) PEO: x $KBrO_3$

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ABSTRACT

Synthesis and ion transport characterizations on hot-pressed solid polymer electrolytes (SPEs): (1-x) PEO: x $KBrO_3$, where x in wt. (%), are reported. The compositional (x) dependent conductivity (σ) studies revealed SPE film: (70PEO: 30$KBrO_3$) as the Optimum Conducting Composition (OCC) with room temperature conductivity $\sigma \sim 4.36 \times 10^{-7}$ Scm^{-1}, which is more than two orders of magnitude higher than that of pure PEO. To understand the ion transport behavior in SPE films, the measurement on some basic ionic parameters viz. ionic conductivity (σ), ionic mobility (μ) and mobile ion concentration (n) have been carried out using different experimental techniques. Material characterizations were done with the help of XRD, SEM, DSC and TGA techniques. The activation energies (E_a) values have been computed from 'log σ - 1/T' Arrhenius plots. Thin film solid-state polymeric batteries were also fabricated using SPE OCC as electrolyte and the cell-potential discharge characteristics were studied under different load conditions.

Keywords: Solid polymer electrolyte, Hot-press technique, Ionic mobility, XRD, SEM, DSC, TGA, Solid-state polymeric battery.

INTRODUCTION

The development of new polymer electrolytes is one of the important areas of research in the last 35 years. Among the known polymer electrolytes, the ion conducting Solid Polymer Electrolytes (SPEs) having great technological relevance's in the fabrication of all-solid-state electrochemical devices such as batteries, fuel cells, electro-chromic displays, smart windows, sensors etc.[1-7] SPEs possess both the liquid like conductivity and solid like mechanical stability including flexibility, which are the characteristic materials advantages favoring them for the thin film devices of desirable shape/ sizes. The first ion conducting polymeric material was discovered in 1973[5]. Since then, a large numbers of polymer electrolytes involving variety of mobile ions viz. H^+, Li^+, Ag^+, K^+, Na^+ etc., as principal charge carriers, have been reported in the last nearly three and half decades. PEO has been commonly employed as polymeric host for salt complexation as it possesses exceptional ability to dissolve high concentrations of variety of salts [8,9]. Solid polymer electrolytes are traditionally prepared by solution-cast method. Recently, a solvent-free, hot-press method has been developed for casting polymer electrolyte membranes [10-15]. The present paper reports, synthesis and ion transport property studies of new solid polymer electrolytes (SPEs): (1-x) PEO: x $KBrO_3$, casted by hot-press technique. Based on this hot-pressed SPE OCC, solid state thin film battery fabrication, discharge characteristics and cell parameters were also studied under different load conditions.

RT: 27 °C

MATERIALS AND METHODS

For synthesis of SPEs: (1-x) PEO: x $KBrO_3$, where x = 0, 5, 10, 15, 20, 25, 30, 35, 40, 50 (wt. %), AR grade precursor chemicals: poly (ethylene oxide) PEO (10^5 Mw, Aldrich, USA) and $KBrO_3$ (purity > 98%, Merck, India) were used. Dry powders of constituent chemicals in appropriate wt. (%) ratios were homogeneously mixed for ~ 30 min at room temperature then heated separately ~ 70 °C (close to the melting point of PEO) for ~ 30 min with mixing continued. It resulted into a soft lump/ slurry which was then pressed (~ 1.25 ton/ cm^2) between two SS- cold blocks, giving rise to a uniform film of thickness ~ 0.013 cm. The details related to hot- press casting of SPEs have been given elsewhere in the literature.[11-15] Material characterizations were done with the help of XRD (model: Shimadzu), SEM (model: JEOL, JXA-8100, Japan), DSC (model: Perkin Elmer) and TGA (model: SDT Universal) techniques. The conductivity (σ) -measurements were carried out on different samples at a fixed frequency (i.e. 5 kHz) using an LCR- bridge (model: HIOKI 3520- 01, Japan). Ionic mobility (μ) was determined directly employing dc polarization Transient Ionic Current (TIC) technique using an x-y-t recorder (model: Graphtec WX 2300-1L, Japan)[16]. Subsequently, mobile ion concentration (n) was evaluated from σ and μ data. The activation energy (E_a) values were also determined by temperature dependent conductivity studies.

Thin film solid-state polymeric batteries were fabricated in the following cell configuration:

K (Anode)	(70PEO: 30$KBrO_3$) (SPE OCC membrane)	(C+I_2+Electrolyte) (Cathode film)

The cell performances were studied under different load conditions at room temperature and the important cell parameters were calculated from the plateau of the discharge profiles.

RESULTS AND DISCUSSION

The room temperature conductivity (σ) variation with different salt concentration for hot-pressed solid polymer electrolytes (SPEs): (1-x) PEO: x $KBrO_3$, as shown in Figure 1. The ionic conductivity (σ) increased abruptly (~10^2 times) after the addition of salt in the host polymer. However, a moderate sized σ-maxima appeared at x = 30 wt.(%) and then decreases on further addition of salts. SPE films beyond 50 wt. (%) salt concentration were brittle and appeared physically less stable. SPE film: (70PEO: 30$KBrO_3$), with room temperature conductivity ($\sigma \sim 4.36 \times 10^{-7}$ S/cm), exhibited optimum conductivity and this has been referred to as Optimum Conducting Composition (OCC). The similar system has also been reported, prepared by usual solution-cast technique with room temperature conductivity ($\sigma \sim 7.74 \times 10^{-8}$ S/cm)[4]. The reason for conductivity enhancement in the present hot-pressed SPE OCC film has been identified from the ionic mobility (μ) and mobile ion concentration (n) measurements on different SPE films at room temperature, as mentioned in Section 2. Figure 2 shows 'log μ-x' and 'log n – x' plots for SPE films: (1-x) PEO: x $KBrO_3$.

It can be clearly noted that ionic mobility (μ) slightly increased and a maxima was obtained for mobile ion concentration (n) at: x = 30 (wt. %), akin to that of 'log σ – x' plot of Figure 1. The room temperature values of all these ionic parameters: σ, μ, n, are listed in Table 1 along with the activation energy (E_a) and σ- value of pure PEO.

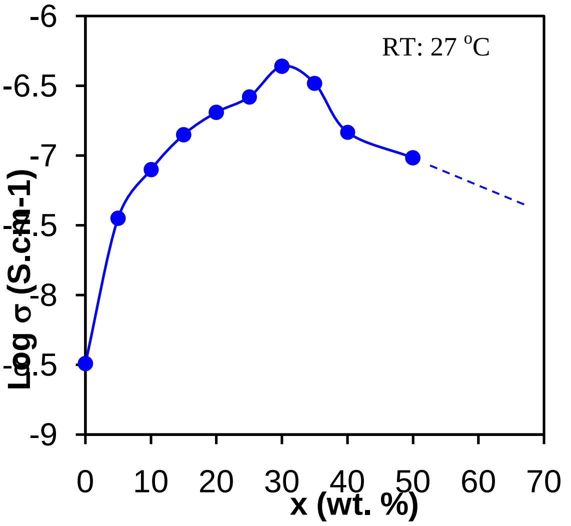

Fig. 1: 'Log □- x' plots for SPEs: (1-x) PEO: x $KBrO_3$

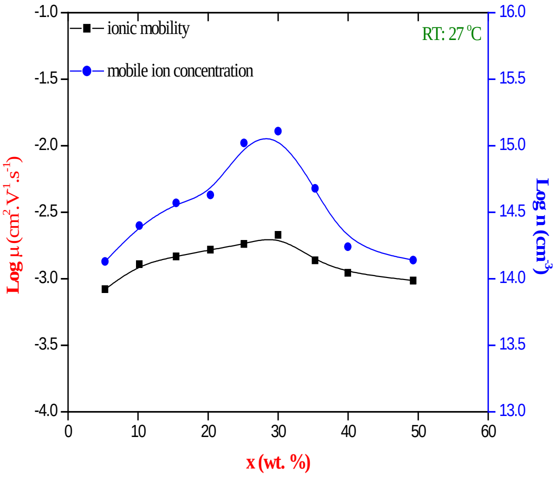

Fig. 2: 'Log μ – x' and 'log n – x' plots for SPEs: (1-x) PEO: x $KBrO_3$

Table 1: Room temperature values of some important ionic parameter: σ, μ, n & E_a for SPE OCC and σ-value of pure PEO.

Film	σ (S/cm)	μ($cm^2\ V^{-1}\ s^{-1}$)	n (cm^{-3})	E_a (eV)
Pure: PEO	3.2×10^{-9}	-	-	-
SPE OCC: (70PEO: 30$KBrO_3$)	4.36×10^{-7}	2.12×10^{-3}	1.28×10^{15}	0.35

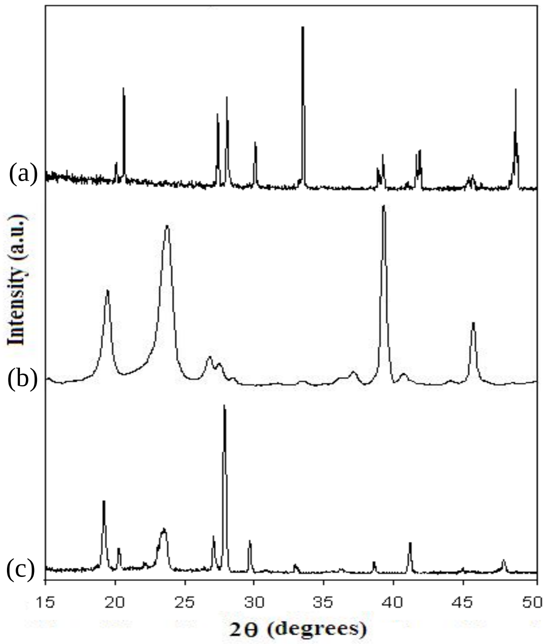

Fig. 3: XRD patterns: (a) $KBrO_3$, (b) pure PEO, (c) SPE OCC: (70PEO: 30$KBrO_3$)

One can obviously note from the table 1 that the reason for the overall increase in conductivity of SPE OCC has been predominantly due to the increase in both μ and n which can be attributed as a consequence availability of relatively larger number of mobile ions at this composition.

The x-ray diffraction patterns for the SPE OCC: [70PEO: 30$KBrO_3$], pure PEO and pure $KBrO_3$ is shown in Figure 3. One can clearly note that from the figure, the some peaks became relatively broader as well as less prominent/ feeble after salt complexation in SPE OCC and this is the indicative of formation of new complex compound as well as polymer-salt complexation. The surface morphology of SPE OCC was observed by scanning electron micrograph (SEM), as shown in Figure 4. The smooth surface morphology of SPE OCC is clearly indication of increase in degree of amorphicity/ reduction in the degree of crystalline of pure PEO after salt complexation. This is due to the cross-linking with polymer and salts, as always observed by the Chu et al[17].

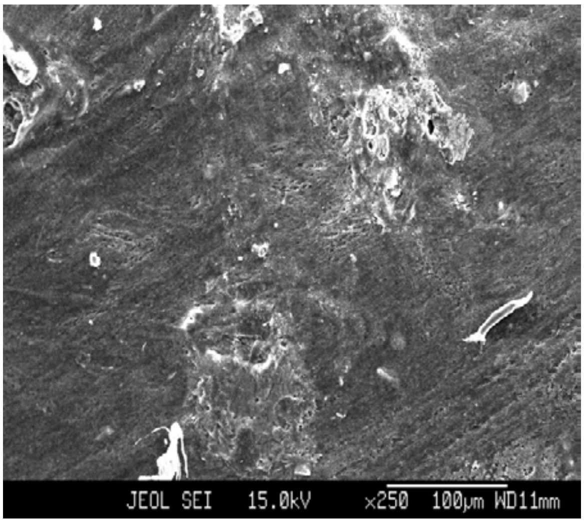

Fig. 4: SEM image of SPE OCC: (70PEO: 30KBrO$_3$)

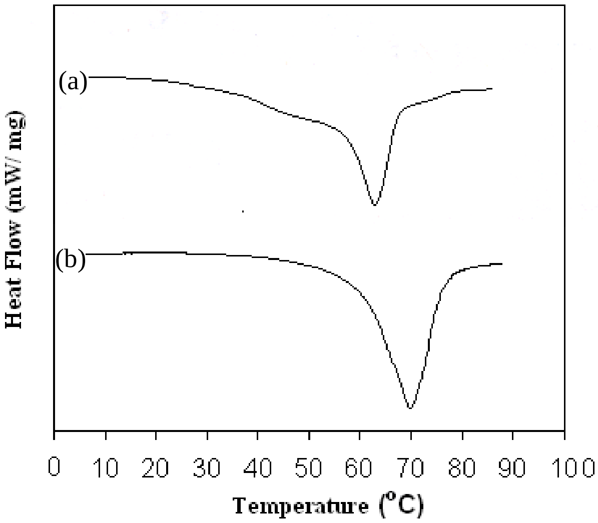

Fig. 5: DSC thermogrames: (a) pure PEO, (b) SPE OCC: (70PEO: 30KBrO$_3$)

Figure 5 shows the DSC thermogrames for the pure PEO and SPE OCC. The broad endothermic peak was observed in SPE OCC at ~ 69 -70 °C and it is corresponding to the melting point temperature of pure PEO. The slightly shifting in the melting point temperature towards higher side is due to the complexation of K$^+$ ion to the ether oxygen of pure PEO and it is also indicative the confirmation of polymer-salt complexation.

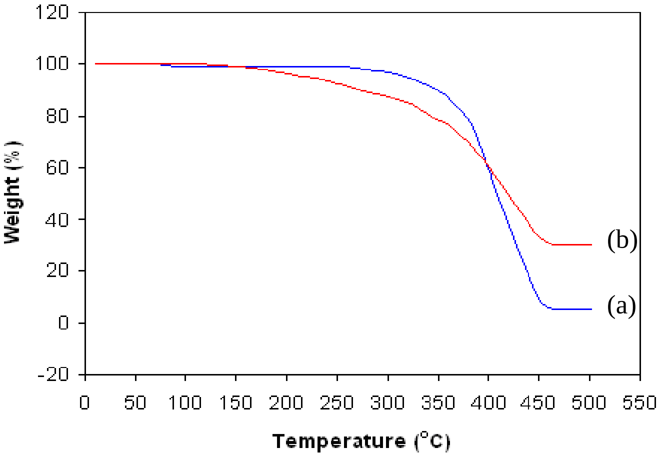

Fig. 6: TGA curves: (a) pure PEO and (b) SPE OCC: (70PEO: 30KBrO$_3$)

Figure 6 shows the Thermo- Gravimetric Analysis (TGA) curves for pure PEO and SPE host: (70PEO:30KBrO$_3$). It can be clearly seen from the figure that the total weight loss for pure PEO is larger as compared to both SPE host and NCPE OCC. The total weight loss for pure PEO is ~ 95 % and SPE OCC is ~ 70 %. The thermal stability of polymer is improved by the polymer-salt complexation

Figure 7 shows the temperature dependent conductivity measurements on SPE films: (1-x) PEO: x KBrO$_3$. The conductivity increased almost linearly with temperature up to ~ 65 ^{o}C at which an upward jump in conductivity was observed at all the compositions.

The sudden jump in conductivity at this temperature corresponds to semi-crystalline to amorphous phase transition temperature (T$_m$) of pure PEO. The linear portion of ‘log σ -1/T’ plots below T$_m$ can be expressed by Arrhenius type equation:

$$\log \sigma = \log \sigma_o \exp(-E_a/kT) \qquad [\mathrm{Scm^{-1}}] \qquad (1)$$

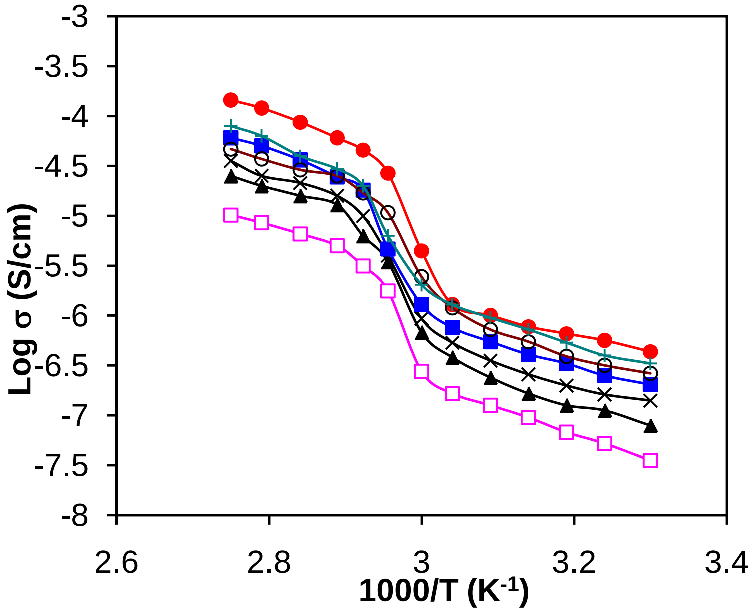

Fig. 7: ‘Log □□- 1/T’ plots for SPEs: (1-x) PEO: x KBrO$_3$. x = 5 (□), 10 (▲), 15 (×), 20 (■, 25 (o), 30 (●, 35 (+)

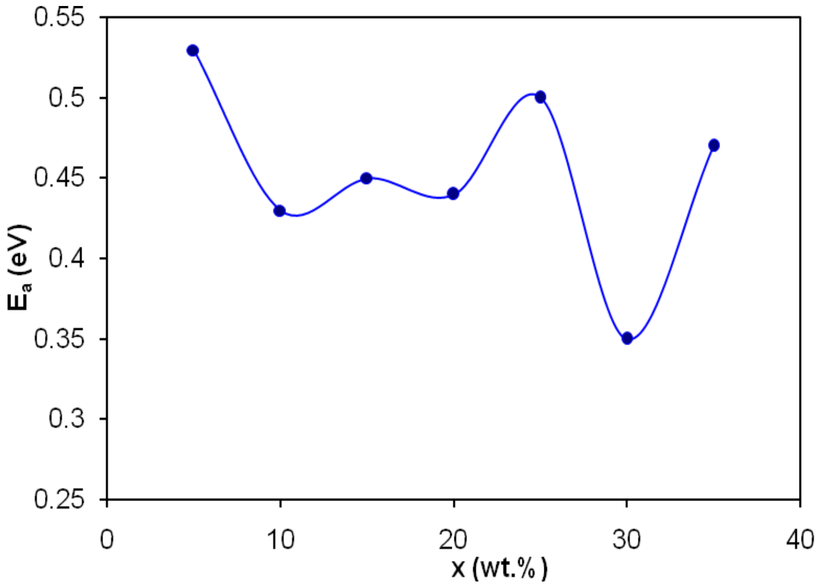

Fig. 8: Variation of activation energy (E$_a$) as a function of x

where σ$_o$ is the pre-exponential factor, k is the Boltzmann constant and E$_a$ is the activation energy (in eV). The E$_a$ values, for all the compositions, were computed from linear least square fitting of the above equation and plotted as a function of x, as shown in Figure 8. The SPE OCC shows low activation energy E$_a$ ~ 0.35 eV, is due to the increase in degree of amorphicity as compared to the other polymer-salt compositions and it is indicative of relatively easier ion migration in the system. The room temperature cell potential discharge characteristics of thin film solid-state polymeric batteries at different load conditions i.e. 100 & 50 kΩ respectively, is shown in Figure 9. An Open Circuit Voltage (OCV) ~ 2.58 V, obtained for all the batteries.

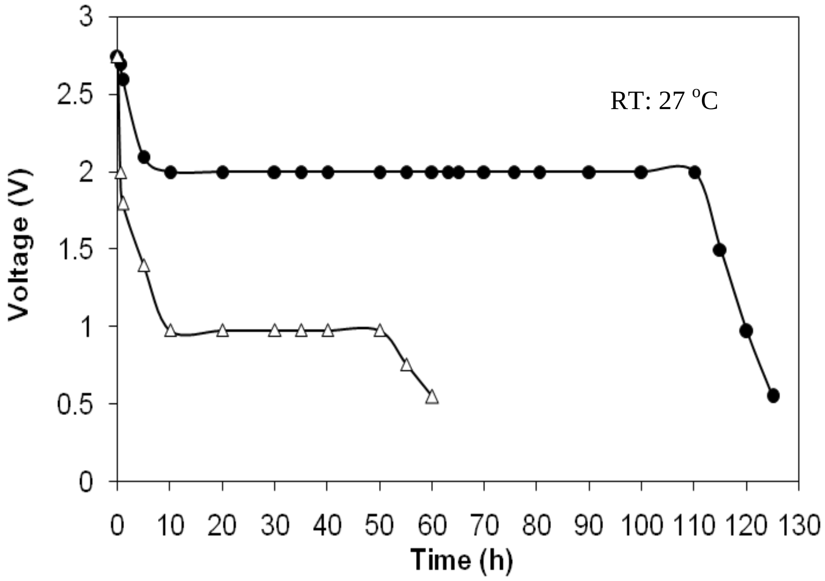

Fig. 9: Cell potential discharge profiles for the thin film solid state battery: K / (70PEO: 30KBrO$_3$) / (C+I$_2$+Electrolyte) under 100 kΩ (●) and 50 kΩ (Δ) loads

The initial sharp decrease in voltage of these thin film solid-state batteries may be due to the initial cell polarization effect and/ or the formation of a thin layer of potassium salt at the electrode/ electrolyte interface. The some important cell parameters calculated in the plateau region of the discharge profiles are listed in Table 2. On the basis of cell parameter studies, one can clearly note that the performances of the batteries have been relatively superior and quit satisfactorily during low current drain states.

Table 2: Some important cell parameters for the thin film solid state battery

Load(kΩ)	Working Voltage(V)	Current Density (μA.cm^{-2})	Discharge Capacity (μA.h)	Power Density (mW.kg^{-1})	Energy Density(mWh.kg^{-1})
100	2.00	1.6	228	24.53	2797
50	0.98	0.78	44.1	5.89	265.14

CONCLUSION

A new hot-pressed solid polymer electrolyte: (70PEO: 30KBrO$_3$) (wt. %) has been synthesized. The conductivity enhancement in SPE OCC is due to the increase in both ionic mobility and mobile ion concentration. XRD, SEM, DSC, TGA studies have been confirmed the polymer-salt complexation. The ion conduction mechanism in SPE film has been explained on the basis of experimental studies on some basic ionic parameters viz. σ, μ and n. A thin film solid-state battery discharge characteristics have been studied under varying load conditions and the cell performed quit satisfactorily under low current drain states.

REFERENCES

1. Scrosati B. Applications of electroactive polymers. London: Chapman and Hall; 1993.
2. Armand MB, Chabagno JM, Duclot JM, editors. Fast Ion Transport in Solids. North Holland; 1979.
3. Khan MS, Shaoor A, Nisar J. Conductance study of PEO and PPO-based polymer electrolytes. Ionics 2010; 16: 539.
4. Sreekanth T, Reddy MJ, Rao UVS. Polymer electrolyte system based on (PEO+KBrO$_3$) -its application as an electrochemical cell. J Power Sources 2001; 93: 268.
5. Fenton DE, Parker JM, Wrigth PV. Complexes of alkali metal ions with PEO. Polymer 1973; 14: 589.
6. Armand MB. Polymer Electrolyte Reviews. London: Amsterdam; 1987.
7. Hashmi SA, Chandra S. Experimental investigations on a sodium ion conducting polymer electrolyte based on PEO complexed with NaPF$_6$. J Materials Sci and Engg B 1995; 34: 18.
8. Bhide A, Kariharan K. A new polymer electrolyte system (PEO)n: NaPO$_3$. J Power Source 2006; 159: 1450.
9. Mohapatra SR, Thakur AK, Choudhary RNP. Studies on PEO-based sodium ion conducting composite polymer films. Ionics 2008; 14: 255.
10. Appetecchi GB, Hasson J, Scrosati B, Salomon M, Cassel F. Hot-pressed, dry, composite, PEO-based electrolyte membranes: I. Ionic conductivity characterization. J Power Sources 2003; 114: 105.
11. Agrawal RC, Chandra A. Ion transport and electrochemical cell performance studies on hot-press-synthesized Ag$^+$ ion conducting electroactive polymeric membranes: (1-x) PEO : x [0.7(0.75AgI:0.25 AgCl):0.3 MI]. J Phys D Appl Phys 2007; 40: 7024.
12. Agrawal RC, Chandra A, Bhatt A, Mahipal YK. Investigations on ion transport property and battery discharge characteristics studies on hot-pressed Ag$^+$ ion conducting nano-composite polymer electrolytes: (1-x) [90PEO:10AgNO$_3$] : x SiO$_2$. New J Physics 2008; 10: 043023.
13. Chandra A, Agrawal RC, Mahipal YK. Ion transport property studies on PEO-PVP blended solid polymer electrolyte membranes. J Phys D Appl Phys 2009; 42: 135107.
14. Chandra A. Hot-pressed polymer electrolytes: Synthesis and characterization. Germany: Lambert Academic Publisher; 2010.
15. Chandra A. Hot-pressed Na$^+$ ion conducting solid polymer electrolytes: (1-x) PEO: x NaPO$_3$. Eur Phys J Appl Phys 2010; 50: 21103.
16. Watanable M, Sanui K, Ogata N, Kobayashi T, Ontaki Z. Ionic conductivity and mobility in network polymers from poly (propylene oxide) containing lithium perchlorate. J Appl Phys 1985; 57: 123.
17. Chu PP, Reddy JM, Kao HM. Novel composite polymer electrolyte comprising mesoporous structured SiO$_2$ and PEO/Li. Solid State Ionics 2003; 156: 141.