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Improved Electrical Properties of Free Standing Blend Polymer for Renewable Energy Resources

Anil Arya, Sweety Sharma and A. L. Sharma*

Centre for Physical Sciences, Central University of Punjab, Bathinda-151001, INDIA.
**Correspondence: alsharmaiitkgp@gmail.com*

Abstract. Blend polymer electrolytes are prepared for salt concentration (Ö/Li = 4) with the constant ratio (0.5 gm) of PEO and PAN using solution casting technique. The prepared free standing solid polymeric film is characterized by Field Emission Scanning Electron Microscopy (FESEM) which confirms the homogeneous distribution of dissociated salt in blend polymer matrix. After addition of salt the ionic conductivity value is found to be of the order of 7.13×10^{-5} Scm^{-1} which is three orders higher when compared with pure blend polymer films. The microscopic interaction among the polymer-ion, ion-ion has been confirmed by the Fourier Transform Infrared (FTIR) Spectroscopy. A very fine correlation has been built in the electrical conductivity and FTIR result. On the basis of above finding, a prepared free standing solid polymeric film appears to be appropriate for the energy storage/conversion device applications.

Keywords: Polymer Nanocomposites, Microstructure, Electrical Properties, FTIR, PEO
PACS: 88.80.ff

INTRODUCTION

Development of free standing thin polymer films electrolytes has been the emerging field of research for scores of years since the first report by Armand and co-workers in 1979[1]. Polymer electrolytes studies have gained much interest due to their potential applications such as high energy density lithium ion rechargeable batteries, supercapacitors, fuel cells and electrochromic devices [2]. The development of a polymer system with high ionic conductivity and stability is the inherited objectives in polymer research as most of the devices. The high molecular weight Poly (ethylene oxide) based polymer electrolytes at present are the thebest candidate of polymer matrix for lithium ion conductors due to their salvation power, complexation ability and ion transport mechanism directly connected to the alkaline cell [3]. Several salts have been used to increase the conductivity of polymer electrolytes such as $LiClO_4$ [4,5], $LiCF_3SO_3$ [6], $LiBF_4$ [7] and $LiPF_6$ [8]. From the various salts mentioned, lithium hexafluorophosphate ($LiPF_6$) remains the only salt used in practical lithium ion batteries, as it offers good electrolyte conductivity and better film formation than others [9].

In the present work, solid polymer electrolyte film consisting of PEO, PAN and $LiPF_6$ are examined for salt concentration(Ö/Li = 4), of lithium salt by keeping PEO/PAN blend ratio as a constant with a view to notice theeffect of salt on conductivity.

MATERIALS PREPARATION

Polymer blend-based solid electrolyte separator films were prepared via a standard solution cast technique reported elsewhere [8]. The polymer salt (PS) complexation was performed using polyethylene oxide (PEO; M/S Aldrich, average M.W. 6×10^5 ,(USA).) and polyacrylonitrile (PAN; M/S Aldrich M.W. 1.5×10^5 along with theaprotic solvent, theappropriate stoichiometry of lithium hexafluorophosphate ($LiPF_6$; Sigma Aldrich) as the salt.The detail of stoichiometric calculation has been reported by Das et al., [8].

Material Characterization

The surface morphology/microstructural studies of the material sample are examined by using a computer-controlled scanning electron microscope (CARL Zeiss). Fourier transform infrared (FTIR) spectroscopy analysis has been carried out in the mid-IR region (600–4000 cm^{-1}) with a wave number resolution of 0.5 cm^{-1} using Bruker, Tensor 27 (Model:

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NEXUS –870) to investigate the role of salt concentration on the nature of polymer–ion interaction. Electrical conductivity measurement on the composite films has been performed using a computer-controlled impedance analyzer (Model 6500B series U.K, CHI760E) in the frequency range of 1 Hz to 1 MHz.

Results and Discussion

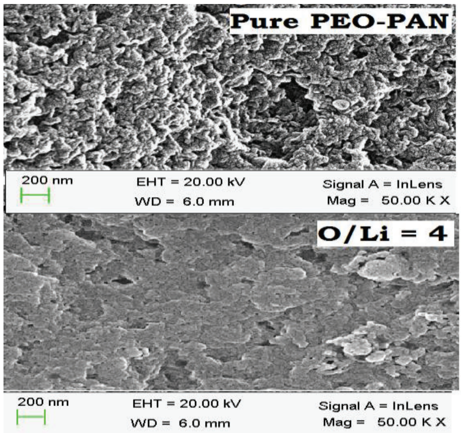

FIGURE 1. FESEM micrographs for a pure PEO-PAN blend, and blend-based SPE with Ö/Li = 4

Fig.1 depicts field emission scanning electron micrograph (FESEM) of free standing polymer films of two polymer system one blends polymer (PEO-PAN) and other having blended polymer along with stoichiometrysalt concentration, Ö/Li = 4. It can be seen that polymer blend matrix without salt has its characteristic porous which may be formed during rapid evaporation of the solvent under room temperature drying.

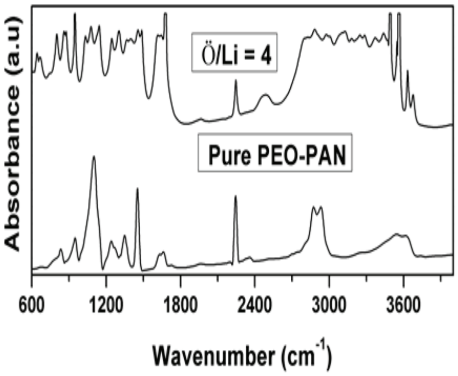

FIGURE 2. FTIR Spectrum of Pure PEO-PAN and LiPF$_6$ (O/Li = 4)

The addition of lithium hexafluorophosphatesalt (LiPF$_6$) in the blended polymer matrix modulates the surface microstructure of the blend that is clearly visible. Surface morphology of pure PEO-PAN is different from PEO–PAN + LiPF$_6$ blend

Fourier transform infrared (FTIR) spectroscopy has been used to probe the possibility of interaction among the composite components at the microscopic level. Fig. 2 shows the FTIR pattern of polymer salt complex (O/Li=4) in the range of (600 to 4000 cm^{-1}).

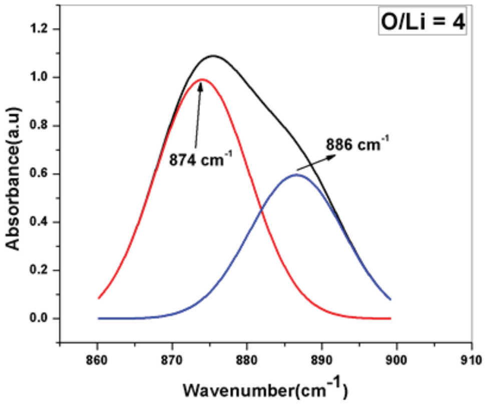

FIGURE 3. Deconvoluted pattern of free anion in PEO-PAN + LiPF$_6$ (Ö/Li = 4) film

On the the basis of asymmetry peak of PF$_6^-$pattern is deconvoluted. The deconvoluted PF$_6^-$ anion band profile of the PEO-PAN and LiPF$_6$ based polymer film is shown in the Fig.3.

The deconvoluted patterns of PF$_6^-$ band for polymer films with O/Li = 4 salt concentration is shown in Figure 3..From the figure it is clearly seen that the loss ofdegeneracy in the vibrational modes of PF$_6^-$, which causes peak asymmetry, appears in the spectrum as two distinctly resolved contributions are assigned to spectroscopically free anion (874 cm^{-1}) and ion-pair (886 cm^{-1}), respectively. The deconvoluted profile of the polymer film with Ö/Li = 4 shows a significantly smaller peak area for the ion-pair contribution in comparison with the free anionpeak area. Themaximum value of free anion peak area for Ö/Li = 4 provides a direct evidence of the enhancement of the free anion fraction in the composite matrix suggesting the possibility of a strong interaction which results in maximum conductivity [10].

Studies of conductivity measurement were carried out of the samples with a different stoichiometry of salt in the polymer blend (PEO–PAN) at room temperature. The samples were placed in a symmetric cell configuration; SS|PS|SS (SS stands for steel blocking electrodes) with an a.c. input signal of ~20mV applied across the cell [11]. The typical impedance plots (Z’ vs. Z”) for the different compositions of PEO-PAN with varying salt concentrations (Ö/Li) at room temperature are shown in Fig. 4.

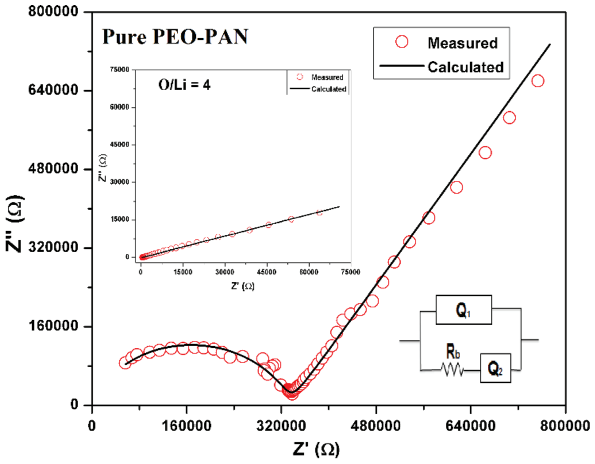

FIGURE 4. Nyquist plot of PS films at room temperature (30 °C) for Pure PEO-PAN and PS complex (Inset)

The intercept of the spike on real axis gives an estimate of bulk resistance (R_b) of the sample. An NLS fitting of the experimental data shows good agreement with the corresponding theoretical pattern suggesting validity and accuracy of the experimental results. An electrical equivalent circuit model of the sample impedance response appears to be consistent with a fit containing of theparallel combination of constant phase element (CPE) and another constant phase element (CPE) connected in series with aresistance (R).The presence of a CPE in the material sample is an evidence of its multiphase character comprising of amicrostructure having both crystalline, amorphous and a mixture of the two phases in the PS complex film. On the addition of salt, the CIS pattern shows a drastic change. In the high-frequency region for Pure PEO-PAN traces of semicircular arc followed by a steep spike in the low frequency region of the intercalated pattern are noticed. Such modification in the impedance spectrum of the PS films suggests a drastic change in the electrical properties upon the addition of salt (O/Li = 4) into polymer complex. As electrical conductivity of the prepared material has been estimated using the formula

$$\sigma_{dc} = \frac{l}{R_b . A}$$

Where, l is the thickness of prepared materials, A is the area of contact electrode surface and R_b is the bulk resistance calculated from Nyquist plot. The bulk resistance (R_b) obtained by noting down the value where intercept cuts on the real (Z′) axis of the Nyquist estimated value has been found to be pure blend polymer 349747 and 490.26 for PS complex films. The conductivity enhancement is three order when compared with the pure blend polymer films. The estimated result of the conductivity is well matched with observed FTIR results.

CONCLUSION

The surface morphology of the prepared polymer film is examined by FESEM. Pure PEO-PAN shows its characteristic porous nature. With the addition of salt porosity is reduced and surface modulation occurs which leads to a homogenous surface formation. The evidence of ion-ion interaction that is strongly a function of salt concentration has been observed in the free standing polymer salt complex films by FTIR. The conductivity ~7.13 x 10^{-5} S cm^{-1} at room temperature has been observed for Ö/Li~4.

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