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Role of low salt concentration on electrical conductivity in blend polymeric films

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ABSTRACT

A new blend polymer electrolyte based on polyethyelene oxide (PEO) and polyacrylonitrile (PAN) doped with Lithium Hexafluorophosphate ($LiPF_6$) has been prepared by solution casting technique using Dimethyalformamide (DMF) as solvent. The prepared samples were characterized by FTIR, FESEM and ac impedance spectroscopic measurements. The complex formation between blend polymer (0.5g PEO: 0.5g PAN) and $LiPF_6$ has been studied using Fourier transform infrared spectroscopy (FTIR). From AC impedance spectroscopic analysis there is enhancement of two order on addition of salt than pure PEO-PAN. The effect of low salt concentration on the conductivity and surface morphology of the blend polymer electrolyte has been discussed.

Keywords: Polyethylene oxide, Impedance, FTIR, Solid Polymer Electrolyte (SPE), Constant Phase Element

INTRODUCTION

Since Wright[1] reported ionic conductivity in a PEO: Na^+ complex in 1975, the research and development effort has become somewhat vigorous on solid polymer electrolyte (SPE) for improvement of the ionic conductivity and stability properties. Ever since Armand[2] proposed the application of SPE to lithium batteries in 1978, the research and development get more focus throughout the world. Development of energy storage devices with superior energy density has ever been a desired R&D goal in response to the need for the miniature power supply for consumer applications.[2-8] A wide variety of polymeric ionic conductors like solid polymer electrolytes (SPEs), gel polymer electrolyte (GPEs), composite polymer electrolytes (CPEs) are expected to play a major role in achieving this goal. The work in this field is therefore very popular. SPEs in rechargeable Lithium batteries are preferred due to their advantageous features like safety, non-volatility, less weight, high energy density, high single voltage, geometry and no memory effect.[9]

The ionic transport in these polymer electrolytes is associated with the metal salt dissolution and the coupling between the ions and segmental motions of the polymer chains.[10] Thus, to solve the safety issue of lithium batteries, solid polymer electrolytes have been widely used in solvent-free lithium batteries in addition to their attractive features of high flexibility and light weight.

The host polymer used in SPEs must contain a Lewis base (usually ether oxygen) for supporting dissolution of the salt and hoping process for motion of cation. Among all polymers, poly(ethylene oxide) (PEO) has been widely investigated so far because of its efficiency in coordinating metal ions, due to the finest distance and alignment of the ether oxygen atoms in polymer chains.[11] The weak coordination in presence of the salt makes possible the incorporation of ion with the polymer PEO and reduces the PEO degree of crystallinity. The increased amorphous phase favors the inter- and intra-chain hoping of ion and develops faster transport of ions.[12,13]

The investigations of solid polymer electrolytes have focused on the enhancement of electrical and mechanical properties for their commercial applications in the field of solid-state electrochemical devices. Various methods have been adopted to reduce crystallinity of polymer electrolytes and to increase segmental mobility of host polymer such as blending, copolymerization, cross-linking, and plasticization of matrix polymer.[14] Among the above, blending of two polymers is easy for preparation using structurally different polymers that interact by hydrogen bonding, ionic and dipolar interactions. We can alter the physical properties as per our requirement by composition of blend polymer which can't be tailored by single polymer. The most common interactions present in blends are hydrogen bonding and ionic and dipole interactions. Main advantages of the blend system are simplicity of preparation and ease of control of physical properties by compositional change.[15]

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In the present study 0.5 g PEO: 0.5 g PAN blend polymer with different stoichiometric ratio (Ö/Li)[16] of lithium salt ($LiPF_6$) are prepared by solution cast technique. The characteristics of blend polymer have been analyzed in terms of ac impedance and FTIR studies have been carried out to confirm the blend polymer salt complex.

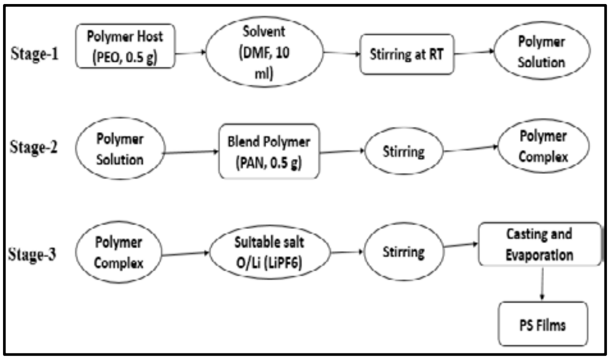

Figure 1. Flow chart of solution cast technique

EXPERIMENTAL DETAILS

PEO (M/S Aldrich, Av. Mw 6×10^5,0.5 gm.), PAN (M/S Aldrich, Av. Mw 1.5×10^5, 0.5 gm) and Lithium hexaflorophosphate ($LiPF_6$; Sigma Aldrich) have been used in the present study. Dimethyalformamode (DMF, E-Merck Germany, 10 ml) is used as a solvent. The blend polymeric electroltes of constant composition (0.5 g PEO: 0.5g PAN) with $LiPF_6$ have been prepared with different stoichiometric ratio (Ö/Li)[10] of salt by solution cast technique (Figure 1).[17] The complex solution with different composition were stirred continuously with a magnetic stirrer for several hours for getting homogenous solutions. The solution was thenkept in glass petri dishes at room temperature up to when all solvent (DMF) was evaporated and prepared films were then characterized. FTIR studies have been carried out on Lithium ion based conducting SPEs at room temperature in the range of 400 cm^{-1} – 4000 cm^{-1} with a resolution of 0.2 cm^{-1} by FTIR (Bruker, Tensor 27 NEXUS –870) instrument. The surface morphology/microstructure of the material sample was studied by using a computer-controlled Scanning Electron Microscope (CARL Zeiss). Impedance measurement were carried out using a computer-controlled impedance analyser (Wayne Kerr Precession Impedance Analyzer, Model 6500B series U.K,CHI660E) in thefrequency range of 1Hz to 1 MHz at ac signal of 20 mV at room temperature.

Figure 2 depicts field emission scanning electron micrograph (FESEM) of free standing polymer films of blend polymer with doped $LiPF_6$ (Ö/Li = 14, 16, 18, 20)

The characteristic porous nature of pure PEO-PAN matrix is clearly visible in Figure2 and it is due to faster evaporation of solvent at room temperature.[16] After even a small amount of salt affects the surface morphology and effect is visible in FESEM graph. On addition of salt change in grain contacts of polymer blend takes place and porosity is reduced. With increase of slat concentration porous microstructure of the polymer–salt complex system is decreasing and spheroid structures are formed.

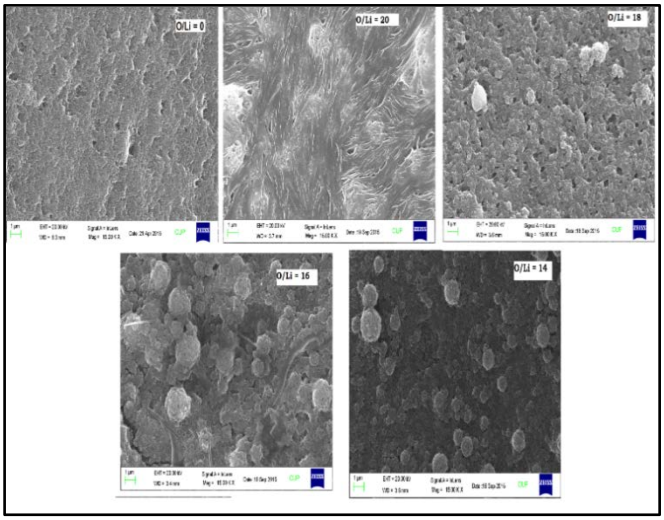

Figure 2. FESEM micrograph for Pure PEO-PAN and Ö /Li= 20, 18, 16, 14. (Scale 1µm)

A clear modification in grain contacts shows improved mechanical properties. The lowering of porous nature clearly indicates PEO–PAN blend formation. Addition of salt into polymer films leads to composite formation and modification in the surface morphology and homogeneity can be seen. On addition of even a small amount of salt (Ö/Li ~ 20), the image shows an uneven appearance due to complex formation of PS films. The PS film with Ö/Li = 14 shows modulation at microscopic level with modification in morphology. This existence of additional surface with salt addition shows better ionic properties in PS films.

Fourier transform infrared (FTIR) spectroscopy has been used to probe the possibility of interaction among the composite components at the microscopic level.

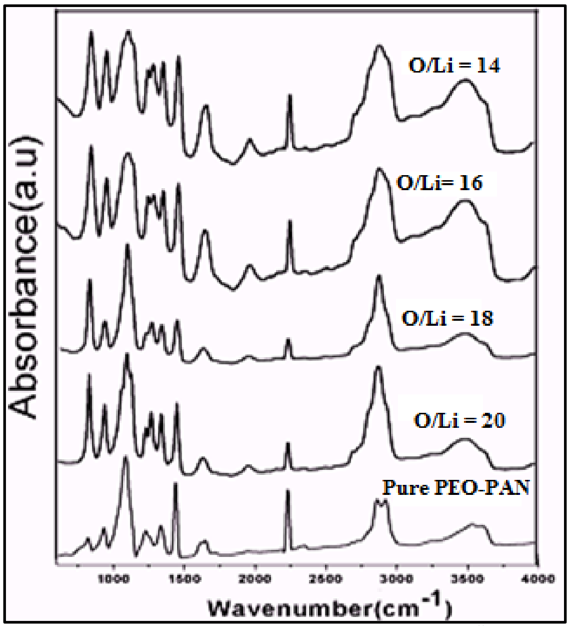

Figure 3. FTIR spectrum of Pure PEO-PAN and Ö/Li = 14, 16, 18, 20

Figure 3 shows the FTIR spectrum of (PAN-PEO)-$LiPF_6$; i.e., for Ö/Li = 14, 16, 18 and 20, representing a broad range of salt concentration in the wavenumber region 600-4000 cm^{-1}. The spectral pattern shows noticeable changes in the vibrational modes of PEO observed in terms of shift in band position, band width and band intensity with a corresponding change in salt concentration; i.e., Ö/Li ratio. The FTIR bands corresponding to the molecular vibration of the various groups in the polymer-salt complex have been identified.

The peak in the wavenumber range 800 cm^{-1} to 900 cm^{-1} corresponds to C-O-C of PEO and salt $v_s(PF6^-)$. The characteristic absorption peak observed in the spectral pattern at the wavenumbers ~644, ~850, ~1080, ~ 1250, ~1666, ~ 2245, ~2864 and 2935 $cm^{-1}$are attributed to Def (CH_2), $v_s(PF_6^-)$, t$(CH_2)_s$, t$(CH_2)_s$, υ(C=O) , υ(C≡N), $v_s(CH_2)$ and $v_{as}(CH_2)$ respectively. The anti-symmetric stretching vibration band at 1,100 cm^{-1} of pure PEO-PAN is shifted to 1118 cm^{-1}, 1110 cm^{-1}, 1114 cm^{-1} and 1114 cm^{-1} as $LiPF_6$ concentration increases.[18-19] The vibrational peak near 1280 cm^{-1} which is assigned to the t$(CH_2)_s$ twisting mode of Vibration due to PAN.[20] Two clear CH_2 vibrational modes appear due to PEO near 1468 cm^{-1} which, correspond to asymmetric CH_2 bending ($\delta(CH_2)_a$) and near 1353 cm^{-1} which, corresponds to symmetric CH_2 wagging and some C-C stretching ($w(CH_2)_s + \nu$(C—C)).[21] The FTIR peaks at 1959 cm^{-1}, 1959 cm^{-1}, 1957 cm^{-1}, 1953 $cm^{-1}$and 1966 cm^{-1} are related to asymmetric stretching of CH2 in PEO. The C≡N stretching band in the IR spectrum appearing at 2245 cm^{-1} the most characteristic feature of nitrile group in pure PEO-PAN. As $LiPF_6$ salt concentration increases, intensity of symmetric stretching vibration band of pure PEO increases and shifts to 2,864 cm^{-1}, 2,883 cm^{-1}, 2890 cm^{-1}, 2890 cm^{-1} and 2,890 cm^{-1}. This is due to the additional amount of Li^+ in the complexes. Pure PEO shows a large, broad band of CH_2 stretching between 2950 and 2840 cm^{-1}. However, the band is splitting into two near 2935 cm^{-1} and 2884 cm^{-1} corresponding to asymmetric CH2 stretching ($\upsilon(CH_2)_a$) and symmetric CH_2 stretching ($\upsilon(CH_2)_s$), respectively. The FTIR analysis gives us the information of role of salt in the polymer and salt interaction in the polymer film.

Figure 4 shows complex impedance spectrum (CIS)

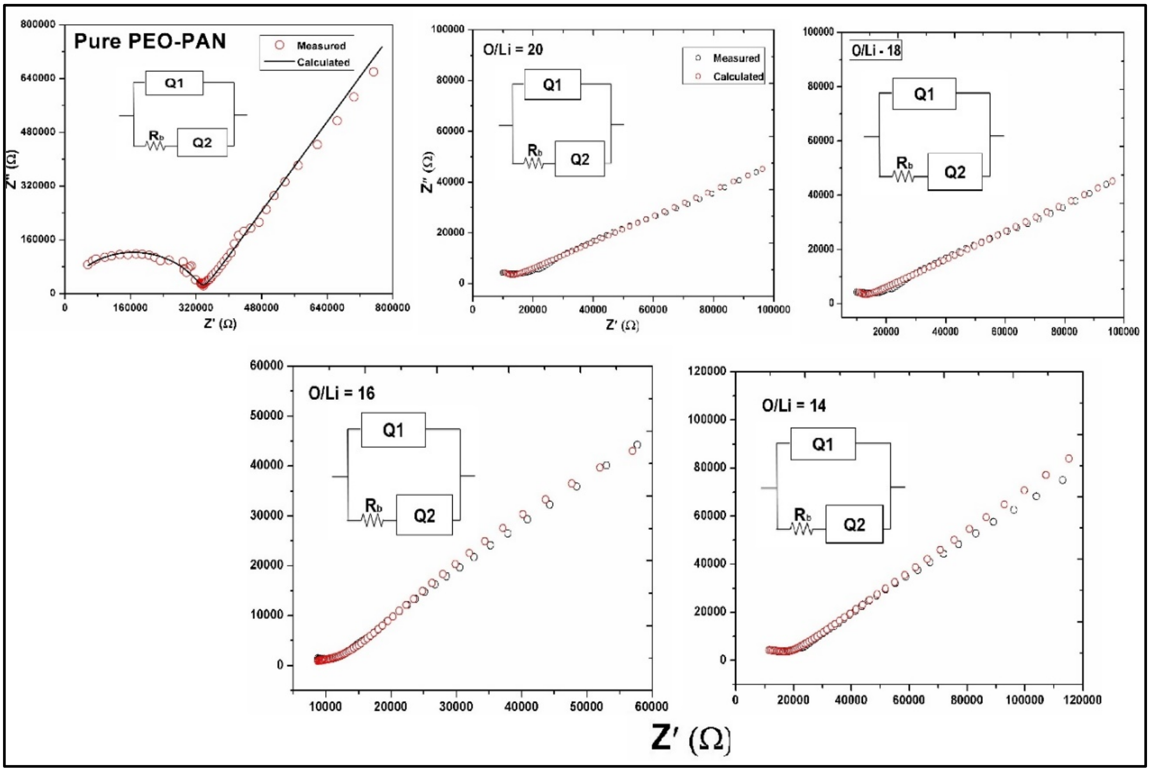

Figure 4. Nyquist plot of PS films at 30° C for Pure PEO-PAN and Ö/Li = 20, 18, 16, 14

Table 1. Fitted Parameters of Nonlinear Least Squares (NLS) Fit of the samples comprising of (PAN-PEO)-$LiPF_6$

Ö/Li	**Q_1**	**n_1**	**Q_2**	**n_2**	**t (mm)**	**R_b**	**σ (S cm^{-1})**
Pure	2.09×10^{-8}	0.8	3.49×10^{-7}	0.6	0.4	349747	7.99×10^{-8}
20	4.5×10^{-6}	0.33	6.58×10^{-11}	0.8	0.5	29484	1.18×10^{-6}
18	4.2×10^{-6}	0.33	6.51×10^{-11}	0.8	0.6	18036	2.32×10^{-6}
16	4.25×10^{-5}	0.34	3.4×10^{-5}	0.8	0.6	15667	2.37×10^{-6}
14	2.61×10^{-6}	0.44	3.08×10^{-9}	0.8	0.5	21000	1.66×10^{-6}

pattern of PEO-PAN and (PEO-PAN)-LiPF$_6$based solid polymer films for Ö/Li = 14, 16, 18 and 20at room temperature. The intercept of the spike on real axis gives an estimate of bulk resistance (R$_b$) of the sample.[22] The experimental impedance response, when fitted using non-linear least squares model by means of a computer program (ZS$_{imp}$Win), agrees well with the theoretical plot (solid lines) and electrical equivalent circuit model appears to be consistent with a fit containing of series combination of constant phase element, resistance in parallel with another constant phase element.[6,23]

The model of electrical equivalent circuit remains identical in pattern for the pure and PS films with essential difference in the values of bulk resistance (R$_b$), constant phase elements Q$_1$ and Q$_2$ and their exponent's n$_1$ and n$_2$, respectively (Table 1). On the addition of salt, the CIS pattern shows a drastic change.[18] In the high-frequency region for Pure PEO-PAN traces of semicircular arc followed by a steep spike in the low frequency region due to electrode effects.[24-26] Such modification in the impedance spectrum of the PS films suggests a drastic change in the electrical properties on addition of salt (Ö/Li = 14, 16, 18, 20) into blend polymer films.

CONCLUSIONS

The surface morphology of the prepared polymer film is examined by FESEM and surface modulation is seen with addition of salt. With the addition of salt porosity is reduced and surface modulation is observed which leads to a homogenous surface formation. An increase in conductivity is obtained with addition of salt due to more free ions and conductivity ~10^{-6} Scm^{-1} at room temperature. Fourier transform infrared (FTIR) spectroscopy spectral pattern shows noticeable changes in the vibrational modes of PEO observed in terms of shift in band position, band width and band intensity with a corresponding change in salt concentration and confirms complex formation.

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