

Structural, Morphological and FTIR of PVDF-HFP and Lithium Tetrafluoroborate Salt as Polymer Electrolyte membrane in Lithium ion Batteries

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Abstract: Thin film solid polymer electrolyte membrane used in Lithium ion batteries consisting of Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) with various concentrations of lithium tetrafluoroborate (LiBF_4) salt have been prepared by solution casting technique. The structural and Morphological properties of the polymer films are studied by XRD and SEM. The result analysis of XRD reveals the amorphous nature of PVDF-HFP – LiBF_4 polymer-salt composite matrix. SEM studies reveals good blending of polymer - salt composite matrix and enhancing morphology. The complexation of the polymer and salt matrix was confirmed by FTIR analysis. Enhancement in ionic conductivity was explained on the basis of amorphous phase of PVDF-HFP complexed with LiBF_4 salt. The highest ionic conductivity was $1.965 \times 10^{-3} \text{ S cm}^{-1}$ for 60 wt% PVDF – HFP polymer: 40 wt of LiBF_4 salt at 363 K. The temperature dependence ionic conductivity of the polymer electrolyte obeys the Volgel – Tamman - Fulcher (VTF) relationship.

Keywords: Solution casting technique, PVDF-HFP, LiBF_4 , Morphology, XRD, SEM, VTF relationship and FTIR.

1. Introduction:

Solid polymer electrolyte membranes have shown great enthusiasm in the research work due to their wide range of applications in Electrochemical devices such as Fuel cells, Cell phone batteries, Sensors, Rechargeable batteries, Capacitors, Memory devices, Electro chromic display devices etc.¹ Solid polymer electrolytes in Lithium ion batteries is an interesting field due to numerous characteristics such as no leakage, more flexibility, high energy density, more safety, and ease to manufacture. This made researchers in the development of Lithium polymer batteries.²⁻³ Lithium polymer batteries consist of polymer electrolyte as separator and charge carrier of ions which have been used as power sources for portable devices due to high energy density.⁴ Fenton et. al⁵ in the year 1973 first suggested ion conducting polymer electrolyte with the interaction of alkali metal ions with PEO based polymer electrolytes. But the conductivity of this kind of polymer electrolytes is very low and it depends on high cost, moisture that made to the search of new alternatives.⁶ Solid polymer electrolytes are less reactive to electrodes but more mechanically stable, safer to

use, offers any desirable size, shape,⁷ flexibility, lightness etc in the modern trends of electronic miniaturization.⁸ They can be used as both the separator which prevents the electrode-electrolyte contact and used as ionic conductor in case of Secondary rechargeable batteries.⁹ Generally polymer electrolytes of high molecular weight with suitable concentration of salt act like a membrane which allows formation of anions and cations by dissociation of the salt that enhances the ionic conductivity due to mobility of cations.¹⁰

Poly (ethylene oxide) (PEO),¹¹ Poly(Vinylchloride) (PVC),² Polyacrylonitrile (PAN),¹³ Poly (methyl methacrylate) (PMMA) ¹⁴⁻¹⁶ and Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)¹⁷ are most frequently used gel polymer electrolytes. Among them PVDF-HFP has more flexibility, high dielectric constant of $\epsilon_r = 8.4$ and low glass transition temperature ' T_g ' provides more number of charge carriers due to great dissociation of salt.^{18, 19, 20, 21} Hence it also exhibits low glass transition temperature, low melting point, low crystallinity and good solubility.²² In the polymer PVDF-HFP, VDF has crystalline nature that has chemical stability and amorphous nature of HFP provides plasticity.²³ Crystalline nature of PVDF, amorphous nature of HFP provides mechanical stability and enhancement in ionic conductivity. Dissolution of the salt further increases the conductivity and reduces crystallinity of the polymer. In addition, the strong electron withdrawing functional group (-C-F) in PVDF-HFP makes the polymer highly anodically stable. In the present research work; Solid polymer electrolyte films of PVDF-HFP and LiBF₄ salt are prepared with different concentrations and characterized by XRD, SEM, FTIR and DSC. XRD reveals the semi crystalline, amorphous nature of the polymer film. Surface morphology through SEM reveals the smooth homogeneous texture by reducing the pore size with different concentrations of salt which confirms the amorphous nature of the polymer film. FTIR analysis provides the complexation and the extent of blending between the polymer and salt. DSC study reveals the thermal properties of the polymer; melting point, melting enthalpy and relative percentage of crystallinity of the polymer electrolyte system.

2. Experimental

2.1 Materials:

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) of average molecular weight 400, 000 CAS: 9011-17-0 used as a polymer and Lithium tetrafluoroborate (LiBF₄) salt of molecular weight 93.7 g/mol, 98% pure, CAS: 14283-07-9 used as the source of conducting ions was purchased from Sigma-Aldrich USA and Tetra hydro Furan (THF) from Merck Millipore, Germany was directly used as a solvent. All the materials were used without any further purification.

2.2 Preparation:

The polymer electrolyte films were prepared by Solution casting technique. Different amounts of PVDF-HFP polymer (90 wt % to 50 wt %) with different concentrations of LiBF₄ salt (10 wt % to 50 wt %) were dissolved in THF for 24 hours and stirred continuously for another 24 hours using magnetic stirrer until the solution becomes homogeneous. The polymer – salt solution was then poured in glass Petri dish and the solvent was allowed to evaporate slowly then left to dry for few days to form films at room temperature. These samples of polymer films were stored in desiccators for further use and analysis.

3. Characterization Techniques

3.1 Fourier Transform Infrared Spectroscopy:

The FTIR spectral data was collected using Perkin Elmer spectrophotometer [Model 1605] in the frequency range of 450 – 4500 cm^{-1} with scan resolution of 5 cm^{-1} .

3.2 Scanning Electron Microscope:

The morphology of the polymer samples were examined by ZIESS SEM at magnification of X5000 magnification.

3.3 X –ray diffraction measurements:

The XRD patterns of the polymer samples were recorded using SEIFERT X – ray diffractometer. The MoK_{α} radiation was used along with Zr filter as monochromatic radiation. The data was collected in the 2θ range from 10° to 80° at the rate of 0.2 sec with operating voltage and current of 40 kV and 30 mA. X – rays of wavelength 1.5406 \AA were emitted by Mo K_{α} source. It has been used to determine the crystalline or amorphous nature of the sample.

3.4 Ionic conductivity:

The ionic conductivity is an important analysis to produce better polymer electrolyte. The DC conductivity measurements were carried out in a specially designed instrument. It consists of Nickel coated electrodes with a spring load arrangement placed in a heat furnace which in turn has temperature indicator. A battery of 3V and Keithley electrometer is connected in series between electrodes. A constant voltage of 3V is applied, and with respect to increase of temperature (303K to 363K); the respective currents are noted. During recording reading the electrodes were short circuited in order to avoid polarization happening near electrode-electrolyte interface.

4. Results and Discussion:

4.1 FTIR Analysis:

The FTIR spectra were recorded to study the structure of polymer, polymer-salt interactions and complexation in polymer electrolytes. The interaction between polymer and salt influence vibrational modes of atoms or molecules which in turn generates change in chemical and physical properties of the polymer. The FTIR polymer electrolyte films of PVDF – HFP, $LiBF_4$ salt and their complexes are shown in the FIG.1. The vibrational bands at 795, 760, 728 and 616 cm^{-1} corresponds to crystalline nature of PVDF – HFP which has been shifted to low frequencies at 714, 709, 708 and 706 cm^{-1} of reducing intensity due to increase of $LiBF_4$ salt concentration; which shows the decrease of crystalline nature of the pure PVDF – HFP polymer. It means amorphous nature of the polymers enhances the ionic conductivity of the sample.²⁴ The vibrational band at 874 cm^{-1} in pure PVDF – HFP has been shifted to higher frequency with increasing intensity transmittance at 878 cm^{-1} , due to inclusion of $LiBF_4$ salt which confirms presence and complexation of salt with host polymer matrix.

The band at 1064 cm^{-1} corresponds to symmetrical stretching mode of CF_2 which is shifted to higher frequencies at 1068, 1069, 1079 1071 cm^{-1} due to inclusion of salt concentration which confirms the complexation of the polymer electrolyte, shows an indicator for the dissociation of $LiBF_4$ salt.^{25, 26} This indicates only certain amount of salt is able to dissolve which limits the number of Lithium ions generated which affects the ionic conductivity.²⁷ The absorption band at 1141 cm^{-1} and 1178 cm^{-1} corresponds to CF_2 symmetrical stretching vibration of PVDF – HFP which is shifted to higher frequencies from 1175 cm^{-1} to 1182 cm^{-1} .^{28, 29, 30} The vibration band at 1289 cm^{-1} corresponds to CF stretching vibration which has been shifted to 1228 cm^{-1} , 1229 cm^{-1} but found to be missing in some peaks of absorption bands. The absorption band at 1402 cm^{-1} corresponds to –C-F stretching, shifted to high frequency at 1403, 1404 and 1406 cm^{-1} for increase of concentration of $LiBF_4$ salt. This happens due to weak interaction between H atoms of CH_2 groups and F atoms of CF_2 groups.^{25, 31, 32} The absorption peaks at 1641 cm^{-1} to 1644 cm^{-1} corresponds to –CH=CF-skeletal breathing of PVDF – HFP polymer.³³ The peaks at 3000 cm^{-1} to 2900 cm^{-1} frequencies correspond to C-H stretching vibration of PVDF – HFP.³⁴ The observed peaks at 3650 cm^{-1} to 3000 cm^{-1} show OH and –OOH groups.³⁵ This occurs due to highly hygroscopic nature of $LiBF_4$ salt and Tetrahydrofuran solvent that absorbs moisture from the atmosphere.

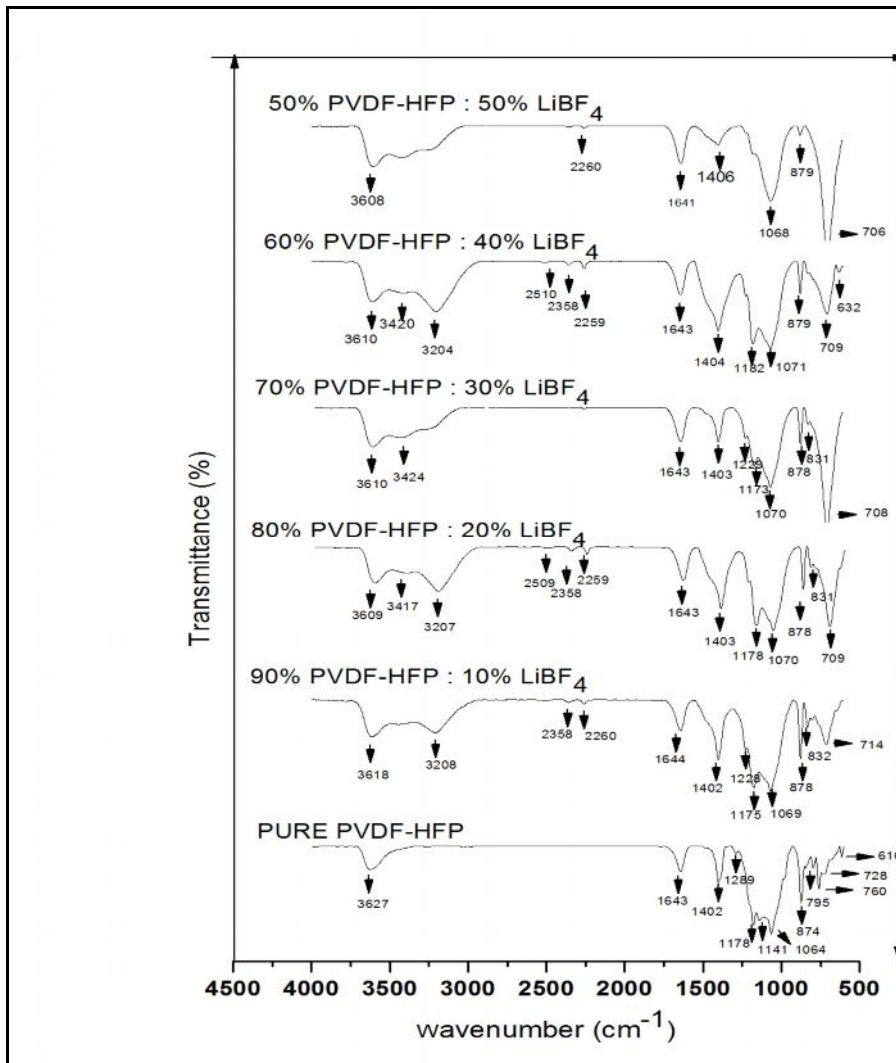


FIG.1. FTIR spectra with various concentrations of PVDF – HFP and LiBF₄

4.2 Scanning Electron Microscope Analysis:

SEM analysis promotes the morphological studies of lithium ion conducting polymer electrolyte films under consideration. In the present research work, a comparison has been made for pure PVDF- HFP polymer film and polymer - salt complex blending with different concentrations of PVDF – HFP and LiBF₄ salt which is shown in the FIG. 2.

From the SEM micrographs it was observed that pure PVDF- HFP polymer film has rough, granular, uneven surface having dark micro pores with lamellar distribution confirms the semi crystalline nature of the film. The dark regions of the pores may be due to evaporation of the tetrahydrofuran solvent. With the addition of concentration of LiBF₄ salt, a smooth lamellar texture of homogeneous appearance as the back ground obtained confirms increase in the interaction between polymer and salt.^{35, 36} Also the pore size decreases with increase of different concentrations of salt promotes the amorphous nature of the polymer.³⁷ The amorphous nature of polymer will enhance the ionic conductivity. The reason is as Lithium ions move freely in the electrolyte with smoother amorphous polymer films.^{27, 38} But re-crystallization occurred at high amount of concentration of salt (greater than 40% of salt) due to uniform distribution and aggregation of LiBF₄ salt at the surface of the polymer which is shown in the FIG. 2 (f).

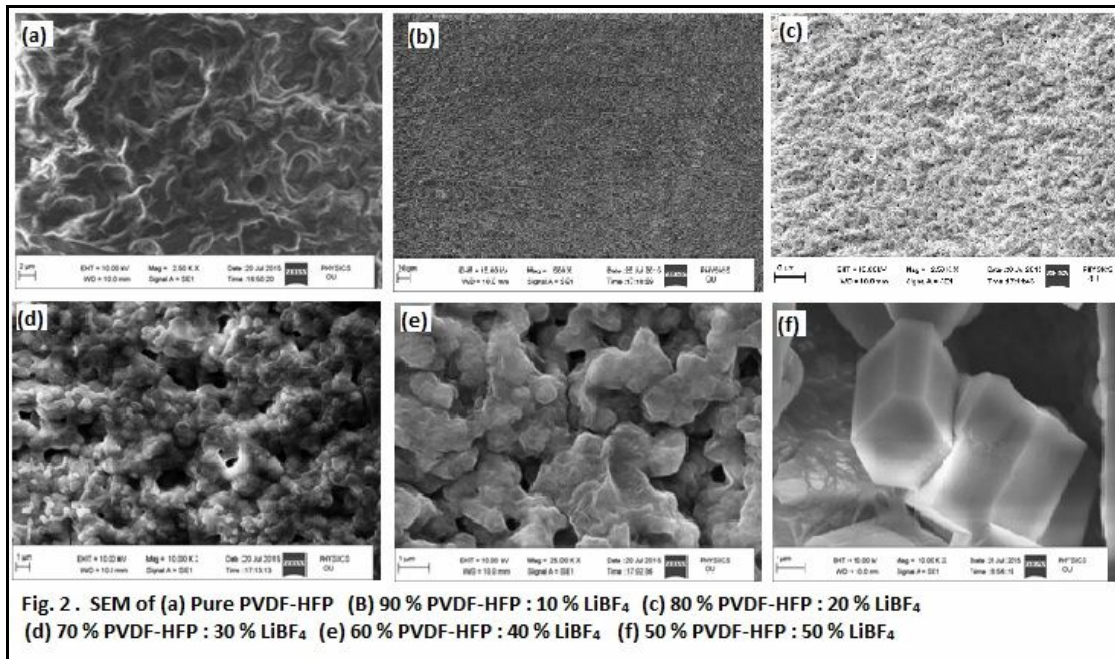


FIG.2. SEM micrographs with various concentrations of PVDF – HFP and LiBF₄

4.3 X – Ray Diffraction Analysis:

X-ray diffraction analysis provides the information on the nature of the sample, crystal structure, crystal orientation, crystallite size, crystallinity, amorphosity and change in phase of the materials which are characterized by the presence of sharp peaks. But in amorphous material, there is no long order and non-crystalline samples are analyzed by one or two broad humps or peaks. Amorphous nature of the polymers enhances the ionic conductivity of the sample.²⁴

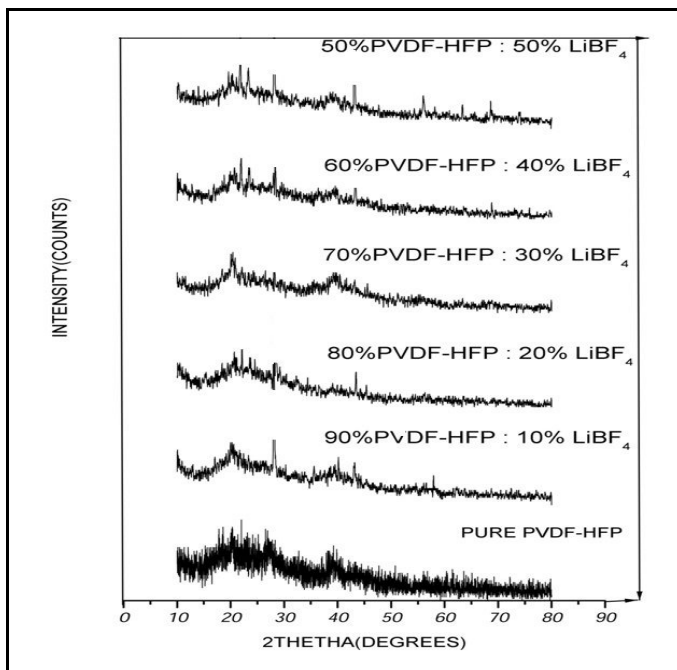


FIG.3. XRD patterns with various concentrations of PVDF – HFP and LiBF₄

X- ray diffraction patterns obtained at room temperature for pure PVDF–HFP film and samples containing various wt% of LiBF₄ are shown in the above FIG 1. The X – ray diffraction major peak recorded in

pure PVDF – HFP observed at $2\theta = 20.3^\circ, 28^\circ, 39^\circ$ are due to the presence of crystalline of PVDF in PVDF – HFP polymer confirms the semi crystalline nature of the polymer.³² With addition of LiBF₄ salt new peaks are observed at $21^\circ, 23^\circ, 28^\circ, 39^\circ, 43^\circ, 56^\circ$ which confirms the complexation of salt with the polymer PVDF – HFP. Also with increase of concentration of salt the intensity of the peaks are reduced, shifted and broadened; which shows the amorphous nature of the salt-polymer matrix.³⁸ At the concentration of PVDF – HFP (60 wt %) – LiBF₄ (40 wt %) polymer- salt matrix, there is good enhancement in the ionic conductivity of the sample. It is shown in the FIG. 3.

4.4 Ionic conductivity Analysis:

The DC conductivity measurements were carried out in a specially designed instrument. It consists of Nickel coated electrodes with a spring load arrangement placed in a heat furnace which in turn has temperature indicator. A battery of 3V and Keithley electrometer is connected in series between electrodes. A constant voltage of 3V 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)

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

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

In the present study, ionic conductivity of PVDF – HFP polymer with different concentrations of LiBF₄ salt has been analyzed and tabulated in table (1). The respective graphs are shown in the FIG.4. It is observed that there is an enhancement in the ionic conductivity of the polymer – salt matrix as the temperature increases. This is due to decrease in the viscosity, increased chain flexibility and segmental motion of the polymer^{39, 40} which either permits ions to hop or transfer from one site to another in the same polymer chain or to the neighbor polymer chain.¹⁹ 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.⁴¹ The enhancement in temperature dependence ionic conductivity represents the ion mobility and amorphous nature provides a greater free volume of the polymer electrolyte system.⁴²

The temperature dependence of ionic conductivity of the polymer electrolyte is generally given by Arrhenius relation Eq. (2).⁴³

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

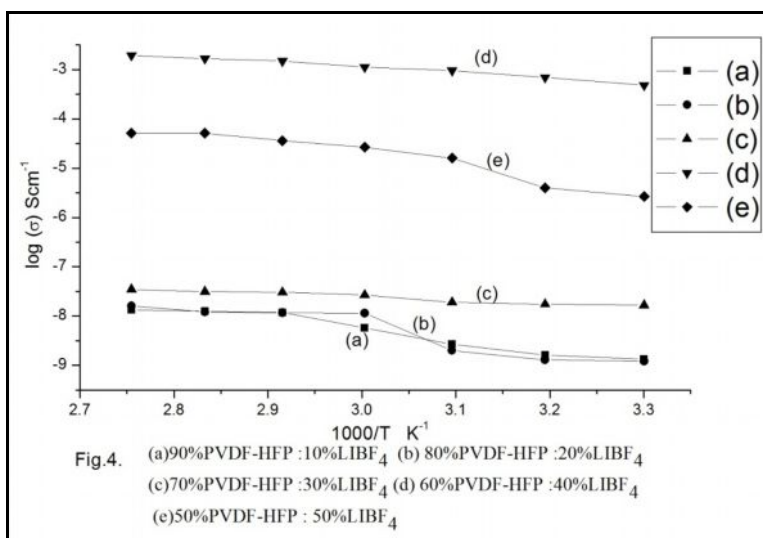


FIG.4. Temperature dependence ionic conductivity of PVDF – HFP and LiBF₄

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 – Tamman – Fulcher (VTF) relation Eq. (3).^{44, 45}

$$\sigma = \sigma_0 \exp\left[\frac{-B}{K_B (T - T_0)}\right] \quad \text{Eq. (3)}$$

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

Table 1. Ionic conductivity of the Polymer – Salt complex system at different temperatures

PVDF-HFP LiBF ₄	Ionic conductivity (σ) S cm ⁻¹						
	303 K	313 K	323 K	333 K	343 K	353 K	363 K
90 : 10	1.33×10^{-9}	1.60×10^{-9}	2.67×10^{-9}	5.70×10^{-9}	1.18×10^{-8}	1.25×10^{-8}	1.33×10^{-8}
80 : 20	1.20×10^{-9}	1.30×10^{-9}	2.00×10^{-9}	1.10×10^{-8}	1.20×10^{-8}	1.20×10^{-8}	1.60×10^{-8}
70 : 30	1.67×10^{-8}	1.75×10^{-8}	1.90×10^{-8}	2.67×10^{-8}	3.03×10^{-8}	3.13×10^{-8}	3.48×10^{-8}
60 : 40	4.82×10^{-4}	6.92×10^{-4}	9.64×10^{-4}	1.125×10^{-3}	1.50×10^{-3}	1.68×10^{-3}	1.965×10^{-3}
50 : 50	2.67×10^{-6}	4.00×10^{-6}	1.60×10^{-5}	2.67×10^{-5}	3.64×10^{-5}	5.13×10^{-5}	5.13×10^{-5}

In addition, the ionic conductivity had increased with variation of concentrations of LiBF₄ salt which is shown in the FIG. 5. It is observed that ionic conductivity increases as the salt concentration of 40 wt% LiBF₄ increases up to optimum level. The number of free charge carriers increases as the ion pair dissociates.⁴²

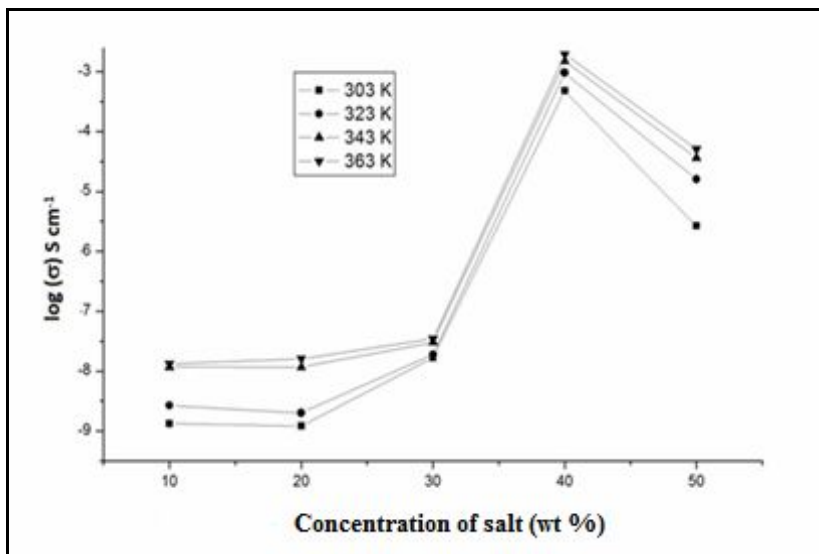


Fig. 5. Variation of ionic conductivity with concentration of salt

Further increase of salt concentration of 50 wt% LiBF₄ reduces the mobility of charge carriers, hence decreases the ionic conductivity as recrystallization and association of LiBF₄ salt take place. The highest ionic conductivity of $1.965 \times 10^{-3} \text{ S cm}^{-1}$ for 60 wt% PVDF – HFP polymer: 40 wt% LiBF₄ salt is observed at 363 K. This is due to low lattice energy of the LiBF₄ salt (699 KJ/mol).^{8, 46}

5. Conclusions:

Polymer –salt matrix electrolytes find applications as Polymer membrane in Lithium ion Batteries. Polymer – salt matrix electrolyte system consisting of PVDF – HFP and LiBF₄ have been prepared using solution casting method. X-ray diffraction and SEM result reveals the amorphous nature of the electrolyte

complex system, for different concentrations of PVDF – HFP polymer and LiBF₄ salt. It is observed that semi crystalline nature gradually decreases up to optimum level and then increases. The analysis of functional groups and the interaction between the constituents was observed by FTIR studies. Also the complex formation between polymer and salt was confirmed by FTIR and XRD studies. The ionic conductivity gradually increases with increase of temperature for various amounts of polymer – salt matrix electrolyte system. It is found that the maximum ionic conductivity of $1.965 \times 10^{-3} \text{ SCm}^{-1}$ was for 60 wt% PVDF – HFP polymer: 40 wt% LiBF₄ salt at 363 K.

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References:

1. Benedict, T.J.; Banumathi, S.; Veluchamy, A.; Gangadharan, R.; Ahmad A.Z.; Rajendran, S. Characterisation of Plasticized Solid Polymer Electrolyte by XRD and AC Impedance Methods *J. Power Sources* 1998, 75, 171-174.
2. Feng, W.; Ting, F.; Ying, B.; Chuan, W.; Lin, Y.; Zengguo, F. Preparation & Characterization of Solid Polymer Electrolytes Based on PHEMO and PVDF – HFP *Solid State Ionics* 2009, 180, 677-680.
3. Gray, F.M. Solid Polymer Electrolytes – Fundamentals & Technological Applications, First ed; VCH: London, New York, 1991.
4. Li, Z. H.; Zhang, H.P.; Zhang, P. et al. P(VDF-HFP) Based Microporous Composite Electrolyte by *in situ* Hydrolysis of Titanium Tetrabutoxide *The Journal of Applied Electrochemistry* 2004, 38, 109-114.
5. Fenton, D. E.; Parkar J.M.; Wright, P.V. Complexes of Alkali Metal ions With Poly (Ethylene Oxide) *Polymer* 1973, 14, 589.
6. Singh, H.P.; Sekhon, S.S. Non-aqueous Proton Conducting Polymer Gel Electrolytes *Electrochim. Acta* 2004, 50, 621.
7. Song, J.Y.; Wang, Y.Y.; C.C. Wan, C.C. Review of Gel type Polymer Electrolytes for Lithium ion Batteries *J. Power Sources* 1999, 77, 183-197.
8. Ali, M.A.M.; Subban, H.R.Y.; Bahron, H; Winie, T.; Latif, F; Yahya, M.Z.A. Grafted Natural Rubber Based Polymer Electrolytes: ATR – FTIR and Conductivity Studies *Solid State Ionics* 2008, 14, 491-500.
9. Jacob, M.M.E.; Hackett, E.; Glannelis, E.P. From Nano Composite to Nano Gel Polymer Electrolytes *Journal of Material Chemistry* 2003, 13, 1-5.
10. Abdullah, M.; Lenggoro, I.W.; Okuyama, K. Polymer electrolyte Nanocomposites *Encyclopedia of Nano Science and Nano Technology* 2004, 8, 731-762.
11. Choi, B.K.; Kim, Y.W. Conductivity Relaxation in the PEO-Salt Polymer Electrolytes *Electrochim. Acta* 2004, 49, 2307-2313.
12. Jung, H.R.; Lee, W.J. Electrochemical Characteristics of Electrospun Poly(Methyl Methacrylate) / Polyvinylchloride as Gel Polymer Electrolytes for Lithium ion Battery *Electrochim. Acta* 2011, 58, 674.

13. Yu, B.; Zhou, F.; Wang, C.; Liu, W. A Novel Gel Polymer Electrolyte Based on Poly ionic Liquid 1-ethyl 3-(2-methacryloyloxy ethyl) imidazolium iodide *Euro. Polym. J.* 2007, 43,2699.
14. Sharma, J.P.; Sekhon, S.S. Nanodispersed Polymer Gel Electrolytes: Conductivity Modification with the Addition of PMMA and Fumed Silica *Solid State Ionics* 2007, 178,439.
15. Krejza, O.; Velicka, J.; Sedlarikova, M.; Vondrak, J. The Presence of Nano Structured Al₂O₃ in PMMA-based Gel Electrolytes *J. Power sources* 2008, 178, 774-778.
16. Kim, C.S.; Oh, S.M. Spectroscopic and Electrochemical Studies of PMMA-based Gel Polymer Electrolytes Modified with Interpenetrating Networks *Journal Of Power Sources*2002, 109, 98-104.
17. Lee, C.; Kim, J.H.; Bae, J.Y. Polymer Gel Electrolytes Prepared by Thermal Curing of Poly(vinylidene fluoride) – Hexafluoropropylene / Poly(ethylene glycol) / Propylene carbonate / Lithium Perchlorate Blends *Polymer* 2003, 44, 7143.
18. Sim, L.N.; Majid S. R.; Arof, A.K. FTIR Studies of PEMA / PVDF-HFP Blend Polymer Electrolyte System incorporated with LiCF₃SO₃ Salt *Vibrational Spectroscopy* 2012, 58, 57.
19. Ramesh, S.; Ong, P.L. Effect of Ethylene Carbonate on the Ionic Conduction in Poly (vinylidene fluoride-hexafluoropropylene) Based Solid Polymer Electrolytes *J. Polym. Chem.* 2010, 1, 702-707.
20. Agarwal, R.C.; Pandey, G.P. Solid Polymer Electrolytes: Materials Designing and all-Solid State Battery Applications: An Overview *J. Phys. D Appl. Phys.* 2008, 41, Article I.D. 223001.
21. Hui, X.; Zhiyuan, T.; Zhongyan, L.; Yanbing, H.; Yong, L.; Hong, W. PVDF - HFP Composite Electrolyte with Excellent Electrochemical Properties of Li-ion Batteries *Solid State Electrochem.* 2008, 12, 1497-1502
22. Elmer, A.M.; Wessien, B.; Sommer-Larsen, P.; West, K.; Hassandera, H.; Jannasch, P. Ion Conductive Electrolyte Membranes Based on Co-continuous Polymer Blends *J. Mater. Chem.* 2003, 13, 2168-2176..
23. Ulaganathan, M.; Rajendran, S. Effect of Different Salts on PVAc / PVdF –co- HFP based Polymer Blend Electrolytes *J. Appl. Poly. Sci.* 2010, 118, 646-651.
24. Rajendran, S.; Babu, R.S.; Siva Kumar, P. Investigations on PVC/PAN Composite Polymer Electrolytes *Journal of Membrane Science* 2008, 315, 67-73.
25. Rajendran, S.; Uma, T. Characterization of Plasticized PMMA– LiBF₄ based Solid Polymer Electrolytes *Bulletin of Materials Science* 2000, 16, 27-29.
26. Ahmad, A.; Rahman, M.Y.A.; Low, S.P.; Hamzah, H. Effect of LiBF₄ Salt Concentration On the Properties of Plasticized MG49 – TiO₂ Based Nano Composite Polymer Electrolyte *ISRN Material Science* 2011, Article ID 401280 , 1-7.
27. Noor, S. A.M.; Ahmad, A.; Talib, I.A.; Rahman, M.Y.A. Morphology, Chemical interaction and Conductivity of a PEO – ERN50 Based on Solid Polymer Electrolytes *Solid State Ionics* 2010, 16, 161-170
28. Aravindan V.; Vickraman, P. Characterization of SiO₂ and Al₂O₃ Incorporated PVDF – HFP based Composite Electrolytes with LiPF₃(CF₃CF₂)₃ *J. App. Poly. Sci.* 2008, 108, 1314.
29. Ataollahi, N.; Ahmad, A.; Hamzah, H.; Rahman, M.Y.A.; Mohamed, N.S.Preparation and Characterisation of PVDF – HFP / MG49 based Polymer Blend Electrolyte *International Journal of ElectroChemical Science* 2012, 7, 6693-6703.
30. Aravindan, V.; Vickraman, P.; Prem Kumar, T. Polyvinylidene fluoride -hexafluoropropylene (PVDF – HFP) - based Composite Polymer Electrolyte Containing LiPF₃(CF₃CF₂)₃ *J. Non - Cryst. Sol.* 2008, 354, 3451-3457.
31. Zhaohui, L.; Guangyao, S.; Xiayu,W.; Deshu, G. Microporous P (VDF – HFP) based Polymer Electrolyte Filled with Al₂O₃ Nano particles *Solid State Ionics* 2005, 176, 1903-1908.
32. Saikia, D.; Kumar, A. Ionic Conduction in P (VDF – HFP) – (PC + DEC) - LiClO₄ Polymer Gel Electrolytes *Electrochim. Acta.* 2004, 49, 2581-2589.
33. Usha Rani, M.; Ravishanker Babu; Rajendran, S. Conductivity Study on PVDF – HFP /PMMA Electrolytes for Lithium Battery Applications *International Journal of Chem Tech Research* 2013, 5, 1724-1732.
34. Saika, D.; Kumar, A. Fast ion transport in P (VDF – HFP) - PMMA – PC – LiClO₄ – TiO₂ Composite gel polymer electrolytes, *Indian Journal Of Pure & Applied Physics*, 41 (2003)
35. 961-966.

36. SivaKumar, M.; Subadevi, R.; Rajendran, S.; Wu, H.C.; Wu, N.L. Compositional Effect of PVDF – PEMA blend Gel Polymer Electrolytes for Lithium Polymer Batteries *European Polymer Journal* 2007, 43, 4466-4473.
37. Lily Margaret Priya, W.; Austin Suthanthiraraj, S. FTIR and SEM Studies of Polymer Electrolytes Composed of Poly(vinylidene fluoride – co- hexafluoropropylene) and Zinc Trifluoromethanesulfonate *Int. J. Chem. Environ. & Tech* 2013, 1, 1-8.
38. Monikowska, E.Z.; Florajmczyk, Z.; Jonska, E. et al. Lithium ion Transport of Solid Electrolytes based on PEO / LiCF₃SO₃ and Aluminium Carboxylate *Journal of power sources* 2007, 173, 734-742.
39. Ulaganatham, M.; Sunder Pethaiah, S.; Rajendran, S. Li-ion Conduction in PVAc based Polymer Electrolytes for Lithium Battery *Mater. Chem. Phys.* 2011, 129, 471-476.
40. Michael, M.S.; Jacob, M.M.E.; Prabakaran, S.R.S.; Radhakrishna, S. Enhanced Lithium ion Transport in PEO-based Solid Polymer Electrolytes Employing a Novel Class of Plasticizer *Solid state Ionics* 1997, 98, 167-174.
41. Mahendran, O.; Rajendran, S. Ionic Conductivity Studies in PMMA/ PVF – HFP Polymer blend Electrolyte studies in PMMA/ PVDF polymer blend electrolyte with Lithium Salts *Ionics*, 2003, 9, 282-288.
42. Subramania, A.; Kalyana Sudaram, N.T.; Vijaya Kumar, G.; Vasudevan, T. New Polymer Electrolyte based on (PVA-PAN) blend for Li ion Battery Applications *Solid State Ionics* 2006, 12, 175-178.
43. Ramya, C.S.; Selvasekarapandian, S.; Savitha, T.; Hiran Kumar, G.; Angelo, P.C. Vibrational and Impedance Spectroscopic Study on PVP – NH₄SCN based Polymer Electrolyte *Physica B* 2007, 393, 11-17.
44. Wu, T.Y.; Su, S.G.; Gung, S.T.; Lin, M.W.; Lin, Y.C.; Lai, C.A.; Sun, I.W. Ionic Liquids Containing an Alkyl Sulfate group as Potential Electrolytes *Electrochim Acta* 2010, 55, 4475-4482.
45. Wu, T.Y.; Hao, L.; Kuo, C.W.; Lin, Y.C.; Su, S.G.; Kuo, P.L.; Sun, I.W. Ionic Conductivity & Diffusion in Lithium Tetrafluoroborate-Doped 1- Methyl-3-Pentylimidazolium Tetrafluoroborate Liquid *Int. J. Electrochem. Sci.* 2012, 7, 2047-2064.
46. Kuo, C.W.; Li, W.B.; Chen, P.R.; Liao, J.W.; Tseng, C.C.; Wu, T.Y. Effect of Plasticizer and Lithium Salt Concentration in PMMA-based Composite Polymer Electrolytes *Int. J. Electrochem.Sci.* 2013, 8, 5007-5021.
47. Othman, L.; Chew, K.W.; Osman, Z., Impedance Spectroscopy Studies of PMMA- Lithium Salts Polymer Electrolyte System *Ionics* 2007, 13, 337-342.
