

Effect of low molecular weight plasticizer on PEO/PVP based solid polymer electrolytes

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Abstract—The ion transport property studies on plasticized 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. 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; frequency dependent conductivity; transference numbers; discharge profiles

I. INTRODUCTION

Recently, polymer electrolytes have been widely studied due to their applicability for a variety of solid state and electrochemical device applications including batteries, fuel cells, supercapacitors, electrochromic devices and chemical sensors [1]. Polymer electrolytes have many advantages, such as flexibility, ease of processing into thin films of large surface area, electrochemical stability and leak-proof nature [2]. Various approaches such as blending [3, 4], copolymerization [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, electrical, transference measurements and discharge profiles were performed to characterize these plasticized polymer blend electrolytes.

II. 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 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 .

III. RESULTS AND DISCUSSION

A. 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

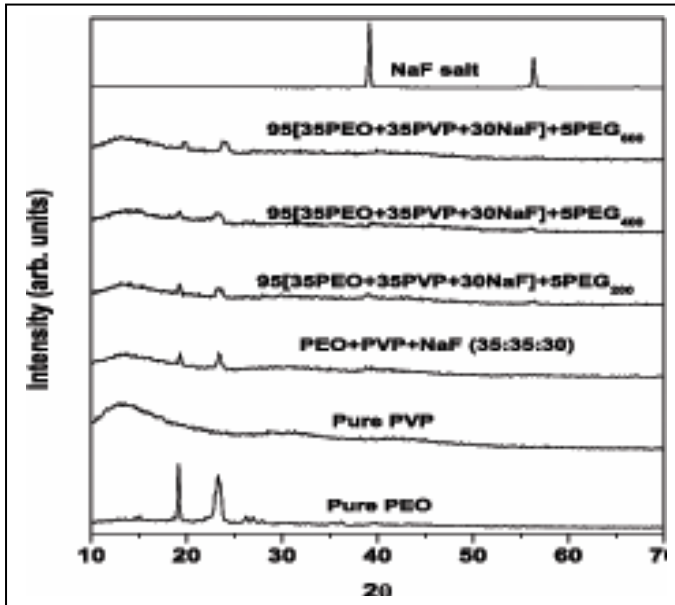


Figure 1. XRD patterns of 95[35PEO:35PVP:30NaF]:5x where x = PEG₂₀₀, PEG₄₀₀, PEG₆₀₀ SPE films

be less intense in PEG₂₀₀ doped films compared to PEG₄₀₀ & PEG₆₀₀ doped systems. 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].

B. Conductivity studies

Fig. 2 shows the variation of log conductivity with inverse absolute temperature for 95[35PEO:35PVP:30NaF]:5x where x = PEG₂₀₀, PEG₄₀₀, PEG₆₀₀ 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. The curvature behaviour of the plots suggests that the data can be better described by the Vogel-Tamman-Fulcher (VTF) relation [21], 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 2. 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 [22].

C. 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. 3. 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 [23].

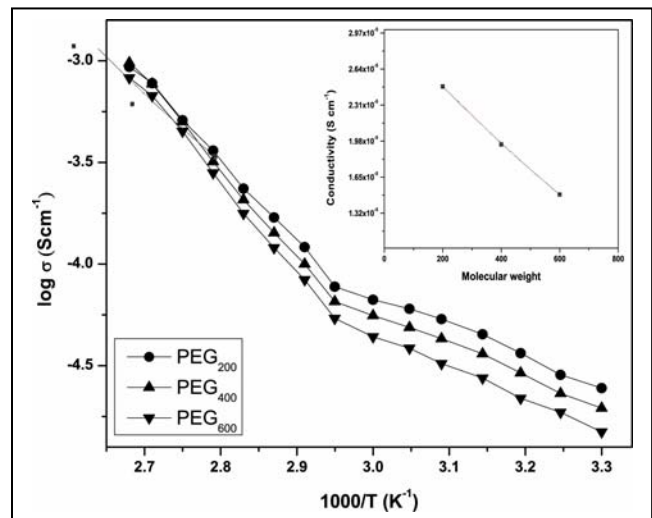


Figure 2. Temperature-dependant conductivity of 95[35PEO:35PVP:30NaF]:5x where x = PEG₂₀₀, PEG₄₀₀, PEG₆₀₀ SPE films

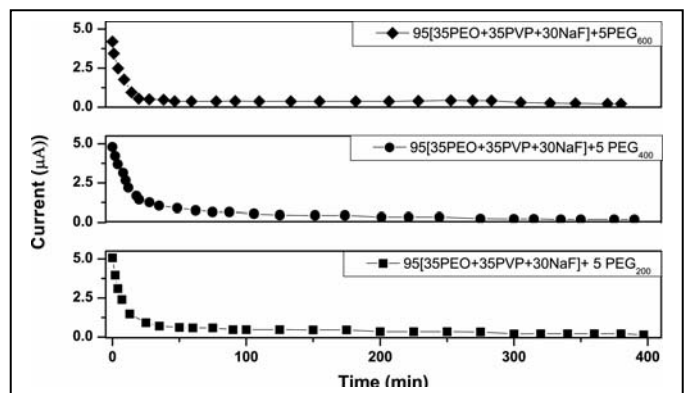


Figure 3. Current versus time plots of SPE films

D. Discharge profiles

The discharge profiles of SPE films at ambient temperature for constant load of 100 kΩ were presented in Fig. 5. 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.

IV. 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. 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. 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.

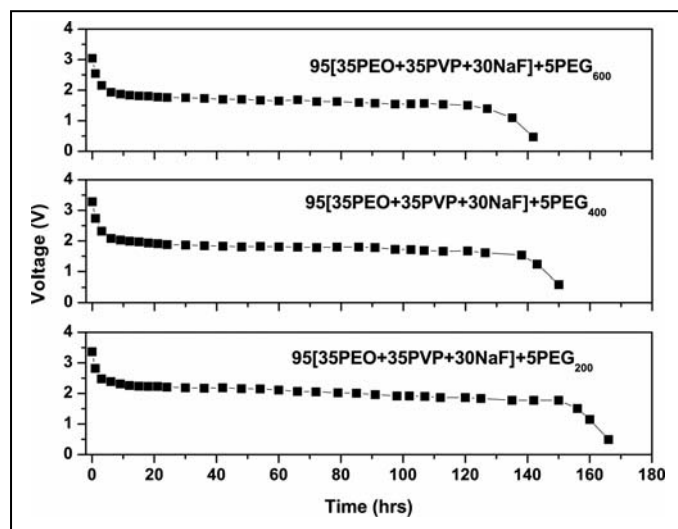


Figure 4. Discharge profiles of SPE films

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