

Synthesis and characterization of hot pressed ion conducting solid polymer electrolytes: $(1 - x)$ PEO: x NaClO₄

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Abstract. Synthesis and ion transport characterization of hot-pressed poly(ethylene oxide) PEO-based solid polymer electrolytes (SPEs): $(1 - x)$ PEO: x NaClO₄, where $0 < x < 50$ wt.%, are reported. The composition: (70PEO: 30NaClO₄) with ionic conductivity (σ) $\sim 7.07 \times 10^{-7}$ S cm⁻¹ shows the highest conducting composition and this have been referred to as optimum conducting composition (OCC). Materials characterization and thermal behavior of the present SPEs have been done with the help of XRD, FTIR, SEM, DSC and TG analysis. To determine the activation energy, temperature dependent ionic conductivity (σ) of different compositions has been measured. Ionic nature of the SPEs has been explained with the help of ionic transference number (t_{ion}) measurements. Finally, the thin film polymer battery is also fabricated using the SPE OCC as electrolyte and calculated their cell parameters at room temperature.

1 Introduction

Ion conducting 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 [1–4]. The main materials advantages of the solid polymer electrolytes are their good mechanical processability, 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 [5]. Since then, a large number of different ion conducting solid polymer electrolytes (SPEs) have been reported [6–8]. 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 [9–12]. 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 [13,14].

To understand the ion conduction phenomenon and ionic behavior of Na⁺ ion conducting polymeric systems, the present investigation reports synthesis, characterization and device applications of hot-pressed solid polymer electrolytes (SPEs): $(1 - x)$ PEO: x NaClO₄, where $0 < x < 50$ wt.%. Materials characterization and polymer-salt complexations have been reported with the help of different experimental techniques, as mentioned in Section 2.

2 Experimental

Poly(ethylene oxide) PEO (10⁵ MW, Aldrich, USA) and sodium chlorate NaClO₄ (>99%, Merck), have been used as the starting materials for the synthesis of hot-pressed solid polymer electrolytes (SPEs): $(1 - x)$ PEO: x NaClO₄, where $0 < x < 50$ wt.%. By using NaClO₄ as complexing salt in poly(ethylene oxide) PEO, SPE films were cast employing hot-press technique. The details about the hot-press technique used for casting SPEs have been discussed in our earlier communications [10–12]. The polymer-salt complexation were done with the help of X-ray diffraction (XRD) (model: Shimadzu), scanning electron micrograph (SEM) (model: JEOL, JXA-8100, Japan). To explain the thermal behavior of the present system,

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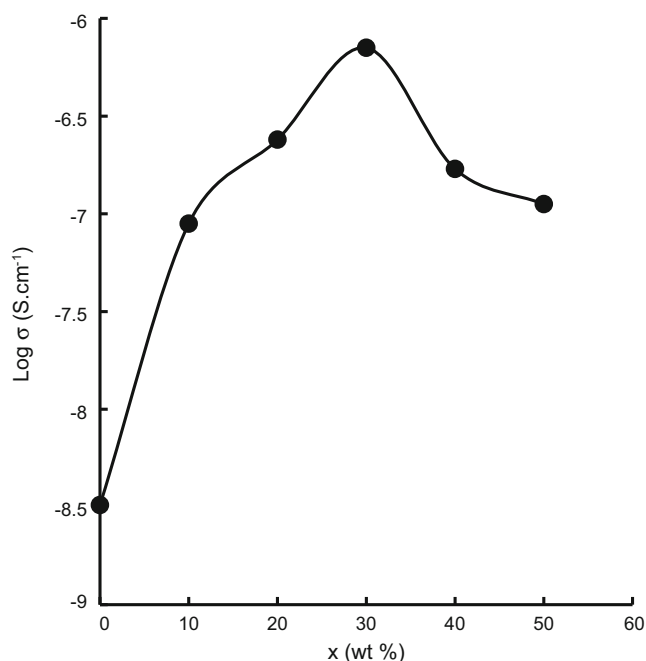
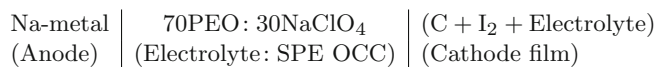


Fig. 1. Compositional dependent conductivity of SPEs: $(1-x)$ PEO: x NaClO₄, where x in wt.%.

DSC analysis (DSC) (model: Perkin Elmer) and thermogravimetric analysis (TGA) (model: SDT Universal) has been carried out for the both pure PEO and SPE OCC. The conductivity measurements were carried out using an LCR-bridge (HIOKI 3520-01, Japan) at room temperature and above with the help of equation: $\sigma = [l/RA]$, with l , thickness; R , bulk resistance and A , area of the polymeric film. The ionic transference number (t_{ion}) of the SPE OCC has been determined at room temperature with the help of dc polarization transient ionic current (TIC) technique [15,16].

A solid-state polymeric battery was fabricated using SPE OCC as electrolytes in the following cells configuration:



The cathode film has been prepared by hot-pressing the physical mixture of elemental iodine (I₂), conducting graphite (C) and SPE OCC in 1:1:1 weight ratios at ~50 °C. The cell performances were studied under different load conditions at room temperature and some important cell parameters were also calculated from the plateau of the discharge profiles.

3 Results and discussion

Figure 1 shows the room temperature conductivity (σ) variations for the hot-pressed SPE films: $(1-x)$ PEO: x NaClO₄, $0 < x < 50$ wt.%. The conductivity increased when the Na⁺ ion salt NaClO₄ concentration increased initially from 0 to 30 wt.% and then decreased on further

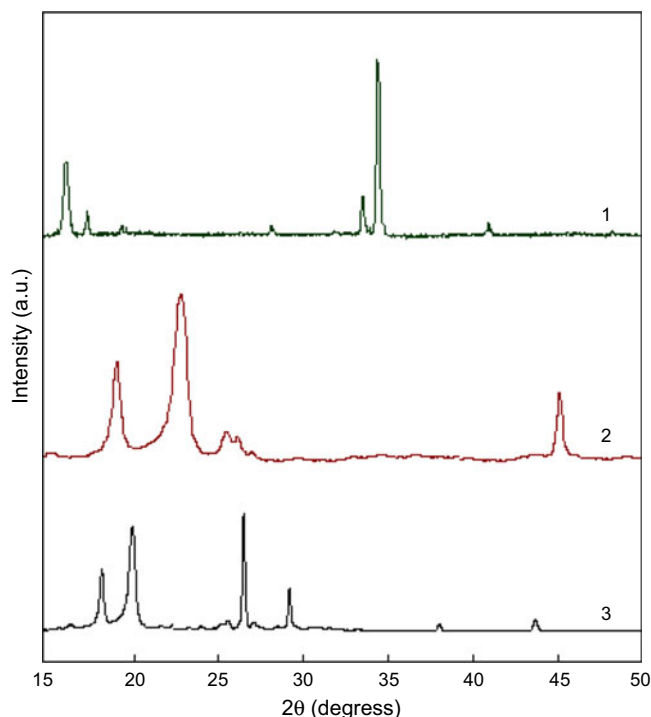


Fig. 2. XRD patterns: (1) NaClO₄, (2) pure PEO and (3) SPE OCC: (70PEO: 30NaClO₄).

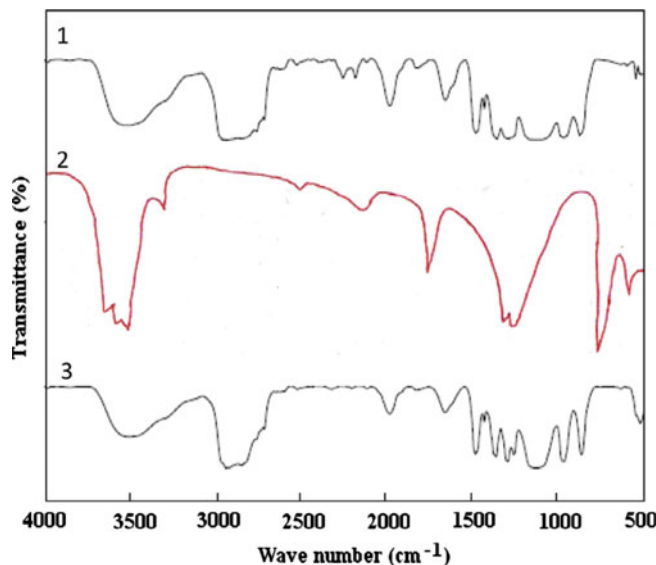


Fig. 3. FTIR Spectrums: (1) pure PEO, (2) NaClO₄ and (3) SPE OCC: (70PEO: 30NaClO₄).

addition of salts. The conductivity maxima appeared at $x = 30$ wt.% i.e., the composition: [70PEO: 30NaClO₄] with $\sigma \sim 7.07 \times 10^{-7}$ S cm⁻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 the present SPE OCC from that of the pure PEO ($\sigma \sim 3.2 \times 10^{-9}$ S cm⁻¹). The increase in conductivity

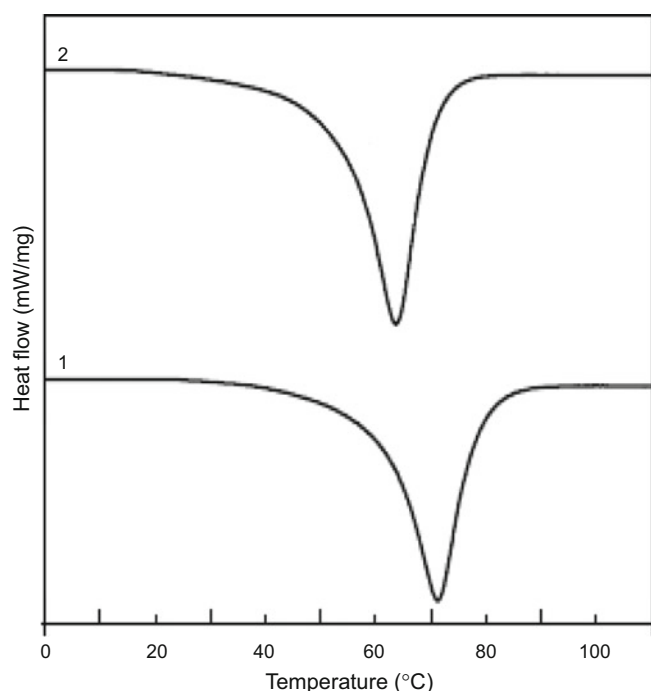


Fig. 4. DSC curves: (1) pure PEO and (2) SPE OCC: (70PEO: 30NaClO₄).

Table 1. Melting temperature (T_m), degree of crystalline (χ), weight loss and decomposition temperature (T_d) for pure PEO and SPE OCC: (70PEO: 30NaClO₄).

Systems	T_m (°C)	χ (%)	Weight loss (%)	T_d (°C)
Pure PEO	69	100	95	220
SPE OCC	62	81	75	275

is due to the increase in degree of amorphicity and this has been confirmed from XRD, SEM and TG analysis, as discussed below. The decrease in ionic conductivity after 30 wt.% or at higher salt concentration is due to the usual blocking effect created by the ion-ion association (pairing) effect, as reported elsewhere [17].

Figure 2 shows the XRD patterns of pure salt NaClO₄, pure PEO and SPE OCC: (70PEO: 30NaClO₄). It can be clearly seen from the figure that characteristic peaks of pure PEO appeared between $2\theta = 15-30^\circ$ is decreased after the addition of salt NaClO₄. Some of the peaks of pure PEO became relatively less-prominent/feeble and disappears after polymer-salt complexation. This is usually attributed to the increase in the degree of amorphicity or decrease in degree of crystallinity and it is strong evidence of confirmation of polymer-salt complexation.

Figure 3 shows the FTIR spectra of complexation between PEO with salt NaClO₄. Peaks between 550 to 820 cm⁻¹ are assigned to the presence of free ClO₄⁻ anions. Peaks in the region 850–1450 cm⁻¹ correspond to -C-O-C- stretching. Some important peaks related to PEO at about 1050, 1080 and 1170 cm⁻¹ related to -C-O-C- symmetric and asymmetric stretching vibrations are characteristics of crystalline PEO phase.

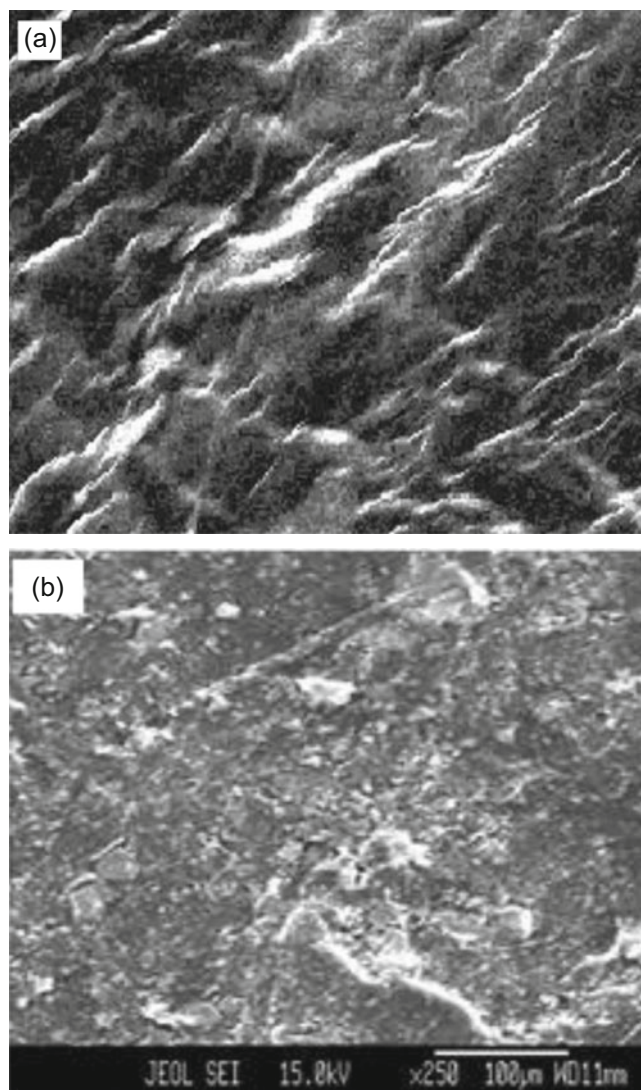
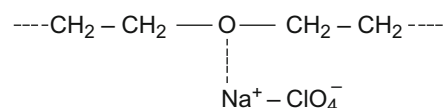


Fig. 5. SEM images: (a) pure PEO [21] and (b) SPE OCC: (70PEO: 30NaClO₄).

The width of the absorption band of the C-H stretching modes between the region 3200–2900 cm⁻¹ decreases with addition of the salt, as reported in our earlier communications [17,18]. These FTIR results are in agreement with the ionic conductivity results as the dissociation of ion aggregates with the addition of salt enhances the free ion concentrations and hence ionic conductivity. With the addition of NaClO₄, changes in the frequencies of -C-O-C- vibrations of PEO may be due to the weakening of interaction between ether oxygen of PEO and NaClO₄ and it is also observed from FTIR spectra that peaks at around 1000–1150 cm⁻¹ corresponding to the crystalline PEO phase disappeared. The possible configuration of newly synthesized hot-pressed SPE OCC illustrated:



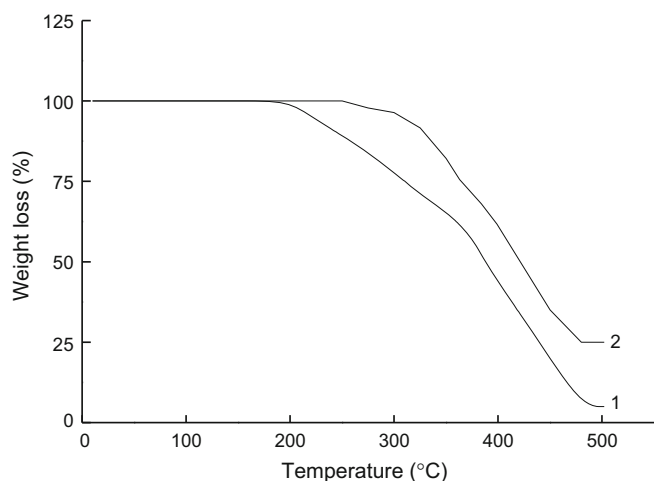


Fig. 6. TGA curves: (1) pure PEO and (2) SPE OCC: (70PEO: 30NaClO₄).

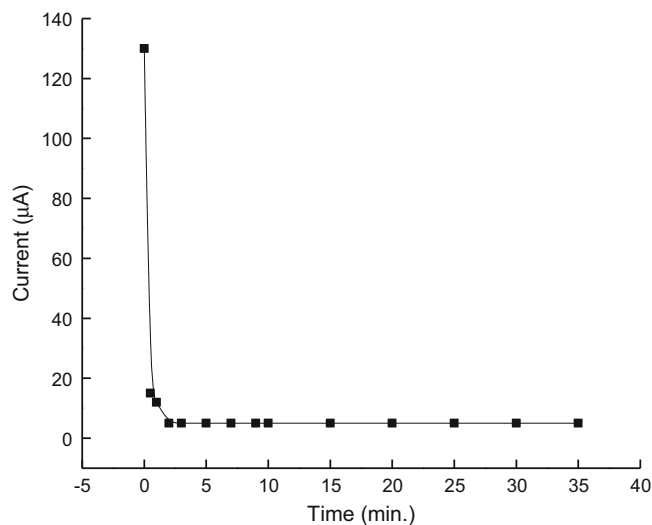


Fig. 8. “Current vs. time” plot for the cell: [SS // SPE OCC // SS].

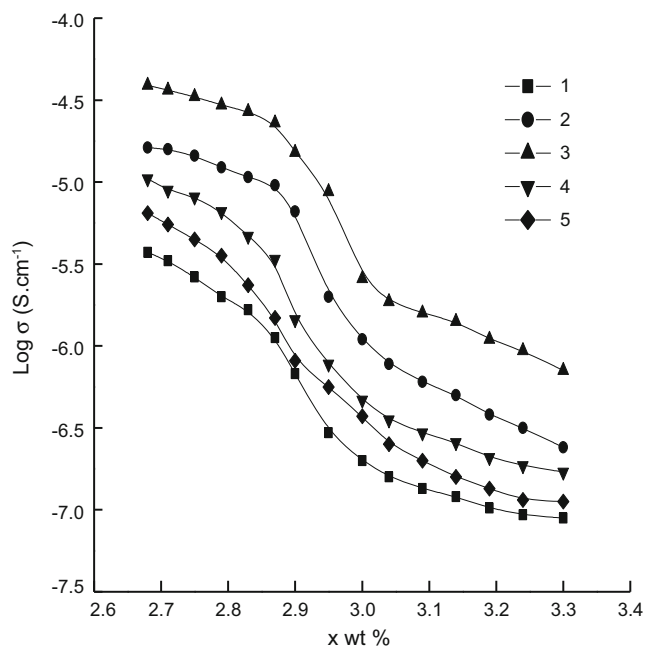


Fig. 7. “Log $\sigma - 1/T$ ” plots for the hot-pressed SPEs: (1 - x) PEO: x NaClO₄, where x in wt. %: 1 (10), 2 (20), 3 (30), 4 (40) and 5 (50).

Table 2. Pre-exponential factor (σ_0) and activation energy (E_a) values for all the compositions of SPEs: (1 - x) PEO: x NaClO₄, where x in wt. %

Systems	σ_0	E_a (eV)
90PEO: 10NaClO ₄	1.50×10^{-2}	0.31
80PEO: 20NaClO ₄	9.40×10^{-1}	0.39
70PEO: 30NaClO ₄	4.63×10^{-1}	0.34
60PEO: 40NaClO ₄	3.19×10^{-3}	0.25
50PEO: 50NaClO ₄	6.27×10^{-3}	0.29

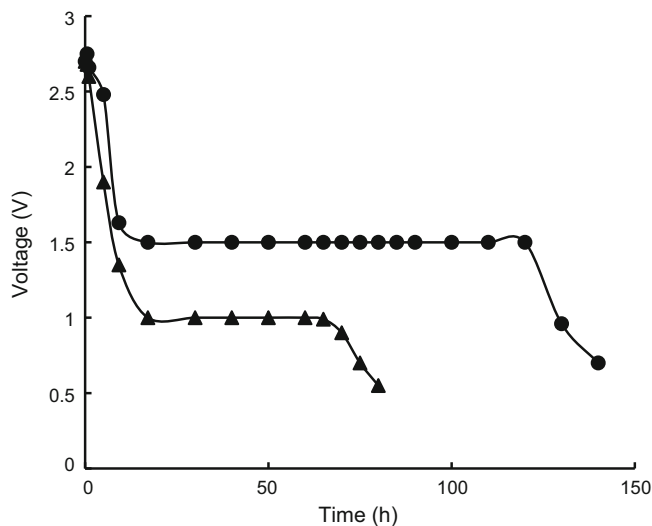


Fig. 9. Discharge characteristics of a solid state polymeric cell: [Na // SPE OCC // (C + I₂ + SPE OCC)] at different loads: 100 k Ω (●) and 50 k Ω (▲).

All the above changes in the FTIR spectra of SPE OCC indicated that an increase in PEO flexibility and amorphicity which leads to further increase in the ionic conductivity of the polymeric system.

Figure 4 shows the DSC thermograms for pure PEO and a hot-pressed SPE OCC: (70PEO: 30NaClO₄). The broad endothermic peak in SPE OCC ~ 62 °C is corresponding to the melting point temperature of pure PEO. The slight shift in the melting point temperature towards lower side (i.e., 72–62 °C) has also been observed and it is due to the decrease in degree of crystallinity after polymer-salt complexation. The degree of crystallinity (χ) has been calculated by assuming that pure PEO being 100% with the equation $\chi = (\Delta H_f / \Delta H_f^0)$ (where ΔH_f^0 is the heat of

Table 3. Some important cell parameters of the solid state polymeric cell at room temperature.

Load (kΩ)	Working voltage (V)	Current density ($\mu\text{A cm}^{-2}$)	Discharge capacity ($\mu\text{A h}$)	Power density (mW kg^{-1})	Energy density (mWh kg^{-1})
100	1.5	1.00	180	13.9	1677
50	1.0	0.67	65	6.21	403.7

fusion of pure PEO and ΔH_f is the heat enthalpy related to salt in PEO), as reported in various workers [19,20]. Table 1 shows the melting temperatures (T_m), degree of crystalline (χ) and weight loss for pure PEO and SPE OCC for direct comparison. It can be clearly shown from the table that the lower T_m and χ in SPE OCC is due to the increase in degree of amorphicity and it also indicates the polymer-salt complexation.

Figure 5 shows SEM images of pure PEO and hot-pressed SPE OCC: (70PEO: 30NaClO₄). It can be clearly seen from the figure that the addition of salts in polymer resulted in improved surface morphology in the present SPE OCC while the pure PEO shows the rough morphology structure. The change in morphology is closely related to the reduction of pure PEO crystallinity or increase in degree of amorphicity after the polymer salt complexation [21,22].

Figure 6 shows the TGA curves of pure PEO and SPE OCC: (70PEO: 30NaClO₄). TGA curve indicated that there is no weight loss up to 200 °C. A gradual weight loss has been observed up to 350 °C and above this temperature there is a rapid weight loss which could be due to the degradation of polymer electrolytes. The total weight loss for pure PEO is $\sim 95\%$ and SPE OCC is $\sim 75\%$. The higher thermal stability has been observed in the present SPE OCC and it is due to the interaction of pure PEO with salt. The increase in decomposition temperature (T_d) is also responsible for thermal stability of the system, as listed in Table 1.

Figure 7 shows the temperature dependant conductivity variations for hot-pressed SPEs: $(1 - x)$ PEO: x NaClO₄. “Log $\sigma - 1/T$ ” plots exhibited straight line behavior with an upward change in slope at ~ 70 °C which is due to the well-known semi-crystalline to amorphous phase transition. The change in ionic conductivity with temperature in PEO-based SPEs can be explained in terms of polymer segmental motion and increase in free volume [23,24]. The linear portion below the transition temperature (~ 70 °C) of SPEs exhibits following Arrhenius type equation:

$$\sigma(T) = \sigma_o \exp(-E_a/kT) \quad [\text{S cm}^{-1}], \quad (1)$$

where σ_o is the pre-exponential factor, E_a is activation energy in eV, k is Boltzmann constant and T is temperature in Kelvin. The σ_o and E_a for all the compositions have been determined by least square linear fitting of the data and listed in Table 2. The lower E_a values in the present SPE films have been observed as compared to hot-pressed film of pure PEO ($E_a \sim 0.91$ eV [22]) and this can be potentially used for solid state device fabrications.

The variation of current with time is shown in Figure 8. Ionic transference number (t_{ion}) ~ 0.95 obtained for the present SPE OCC at room temperature and it indicates the majority of charge carriers ($\sim 95\%$) are cations Na⁺ and only a very small contribution ($\sim 5\%$) of anions. Figure 9 shows the cell potential discharge profiles for the solid state polymeric cell: [Na // SPE OCC // C + I₂ + SPE OCC] under two different loads viz. 100 kΩ, 50 kΩ at room temperature. The elemental iodine (I₂) acts as “active cathode”. The addition of conducting graphite powder to the cathode material enhances its electronic conductivity and hence, cathode can also act as a current collector. The addition of polymer electrolyte to the cathode mixture provides more interfacial contact area between the cathode and electrolyte and hence, reduces the interfacial resistance and resulting better battery performance [25,26]. The open circuit voltage (OCV) is ~ 2.7 V obtained for both the cells. It can be clearly noticed that except for the initial potential drop, OCV value remained practically stable for ~ 120 h. (i.e., during a low current drain state). However, the cell potential decreased relatively faster when discharge through 50 kΩ load (i.e., during higher current drain states). The initial sharp decrease in voltage may be due to polarization and/or the formation of thin layer of sodium salt at electrode-electrolyte interface [27,28]. For direct comparison of cell parameters, are listed in Table 3. On the basis of these studies, it can be observed that the present polymeric cell, performed fairly satisfactorily especially during low current drains at room temperature.

4 Conclusions

A new hot-pressed solid polymer electrolyte: (70PEO: 30NaClO₄) have been investigated. Two orders of conductivity enhancement were achieved from that of the pure PEO. The ionic conductivity enhancement, materials characterization and polymer-salt complexation have been successfully explained with the help of XRD, FTIR, DSC and TGA studies. The low activation energy in the present SPE indicated that it can be potentially used for electrochemical device applications. A solid-state polymeric battery discharge characteristics have been studied under varying load conditions and the cell performed quite satisfactorily under low current drains.

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References

1. M.B. Armand, J.M. Chabagno, J.M. Duclot, *Fast Ion Transport in Solids* (North Holland Pub. Co., North Holland, 1979)
2. F.M. Gray, *Polymer Electrolytes: Fundamentals and Technological Applications* (Wiley-VCH Pub., New York, 1991)
3. B. Scrosati, *Applications of Electroactive Polymers* (Chapman and Hall, London, 1993)
4. R.C. Agrawal, G.P. Pandey, *J. Phys. D: Appl. Phys.* **41**, 22300 (2008)
5. D.E. Fenton, J.M. Parker, P.V. Wright, *Polymer* **14**, 589 (1973)
6. L.R.A.K. Bandara, M.A.K.L. Dissanayake, B.E. Mellander, *Electrochim. Acta* **43**, 1447 (1998)
7. P.S. Anantha, K. Hariharn, *J. Phys. Chem. Solids* **64**, 1131 (2003)
8. T. Sreekant, M.J. Reddy, U.V.S. Rao, *J. Power Sources* **93**, 268 (2001)
9. G.B. Appetecchi, F. Croce, J. Hasson, B. Scrosati, M. Salomon, F. Cassel, *J. Power Sources* **114**, 105 (2003)
10. R.C. Agrawal, A. Chandra, *J. Phys. D: Appl. Phys.* **40**, 7024 (2007)
11. A. Chandra, *Eur. Phys. J. Appl. Phys.* **50**, 21103 (2010)
12. A. Chandra, A. Chandra, K. Thakur, *Composites: B* **60**, 292 (2014)
13. P.S. Anantha, K. Hariharn, *Solid State Ion.* **176**, 155 (2005)
14. S.R. Mohapatra, A.K. Thakur, R.N.P. Choudhary, *Ionics* **14**, 255 (2008)
15. S. Chandra, S.K. Tolpadi, S.A. Hashmi, *Solid State Ion.* **28–30**, 651 (1988)
16. A. Chandra, A. Chandra, K. Thakur, *Russ. J. Gen. Chem.* **83**, 2375 (2013)
17. A. Chandra, A. Chandra, K. Thakur, *Chinese J. Polym. Sci.* **31**, 302 (2013)
18. A. Chandra, A. Chandra, K. Thakur, *Polym. Bull.* **71**, 181 (2014)
19. A. Bhide, K. Hariharan, *J. Power Sources* **159**, 1450 (2006)
20. J.P. Sharma, S.S. Sekhon, *Bull. Mater. Sci.* **36**, 629 (2013)
21. M.J. Reddy, P.P. Chu, *Solid State Ion.* **149**, 115 (2002)
22. A. Chandra, A. Chandra, *Hot-Pressed Polymer Electrolytes: Synthesis and Characterization* (Lambert Academic Pub., Germany, 2010)
23. T. Miyamoto, K. Shibayama, *J. Appl. Phys.* **44**, 5372 (1973)
24. S.D. Druger, A. Nitzan, M.A. Ratner, *Phys. Rev. B* **31**, 3939 (1985)
25. B.B. Owens, G.R. Argue, J.J. Groce, L.D. Hermo, *J. Electrochem. Soc.* **116**, 312 (1969)
26. C.V.S. Rao, M. Ravi, V. Raja, P.B. Bhargav, A.K. Sharma, V.V.R.N. Rao, *Iranian Polym. J.* **21**, 531 (2012)
27. P.B. Bhargav, V.M. Mohan, A.K. Sharma, V.V.R.N. Rao, *Ionics* **13**, 441 (2007)
28. B.L. Ellis, L.F. Nazar, *Curr. Opin. Solid State Mater.* **16**, 168 (2012)