

MESCon 2014 [4th -5<sup>th</sup> September 2014]  
National Conference on Material for Energy Storage and Conversion- 2014

## Effect of plasticizer on Poly (vinyl alcohol): Poly (vinylidene fluoride) blend polymer electrolyte

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**Abstract :** Free standing film of Gel polymer electrolyte (GPE) based on Poly(vinyl alcohol) (PVA): Poly(vinylidene fluoride) (PVdF): Lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ): Ethylene carbonate (EC) have been prepared by solution casting technique. Effect of lithium salt and plasticizer in PVA:PVdF blend polymer electrolytes have been analyzed using AC impedance spectroscopy and Fourier transform Infrared spectroscopy (FTIR) studies. The ionic conductivity ( $\sigma$ ) of pure PVA: PVdF blend system is low ( $\sim 10^{-10} \text{ Scm}^{-1}$ ) because of the crystalline nature of PVdF and Semi crystalline nature of PVA. This value has been enhanced by the addition of lithium salt ( $\sigma = 10^{-3} \text{ Scm}^{-1}$ ). However on the addition of Ethylene carbonate, the ionic conductivity has been decreased slightly by one order of magnitude. This may be due to the increase in viscosity of gel polymer electrolyte which may restrict the segmental motion of polymer chains at ambient temperature. This is inturn reflected in the dielectric spectra in which a very low value of dielectric constant is observed for GPE compared to salt doped system. Interaction of lithium salt and plasticizer with the polymer blend matrix has been confirmed from FTIR spectra analysis.

**Keywords:** Gel polymer electrolyte; Fourier transform Infrared spectroscopy; modulus; ethylene carbonate

### Introduction

Solid polymer electrolytes (SPE) have been extensively studied in recent years as they find technological applications in solid state ionic devices due to their dimensionality, easy processability, flexibility, electrochemical stability, safety, and long life[1, 2]. Blending technique for polymer electrolytes has been considered as greatest advantageous for enhancing the properties because of ease of preparation and control of the properties by changing blended polymer matrix composition[3]. In recent years, polymer electrolytes containing liquid plasticizers (non-aqueous solvents) are attractive as novel electrolytes because of its high ionic conductivity, mechanical stability and processability at ambient temperature[4]. The plasticizer used for the hybrid film is generally a low molecular weight solvent having a high dielectric constant like Ethylene carbonate, Propylene carbonate, Dimethyl formamide, etc.

The aim of the present work is to investigate the effect of lithium triflate salt and ethylene carbonate plasticizer in Poly(vinyl alcohol) [PVA] : Poly(vinylidene fluoride) [PVdF] blend polymer electrolyte on the ionic conductivity, complex formation and interaction of Polymer, salt and plasticizer using Impedance spectroscopy and Fourier-transform infrared spectroscopy (FTIR) respectively.

## Experimental:

PVA ( $M_w$ : 1,25,000) and PVdF ( $M_w$ : 5,30,000) were purchased from S. d. Fine, Lithium triflate,  $\text{LiCF}_3\text{SO}_3$  from Alfa Aesar, Ethylene carbonate (Himedia) and N, N-Dimethyl formamide, DMF from Merck. The purchased raw materials were used without further purification.

Solid polymer electrolyte of PVA and PVdF doped with Lithium triflate,  $\text{LiCF}_3\text{SO}_3$  in the presence of N, N-Dimethyl formamide, DMF (Merck) solvent has been prepared using solution casting technique as reported elsewhere[5]. Gel polymer electrolyte has been prepared by the addition of EC plasticizer into the polymer salt matrix as mentioned in the above method. The resulting films were flexible and free standing.

The FTIR spectrum was recorded for the polymer film in the range  $400\text{--}4000\text{ cm}^{-1}$  using JASCO 460 plus FT-IR Spectrophotometer at room temperature. Impedance measurements have been performed on a HIOKI make LCZ meter (model 3532) in the frequency window,  $42\text{Hz--}5\text{MHz}$  at room temperature (303K) with stainless steel blocking electrodes.

## Results

### FTIR studies

FTIR spectroscopy was used to observe the vibration energies of covalent bonds in the polymer host and the interactions that occur in the polymer - salt complexes. Figure 1 shows the FTIR spectra of i) PVA:PVdF:  $x\text{ LiCF}_3\text{SO}_3$  ( $x=0, 15$ ) blend and (ii) gel polymer electrolyte. FT-IR spectral studies have been carried out to confirm the polymer-salt complex.

### Complex Impedance Plot

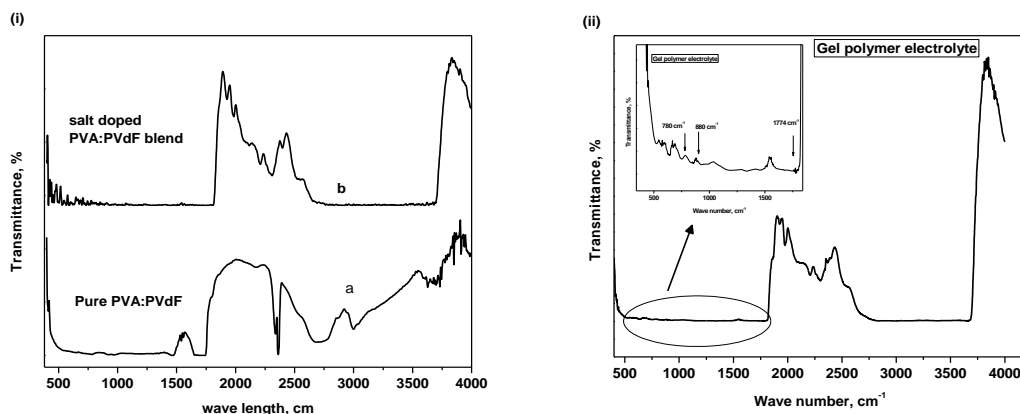
Impedance spectroscopy measurements were used to determine the conductivity of the films. Figure 2 shows the complex impedance plot of i) pure (ii) lithium salt doped solid polymer electrolyte and (iii) gel polymer electrolyte at 303 K. Conductivity ( $\sigma$ ) of the samples was calculated using  $\sigma=t/R_bA$ ; where  $t$  is the sample thickness (cm),  $A$  the effective contact area of the electrode and the sample ( $\text{cm}^2$ ), and  $R_b$  is the bulk resistance ( $\Omega$ ) obtained from the impedance plots.

### Dielectric Measurements

Figure 3 represents Real and imaginary part of dielectric spectra of pure, lithium triflate doped and EC complexed gel polymer electrolyte. A broad frequency range of dielectric relaxation spectroscopy is a very useful tool to study the relaxation of dipoles in polymer electrolytes.

## Discussion

In Fig 1(i) the major O–H stretching of alcohols appearing near  $3005\text{ cm}^{-1}$  in pure PVA:PVdF blend polymer electrolyte has been found to be broad and displaced in the salt doped and plasticized polymer electrolyte. It may be due to the interaction of lithium salt and ethylene carbonate plasticizer.



**Fig. 1.** FTIR spectra of (i) pure and  $\text{LiCF}_3\text{SO}_3$  doped PVA:PVdF blend (ii) EC complexed gel polymer electrolyte

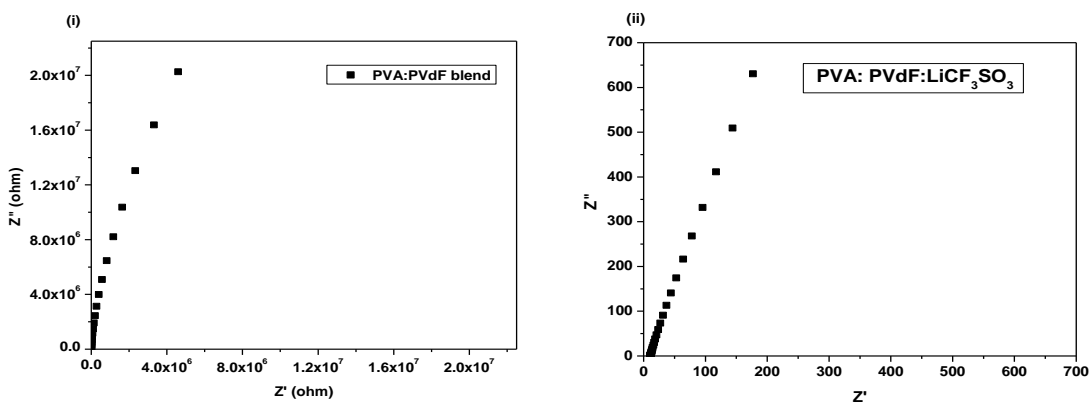
The vibrational peak at  $2991\text{ cm}^{-1}$ ,  $2699\text{ cm}^{-1}$ ,  $2356\text{ cm}^{-1}$ ,  $1745\text{ cm}^{-1}$  corresponding to C-H symmetric stretching, C-H asymmetric stretching,  $\text{CH}_2$  symmetric stretching and C=O stretching vibrations present in acetate group of PVA in blend polymer electrolyte get shifted and disappeared in the salt doped and plasticized system (Fig. 1(ii)). Strong characteristic peak for pure PVdF at  $1170\text{ cm}^{-1}$  has been absent in all spectra which is attributed to specific interaction of fluorine in PVdF with the carbon and hydrogen bonds of PVA. The symmetric stretching, bending and wagging vibrations of  $-\text{CF}_2$  present in PVdF, have been found in blend system was shifted to higher wavenumber for salt doped and gel polymer electrolyte as shown in Table 1.

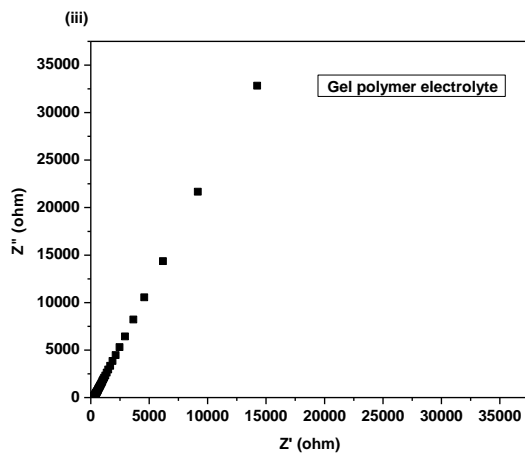
The presence of peak at  $1258\text{ cm}^{-1}$  in GPE denotes the C-N symmetric vibrations of DMF solvent which is shifted from the other two. The existence of solvent peak reveals the presence of excess solvent (residual solvent) which acts as the plasticizer in the polymer electrolyte system thereby enhancing the ionic conductivity. The new minor peak obtained at  $1031\text{ cm}^{-1}$  for salt doped polymer complex shows  $\text{SO}_3$  symmetric vibrations of  $\text{CF}_3\text{SO}_3^-$  anion[7]. It specifies the strong interaction of the lithium salt with the host polymer matrix by the dissociation process. The increase of intensity in the salt doped system indicates increase in the number of free ions, which are responsible for ionic conductivity[8]. The other new peak found at  $748\text{ cm}^{-1}$  corresponds to ring breathing mode of EC present in the gel polymer electrolyte[7]. The peak shift, disappearance and presence of new peaks in FTIR spectra confirm the complex formation between the polymer blend, lithium salt and the plasticizer[9].

**Table 1. FTIR band assignments for pure, lithium triflate doped and gel polymer electrolytes**

Band assignments	Absorption peak in $\text{cm}^{-1}$		
	80PVA:20PVdF	80PVA:20PVdF :15 $\text{LiCF}_3\text{SO}_3$	80PVA:20PVdF: 15 $\text{LiCF}_3\text{SO}_3$ :5EC
C-H (stretching)	2991	-	-
C-H (asymmetric stretching)	2699	-	-
$\text{CH}_2$ (symmetric stretching)	2356	2315	2315
C=O (stretching)	1745	-	1774
C-N (symmetric)	1301	1251	1258
$\text{SO}_3$ (symmetric)	-	1031	1022
$-\text{CF}_2$ (symmetric stretching)	968	-	929
$-\text{CF}_2$ (bending)	548	578	566
$-\text{CF}_2$ (wagging)	420	446	439

From the Figure 2, the absence of the high-frequency semicircle in each plot, confirms that the total conductivity is mainly due to the result of ionic conduction. Ionic conductivity for pure 80PVA-20PVdF blend has been calculated from above equation and found to be in the range of  $10^{-10}\text{ S cm}^{-1}$ . It may be due to the blending of semi crystalline nature of PVA with crystalline nature of PVdF. From the Fig 2 (i), it is clear that the complex impedance plot shows a straight line almost parallel to the imaginary axis; and, the curvature has been caused by the double layer at the blocking electrodes<sup>10</sup>. The addition of lithium triflate salt (15 mol%) into the blend polymer electrolyte increases the conductivity to its maximum level in the blend polymer host and it is found to be in the range  $10^{-3}\text{ S cm}^{-1}$ . This is because of the increase of the number of conducting species and also increase in the amorphous nature of the electrolyte which facilitating the fast ion transports. The optimum ionic conductivity value indicates the maximum and effective interactions between  $\text{Li}^+$  ions with the polymer blend in the electrolyte.



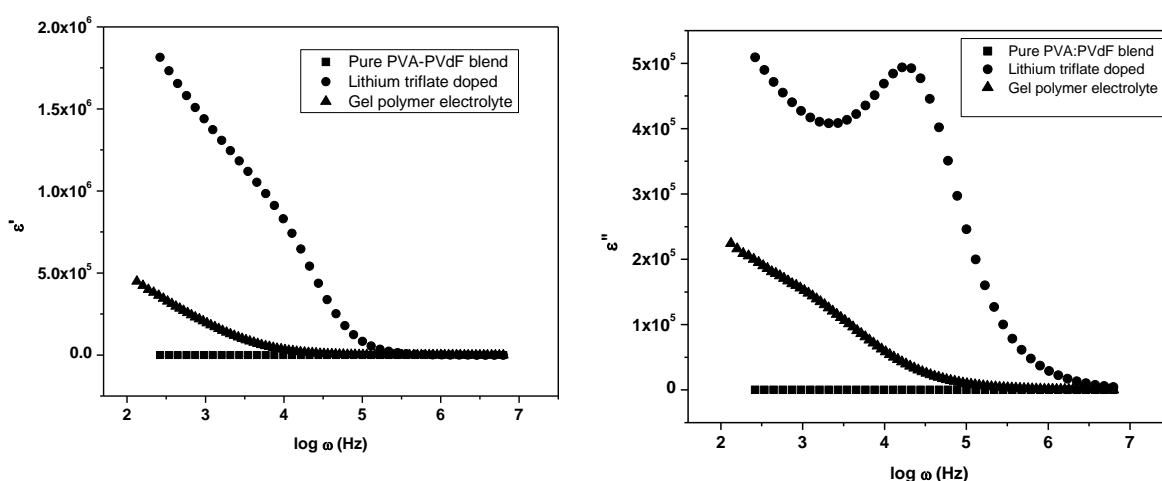


**Fig 2: Complex impedance plot of (i) PVA:PVdF blend (ii) LiCF<sub>3</sub>SO<sub>3</sub> doped PVA:PVdF (iii) EC plasticized LiCF<sub>3</sub>SO<sub>3</sub> doped PVA:PVdF gel polymer electrolyte**

However ionic conductivity of gel polymer electrolyte has been slightly decreased of the one order ( $10^{-4}$  S cm<sup>-1</sup>) due to the addition of 5 mol% of EC in SPE. The decrease in conductivity by the addition of plasticizer may be due to the increase of viscosity which restricts the mobility of the lithium ions. Hence in the present, EC has been least effective in elevating the conductivity[9] at ambient temperature.

Fig 3 shows the variation of real and imaginary parts of the dielectric constant as a function of angular frequency. It shows the dielectric constant value increase with decreasing frequency. This is attributed to the high contribution of charge accumulation at the electrode–electrolytes interfaces, which is explained in terms of ion diffusion[11]. At higher frequencies the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field[12]. Hence the decrease of dielectric value occurs at high frequencies.

Effect of lithium salt in the system shows the high frequency  $\beta$ -relaxation peak at low temperature (303 K) which may be due to movement of side group dipoles. Plasticized polymer electrolyte possesses lower dielectric constant value. This is reflected by its low ionic conductivity compared to other two systems.



**Fig 3: Dielectric spectra of PVA:PVdF based solid and gel polymer electrolytes**

## Conclusion

Flexible gel polymer electrolyte of PVA:PVdF: LiCF<sub>3</sub>SO<sub>3</sub>:EC has been prepared using solution casting technique. Interaction of lithium salt and the plasticizer with the host polymer matrix has been studied. FTIR analysis confirms the interaction of lithium ion with blend, EC and solvent. LiCF<sub>3</sub>SO<sub>3</sub> doped blend polymer electrolyte system exhibits the maximum ionic conductivity in the range of  $10^{-3}$  S cm<sup>-1</sup> at ambient temperature. This system also possesses high dielectric constant when compared to gel polymer electrolyte. In the present

study, incorporation of 5 mol% EC does not increase the ionic conductivity. Hence addition of still higher amount of plasticizer has been planned to be prepared for the conductivity enhancement.

### Acknowledgment

Authors are thankful to the Prof. Dr. Hiran kumar, PSN College of Engineering and Technology, Tirunelveli, TamilNadu for providing the Impedance characterization facility.

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