

Influence of Plasticizer on (PEO+PVP) Based Blended Solid Polymer Electrolyte Membranes

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Abstract

The influence of low molecular weight plasticizer on the properties of Na⁺ ion conducting PEO/PVP blended solid polymer electrolyte (SPE) membranes, 95[35PEO:35PVP:30NaF] : 5x, where x = PEG₂₀₀, PEG₄₀₀, PEG₆₀₀ were reported. SPE films were prepared using solution cast technique. The solid polymer electrolyte film, (35PEO:35PVP:30NaF), also prepared and identified as the highest conducting composition at room temperature. Complexation of the prepared electrolytes was studied by X-ray diffraction (XRD) analysis. The optical behaviour of the SPE films was studied from ultraviolet-visible (UV-vis) spectroscopy, and the optical parameters viz. absorption edge, direct energy bandgap and indirect energy band gap were determined. Frequency dependent conductivity (σ_{ac}) values were obtained from complex impedance (cole-cole) plots. It was observed that the magnitude of conductivity increased with the decrease of molecular weight of the plasticizer at room temperature. The charge transport mechanism in this SPE is mainly due to ions which were confirmed by the transference number experiment. Using this electrolyte, cells were fabricated and their discharge profiles were studied under constant load. Several cell parameters associated with the cells were evaluated.

Keywords: *solid polymer electrolytes, XRD analysis, Optical behaviour, frequency dependent conductivity, transference numbers, discharge profiles.*

Introduction

Various sources of alternative energy are continuously evolving to reduce the long-term dependence on oil, nuclear and other fossil fuels. The other environmentally friendly fuel cells, such as batteries, super [capacitors](#) and dye sensitized solar cells, are strong candidates for this reason [1]. The conception of [polymer electrolytes](#) is a highly specialized and multidisciplinary field that covers the disciplines of electrochemistry, polymer science, organic and inorganic chemistry [2].

Various approaches such as blending [3, 4], co-polymerization [5], plasticization [6], addition of ceramic fillers [7] etc. have been made to enhance the ionic conductivity of polymer electrolytes [8]. The most important advances in increasing the ionic conductivity of polymer electrolytes were brought into effect by the incorporation of suitable amounts of plasticizers [9]. Generally, low molecular weight, high dielectric constant polar organic solvents such as ethylene carbonate (EC) [10, 11], propylene carbonate (PC) [12], polyethylene glycol (PEG) [13], dimethylformamide (DMF) [5], dimethylsulfoxide (DMSO) [14], dioctyl phthalate (DOP) [15] and dibutyl

phthalate (DBP) [16] have been used in polymer electrolytes to enhance their room temperature ionic conductivities. The conductivities of these electrolytes critically depend on the physical properties of the plasticizer such as its viscosity and dielectric constant. A plasticizer improves the electrical conductivity of polymer electrolyte by (i) increasing the amorphous content of polymer electrolytes; (ii) dissociating ion aggregates present in polymer electrolytes; (iii) lowering the glass transition temperature, T_g [17].

The present work is concerned with PEG (Average $M_w=200$, 400 and 600) used as a plasticizer in (PEO+PVP+NaF) polymer electrolyte. Several experimental techniques such as XRD, Optical studies, electrical, transference measurements and discharge profiles were performed to characterize these plasticized polymer blend electrolytes.

Experimental

Polymer electrolyte films of PEO/PVP complexed with NaF at different compositions were prepared by solution cast technique using methanol (water-free) as solvent. Film of (35PEO:35PVP:30NaF) composition was identified as the highest conducting composition at room temperature on the basis of PEO/PVP – NaF salt concentration dependent conductivity which were obtained from complex impedance plots. Na^+ ion conducting plasticized PEO/PVP blended solid polymer electrolyte (SPE) membranes, 95[35PEO:35PVP: 30NaF] : 5x where x = PEG₂₀₀, PEG₄₀₀, PEG₆₀₀ were also prepared. The X-ray diffraction studies of these films were performed by means of a SEIFERT X-ray diffractometer system with Ni-filtered Cu k_α radiation. The optical behaviour of the SPE films was studied from ultraviolet-visible (UV-vis) spectroscopy, and the optical parameters viz. absorption edge, direct energy bandgap and indirect energy band gap were determined. Frequency dependent conductivity (σ_{ac}) values were obtained from complex impedance (cole-cole) plots. The AC conductivity was measured using PSM 1700 Impedance Analyzer in the frequency range 1 Hz – 1 MHz and in the temperature range 303–373 K. The total ionic transport number (t_{ion}) was evaluated by means of Wagner's polarization technique [18]. Electrochemical cells were fabricated with the configuration Na/(PEO+PVP+NaF+Plasticizer) / (I₂+C+ electrolyte). The discharge characteristics were monitored under a constant load of 100 k Ω .

Results and discussion

1. X-ray diffraction studies

Fig. 1 shows the comparative profiles of the XRD patterns of 95[35PEO:35PVP:30NaF]:5x where x = PEG₂₀₀, PEG₄₀₀, PEG₆₀₀ solid polymer electrolytes. The diffraction peaks observed for 2θ values at 19.1° and 23.3° were found to be less intense in PEG₂₀₀ doped films compared to PEG₄₀₀ & PEG₆₀₀ doped systems.

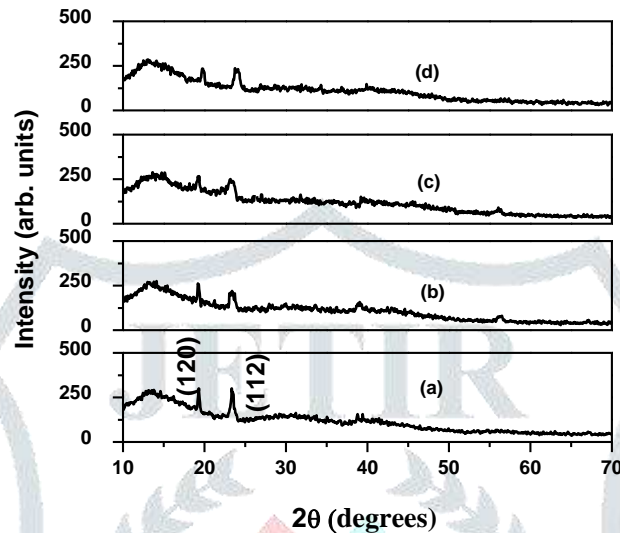


Figure-1: XRD patterns of 95[35PEO:35PVP:30NaF]:5x where x = PEG₂₀₀, PEG₄₀₀, PEG₆₀₀ SPE films

This indicated that the addition of plasticizer caused a decrease in the degree of crystallinity of the film. Among the three systems PEG₂₀₀ doped film was less intense. This indicated that the addition of PEG₂₀₀ is more responsible to decrease the degree of crystallinity of the film than that of PEG₄₀₀ and PEG₆₀₀ doped samples. This may be due to a larger concentration of free ions in systems added with PEG₂₀₀ than PEG₄₀₀ and PEG₆₀₀ [19]. The peaks exhibited a decrease in intensity with broadening at PEG₂₀₀ compared with PEG₄₀₀ and PEG₆₀₀ doped polymer electrolytes. This indicated a decrease in the crystalline phase and a dominant presence of the amorphous phase. This amorphous nature resulted in greater ionic diffusivity with high ionic conductivity, as amorphous polymers have flexible backbone [20].

2. Optical absorption studies

To determine the nature and width of the band gap, α , $(\alpha h\nu)^2$, $(\alpha h\nu)^{1/2}$ were plotted as a function of photon energy ($h\nu$) for 95[35PEO+35PVP+ 30NaF] : 5x polymer electrolytes where x = PEG₂₀₀, PEG₄₀₀ & PEG₆₀₀.

2 (a) Absorption spectra

The optical absorption spectra of 95[35PEO+35PVP+30NaF] : 5x where x = PEG₂₀₀, PEG₄₀₀ and PEG₆₀₀ composite plasticized electrolytes are shown Fig.2(a).

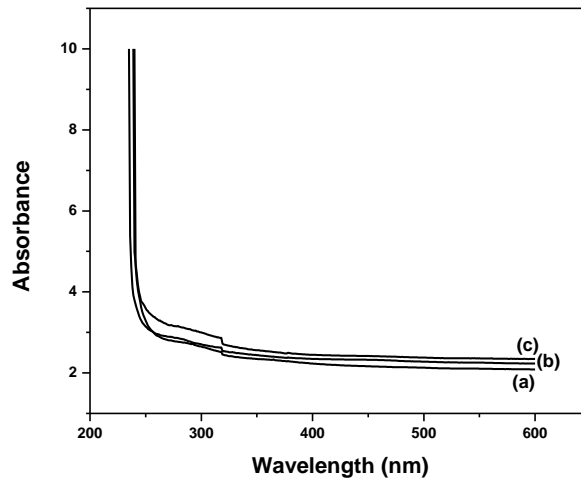


Figure 2(a). Absorption spectra of (a) 95[35PEO+35PVP+30NaF]:5PEG₂₀₀ (b) 95[35PEO+35PVP+30NaF]:5PEG₄₀₀ and (c) 95[35PEO+35PVP+30NaF]:5PEG₆₀₀ polymer blend films

2 (b) Absorption edge

The absorption edge values were obtained by extrapolating the linear portions of the α vs $h\nu$ plots [Fig. 2 (b).] to zero absorption value. It was observed that the electrolyte plasticized with PEG₂₀₀ has low absorption edge (4.30 eV) than PEG₄₀₀ and PEG₆₀₀ polymer electrolytes.

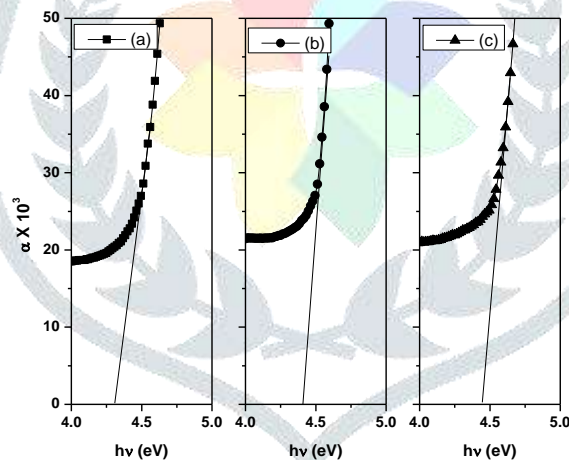
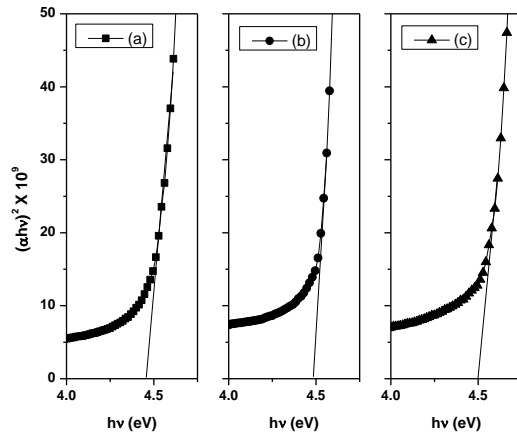


Figure 2(b). α vs $h\nu$ plots of (a) 95[35PEO+35PVP+30NaF]:5PEG₂₀₀ (b) 95[35PEO+35PVP+30NaF]:5PEG₄₀₀ and (c) 95[35PEO+35PVP+30NaF]:5PEG₆₀₀ polymer blend films

2 (c) Direct band gap

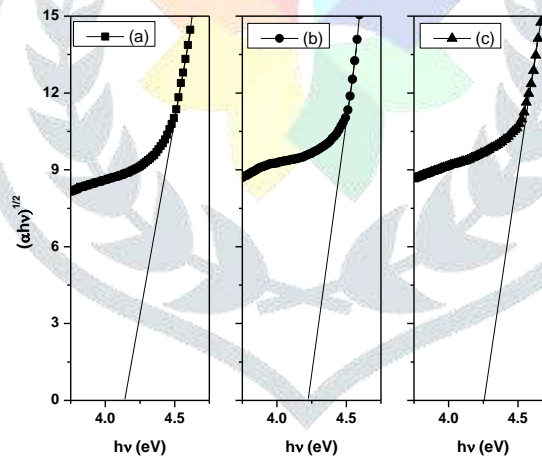
The optical band gaps were evaluated from $(\alpha h\nu)^2$ vs $h\nu$ plots and the allowed direct transition energies were determined by extrapolating the linear portion of the curves to zero absorption [Fig. 2(c)]. It was observed that the electrolyte plasticized with PEG₂₀₀ has low direct band gap than PEG₄₀₀ and PEG₆₀₀ polymer electrolytes.



**Figure 2 (c) $(\alpha h\nu)^2$ vs $h\nu$ plots of (a) 95[35PEO+35PVP+30NaF]:5PEG₂₀₀
(b) 95[35PEO+35PVP+30NaF]:5PEG₄₀₀ and
(c) 95[35PEO+35PVP+30NaF]:5PEG₆₀₀ polymer films**

2 (d) Indirect band gap

The indirect band gaps were obtained from the plots of $(\alpha h\nu)^{1/2}$ versus photon energy as shown in Fig 2(d). It was observed that the electrolyte plasticized with PEG₂₀₀ has low indirect band gap than PEG₄₀₀ and PEG₆₀₀ polymer electrolytes.



**Figure 2(d): $(\alpha h\nu)^{1/2}$ vs $h\nu$ plots of (a) 95[35PEO+35PVP+30NaF]:5PEG₂₀₀
(b) 95[35PEO+35PVP+30NaF]:5PEG₄₀₀ and
(c) 95[35PEO+35PVP+30NaF]:5PEG₆₀₀ polymer films**

Table 1. Absorption edge and band gaps of 95[35PEO+35PVP+30NaF] : 5PEG_x plasticized polymer blend electrolytes

Polymer electrolyte	Absorption edge (eV)	Band gap (eV)	
		Direct	Indirect
95[35PEO+35PVP+30NaF]:5PEG ₂₀₀	4.30	4.45	4.14
95[35PEO+35PVP+30NaF]:5PEG ₄₀₀	4.39	4.48	4.23
95[35PEO+35PVP+30NaF]:5PEG ₆₀₀	4.45	4.51	4.26

The values of absorption edge, direct band gap and indirect band gap are shown in Table 1. It is clear from the table that the band edge, direct band gap and indirect band gap values showed an increasing trend with increase in the molecular weight of the plasticizer. This is because of the fact that low molecular weight plasticizer (PEG₂₀₀) has high conductivity.

3. Impedance plots

Typical impedance plots (Z' vs Z'') for 95[35PEO+35PVP+30NaF] : 5x where x = PEG₂₀₀, PEG₄₀₀ and PEG₆₀₀ composite electrolytes at different temperatures (303 – 373 K) are shown in Fig. 3, which showed a normal impedance behaviour such as a depressed semicircular portion followed by a spike (residual tail).

The ionic conductivity of 95[35PEO+35PVP+30NaF] : 5x where x = PEG₂₀₀, PEG₄₀₀ and PEG₆₀₀ polymer electrolytes was calculated from the relation

$$\sigma = l/R_b A$$

where l , is the thickness of the film, A , the area of the film and R_b , the bulk resistance of the film material which is obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance [21].

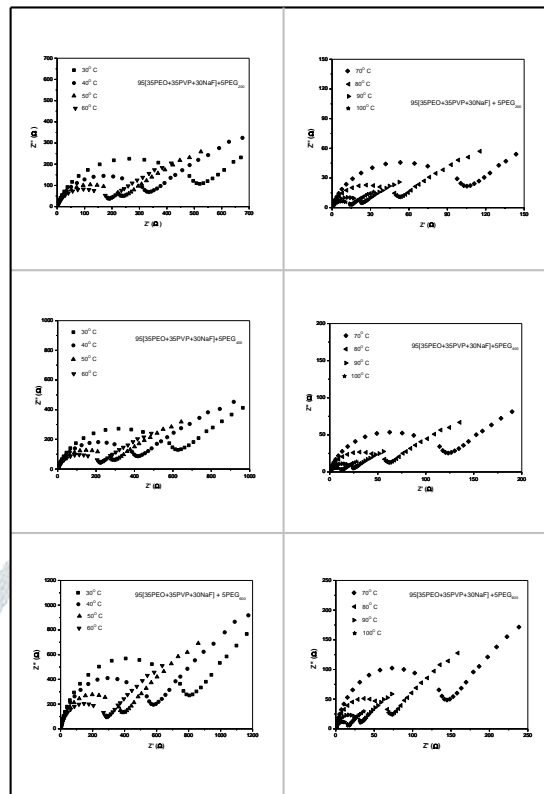


Figure 3. Impedance (Cole-Cole) plots of 95[35PEO+35PVP+30NaF] : 5PEG_x polymer blend films at different temperatures

4. Conductivity studies

Fig. 4 shows the variation of log conductivity with inverse absolute temperature for 95[35PEO:35PVP:30NaF]:5x where $x = \text{PEG}_{200}, \text{PEG}_{400}, \text{PEG}_{600}$ solid polymer electrolytes. From the plot, it has been observed that as temperature increases the conductivity values also increase for all the compositions. The non-linearity in Arrhenius plots indicated that ion transport in polymer electrolytes is dependent on polymer segmental motion.

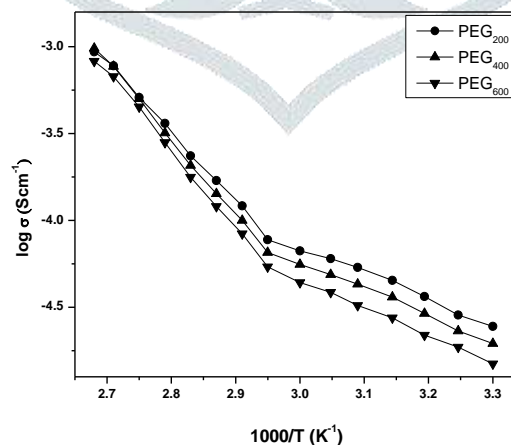


Figure - 4: Temperature – dependent conductivity of 95[35PEO+35PVP+30NaF]:5PEG_x composition polymer electrolytes

The curvature behaviour of the plots suggests that the data can be better described by the Vogel-Tamman-Fulcher (VTF) relation [22], which described the transport properties in a viscous matrix. It supports the idea that the ion moves through the plasticizer-rich phase. The variation of conductivity as a function of molecular weight for 5 wt% PEG added to the system is shown in the inset of Fig. For systems plasticized with PEG₂₀₀ the conductivity value increases than that of the systems plasticized with PEG₄₀₀ and PEG₆₀₀. From the figure, the molecular weight is seen to have an inverse effect, i.e., a decrease in the molecular weight of PEG added increases the conductivity of the polymer complexes. This implies that the lower molecular weight PEG is a better plasticizer for conductivity enhancement. These results are in good agreement with the results obtained by Srivastava and Chandra [19] who reported that higher ionic conductivities were obtained for poly(ethylene succinate) – NH₄ClO₄ plasticized with PEG₂₀₀, followed by those plasticized with PEG₄₀₀, PEG₆₀₀ and PEG₁₅₀₀. The higher ionic conductivities obtained from samples plasticized with PEG₂₀₀ may be due to a larger concentration of free ions in system added with PEG₂₀₀ than PEG₄₀₀ and PEG₆₀₀ [23].

5. Transference number

In Wagner's polarization technique dc current was monitored as a function of time on application of fixed dc voltage across the (anode) Na/SPE/ (cathode) C. After polarization of the cell with 1.5 V dc, the current versus time plots were obtained and shown in Fig. 5. For all the compositions of SPE system, the values of ionic transference numbers are in the range 0.95 - 0.97. This suggests that the charge transport in this polymer electrolyte films are predominantly due to ions; only a negligible contribution comes from electrons [24].

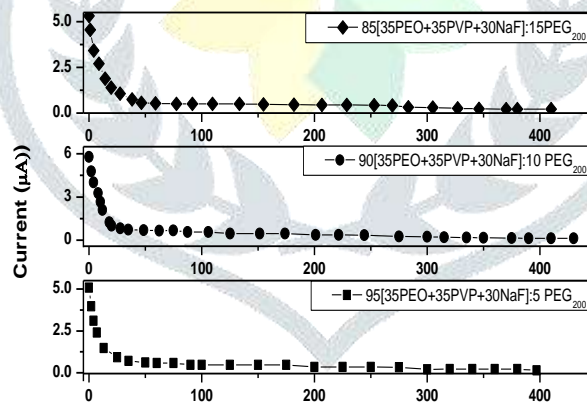


Figure 5. Current versus time plots of SPE films

6. Discharge profiles

The discharge profiles of SPE films at ambient temperature for constant load of 100 k Ω were presented in Fig. 6.

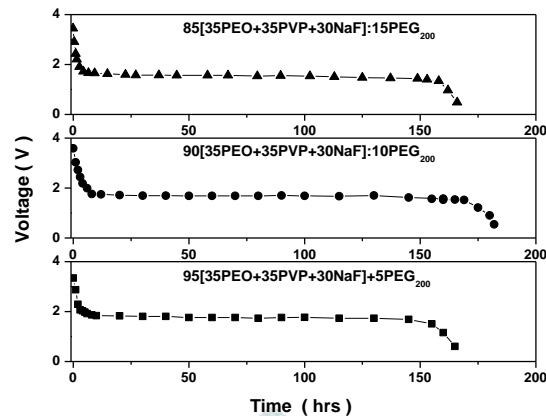


Figure 6. Discharge characteristics of $(100-x)[35\text{PEO}+35\text{PVP}+30\text{NaF}] : x\text{PEG}_{200}$ electrochemical cells at a constant load of 100 k Ω

The sharp initial decrease in voltage may be due to the polarization and/or the formation of thin layer sodium at electrode-electrolyte interface. The open circuit voltage (OCV) and short circuit current (SCC) of SPE doped with PEG₂₀₀ cell has been determined which were 3.34 V and 1.53 mA respectively. The various cell parameters are summarized below:

- Cell weight = 1.82 g
- Area of the cell = 1.33 cm²
- Discharge time = 156 h
- Power density = 2.80 W/kg
- Energy density = 437 Wh/kg

This supports the practical application of the present electrolyte in solid-state battery applications.

Conclusions

A new plasticized Na⁺ ion conducting PEO - PVP blended solid polymer electrolyte membranes: 95[35PEO:35PVP: 30NaF] : 5x, where x = PEG₂₀₀, PEG₄₀₀, PEG₆₀₀ has been synthesized. Complexation of the polymer matrices has been ascertained by XRD analysis. It is clear from absorption studies that the band edge, direct band gap and indirect band gap values showed an increasing trend with increase in the molecular weight of the plasticizer. This is because of the fact that low molecular weight plasticizer (PEG₂₀₀) has high conductivity. The maximum ionic conductivity value has been obtained for PEG₂₀₀ based electrolyte because of larger concentration of free ions in PEG₂₀₀ system compared to PEG₄₀₀ and PEG₆₀₀ systems. From conductivity data it can be seen that PEG₂₀₀ plasticized polymer electrolytes have higher conductivity than PEG₄₀₀ and PEG₆₀₀. The transference number measurements indicated that the newly synthesized SPE is an ionic conductor and the charge transport is due to ions. The electrolyte films doped with low molecular weight plasticizer exhibit better performance, which indicates that such electrolytes are more suitable for fabricating solid-state batteries.

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