



Conductivity and stability properties of solid polymer electrolyte based on PEO-PAN + LiPF₆ for energy storage

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Ionically conducting solid polymer electrolyte (SPE) films has drawn considerable attention because of its many appealing properties such as flexibility, design mouldability, role as leakage free solid separator/electrolyte in devices and improved safety hazard. Polymer blend electrolytes are prepared for various concentration of salt (Ö/Li) with the constant ratio (0.5 gm) of each PEO and PAN polymers (blend polymer) using solution casting technique. The maximum ac ionic conductivity value is found to be of the order of $\sim 10^{-5}$ S cm⁻¹ for the film having Ö/Li = 4 support the applicability of films for the energy storage/conversion device application. The thermo gravimetric analysis (TGA) result shows the stability of the prepared films for use in the device application. Finally the cyclic voltammetry experiment was performed to see the voltage sustainability (~4 Volt) of prepared free standing solid polymeric films for the device applications.

Keywords: Polymeric Films; Ionic Conductivity; PEO; Voltage Window; Thermogravimetric Analysis.

INTRODUCTION

Polymer electrolytes have been the emerging field of research for scores of years since the first report by Armand and co-workers in 1979 [1]. Polymer electrolytes envisage the advantage of solid electrolyte as well as the property of liquid electrolyte. The interest in this study is continually growing due to their potential applications such as ; supercapacitors, electrochromic displays, fuel cells and lithium rechargeable batteries [2]. Polymer electrolytes are flexible and light weight which makes them suitable to put in any desired shape. The development of polymeric systems with high ionic conductivity and good stability properties is congenital objective in polymer research, due to their potential application in energy storage/conversion devices such as solid state rechargeable lithium ion batteries, electrochromic windows, etc [3,4]. As the demand for portable electronics is increasing in our society, and many aspects of our life are now dependent on the performance of our handy electronics, call for a safe, consistent and efficient mean to store electrical energy. Also, modern advances in processing power, screen size and need for thinner and lighter devices, have increased the demand for lighter batteries with higher energy density and long cycle life [5]. Ionic conductivity in solid polymer electrolytes is associated with the amorphous phase of the studied samples [6]. Various approaches have been explored to modify the polymer matrixes with the goal to improve the polymer electrolyte utility and to increase the segmental mobility of host polymer such as blending, copolymerization, cross-linking, and plasticization of matrix polymer [7]. Among the above mentioned approach, blending of polymers is the best approach to develop new polymeric materials with improved thermal/mechanical/electrochemical stability, electrical conductivity and electrochemical properties [8]. In blending hydrogen bonding, ionic/dipole interactions leads to easy preparation and control of physical properties by compositional change [9]. Number of polymers have been attempted to develop

polymer electrolytes such as poly (acrylonitrile), poly(propylene oxide), poly(methyl methacrylate) and poly (maleic anhydridestyrene) etc. are studied by various researchers and high molecular weight PEO-based SPE is the best candidate for technological applications [10].

Polyethylene oxides (PEO) have large dipole moment due to ether oxygen and it dissociate easily in appropriate solvents. It also help to make the salt dissociation into it without any additional additives. Glass transition temperature (T_g) of the selected host matrix (PEO) is low for segmental motion of ion with PEO chain. The crystalline phase is also suppressed for enhancing ion conducting path of electrolytes. In present research work, blending of PEO-PAN is done, as first provides conduction channel for ions and later improves mechanical properties. LiPF₆ is the conductive species; it provides free ions which participate in the segmental motion of host polymer PEO chain.

EXPERIMENTAL

Solution cast technique has been used in the present studies for the sake of simplicity and cost effectiveness. Polymer blend-based solid electrolyte separator films have been prepared by a standard solution cast technique reported elsewhere [11]. A snapshot of the technique is shown by the flow chart (Fig. 1) given below. This is one of the best traditional procedures for casting films of Solid Polymer Electrolyte (SPE). In this technique, appropriate amount of polyacrylonitrile (PAN; M/S Aldrich, average molecular weight 1.5×10^5 , (USA); 0.5 gm.) and polyethylene oxide (PEO; M/S Aldrich, average molecular weight 6×10^5 , (USA); 0.5 gm.), N,N-dimethylformamide (10 ml), (E-Merck Germany) was used as organic solvent, Lithium hexafluorophosphate (LiPF₆; Sigma Aldrich) as the salt.. Although the addition of an appropriate amount of salt by stoichiometric ratio has been calculated considering oxygen of PEO [11]. The formula for this calculation has been shown below;

For Polyethylene oxide (PEO);

$$\frac{\ddot{O}}{\text{Li}^+} = \frac{\text{No. of monomer unit in half a gram of PEO}}{\text{No. of LiPF}_6 \text{ molecular in half a gram of salt}} \times \frac{\text{wt. of PEO taken}}{\text{wt. of salt taken}}$$

AC electrical conductivity measurement on the composite films has been performed using a computer-controlled impedance analyzer (Wayne Kerr Precision Impedance Analyser, Model 6500B series U.K, CHI 760E) in the frequency range of 1 Hz to 1 MHz. The samples were placed in a symmetric cell configuration; SS|PCE|SS (SS stands for stainless steel blocking electrodes) with an a.c. the input signal of ~20 mV. The thermal stability of the polymer film was analyzed by thermogravimetric analysis (TGA) using an SHIMDZU-DTG-60H under dynamic temperature conditions from 30 °C to 600 °C, in a nitrogen atmosphere at a constant heating scan rate of 10 °C min⁻¹. The electrochemical stability window (ESW) was determined by cyclic voltammetry of electrolyte membranes using electrochemical analyzer (Model 608C, CH Instruments, USA) at the potential range was -3 to +3 V (vs./Li⁺) at a voltage scan rate of 10 mV/s under the room temperature.

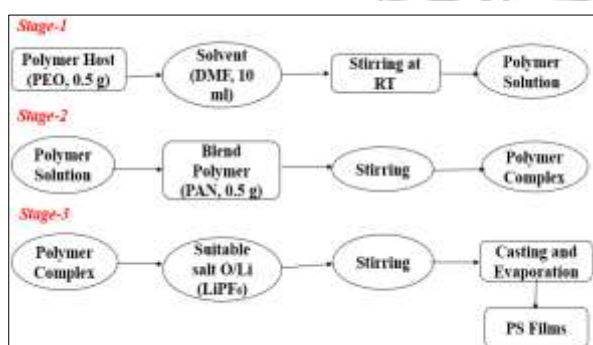


Figure 1. Flow chart of Solution Cast method

RESULTS AND DISCUSSIONS

In the present study, the electrochemical stability window (ESW) was determined by cyclic voltammetry of electrolyte membranes using electrochemical analyzer (Model 608C, CH Instruments, USA). The sample were placed in a cell configuration: SS//PAN-PEO-LiPF₆ films//SS (SS: stainless steel) cell was used for electrochemical measurements measured by cyclic voltammetry at the temperature 30 °C and potential range was -3 to +3 V (vs./Li⁺) at a scan rate of 10 mV/s under the room temperature.

Polymer electrolytes intended for practical applications in commercial devices must support high lithium ion mobility to provide elevated power densities in batteries or rapid response in sensors or optical displays. However, electrolytes must also be chemically stable to enable devices to attain extensive shelf lives. SPEs in high voltage devices, must be able to withstand the range of potential of the electrode couple. The electrochemical stability of an electrolyte during oxidation and reduction cycles is one of the essential parameters for practical use both in energy storage systems and in electrochromic devices. A comparative study of the electrochemical stability of the prepared free standing polymeric electrolyte systems is carried out using cyclic voltammetry over the potential range from -3 to 3V (Fig. 2).

Thermogravimetric analysis (TGA) technique is used to study the physical changes faced by the polymer electrolyte and it gives an idea of the kind of changes undergoing in the polymer electrolyte

at working atmosphere. The process involves a change in weight attributed to moisture acceptance and thermal stability of the polymer electrolyte.

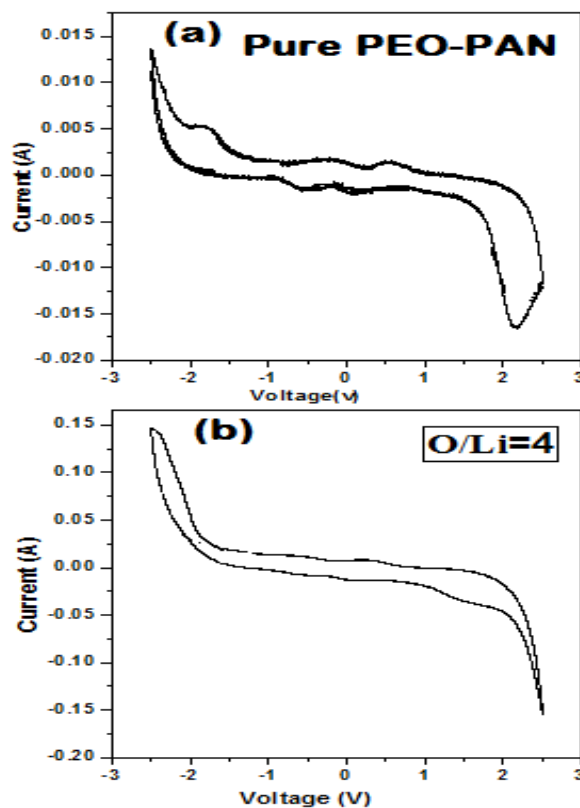


Figure 2. Current–voltage response of a SS electrode in the PEO–PAN copolymer SPE with (a) pure PEO-PAN (b) $\ddot{O}/\text{Li} = 4$.

Typical thermogram obtained for the films containing constant PEO/PAN ratio (50:50) with stoichiometric ratio $\ddot{O}/\text{Li} = 4$ of conducting species LiPF₆ are shown in Fig. 3.

TGA curve shows that there is a gradual weight loss of 5% until the sample reaches 120 °C irrespective of the salt concentration which could be due to the evaporation of moisture absorbed while loading the sample. This loss is attributed to traces of trapped solvent (DMF) in polymer network and release of surface adsorbed moisture. As we can see from Fig. 3, there is sudden weight loss for PEO-PAN sample at 200 °C. This may be due to structural decomposition of host polymer PEO. But as we increase the salt weight loss is a little up to 150 °C for $\ddot{O}/\text{Li} = 4$, so we can see from TGA spectrum that sample is almost stable up to 200 °C. At higher temperature about 300 °C sample starts decomposing and weaker bonds of PEO start breaking and at a very high temperature about 500 °C weight loss is maximum, which could be due to the decomposition of the polymer. The constant line after 400 °C is due to some inorganic residue after decomposition of the polymer. On addition of salt ($\ddot{O}/\text{Li} = 4$) the second region gets broad due to the interaction of salt with PEO and shows less weight loss than pure PEO-PAN. Now near 450 °C there is gradual weight loss.

We can see from the graph that upto 200 °C, both samples are thermally stable after which weak bond starts breaking and weight loss is more. As for $\ddot{O}/\text{Li} = 4$ concentration second region is

broader than others which make it more stable for applications purpose. In the third region, it is observed that the the weight loss has been improved.

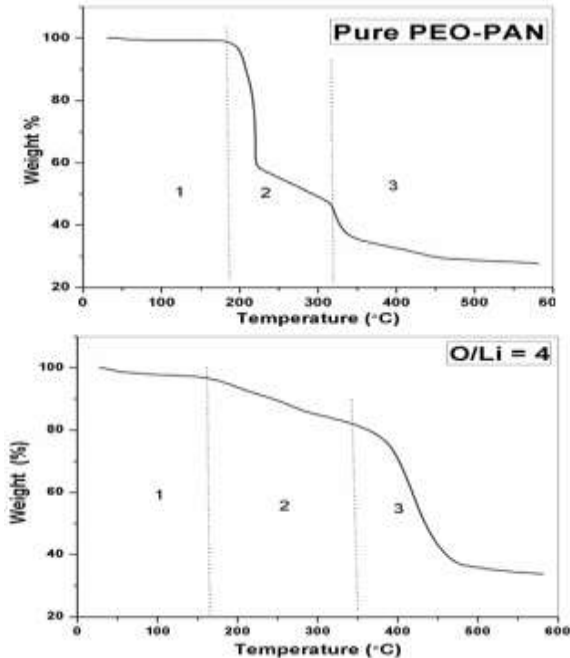


Figure 3. TGA analysis of Pure PEO-PAN and LiPF_6 ($\text{O}/\text{Li} = 4$).

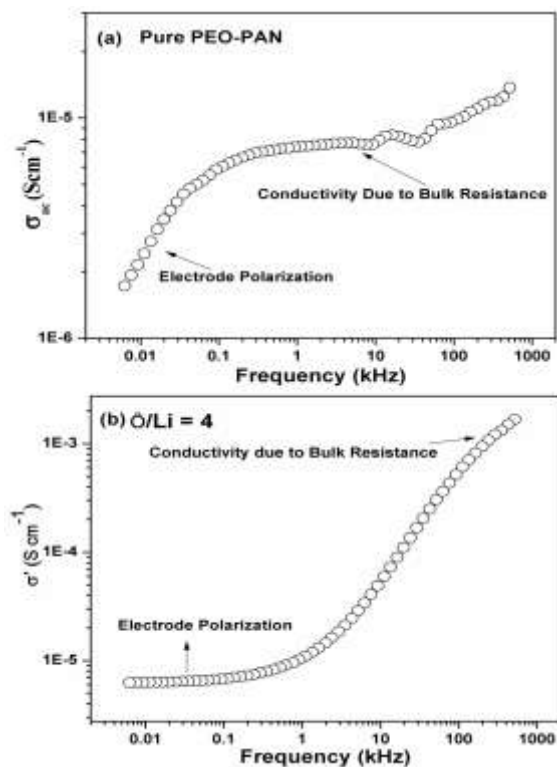


Figure 4. Variation of σ_{ac} as a function of frequency for pure PEO-PAN and $\text{O}/\text{Li} = 4$ at 30°C .

Figure 4. shows the variation of σ_{ac} (ac conductivity) as a function of frequency for pure PEO-PAN and $\text{O}/\text{Li} = 4$ at 30°C . At 30°C , the spectrum for σ_{ac} (ac conductivity) shows two frequency regions: (1) a frequency independent region at a lower frequency, (2) followed by a high frequency dispersion region. The observation observed in the region 1 is due to electrode polarization or space charge polarization effect and is a fundamental characteristic of an ionic conductor. In region (1), the lowering in frequency decreases the conductivity value. It is because at lower frequencies, accumulation of more charge occurs at the interface between electrode electrolytes interface and increase in time for ionic motion leads decrease in electrical conductivity value. This phenomenon becomes dominant at high temperature due to increase in mobility of charge carriers. At low frequency the applied electric field forces the charge carriers to drift over large distances and increase in time for ionic motion takes place which directly affects the electrical conduction of ions (Li^+).

In the high frequency region (region 2), the ac electrical conductivity (σ_{ac}) is increasing with the increase in frequency. This enhancement of electrical conductivity may be primarily due to the dielectric contribution (transient dipole). It refers to the region in the conductivity spectrum where strong frequency dependence of conductivity is observed. The slope of the low frequency dispersion curve is different for pure PEO-PAN (Figure 4(a)) and PS films associated with $\text{O}/\text{Li} = 4$ (Figure 4(b)). As we add salt ($\text{O}/\text{Li} = 4$), low frequency region disappears and it may be due to change in polarization strength. For the blend polymer salt complex (PS) film, the low frequency dispersion region disappearance may be due to the faster ion dynamics in PS complex film when compared with the pure blend polymer film.

CONCLUSION

Polymer electrolytes films have been synthesized by solution cast technique. The real part of electrical conductivity has been analyzed in terms of frequency. This analysis has confirmed electrode polarization at a lower frequency due to its charge accumulation. On addition of salt concentration ($\text{O}/\text{Li} = 4$) reduces the relaxation time which in turn the increase in electrical conductivity. The thermal analysis confirms the suitability of sample films up to 200°C after addition of salt in blend polymer films. Cyclic voltammetry graph shows a broad electrochemical voltage window ($\sim 4\text{V}$).

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