



## Optimization of Free standing Polymer Electrolytes films for Lithium ion batteries application

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### ABSTRACT

The free standing polymer salt complex films consisting of blend polymer based on Poly(acrylonitrile) (PAN) as host polymer–Poly(ethylene oxide)(PEO) as a copolymer, Dimethylformamide (DMF) as solvent and Lithium hexafluorophosphate (LiPF<sub>6</sub>) as a conducting species were prepared. Keeping in view of characterization of solid state film such as, Fourier transform infrared (FTIR) spectroscopy is done for an understanding of the microscopic interaction among the different component present in the material system. The energy storage/conversion device applications have been analyzed by the impedances spectroscopy. The surface morphology or micro-structural of the polymer electrolytes film was analyzed by FESEM. The electrochemical stability window was about ~4V for the polymer electrolyte film at (N̄/Li=6). The advantageous outcome of PAN combining with PEO based electrolytes is in comparable good electrical conductivity and wider electrochemical stability window. Further optimization might lead to practical solid state polymer electrolytes for lithium ion batteries.

*Keywords: Polyethylene oxide, Impedance Spectroscopy, FTIR, Solid Polymer Electrolyte (SPE), FESEM*

### INTRODUCTION

Recently, from three decades main concentration is on the preparation and characterization of high quality new series free standing solid polymer electrolytes films. Although the free standing solid polymer electrolytes films are multicomponent systems comprising of the polymer as a host matrix and salt as conducting species. Prepared films will be expected to serve the purpose in the field of new generation high energy density storage/conversion device such as high energy density lithium ion battery, supercapacitor, PEM fuel cell and portable applications.<sup>1-3</sup> The most challenging aspects of the evolution of this solid state (polymer salt) PS films are; the inherent viscous property of polymer, presence of cation and anion which results in concentration polarization and internal friction of the polymer. On the basis of exhaustive literature survey, it has been noted that there are number of parameters which imposes serious limitation

to use of solid state PS films for applications in energy storage/conversion devices such as; a) Low ambient/sub ambient ionic conductivity, b) Poor stability properties in terms of electrochemical, thermal and mechanical under desired operating condition of the device, c) Compatibility with existing electrode, d) Poor charging/discharging performance.<sup>4-5</sup> However the ionically conducting polymer electrolytes might enhance the ionic conductivity of this system. The solid polymer electrolytes have advantage over the liquid electrolyte currently in use and thereby enabling the fabrication of flexible, compact, laminated solid state structures free from leaks and are available in varied geometries. The most important challenging aspect in the development of ion conducting solid polymers (also known conventionally as the solid polymer electrolytes; SPEs) till date that imposes serious limitations on their utility for applications in devices are: ambient conductivity, poor mechanical, thermal and voltage stability under desired operating conditions of the device. In addition, the presence of both cation and anion in the solid polymer matrix causes inherent problems of concentration polarization arising due to ion-pairing effect leading to immobilization of the conducting species and consequent lowering of electrical conductivity at an unacceptable level.<sup>6-9</sup>

### EXPERIMENTAL DETAILS

Sample preparation of high quality new series polymeric films based on (PAN-PEO)+LiPF<sub>6</sub> has been prepared via solution cast

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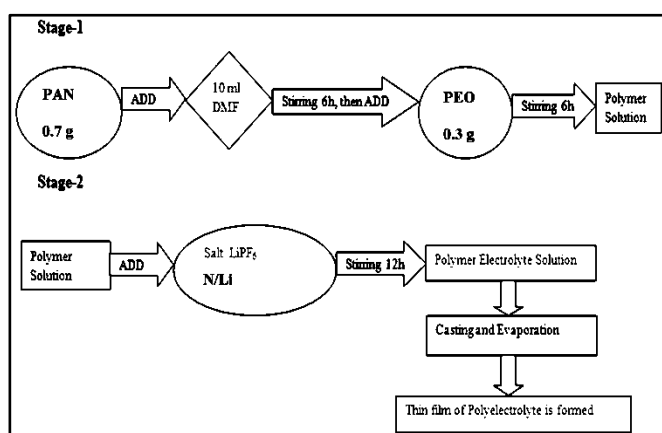
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technique. Polyacrylonitrile (PAN; M/S Aldrich, average molecular weight  $1.5 \times 10^5$ , (USA); 0.7gm) and polyethylene oxide (PEO; M/S Aldrich, average molecular weight  $6 \times 10^5$ , (USA); 0.3gm), N,N-dimethylformamide (10 ml), (E-Merck Germany) was used as organic solvent, Lithium hexafluorophosphate ( $\text{LiPF}_6$ ; Sigma Aldrich) as the salt. Although the addition of an appropriate amount salt by stoichiometric ratio has been calculated considering nitrogen of PAN. The formula for this calculation has been shown below;

For Polyacrylonitrile (PAN);

$$\frac{\dot{N}}{\text{Li}^+} = \frac{\text{No. of monomer unit in half gram of PAN} \times \text{wt. of PAN taken}}{\text{No. of } \text{LiPF}_6 \text{ molecular in half gram of salt} \times \text{wt. of salt taken}}$$

The detail of stoichiometric calculation has been reported by.<sup>10</sup> Finally free standing films polymer electrolyte films having the general formula  $(\text{PAN-PEO})_6 + \text{LiPF}_6$  were obtained.



**Figure 1.** Flow chart of solution cast technique

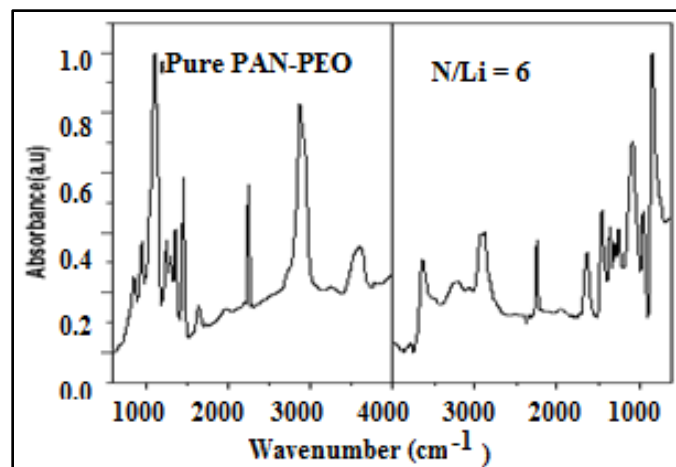
## MATERIAL CHARACTERIZATION

FTIR spectra of all the polymeric film were recorded by using a Bruker Tensor 27 Spectroscopy. The FTIR spectra were recorded in the absorbance mode. The ionic conductivity of polymer film electrolytes was measured by DC impedance methods in the temperature ranging from  $30^\circ\text{C}$  to  $100^\circ\text{C}$  and over the frequency range 100Hz to 5MHz. The sample was placed in a cell configuration: SS |PS|SS (i.e., SS stands for stainless steel blocking electrodes) and placed in a temperature-controlled oven. The experiments were performed in a constant area cylindrical cell of an electrode diameter of  $1.06 \text{ cm}^2$ . The complex impedance/admittance plots of PS have been fitted using the computer program and instrument model is connected to Wayne Kerr Precision Impedance Analyzer, Model 6500B series U.K. The electrochemical stability window (ESW) was determined by cyclic voltammetry of electrolyte membranes using electrochemical analyzer (Model 608C, CH Instruments, and USA). The sample were placed in a cell configuration: SS |PS|SS (SS: stainless steel) cell was used for electrochemical measurements measured by AC impedance methods in the temperature ranging from  $30^\circ\text{C}$ . At potential range was -3 to +3 V (vs.  $/\text{Li}^+$ ) at a scan rate of 10 mV/s under the room temperature.

## RESULTS AND DISCUSSION

### FOURIER TRANSFORMS INFRARED SPECTROSCOPY

The Fourier transform infrared (FTIR) spectroscopy has been used as an important tool to characterize the organics, inorganic and polymeric materials. Infrared spectra can identify the nature of bonding and different functional groups present in a sample by monitoring the vibration energy levels of the molecules, which are essentially the fingerprint of different molecules. The films were subjected to structural, thermal and electrical characterization for their possible use in electrochemical devices. Fourier transform infrared (FTIR) spectra were recorded in the absorbance mode with the resolution of  $0.4 \text{ cm}^{-1}$ .



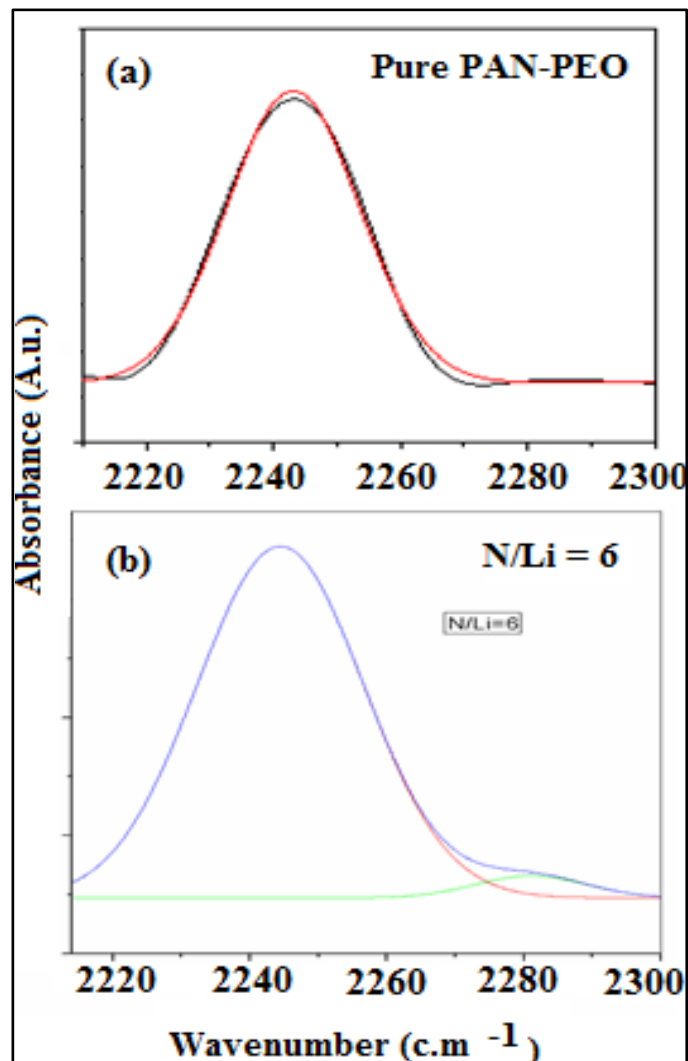
**Figure 2.** FTIR spectrum of PAN-PEO and polymer salt complex films

The band between the range of 700 and  $1000 \text{ cm}^{-1}$  correspond to rocking mode of  $\text{CH}_2$  ( $\rho(\text{CH}_2)$ ), and those between  $1200\text{-}1300 \text{ cm}^{-1}$  correspond twisting mode of  $\text{CH}_2$  ( $\tau(\text{CH}_2)$ ), the bands around  $1300$  to  $1390 \text{ cm}^{-1}$  correspond wagging mode of  $\text{CH}_2$  ( $\omega(\text{CH}_2)$ ) and the bands from  $1400$  and  $1500 \text{ cm}^{-1}$  correspond to scissoring mode of  $\text{CH}_2$  ( $\nu_s(\text{CH}_2)$ ) and wave number is  $2200$  and  $2300 \text{ cm}^{-1}$  correspond to nitrile groups of  $(-\text{C} \equiv \dot{N})$ , the peak appear in wave number  $800$  and  $900 \text{ cm}^{-1}$  correspond to salt ( $(\text{PF}_6^-)$ ), respectively of polymer- salts complex.<sup>11</sup>

### STUDY OF POLYMER-ION INTERACTION

The spectral outline in the wave number ranges  $\sim 2213\text{-}2300 \text{ cm}^{-1}$  with the peak at  $2242 \text{ cm}^{-1}$ . The absorption peak of the blend polymer (PAN-PEO) group is credited to  $\text{CH}_2$  mode of methylene group, nitrile group  $-\text{C} \equiv \dot{N}$  stretching spectra of PS based on PAN can be observed at the wave numbers-  $2239.32$ ,  $2264.33$ ,  $2248.53$ ,  $2242.43$ ,  $2239.32$ ,  $2243.21$ ,  $2243.04$ ,  $2231.54$ ,  $2241.44$  and  $2244.37$  is assigned to  $-\text{C} \equiv \dot{N}$  stretching frequency of pure PAN. The modification in the  $-\text{C} \equiv \dot{N}$  vibration absorbance caused by the existence of the salt can make available the significant change. Moreover the results give strong proof of polymer-ion interaction on the addition of salt ( $\text{LiPF}_6$ ) in solvent inflamed PAN. There is no proof of salt interaction with solvent (DMF) skeletal groups (i.e.,  $\text{CH}_3$ ,  $\text{C-CH}_3$  with  $\text{C-N}$ ) might be

experimental in the FTIR spectra group as shown in previous report.<sup>6</sup>



**Figure 3.** Deconvolution pattern of polymer-ion interaction of (a) blend PAN-PEO and (b) PAN-PEO+LiPF<sub>6</sub>.

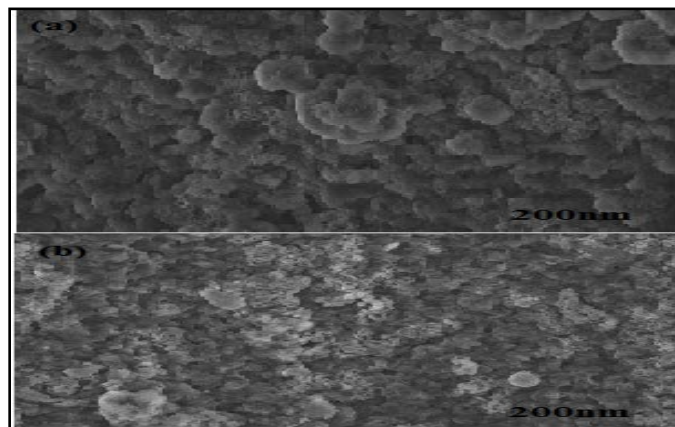
Further, the shoulder peak has appeared at 2280 cm<sup>-1</sup> (close to the -C≡N) as a form of PAN on salt accumulation and in various clay concentrations the shoulder peak (2270 cm<sup>-1</sup>) has shifted as shown in Figure 3. The interaction of ions of the salts shows clear proof with group -C≡N position of PAN backbone.

### FESEM

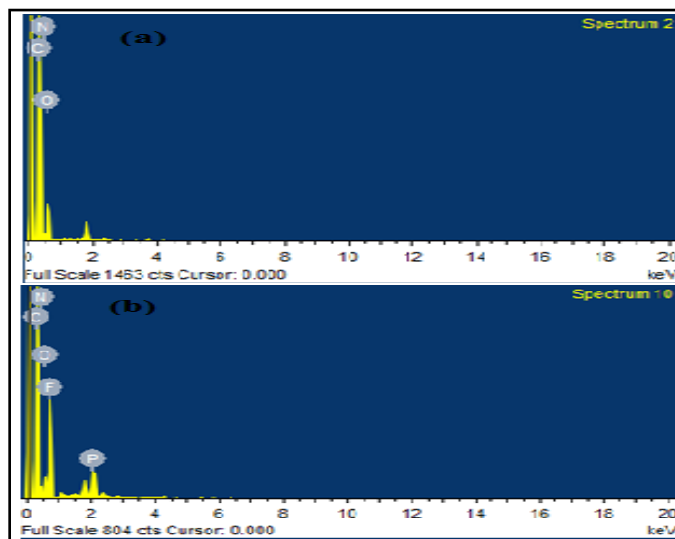
The surface morphology of blend polymer free standing electrolytes was analyzed by the FESEM. This blend electrolyte show the slight change in the addition of salt concentration. These micrographs tell that the polymer electrolytes are crystalline in nature with amorphous boundary. It is clear visible that a heterogeneous structure is due to uneven distribution of crystalline component in the predominantly unstructured boundary. However the crystalline component may be interrelated to PS complex

Whereas the amorphous phase may be certified to pure host polymer phase. Generally, the resulted FESEM photographs show that the salt were homogeneous distributed and dispersed in the

polymer matrix as a consequence of the uniform precipitation of in the polymer matrix through the solution cast method.<sup>11</sup> The addition of salts has modified the PAN-PEO based electrolyte surface morphology. Through the comparison between Fig. 4 and 5. At magnification, a smoother surface morphology was shown after the addition of the salts. However themicrographical image of pure PAN-PEO shows the presence of several spherulitic crystalline domains closely packed to each other in an orderly manner as reported already.<sup>12</sup> The energy dispersive x-ray analysis gives the information of materials contain in the samples. This result can be used as evidence to confirm the existence of LiPF<sub>6</sub> in the electrolyte film after the stirring, mixing and drying processes PAN-PEO based electrolyte surface morphology.



**Figure 4.** FESEM micrographs of PE-based electrolyte films, (a) with Pure PAN-PEO, (b) PAN-PEO+LiPF<sub>6</sub>

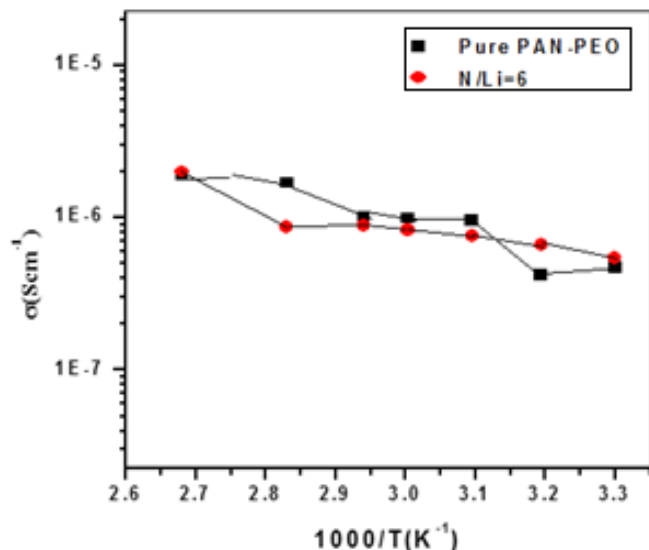


**Figure 5.** EDX elemental analysis pattern of (a) PAN-PEO and (b) PAN-PEO+LiPF<sub>6</sub> polymer salt film.

### IONIC CONDUCTIVITY STUDY

The impedance spectroscopic technique is anew and powerful method which be used to calculate the electrical properties of the polymer blend and polymer electrolyte membranes. The impedance spectra of PS films with pure PAN-PEO and PAN-PEO + LiPF<sub>6</sub>. From this Nyquist plots conductivity values ( $\sigma$ ) were calculated using ( $\sigma = t/R_bA$ ); where 't' is the thickness of

films,  $A$  areas of films and  $R_b$  is the bulk resistance of the sample and also calculated the Arrhenius equation,  $\sigma(T) = \sigma_0 \exp(-E_a/K_B T)$ , where  $\sigma_0$  is the pre-exponential factor,  $E_a$  is the activation energy in eV,  $K_B T$  is Boltzmann constant and  $T$  is the temperature in k. The activation energy,  $E_a$  can be evaluated from the slope of the plots.<sup>13-16</sup> The highest ionic conductivity obtained at 100°C is  $\sim 2.0 \times 10^{-6} \text{ S cm}^{-1}$  and with lower activation energy  $\sim 0.210$  eV. This increase in ionic conductivity at higher temperature can be attributed to increase in number of free charge carriers on addition of salt and results in reduction in activation energy value. It may be due to the lowering of lattice energy and faster transport of charge carriers. This result suggest that the conductivity of the PS films is useful for energy storagesystem.



**Figure 6.** Plot for variation of ionic conductivity with temperature of free standing polymeric film

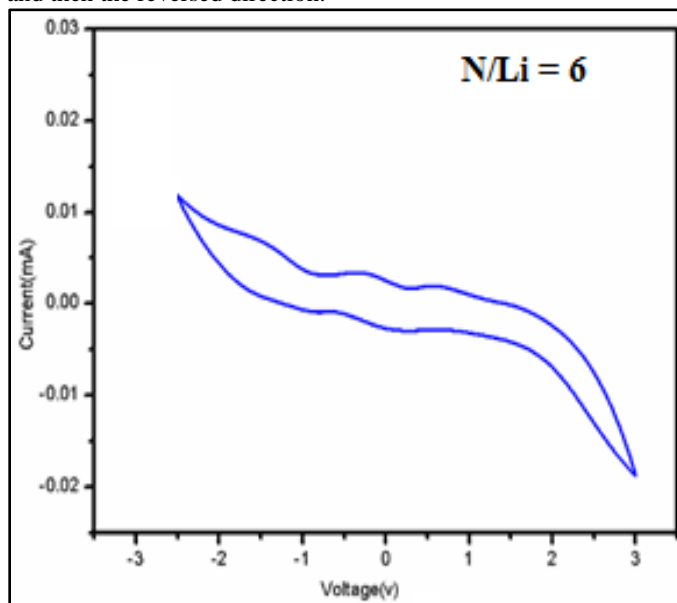
**Table:** dc electrical conductivity and activation energy of blend polymer and polymer salt complex films.

Sample Name	dc electrical conductivity(S cm <sup>-1</sup> )		Activation energy (eV)
	30 °C	100 °C	
Blend PAN-PEO	4.7 × 10 <sup>-7</sup>	1.9 × 10 <sup>-6</sup>	0.460
N/Li =6	5.4 × 10 <sup>-7</sup>	2.0 × 10 <sup>-6</sup>	0.210

### ELECTROCHEMICAL STABILITY

Electrochemical stability window of blend polymer salt system was measured by cyclic voltammetry technique. Cyclic Voltammetry involves applying a potential to the working electrode which changes with time and revealing the capacitive behavior of given material. It records, the current flowing through the working electrode as a function of the applied potential and a plot of current vs. potential is constructed called voltammogram.

Firstly, the cyclic voltammetry analysis is scanned in the forward and then the reversed direction.



**Figure 7.** Current–voltage response of SS electrode with optimized amount (N/Li = 6) with pure PAN-PEO and (PAN-PEO)<sub>6</sub> + LiPF<sub>6</sub> nanocomposite films

Electrochemical stability window of the polymer electrolyte is obtained by the  $\sim 4\text{V}$  and is shown in Fig.7. A blend of PAN with PEO based solid polymer electrolytes has the advantage of wide electrochemical stability window in energy storage devices.

### SUMMARY AND CONCLUSIONS

A new series of Polymer electrolyte film expressed by the blend polymer electrolytes based on PAN-PEO +LiPF<sub>6</sub> were prepared by solution cast technique with fixed N to Li ratio (N/Li=6) where Lithium hexafluorophosphate (LiPF<sub>6</sub>) was taken as salt. The main conclusions drawn from the results obtained may be summarized as follows: The surface morphology of blend polymer salt electrolytes analyzed by the FESEM show the slight change in surface behavior on the addition of salts. The solid polymer salt electrolyte film was visible and flexible with ionic conductivity in the range of at  $1.9 \times 10^{-6} \text{ S cm}^{-1}$ , 100 °C. The highest conductivity value  $2.0 \times 10^{-6} \text{ S cm}^{-1}$  has been observed at 100 °C is found for a film of (N/Li=6). The temperature dependent of the (PAN-PEO)+LiPF<sub>6</sub> blend polymer electrolyte obeys the Arrhenius equation and the activation energy ( $E_a$ ) of this solid electrolyte is estimated. The electrochemical window of polymer blends based on solid polymer electrolytes were calculated by Cyclic Voltammetry ( $\sim 4\text{V}$ ).

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