

# Preparation and characterization of Lithium ion conducting blend polymer (PVA-PVP) with LiBr

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**Abstract:** Lithium ion conducting blend polymer electrolytes based on Poly(vinyl alcohol) (PVA) and Poly(vinyl pyrrolidone) (PVP) doped with different concentrations of lithium bromide (LiBr) have been prepared by solution casting method. The prepared electrolytes have been characterized by XRD, FTIR, DSC and AC impedance techniques. The complex formation between the blend polymer, PVA-PVP and the salt, LiBr has been confirmed by XRD and FTIR analyses. It has been observed that the ionic conductivity of the doped blend polymer electrolyte increases as the salt concentration increases. The maximum ionic conductivity has been found to be  $1.03 \times 10^{-4} \text{ S cm}^{-1}$  for 70 PVA : 30 PVP : 0.25 M wt % LiBr sample at room temperature. Thermal behavior of the samples has been analyzed by differential scanning calorimetry and thermo gravimetry techniques.

**Keywords:** blend polymer, XRD, FTIR, glass transition temperature, ionic conductivity

## I. INTROCUCTION

Polymer electrolytes envisage the advantage of solid electrolytes as well as the property of liquid electrolytes. The interest in this study is continually growing due to their potential applications in lithium batteries, electro chromic devices, etc [1-3]. The development of polymer system with high ionic conductivity and stability is the congenial objectives in polymer research. Hence polymer should possess fundamental properties like low glass transition temperature ( $T_g$ ) so that the conformations of polymer chains and segmental motion can significantly assist transport of ions at the operating temperature ensuing conductivity. Hence, the polymer electrolyte should possess low degree of crystallinity as the conduction in polymer electrolytes is through the amorphous domain of the polymer-salt system. Various approaches viz.co-polymerization [4], grafting [5], physical cross linking [6], blending [7], plasticization [8] and addition of inert ceramic oxides into the matrix [9] were carried out in the preparation of polymer electrolytes with high conductivity and appreciable thermal stability at ambient temperature. Among these techniques, blending of polymers is the most feasible approach, in the past few years it has been intensively investigated.

The blending of polymers may lead to the increase in stability due to one polymer portraying itself as a mechanical stiffener and the other as a gelled matrix supported by the other. The lithium salt is added so as to increase the amorphicity and the introduction of conducting moieties into the matrix. Poly(vinyl alcohol) (PVA) is a water-soluble synthetic polymer and is an odorless, tasteless, translucent, white or cream colored granular powder [10]. The prominent properties of PVA are its biodegradability [11] in the environment and biocompatibility [12-14]. PVA has high tensile strength, flexibility, high oxygen and aroma barrier property. It also has excellent film forming, emulsifying and adhesive properties. Poly(vinyl pyrrolidone) (PVP) is a water-soluble polymer [15]. PVP is derived from vinyl polymer exhibiting highly polar side groups present in the lactam ring [16]. In addition, it is an amorphous polymer with high  $T_g$  due to presence of rigid pyrrolidone functional group, exhibiting property to form complexes with other polymers [17]. PVP has adhesive property, excellent physiological compatibility, low toxicity and reasonable solubility in water and most organic solvents [18,19] which can find wide applications in biomedical field.

The present work deals with the preparation and characterization of blend polymer electrolytes based on PVA and PVP doped with different concentrations of lithium bromide (LiBr) by solution casting technique using DMSO as solvent. In order to characterize the prepared blend polymer electrolytes, various experimental techniques such as X-ray diffraction, Fourier transform infrared spectroscopy, differential scanning calorimetry, Thermogravimetry and AC impedance spectroscopy have been employed.

## II. EXPERIMENTAL TECHNIQUES

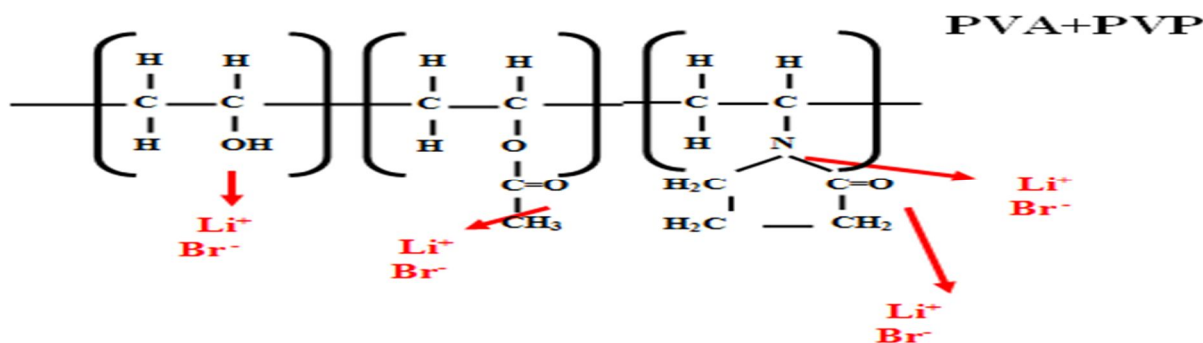
PVA ( $M_w = 1,25,000$ , Sd fine), PVP ( $M_w = 40,000$ , Sd fine) and LiBr (AR grade, Merck) have been used as raw materials in this study. Dimethyl sulfoxide (DMSO) is used as solvent. The blend polymer electrolytes have been prepared using the optimized composition of PVA and PVP (70PVA:30PVP) [20] and lithium bromide (LiBr) of different ratios by solution casting technique. The solutions of the optimized composition of the blend polymer (70 PVA: 30PVP) and various concentrations of LiBr have been stirred continuously with a magnetic stirrer at  $60^\circ\text{C}$  for several hours in order to obtain homogeneous solutions. The solutions have

been poured in polypropylene petri dishes and kept in vacuum oven at 70 °C for five days to remove excess solvent present in the samples. Transparent and flexible films have been obtained.

X-ray diffraction patterns have been recorded at room temperature with X' Pert PRO diffractometer using the  $\text{CuK}\alpha$  radiation in the range of  $2\theta = 10^\circ$  to  $80^\circ$ . FTIR analysis has been done using SHIMADZU IR Affinity – 1 Spectrometer in the range  $400 - 4000 \text{ cm}^{-1}$  at room temperature. DSC thermograms have been obtained using DSC 200F3 Maia. Thermo gravimetric analysis (TG) has been carried out using STA 6000 Build 101 at a heating rate of  $20^\circ\text{C}$  per minute in the range from  $35^\circ\text{C}$  to  $955^\circ\text{C}$ . Electrical measurements of the blend polymer electrolytes have been carried out in the temperature range of 303 to 343 K over the frequency range of 42 Hz to 1 MHz using a HIOKI make LCR meter (model 3532 ) using aluminium blocking electrodes.

### III. POSSIBLE INTERACTION BETWEEN PVA-PVP AND LiBr

The possible interaction between PVA-PVP blend polymer with dissociated salt (LiBr) has been shown in Scheme 1. Lithium ion from the salt interacts with the polar groups of the host blend polymer matrix.



Scheme1. Possible interaction between PVA-PVP matrix and LiBr

### IV. RESULTS AND DISCUSSION

#### A. X-ray diffraction (XRD) analysis

Fig. 1 represents the XRD patterns of blend polymer (70 PVA : 30 PVP) and blend polymer with different concentrations of LiBr. In the salt-doped systems, the relative intensity of the hump decreases and its broadness increases with respect to blend polymer. This result can be interpreted by considering the Hodge et al. [21] criterion, which establishes a correlation between the intensity of the peak and the degree of crystallinity. These changes indicate that the addition of LiBr to blend polymer matrix reduces the crystalline nature and enhances the amorphous nature of blend polymer. This is due to the complexation between the blend polymer (PVA-PVP) and the dopant salt (LiBr). No peaks corresponding to LiBr are observed in the salt-doped blend polymer systems indicating the complete dissociation of the salt in the blend polymer matrices. Thus, the XRD analysis reveals the complex formation between the blend polymer and the salt.

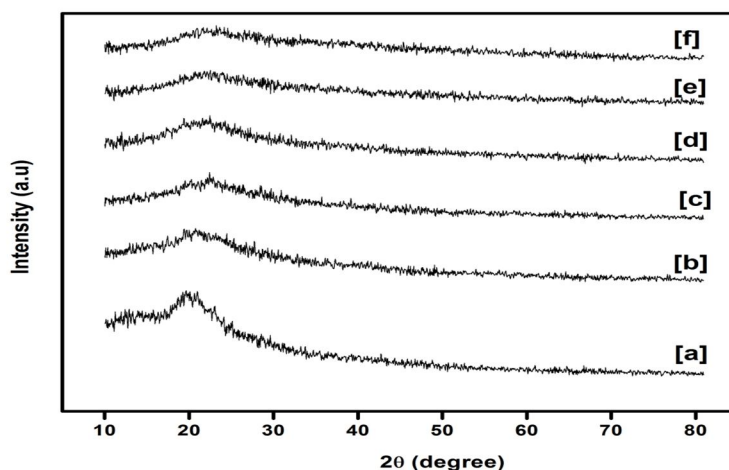


Fig. 1 XRD patterns of a) 70 PVA: 30 PVP b) 70 PVA: 30 PVP: 0.1 M wt% LiBr c) 70 PVA: 30 PVP: 0.15 M wt% LiBr d) 70 PVA: 30 PVP: 0.2 M wt% LiBr e) 70 PVA: 30 PVP: 0.25 M wt% LiBr f) 70 PVA: 30 PVP: 0.3 M wt% LiBr

The crystallite size (D) for all electrolytes has been calculated by Debye-Scherrer equation,

$$D=0.89\lambda/\beta \cos\theta$$

where  $\lambda$ - wavelength of the X-ray radiation,  $\theta$  - diffraction angle, and  $\beta$  - full width at half maximum (FWHM). The diffraction angle, FWHM, and crystallite size of all samples have been tabulated in Table I. It is observed that 70 PVA: 30 PVP: 0.25 M wt% LiBr blend polymer electrolyte has small crystallite size and also it is more amorphous than other compositions. Thus, the X-ray diffraction analysis reveals the increase of amorphous nature of the blend polymer electrolyte films.

Table I Crystallite Size of 70 PVA: 30 PVP: X LiBr (X = 0.1 M wt%, 0.15 M wt%, 0.2 M wt%, 0.25 M wt% and 0.3 M wt%) Blend Polymer Electrolytes

PVA: PVP: LiBr Composition	2 $\theta$ (degree)	FWHM (degree)	Crystallite size (nm)
70 : 30 : 0 M wt %	19.65	1.34	5.9
70 : 30 : 0.1 M wt %	20.57	1.41	5.6
70 : 30 : 0.15 M wt %	22.39	1.60	4.9
70 : 30 : 0.2 M wt %	17.68	2.41	3.3
70 : 30 : 0.25 M wt %	22.38	7.18	1.1
70 : 30 : 0.3 M wt %	23.04	4.02	2.0

**B. Fourier Transform Infrared (FTIR) Analysis**

FTIR characterization is a convenient and sensitive method to detect the interaction between two species. The natural vibrational frequencies of atoms in molecules and crystals fall in the infrared region which facilitates the identification of functional groups present in a material. Fig. 2 depicts the FTIR spectra of blend polymer and blend polymer doped with different concentrations of LiBr. The FTIR spectral assignments for 70 PVA : 30 PVP : LiBr complexes having different concentrations of LiBr are shown in Table II.

The FTIR spectrum of the PVA-PVP blend film reveals absorptions at 1648 cm<sup>-1</sup> corresponding to C=C stretching which is shifted to 1642 cm<sup>-1</sup> -1648 cm<sup>-1</sup> in the salt doped blend polymer electrolytes. In addition to this, the C-H stretching shows an absorption band at 2920 cm<sup>-1</sup> in blend polymer, which is shifted to 2919 cm<sup>-1</sup>, 2926 cm<sup>-1</sup> and 2928 cm<sup>-1</sup>, respectively in the salt doped systems. Similarly, for C-O-C stretching for blend polymer, the peak at 1289 cm<sup>-1</sup> is shifted to the wave number at 1291cm<sup>-1</sup> and 1292 cm<sup>-1</sup> in the salt doped systems [22]. The characteristic peak at 1019 cm<sup>-1</sup> in the blend polymer corresponding to C- C stretching is shifted to lower wave numbers at 1013 cm<sup>-1</sup> and 1016 cm<sup>-1</sup> in the salt doped systems.

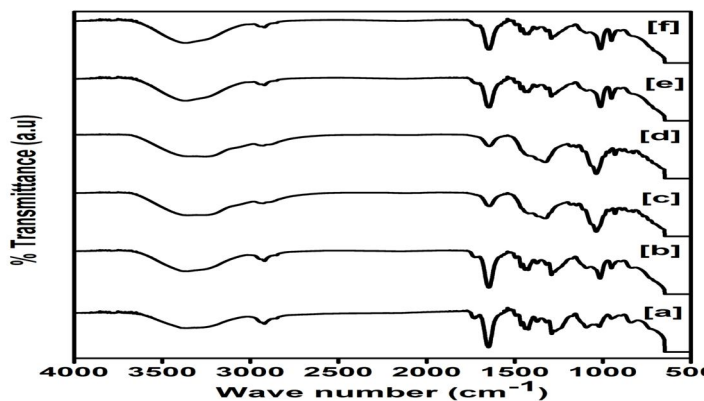


Fig. 2 FTIR spectra of undoped and doped blend polymer electrolytes with different concentrations of LiBr a) 70 PVA: 30 PVP b) 70 PVA: 30 PVP: 0.1 M wt% LiBr c) 70 PVA: 30 PVP: 0.15 M wt% LiBr d) 70 PVA: 30 PVP: 0.2 M wt% LiBr e) 70 PVA: 30 PVP: 0.25 M wt% LiBr f) 70 PVA: 30 PVP: 0.3 M wt% LiBr The vibrational peak at  $1319\text{ cm}^{-1}$  is attributed to  $\text{CH}_2$  wagging of blend polymer (PVA-PVP) and is found to be shifted to the wave numbers at  $1323\text{ cm}^{-1}$ ,  $1321\text{ cm}^{-1}$ ,  $1318\text{ cm}^{-1}$  in the salt doped films. The vibrational peak at  $1372\text{ cm}^{-1}$  attributed to  $\text{CH}_3$  symmetric bending of undoped film is found to be shifted to the wave numbers at  $1370\text{ cm}^{-1}$  -  $1376\text{ cm}^{-1}$  in the salt doped systems. A band at  $950\text{ cm}^{-1}$  in the blend corresponding to O-H out of plane bending is shifted to higher wave numbers at  $951 - 967\text{ cm}^{-1}$  in the complexes [23]. The vibrational peak observed at  $894\text{ cm}^{-1}$  assigned to  $\text{CH}_2$  rocking in pure PVP gets shifted to higher wave numbers at  $895\text{ cm}^{-1}$  and  $896\text{ cm}^{-1}$  in the complexed systems [24]. The broad band around  $3362\text{ cm}^{-1}$  in the blend polymer corresponding to O-H stretching (PVA-PVP) is shifted to higher wave numbers at  $3355\text{ cm}^{-1}$  -  $3373\text{ cm}^{-1}$  in the complexes. The shift in the positions of absorption bands, the change in their intensities and the appearance of new peaks and the disappearance of some peaks in the salt doped blend polymer systems with respect to undoped blend polymer system confirms the complex formation between the blend polymer and the salt.

Table II FTIR Absorption Bands, Positions and Assignments for 70 PVA: 30 PVP: X LiBr (X = 0.1, 0.15, 0.2, 0.25 and 0.3 M wt%) Blend Polymer Electrolytes

PVA:PVP	Wave number ( $\text{cm}^{-1}$ )					Assignment
	PVA : PVP : M wt % LiBr					
70:30	70:30:0.1	70:30:0.15	70:30:0.2	70:30:0.25	70:30:0.3	
894	896	895	895	896	896	$\text{CH}_2$ Rocking
950	951	966	967	951	951	O-H out of plane
1019	1016	1019	1013	1013	1013	C-C stretching
1289	1291	-	1292	1292	1292	C-O-C stretching
1319	1319	1323	1321	1318	1318	$\text{CH}_2$ Wagging
1372	1374	1370	1371	1376	1376	$\text{CH}_3$ symmetric bending
1648	1647	1642	1643	1643	1648	C=C stretching
2920	2919	2926	2928	2919	2920	C-H stretching
3362	3363	3355	3261	3373	3373	O-H stretching

### C. Thermal Analysis

#### 1) Differential Scanning Calorimetry (DSC) Analysis

DSC analysis has been carried out to find the glass transition temperature, ( $T_g$ ) of the blend polymer electrolyte. The DSC curves for blend polymer (PVA-PVP) and blend polymer doped with 0.25 M wt% LiBr are shown in Fig. 3a & 3b. The  $T_g$  value has been determined at the midpoint of the step-like change in the DSC thermograms. It is found that  $T_g$  of the undoped blend polymer electrolyte, 70 PVA : 30 PVP is  $85^\circ\text{C}$  and that of the salt-doped blend polymer electrolyte, 70 PVA : 30 PVP : 0.25 M wt% LiBr is  $78^\circ\text{C}$ . This indicates that the addition of LiBr causes a decrease in the value of  $T_g$  of blend polymer. This reduction in  $T_g$  can be attributed to the plasticizing effect of the salt [25] on the polymer structure which weakens the dipole-dipole interactions between the PVA-PVP chains.

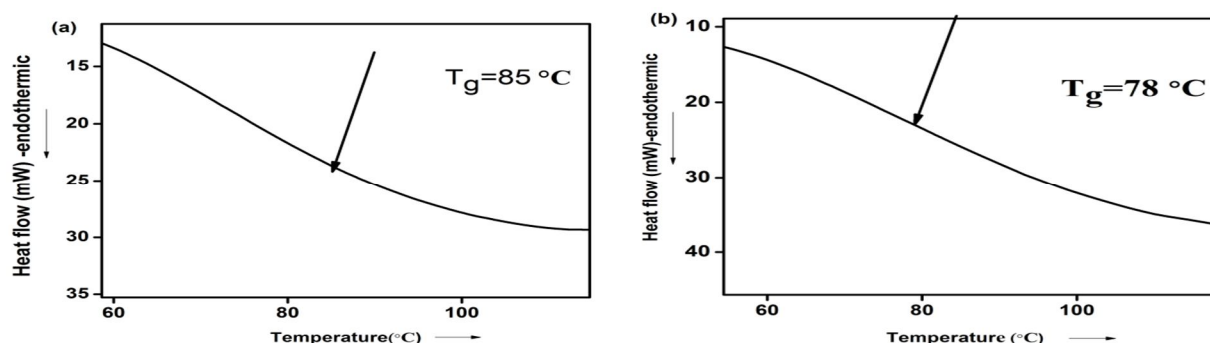


Fig. for (a) 3 DSC thermogram 70 PVA : 30 PVP and (b) 70 PVA : 30 PVP : 0.25 M wt% LiBr.

2) Thermogravimetric (TG) analysis

TG analysis is sensitive enough to record the thermal events such as decomposition and corresponding weight loss of the electrolyte sample. The process involves change in weight attributed to moisture uptake and thermal stability of the polymer electrolyte. Fig. 4 shows the TGA curves of (a) 70 PVA: 30 PVP and (b) 70 PVA: 30 PVP: 0.25 M wt% LiBr membranes. It is found from the figure that, for blend polymer electrolyte the first maximum decomposition temperature is at about 128 °C with 8% weight loss [26] and for salt doped blend polymer electrolyte membrane, it is at about 230 °C with 21% weight loss [27].

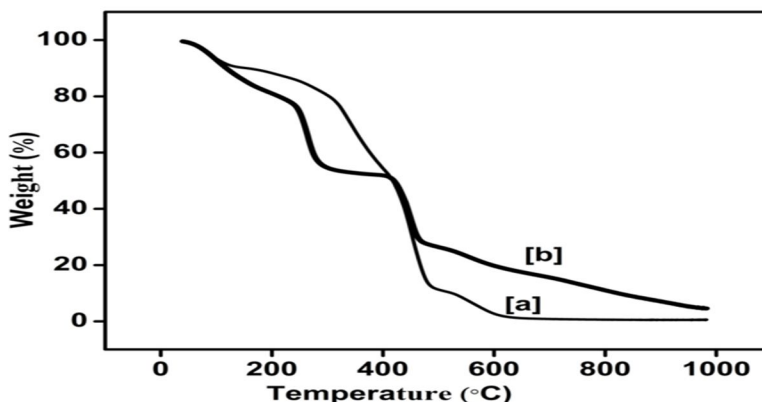


Fig. 4 TGA curves of (a)70 PVA: 30 PVP (b)70 PVA: 30 PVP: 0.25 M wt% LiBr membranes.

This initial weight loss is probably due to evaporation of moisture because these polymer membranes tend to absorb moisture from the surroundings. The second maximum decomposition temperatures are at about 480 °C and 413 °C for blend polymer electrolyte and salt doped blend polymer electrolyte membranes with a weight loss of about 77% and 23%, respectively [28]. This weight loss may be due to evaporation of residual water embedded in the ionic cluster. The third maximum decomposition temperatures are at about 632 °C and 475 °C for blend polymer electrolyte and salt doped blend polymer electrolyte membranes with a weight loss of about 11% and 24% respectively. Hence the thermal stability of 70 PVA: 30 PVP blend polymer doped with 0.25 M wt% LiBr is high compared to 70 PVA: 30 PVP blend polymer.

D. AC Impedance Spectroscopic Analysis

1) Impedance analysis

Fig. 5(a) shows the complex impedance plot for 70PVA: 30PVP blend polymer doped with different concentrations of LiBr at 303 K. The plot shows a high frequency semicircle which is due to the bulk effect of the electrolyte and a low frequency spike corresponding to the effect of the blocking electrodes [29]. As the concentration of the salt increases, the diameter of the semicircle decreases. This indicates that the bulk resistance ( $R_b$ ) of the polymer electrolyte decreases. The  $R_b$  of the polymer electrolyte has been obtained from the intercept of the high frequency semicircle or the low frequency spike on the  $Z'$  axis.

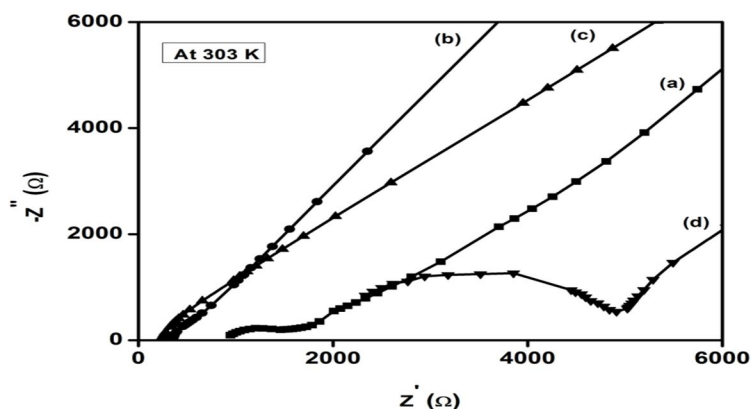


Fig. 5(a) Complex impedance plot of a) 70 PVA: 30 PVP: 0.15 M wt% LiBr b) 70 PVA: 30 PVP: 0.2 M wt% LiBr c) 70 PVA: 30 PVP : 0.25 M wt% LiBr d)70PVA: 30PVP: 0.3 M wt% LiBr at 303 K.



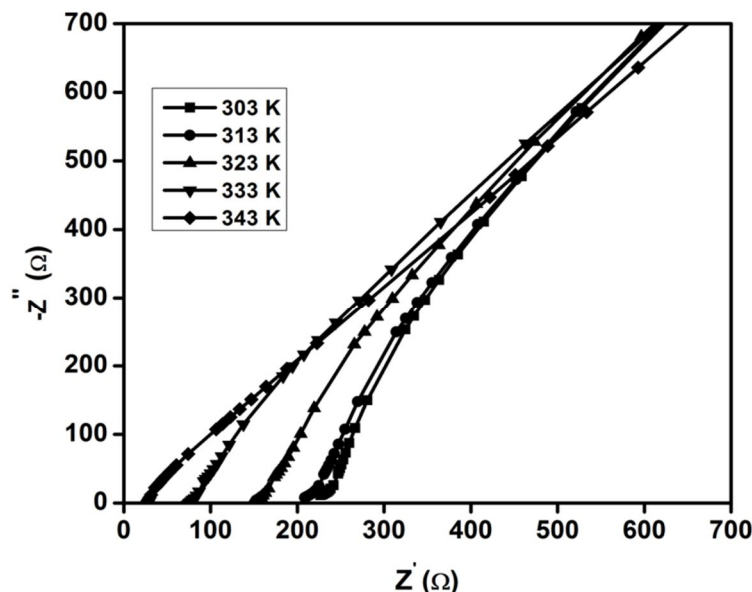


Fig. 5(b) Complex impedance plot of 0.25 M wt% LiBr-doped 70 PVA : 30 PVP blend polymer electrolyte at different temperatures

. The ionic conductivity of the samples has been calculated by using the equation:

$$\sigma = l/A R_b$$

where  $l$ ,  $A$  and  $R_b$  are the thickness, area and bulk resistance of the polymer electrolyte. The ionic conductivity of blend polymer (70 PVA : 30 PVP) electrolyte has been reported as  $1.58 \times 10^{-6} \text{ S cm}^{-1}$  [20]. The highest ionic conductivity at room temperature is found to be  $1.03 \times 10^{-4} \text{ S cm}^{-1}$  for the blend polymer electrolyte (70 PVA : 30 PVP) doped with 0.25 M wt% LiBr. Fig. 5(b) shows the impedance plot of the highest conductivity sample, 70 PVA:30 PVP:0.25 M wt% LiBr at different temperatures. It is seen that the bulk resistance decreases with increase of temperature, hence the ionic conductivity increases.

Table III Ionic Conductivity ( $\sigma_{dc}$ ) for Blend Polymer Electrolyte (70 PVA: 30 PVP) Doped with Different Concentrations of LiBr

PVA:PVP: LiBr Composition	Ionic conductivity, $\sigma_{dc}$ ( $\text{S cm}^{-1}$ )				
	$\sigma_{303 \text{ K}}$	$\sigma_{313 \text{ K}}$	$\sigma_{323 \text{ K}}$	$\sigma_{333 \text{ K}}$	$\sigma_{343 \text{ K}}$
70:30:0.15M wt%	$7.06 \times 10^{-6}$	$2.18 \times 10^{-5}$	$6.63 \times 10^{-5}$	$1.40 \times 10^{-4}$	$3.76 \times 10^{-4}$
70:30:0.2 M wt%	$2.70 \times 10^{-5}$	$2.84 \times 10^{-5}$	$7.76 \times 10^{-5}$	$1.92 \times 10^{-4}$	$4.82 \times 10^{-4}$
70:30:0.25M wt%	$1.03 \times 10^{-4}$	$1.07 \times 10^{-4}$	$1.45 \times 10^{-4}$	$2.92 \times 10^{-4}$	$7.76 \times 10^{-4}$
70:30:0.3 M wt%	$4.16 \times 10^{-6}$	$4.76 \times 10^{-6}$	$2.08 \times 10^{-5}$	$7.92 \times 10^{-5}$	$2.58 \times 10^{-4}$

The ionic conductivity values of the blend polymer electrolytes at different temperatures are given in Table III. From the table, it has been observed that as the salt concentration increases, the ionic conductivity increases. This may be due to the increase in amorphous nature of blend polymer electrolyte on the addition of salt [23] (confirmed by XRD analysis) that enhances the ionic motion in the blend polymer network and the decrease of  $T_g$  reduces the energy barrier of the segmental motion.

## 2) Conductance Spectra Analysis

Fig. 6(a) & 6(b) show the conductance spectra for blend polymer 70 PVA : 30 PVP doped with different concentrations of LiBr at 303 K and for the highest conductivity sample 70 PVA: 30 PVP: 0.25 M wt% LiBr at different temperatures, respectively.

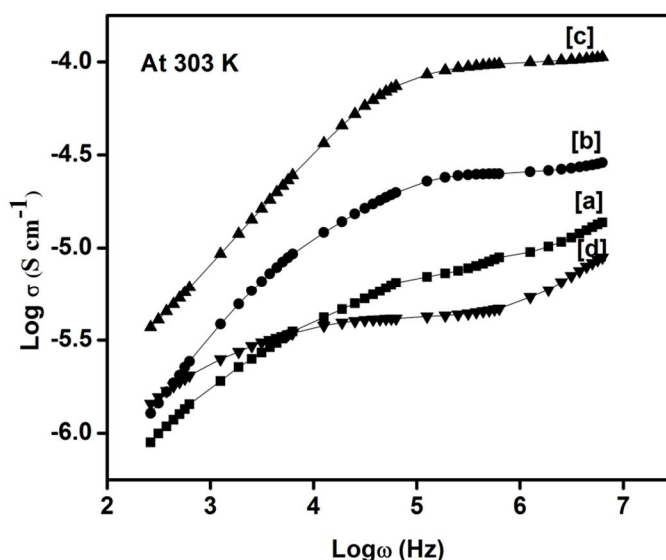


Fig. 6(a) Conductance Spectra of a) 70 PVA: 30 PVP : 0.15 M wt% LiBr b) 70 PVA: 30 PVP : 0.2 M wt% LiBr c) 70 PVA:30PVP : 0.25 M wt% LiBr d) 70PVA: 30PVP: 0.3 M wt% LiBr at 303 K.

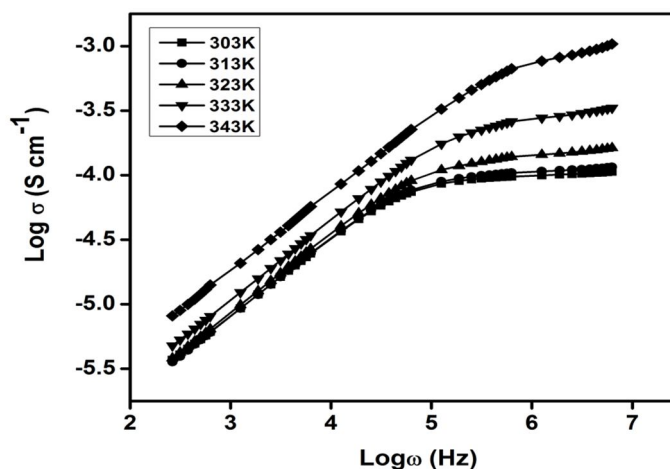


Fig. 6(b) Conductance spectra of 70 PVA: 30 PVP: 0.25 M wt% LiBr at various temperatures.

The plot consists of a low frequency dispersion region describing electrode-electrolyte interface phenomena connected with the space charge polarization at the blocking electrodes followed by the frequency independent plateau region connected with the dc conductivity of the polymer complexes. The high frequency region of the curve corresponds to the bulk relaxation phenomena. The dc conductivity values of the PVA: PVP: LiBr films can be calculated by extrapolating the plateau region to the log  $\sigma$ -axis. Fig. 6(b) shows that the dc conductivity increases with increasing temperature, which suggests that the free volume around the polymer chain enhances the mobility of ions, polymer segments and hence the conductivity [30].

## V. CONCLUSION

Blend polymer electrolytes (70 PVA : 30 PVP) doped with different concentrations of LiBr have been prepared by solution casting technique using DMSO as solvent. Amorphous nature of the complex has been confirmed by XRD analysis. The FTIR analysis confirms the complex formation between blend polymer and the salt. DSC thermograms convey a decrease in  $T_g$  with the addition of salt due to plasticizing effect. Thermal stability has been analyzed using TGA. The AC impedance spectroscopy analysis shows the highest conductivity of  $1.03 \times 10^{-4} \text{ Scm}^{-1}$  for 70 PVA : 30 PVP : 0.25 M wt% LiBr sample at room temperature.

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