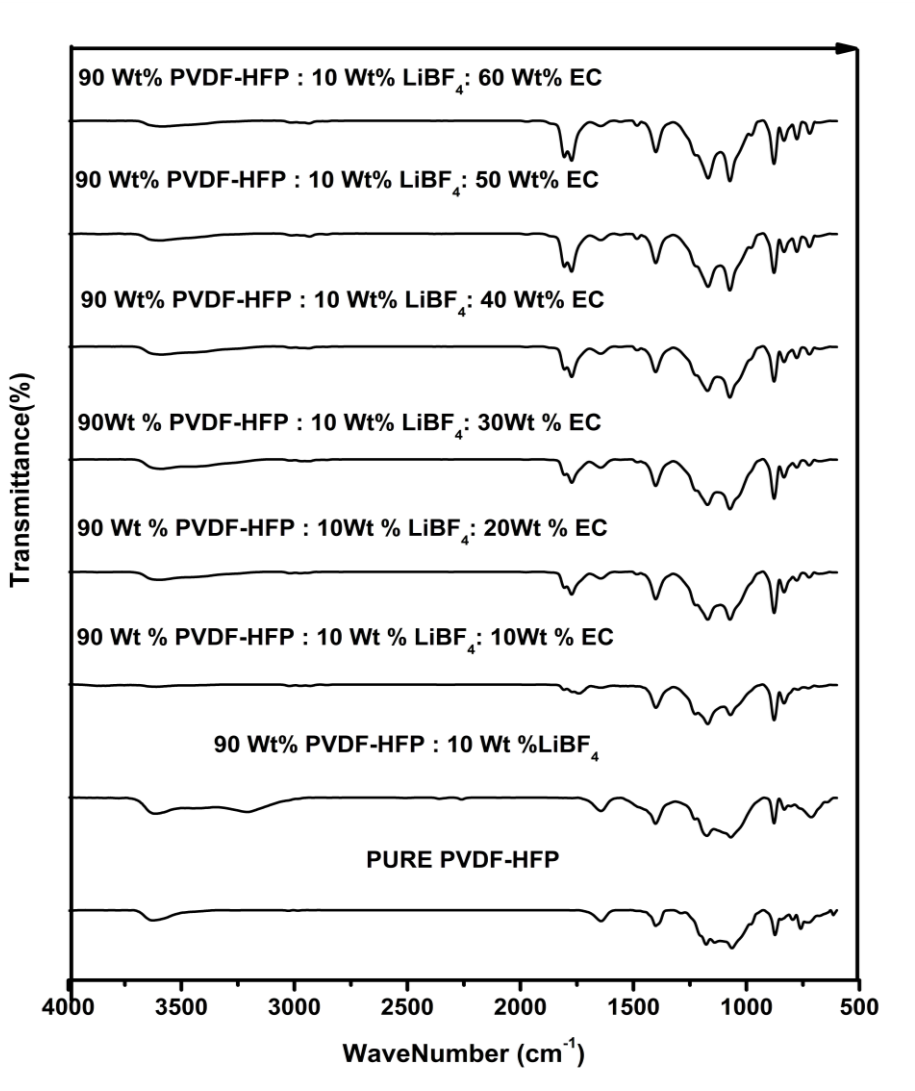

FIG.1. FTIR spectra with various concentrations of EC plasticizer in 90% PVDF – HFP: 10% $LiBF_4$

The vibrational bands in pure PVDF - HFP at 795 (-CF_2 stretching vibration), 760 (-CH_2 rocking vibration), 728 cm^{-1}corresponds to crystalline nature of VDF units which has been shifted to low frequencies at 777, 722 and 676 cm^{-1} of reducing intensity due to addition of $LiBF_4$ salt and increase in concentration of EC plasticizer. This shows the decrease of crystalline nature of the pure PVDF – HFP polymer. It means amorphous nature of the polymer enhances the ionic conductivity of the sample.[41, 42] The vibration band at 874 cm^{-1} (combined CF_2 and C-C symmetric stretching vibration) in pure PVDF – HFP has been shifted to higher frequency with increasing intensity transmittance at 878cm^{-1}. Also a new peak at 834cm^{-1} (mixed

mode of CH_2 rocking and CF_2 asymmetric stretching) is observed due to inclusion of $LiBF_4$ salt and incorporation of various wt% concentrations of EC plasticizer which confirms amorphous nature of HFP units of the Polymer-Salt-Plasticizer matrix.[43,44,45] The band at 1064 cm^{-1} corresponds to symmetrical stretching mode of CF_2which is shifted to higher frequencies at 1068, 1071, 1073, 1074 cm^{-1} due to inclusion of salt and various concentrations (10 wt% to 60 wt%) of Plasticizer which confirms the complexation of the polymer electrolyte, shows an indicator for the dissociation of $LiBF_4$ salt.[26, 46-48] The absorption band at 1073, 1141 cm^{-1} and 1171 cm^{-1} corresponds to $-CF_2$ symmetrical stretching vibration of PVDF – HFP.[26, 46-48] The vibration band at 1226, 1289 cm^{-1} corresponds to -CF stretching vibration and found to be missing in some peaks of absorption bands for increase of EC plasticizer. This happens due to weak interaction between H atoms of CH_2 groups and F atoms of CF_2 groups.[39, 46] The vibration band at 1401, 1484 cm^{-1}corresponds to $-$ CF stretching vibration. The absorption peaks at 1644 cm^{-1}, 1645 cm^{-1}corresponds to –CH=CF- skeletal breathing of PVDF – HFP polymer.[17] The peaks at 1743, 1774 and 1807 cm^{-1} corresponds to C=O bonds in EC plasticizer.[49, 50-51] The transmittance intensity gradually increases for different concentrations (10 wt% - 50 wt% of EC). The peaks at 3000 cm^{-1} to 2900 cm^{-1}frequencies correspond to C-H stretching vibration of PVDF – HFP.[39] The observed peaks at 3650 cm^{-1} to 3000 cm^{-1} show OH and –OOH groups. This occurs due to highly hygroscopic nature of $LiBF_4$ salt and Tetrahydrofuran solvent that absorbs moisture from the atmosphere

D.C. Ionic Conductivity Analysis:

The DC conductivity measurements were carried out in a specially designed instrument. It consists of Copper electrodes with a spring load arrangement placed in a heat furnace which in turn has temperature indicator. A battery of 1.5V and Keithley Model 196 electrometer is connected in series between electrodes. A constant voltage of 1.5V is applied, and with respect to increase of temperature (303K to 363K); their respective currents are noted. During recording reading, the electrodes were short circuited in order to avoid polarization that happens near electrode-electrolyte interface. The resistance of the polymer samples was found using Ohm's law (R = $\frac{V}{I}$). The DC conductivity of the polymer electrolyte can be calculated using Eq. (1)

$$\sigma = \frac{l}{R_b\ A} \quad \text{S/Cm} \qquad \text{Eq. (1)}$$

Where l = Thickness of the polymer sample, R_b = Bulk resistance, A = Area of the electrodes.

In the present study, ionic conductivity of 90 wt% PVDF – HFP polymer: 10 wt% $LiBF_4$ salt and different concentrations (10 wt% - 60 wt %) of EC plasticizer has been analyzed and tabulated in table (1). The respective graphs are shown in the FIG.2. It is observed that as temperature increases there is an enhancement in the ionic conductivity for 10 wt% to 50 wt% plasticizer concentration of polymer – salt – plasticizer matrix. This is due to increase in the degree of salt dissociation and thus produce more mobile ions [52, 53]. Addition of plasticizer decreases viscosity, increases chain flexibility and segmental motion of the polymer [54, 55] which either permits ions to hop or transfer from one site to another in the same polymer chain or to the neighbor polymer chain.[27] As temperature increases, the mobility free volume of the polymer and rate of dissociation of lithium salts also increases which makes lithium ions to move freely in the amorphous phase.[56] The enhancement in temperature dependence ionic conductivity represents the ion mobility and amorphous nature provides a greater free volume of the polymer electrolyte system.[57] The highest ionic conductivity of $1.652\ x\ 10^{-3}\ SCm^{-1}$ for 90 wt% PVDF – HFP polymer: 10 wt% $LiBF_4$ salt: 50 % EC plasticizer observed at 373 K. This can be compared with the ionic conductivity of 90 wt% PVDF – HFP polymer: 10 wt% $LiBF_4$ salt without addition of EC plasticizer which was $1.45\ x\ 10^{-8}$ S cm^{-1} at 373K. [16] It ensures that addition of plasticizer enhanced the ionic conductivity from 10^{-8} to $10^{-3}\ SCm^{-1}$. But at higher content 60 wt % of plasticizer, slightly reduces the ionic conductivity of $1.511\ x\ 10^{-3}\ SCm^{-1}$ at 373 K. As plasticizer EC act like transient crosslinkers resulting immobilization of the polymer chain segments; decreasing the ionic conductivity.[58] The plasticizers interrupt the polymer-polymer interaction by occupying inter and intra chain free volume. The effect of plasticizer on the polymer mobility, ionic conductivity depends on the nature of plasticizer viscosity, dielectric constant, polymer-plasticizer interaction, ion-plasticizer coordination and molecular weight.

The temperature dependence of ionic conductivity of the polymer electrolyte is generally given by Arrhenius relation Eq. (2). [59]

$$\sigma = \sigma_0\, Exp[\frac{-E_a}{K_B\ T}] \qquad \text{Eq. (2)}$$

Where $E_a$the activation energy is needed for an ion to jump to a free volume space, σ_0 is the maximum ionic conductivity and $K_B$is the Boltzman constant. However some temperature dependence of ionic conductivity is not linear but polynomial (n = 2 or n = 3) and obeys the empirical Vogel – Tammann – Fulcher (VTF) relation Eq. (3). [60, 61]

$$\sigma = \sigma_0\, Exp[\frac{-B}{K_B\ (T-T_0)}] \qquad \text{Eq. (3)}$$

'B' is the pseudo activation energy for the redistribution of free volume and T_0 is the reference temperature.

Table 1: Ionic Conductivity for various concentrations of EC plasticizer in polymer-salt matrix at different temperatures

PVDF-HFP : $LiBF_4$: EC	Ionic conductivity (σ) S cm^{-1}							
	303 K	313 K	323 K	333 K	343 K	353 K	363 K	373 K
90 : 10 : 0	1.33×10^{-9}	1.6×10^{-9}	2.67×10^{-9}	5.70×10^{-9}	1.18×10^{-8}	1.25×10^{-8}	1.33×10^{-8}	1.45×10^{-8}
90 : 10 : 10	3.111×10^{-4}	3.569×10^{-4}	3.695×10^{-4}	3.669×10^{-4}	3.881×10^{-4}	4.027×10^{-4}	4.454×10^{-4}	4.642×10^{-4}
90 : 10 : 20	5.856×10^{-4}	6.210×10^{-4}	6.585×10^{-4}	6.689×10^{-4}	6.903×10^{-4}	7.159×10^{-4}	7.303×10^{-4}	9.392×10^{-4}
90 : 10 : 30	1.148×10^{-3}	1.261×10^{-3}	1.288×10^{-3}	1.292×10^{-3}	1.297×10^{-3}	1.322×10^{-3}	1.333×10^{-3}	1.393×10^{-3}
90 : 10 : 40	1.240×10^{-3}	1.342×10^{-3}	1.345×10^{-3}	1.347×10^{-3}	1.379×10^{-3}	1.394×10^{-3}	1.395×10^{-3}	1.412×10^{-3}
90 : 10 : 50	1.562×10^{-3}	1.592×10^{-3}	1.595×10^{-3}	1.600×10^{-3}	1.601×10^{-3}	1.608×10^{-3}	1.614×10^{-3}	1.652×10^{-3}
90 : 10 : 60	1.378×10^{-3}	1.387×10^{-3}	1.438×10^{-3}	1.483×10^{-3}	1.485×10^{-3}	1.492×10^{-3}	1.495×10^{-3}	1.511×10^{-3}

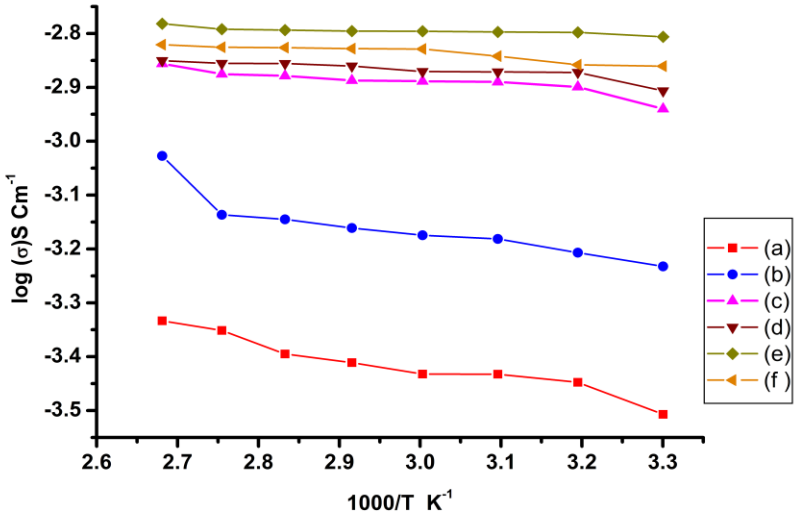

Figure. 2 Temperature dependence Ionic Conductivity for various concentrations of EC Plasticizer in polymer-salt matrix

(a) 90% PVDF-HFP: 10 % $LiBF_4$: 10% EC (b) 90% PVDF-HFP: 10 % $LiBF_4$: 20% EC

(c) 90% PVDF-HFP: 10 % $LiBF_4$: 30% EC (d) 90% PVDF-HFP: 10 % $LiBF_4$: 40% EC

(e) 90% PVDF-HFP: 10 % $LiBF_4$: 50% EC (f) 90% PVDF-HFP: 10 % $LiBF_4$: 60% EC

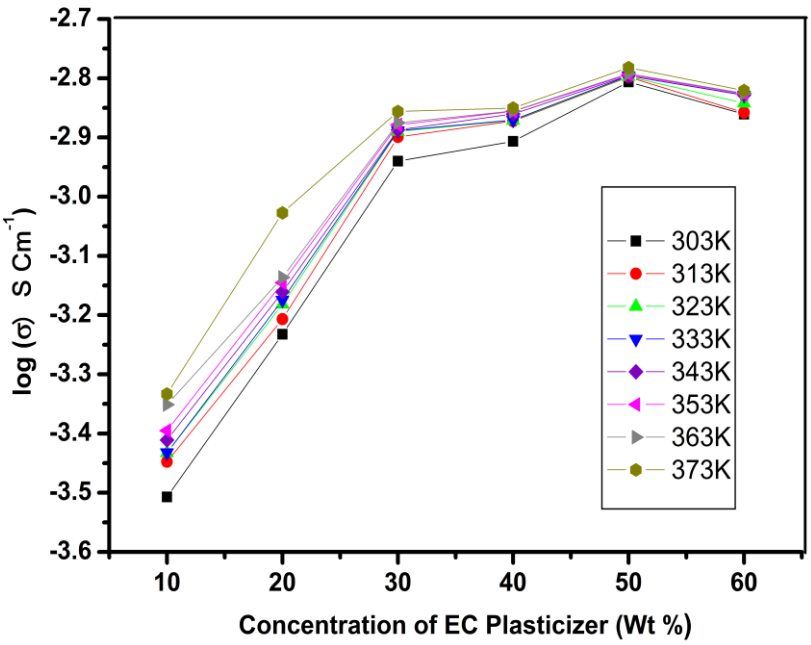

Figure 3: Ionic Conductivity for various concentrations of EC plasticizer at different temperatures

In addition, the ionic conductivity increases with variation of concentrations of EC plasticizers from 10 wt% to 50 wt % in PVDF-HFP: $LiBF_4$ polymer – salt matrix that is up to optimum level. Further increase of 60wt% of EC drops the ionic conductivity which is shown in the FIG. 3. Finally excess of EC plasticizer reduces the mechanical and elastic flexibility of the polymer-salt matrix. The reason for this is initially up to optimum level; addition of plasticizer decreases viscosity, increases chain flexibility and segmental motion of the polymer [54, 55] which either permits ions to hop or transfer from one site to another in the same polymer chain or to the neighbor polymer chain.[27] Hence this enhances the ionic conductivity, but at higher content 60 wt % of plasticizer, reduces the ionic conductivity. This is confirmed in the above table (1). The reason for this is; as plasticizer EC act like transient cross linkers resulting immobilization of the polymer chain segments; decreasing the ionic conductivity.[58] The plasticizers interrupt the polymer-polymer interaction by occupying inter and intra chain free volume. The effect of plasticizer on the polymer mobility, ionic conductivity depends on the nature of plasticizer viscosity, dielectric constant, polymer-plasticizer interaction, ion-plasticizer coordination and molecular weight.

CONCLUSIONS:

Polymer–salt matrix electrolytes find applications as Polymer membrane in Lithium ion Batteries. Plasticized Polymer – Salt - EC matrix electrolyte system consisting of 90% PVDF – HFP polymer, 10% LiBF4 salt with various concentrations (10 Wt% - 60 Wt %) of EC plasticizer has been prepared using solution casting method. X-ray diffraction and SEM result reveals the amorphous nature of the electrolyte complex system. The analysis of functional groups, interaction between the constituents and complex formation between polymer and salt was confirmed by FTIR studies. XRD studies reveal increase in amorphous nature gradually up to optimum level (50 Wt% of EC) and then decreases at 60 Wt% of EC. The ionic conductivity gradually increases with increase of temperature for various amounts (10 Wt% - 60 Wt %) of EC plasticizer in polymer – salt matrix electrolyte system. It is found that the maximum ionic conductivity of $1.652\ x\ 10^{-3}\ SCm^{-1}$ was found for 90 wt% PVDF – HFP polymer: 10 wt% $LiBF_4$ salt and 50 Wt% of EC plasticizer at 373 K. This can be compared with the ionic conductivity of 90 wt% PVDF – HFP polymer: 10 wt% $LiBF_4$ salt without addition of EC plasticizer which was $1.45\ x\ 10^{-8}$ S cm^{-1} at 373K. [16] It ensures that addition of plasticizer enhanced the ionic conductivity from 10^{-8} to $10^{-3}\ SCm^{-1}$ and the temperature dependence ionic conductivity of the polymer electrolyte obeys the Volgel – Tamman - Fulcher (VTF) relationship.

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AUTHOR INFORMATION:

The author declares no competing financial interest.

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