*International Journal of Latest Research in Engineering and Technology (IJLRET)*
*ISSN: 2454-5031*
*www.ijlret.com || Volume 03 - Issue 04 || April 2017 || PP. 54-59*

# Study on Lithium Ion- Conducting Blend Polymer Electrolytes

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**Abstract:** Blending of polymers is one of the most useful methods for synthesizing solid polymer electrolytes. Blend polymer electrolytes have been prepared with Polyvinylalcohol (PVA)-Polyacrylonitrile (PAN) and polyyvinylidenefluoride (PVdF) doped with lithium nitrate with different concentrations by solution casting technique , using Dimethylformamide (DMF) as the solvent . The prepared electrolytes are characterized by Fourier transform infrared (FTIR), Ultraviolet (UV) ,AC Impedance (LCR) and measurement techniques. The ionic conductivity has been found out by the LCR analysis. From AC impedance spectroscopy the maximum ionic conductivity has been found to be 1.0280×10^-4 S/cm at 303 K polymer electrolytes at ambient temperature. The complex formation between the polymers and the salt has been confirmed by FTIR analysis . The band gap studies have been done by UV.
**Keywords:** Polyvinylalcohol, Polyacrylonitrile, Polyyvinylidenefluoride, UV , FTIR,LCR.

## 1. Introduction

**The polymer electrolytes** which have higher ionic conductivity play a major role in the ionic devices viz. electro chromic devices, sensors, and super capacitors [1][13][9]. Various methods have been adopted to enhance the ambient temperature ionic conductivity of the polymer electrolyte. One such method is to dissolve inorganic salt in polymer matrix. Various polymers like PVA, PAN, and PVdF have been used to develop polymer electrolytes.

**Polymer blending** is one of the most promising ways by which these properties could be changed. Polymer blends are physical mixtures of structurally different polymers that interact through secondary forces and that are miscible to the molecular level. The significant advantages of polymer blends are that the properties of the final product can be tailored to the requirement of applications ,which cannot be achieved by one polymer. Generally, blending of two polymers not only results in the improvement of mechanical strength but also helps increasing the conductivity by suppressing the crystallization of polymer chain. Blending a mix (a substance) with another substance so that they combine together put or combine (abstract things together ).polymer blend mixture of atleast two polymers or co-polymers. It has attracted much attention as an easy and cost effective method of developing polymeric materials. A polymer blend or polymer mixture is a member of a class of materials analogous to metal alloys in which atleast two polymers are blended together a new material with different physical properties[8][10].

**Poly (vinyl alcohol) (PVA)** is a polymer that has been studied intensively because of its good film forming and physical properties, high hydrophilicity, processability biocompatibility, and good chemical resistance. It is a semi-crystalline polymer,containing crystalline and amorphous phase. Poly vinyl alcohol (PVA) is a cheap polymer having excellent film forming and adhesive properties, good chemical and mechanical stability and high potential for chemical cross-linking. However, PVA has highly swelling and low proton conductivity[12][11].

**Polyacrylonitrile (PAN)**, a commercially important polymer is a predominant precursor activated PAN films can find application as electrochemical supercapacitor electrodes[8][2][3]. This study is focused on the structure, processing and properties of polyacrylonitrile composite films[11][12].

**Polyvinylidene fluoride (PVdF)** is a polycrystalline polymer started drawing scientific interest in the seventies, because of its extraordinary pyroend piezoelectric properties. These properties combined with both high elasticity and processing ability lend this material numerous technological applications . PVDF has been chosen as polymer host for the present study because of its combination of flexibility, low weight, low thermal conductivity, high chemical corrosion resistance, and heat resistance . Poly (vinylidene fluoride) (PVDF) is a thermoplastic material used in a variety of products and parts such as piezoelectric film, fiber, belt, and pipe. For advanced applications of PVDF, it is highly desirable to enhance and control its physical properties such as thermal stability, mechanical modulus, and electrical conductivity[1][6] .

**Lithium nitrate salt ($LiNO_3$)** we have been chosen for getting good conductivity and properties of Lithium metal has shown great promise as an anode material for high-energy storage systems, owing to its high theoretical specific capacity and low negative electrochemical potential. Unfortunately, uncontrolled dendritic and mossy lithium growth, as well as electrolyte decomposition inherent in lithium metal-based batteries, cause safety issues and low Coulombic efficiency[4][7][5].

In the present work $LiNO_3$ doped PVdF polymer electrolytes have been prepared and subjected to various characterizations such as LCR, FTIR, AC impedance spectroscopy, UV-visible spectroscopy.

## 2. Experimental Details

### 2.1. Solution Casting Technique:

In the present study, Lithium nitrate salt doped PVdF,PAN,PVA thin film electrolytes have been prepared by solution casting technique. In this technique suitable amount of the polymer PVdF,PVA,PAN was dissolved in DMF at about 60°C and continuously stirred with a magnetic stirrer until the solution became transparent. Then the salt $LiNO_3$ was added and stirred well until they became homogeneous. Then the homogeneous solutions were poured in poly propylene petridishes and kept in a vacuum oven for solvent evaporation at 90°C for two days. After the complete evaporation of the solvent, the stand alone films were carefully removed from th petridishes and sealed in an air tight cover.

### 2.2characterization

**Vibrational Study**

FTIR spectra have been recorded for the polymer electrolyte films using a SHIMADZU- IR Affinity-1 Spectrometer in the Range of 400cm$^{-1}$ to 4000cm$^{-1}$ at room temperature.

**Ac Impedance Study**

Conductivity measurements have been carried out by using a HIOK*I – 3532 LC*Z meter in the frequency range of 42 Hz – 1MHz over the temperature range of 303K – 343K.

**Uv-Vis Spectral Analysis**

The UV-visible absorption spectroscopy technique is used for the investigation of optical properties of polymer.It was observed that the band gap energy was calculated from the plot.

## 3. Results and Discussions

### 3.1. Fourier Transform Infrared Analysis:

FTIR has been performed to study the complex formation between the blend polymer and salt. Generally FTIR is also used to study the interaction between cations, anions, solvents and polymers.

This interaction is determined by the shift in the IR spectrum as well as the alteration in band shapes and the intensities of internal vibrational modes. Figure 3.1 represents the FTIR spectra of 0.9PVA:0.08 PAN: 0.02PVdF blend polymer electrolyte with $LiNO_3$ .The vibrational frequencies observed in the FTIR spectra are given in Table 3.1

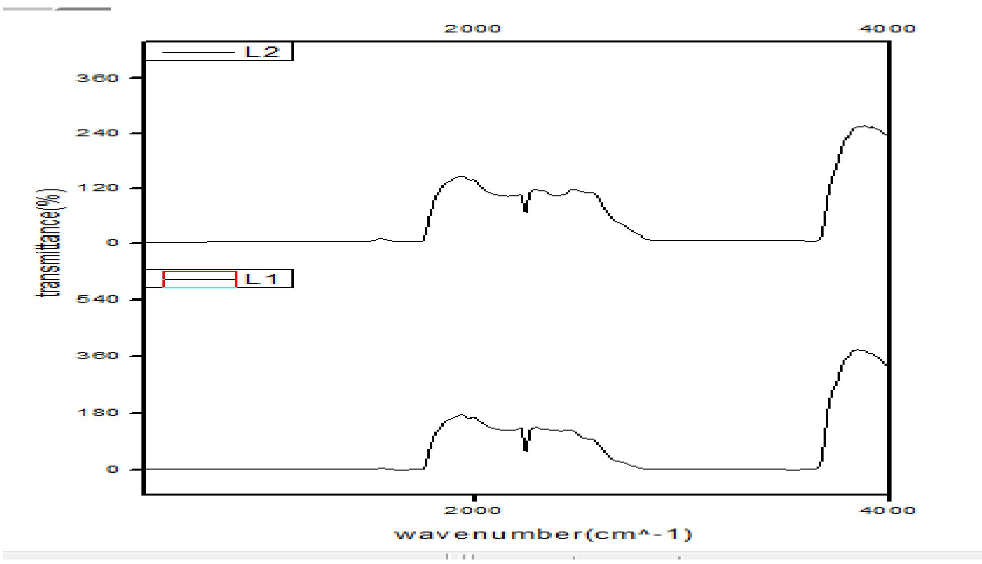

Table 3.1. FTIR transmission bands, positions and assignments for 0.9 PVA : 0.08PAN:0.02 PVdF:X $LiNO_3$ (X =0.1,0.2 wt %) blend polymer electrolytes.

| **Wave number ($cm^{-1}$)** | **PVA:PAN: PVdF M wt% $LiNO_3$** | | **Assignments** |
|---|---|---|---|
| | **0.9:0.08:0.02:0.1** | **0.9:0.08:0.02:0.2** | |
| **1489.05$cm^{-1}$** | **1489.05$cm^{-1}$** | **1473$cm^{-1}$** | **$CH_2/CH_2$** |
| **4343.68$cm^{-1}$** | **4343.68$cm^{-1}$** | **4359$cm^{-1}$** | **$CH_2$** |

The vibration peak at 1489.05$cm^{-1}$, 1473cm-, assigned to $CH_2/CH_2$ stretching of pure PVA,PVdF,PAN has shift in the LITHIUM NITRATE added electrolytes. **[ Brandon H. Holder et al 2012].** The absorptions peak at 4343.68$cm^{-1}$ and 4359cm-1 attributed to CH2 stretching of pure lithium nitrate has been shifted .**[ Tiwari, Srivastava, et al 2011; V.Singh, et al 2006 ].** The interaction is determined by the shift in the IR spectrum Interval Variation Mode.

### 3.2 Conductance Spectra Analysis

**The conductance spectra consists of two regions:**

- **low frequency dispersion region.**
- **frequency independent plateau region.**

The low frequency dispersion region describing electrode-electrolyte interface phenomenon, which is connected with the space change polarization at the blocking electrodes followed by the frequency independent plateau region connected with the dc conductivity ($\sigma_{dc}$) of the polymer electrolyte.

As the frequency increases, more and more charge accumulation occurs at the electrode-electrolyte interface, which leads to a decrease in number of mobile ions and eventually to a drop in conductivity.The second region corresponds to the frequency- independent plateau region and the extrapolation of the plateau to the logσ gives the value of dc conductivity. The dc conductivity values for all compositions of PVA: PAN: PVdF $LiNO_3$ polymer electrolytes at room temperature.

### 3.2.1 Conductance Spectra Analysis

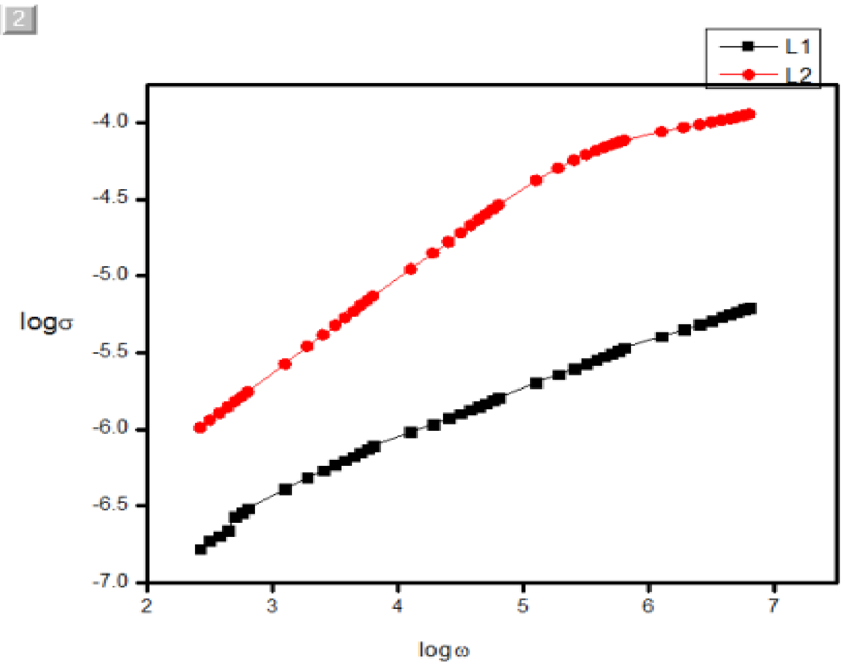


Figure 3.3.1 Conductance Spectra of a) 0.9 PVA:0.08 PAN:0.02PVdF 0.1 M wt% $LiNO_3$ b) 0.9PVA: 0.08PAN:0.02 PVdF: 0.2 M wt% $LiNO_3$ blend polymer electrolytes at 303K.

### 3.2.2 Temperature Dependence of Conductance Spectra for Different Temperature

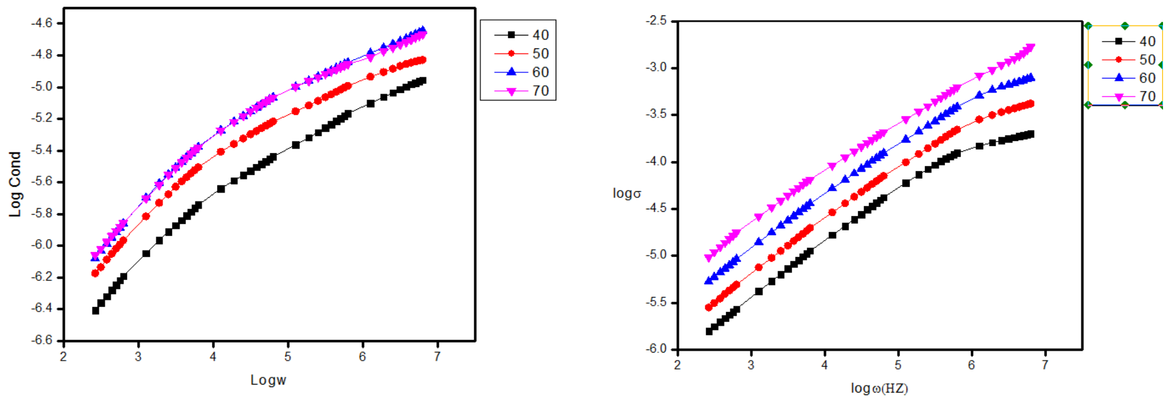


Figure 3.3.2.a) Conductance Spectra at 40$^0$C , b) Conductance spectra at 50$^0$C, c) Conductance spectra at 60$^0$C, d) Conductance spectra at 70$^0$CSpectra 70$^0$C

### 3.2.3 Modulus Spectra Analysis

Macedo et al. have presented the electric modulus M in order to overcome the effect of electrode polarization. The electric modulus is defined as,

**M*=M□□jM''------------(1)**

Where M′ and M″ are real and imaginary part of the complex electric modulus.

depict the frequency dependence of M'(ω) and M"(ω) **a) 0.9PVA:0.08 PAN:0.02PVdF 0.1 M wt% $LiNO_3$ b) 0.9PVA:0.08 PAN:0.02 PVdF: 0.2 M wt% $LiNO_3$** polymer electrolytes at 303 K. Both plots show an increase at the high frequency end, and well-defined dispersion peaks are observed for M'. The increase of M'(ω) and M"(ω) plot at higher frequencies may be allotted to the bulk effect. At lower frequencies, it is observed that the value of M'(ω) and M"(ω) is in the locality of zero, due to the negligible contribution of electrode polarization. **[et al 2014].**

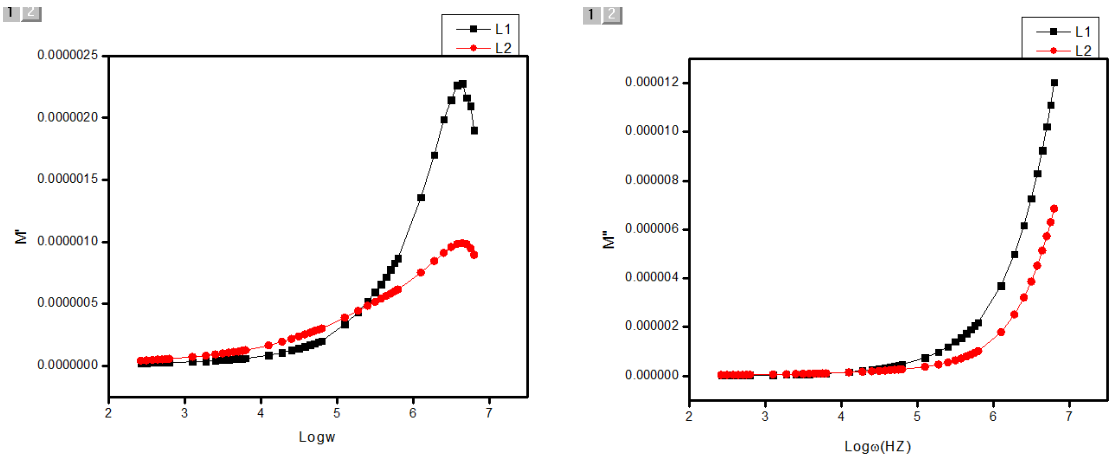


Figure 3.2.3 (a & b)Frequency dependence of M′(ω) and M"(ω) Conductivity of a) 0.9PVA:0.08 PAN:0.02PVdF 0.1 M wt% $LiNO_3$ b) 0.9PVA: 0.08PAN:0.02 PVdF: 0.2 M wt% $LiNO_3$ blend polymer electrolytes at 303K.

### 3.3 UV-VIS Spectral Analysis

The UV-visible absorption spectroscopy technique is used for the investigation of optical properties of the PVdF polymer.Figure 4 (a,b) shows A plot of $(\alpha h\nu)^2$ versus photon energy (hν) for pure PVdF and 80% PVdF doped with 20% $LiNO_3$

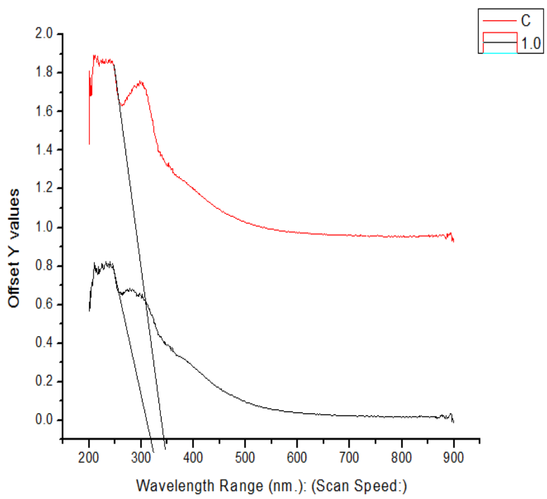


Figure 3.3 UV spectrum of a) 0.09 PVA:0.08PAN:0.02PVdF 0.1 M wt% $LiNO_3$ b) 0.09PVA:0.08 PAN: 0.02PVdF: 0.2 M wt% $LiNO_3$ blend polymer electrolytes at 303K

It was observed that the band gap energy was calculated from the plot by extrapolating the straight line portion of the curve to zero absorption coefficient value. The value thus calculated was equal to 4.16 eV for pure PVdF and 4.08 eV for 80%PVdF: 20% $LiNO_3$. It is clear that the band gap energy decreases with addition of $LiNO_3$.

## 4. Conclusions

PVdF,PAN@ PVA based blend spolymer electrolyte with different concentration of LithiumNitrate have been prepared by solution casting technique.The polymer electrolyte having 0.02PVdF,0.09 PAN,0.09PVA doped with 0.01$LiNO_3$ and 0.02 $LiNO_3$has low bulk resistance and high conductivity of 1.0280×10^-4 S/cm at 303 K. The direct optical band gap for PVdF and $LiNO_3$ doped -and is calculated and it is found that the band gap energy decreased with the addition of $LiNO_3$.

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