

FTIR Spectroscopic and DC Ionic conductivity Studies of PVDF-HFP: LiBF₄: EC Plasticized Polymer Electrolyte Membrane

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Abstract. In the present paper; the FTIR and Temperature dependent DC Ionic conductivity studies of polymer (80 Wt% PVDF-HFP) with inorganic lithium tetra fluoroborate salt (20 Wt% LiBF₄) as ionic charge carrier and plasticized with various weight ratios of Ethylene carbonate plasticizer (10 Wt% to 70 Wt% EC) as gel polymer electrolytes. Solution casting method is used for the preparation of plasticized polymer-salt electrolyte films. FTIR analysis shows the good complexation between PVDF-HFP: LiBF₄ and the presence of functional groups in the plasticized polymer-salt electrolyte membrane. Also the analysis and results show that the highest DC ionic conductivity of $1.66 \times 10^{-3} \text{ S cm}^{-1}$ was found at 373 K for a particular concentration of 80 Wt% PVDF-HFP: 20 Wt% LiBF₄: 40 Wt% EC porous gel type polymer-salt plasticized porous membrane. Increase of temperature results expansion and segmental motion of polymer chain that generates free volume in turn promotes hopping of the lithium ions satisfying Vogel-Tammann-Fulcher equation.

1. Introduction

For the past few decades solid polymer electrolytes rules over liquid electrolytes as they overcome the problem of large size, consumption of more space, corrosion, electrolyte leakage, poor electrode-electrolyte contact and flammable. Solid polymer electrolytes such as PEO, PVC, PVA, PMMA, PAN etc finds application in the electro chemical energy storage devices like high power energy density batteries, lithium ion solid polymer batteries, super capacitors, fuel cells, solar cells, electro chromic displays, chemical sensors etc [1]. But now for the past recent years solid polymer electrolytes are replaced with gel type polymer batteries as of their amorphous nature, good electro-electrolyte contact, avoids dendrite growth, compact size, and flexible, mechanical stability, thermal stability and high ionic conductivity [2]. In the present paper we study the preparation and analysis of porous gel polymer electrolytes. The temperature dependent DC Ionic conductivity for various concentrations of low viscosity plasticizer in a constant ratio of gel polymer-salt matrix are measured and calculated. The gel type porous polymer Poly (Vinylidene-co-Hexafluoropropylene) (PVDF-HFP) has semi crystalline, amorphous nature and high dielectric constant that improves good ionic conductivity [3]. Inorganic lithium tetra fluoroborate (LiBF₄) salt has high dissociation energy of lithium ions as charge carriers. And Ethylene carbonate (EC) plasticizer of high dielectric constant, low viscosity is used. Effect of



various weight concentrations of EC plasticizer provides good mechanical strength, flexibility, low degradation of the polymer and dissociates more number of lithium ionic charge carriers [4]. Also increase of temperature allows segmental motion of polymer, creates large amount of voids or free spaces for the mobility of lithium ions to increase the ionic conductivity of plasticized polymer-salt electrolyte film [5, 6].

2. Experimental

2.1 Materials

Materials used in the present investigation are micro porous gel polymer Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) of molecular weight 400,000 (Sigma-Aldrich), Inorganic Lithium tetrafluoroborate (LiBF_4) salt of molecular weight 93.7 g/mol (Sigma-Aldrich) as ionic charge carrier and Ethylene carbonate as an plasticizer of molecular weight 88.06 g/mol (Sigma-Aldrich) and Tetra hydro Furan (THF) solvent analytical grade from Merck Milliopore, Germany.

2.2 Preparation

The plasticized gel polymer electrolyte films preparation is done using Solution casting method. 80 wt % of PVDF-HFP polymer, 20% wt of LiBF_4 salt are mixed with different weight ratios of (10 % to 70 %) of Ethylene carbonate plasticizer. These are dissolved in THF solvent for 24 hours then stirred continuously for another 24 hours with magnetic stirrer to get homogeneous solution. Then the solution was then poured in glass Petri dish and the solvent was allowed to evaporate slowly for several days to get thin films. Finally the polymer films are stored in desiccators for analysis.

3. Characterization Techniques

3.1 Fourier Transform Infrared Spectroscopy

The FTIR spectral analysis was done with Perkin Elmer FTIR spectrophotometer [Model 1605] in the frequency range of $450 - 4500 \text{ cm}^{-1}$ with scan resolution of 5 cm^{-1} .

3.2 Ionic conductivity

The DC conductivity was performed with a laboratory designed conductivity set up [7]. A nickel coated electrodes with a spring load arrangement connected to a heat furnace and temperature indicator. A battery of 1.5V and Keithley (Model 196) electrometer are connected in series between electrodes where testing samples placed. Applying a uniform voltage of 1.5V along with increase of temperature (303K to 373K); the respective currents are measured. Readings are recorded between the electrodes with short circuiting in order to avoid polarization that occurs at the interface of electrode-electrolyte of the polymer electrolyte film.

4. Results and Discussion

4.1 FTIR Analysis

The FTIR spectra are an important tool to characterise and analyze the structural changes in polymer, to identify functional groups, interactions and complexation of polymer-salt-plasticizer. The interaction between polymer, salt and plasticizer influence vibrational modes of atoms or molecules which generates change in chemical and physical properties of the polymer. The FTIR transmittance spectra of polymer electrolyte films consist of polymer PVDF – HFP, LiBF_4 salt and different compositions (10 Wt% - 70 Wt %) of Ethylene Carbonate plasticizer as shown in the figure 1. The vibrational bands of pure PVDF - HFP polymer at 760 cm^{-1} ($-\text{CH}_2$ rocking vibration), 789 cm^{-1} ($-\text{CF}_2$ stretching vibration) belongs to crystalline nature of VDF units of the polymer [8]. On addition of LiBF_4 salt, the vibrational peaks shift to lower wave number of decreased intensity at 708 cm^{-1} , 712 cm^{-1} and 716 cm^{-1} respectively. This indicates structural change of semi crystalline nature of PVDF

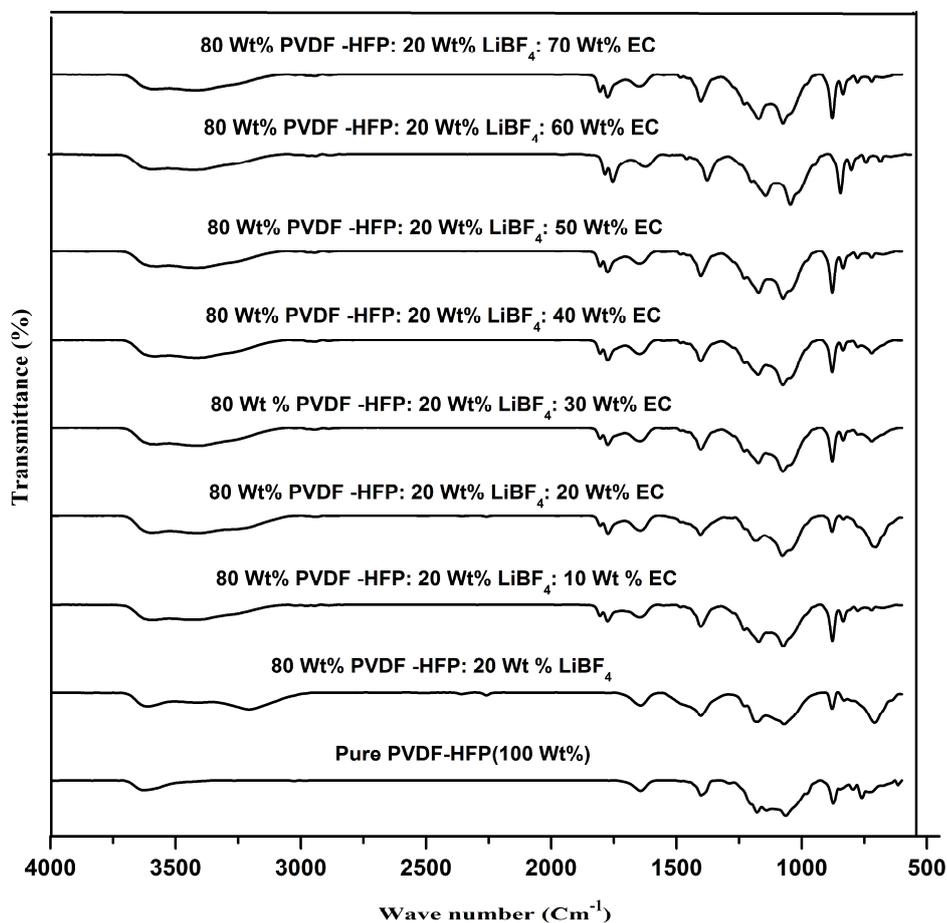


Figure 1. FTIR of various concentrations (10Wt% to 70 Wt %) of EC plasticizer in 80% PVDF – HFP: 20% LiBF₄ polymer-salt matrix electrolyte membrane.

–HFP to amorphous one. The vibration band of pure PVDF-HFP at 870 cm^{-1} due to combined CF_2 and $\text{C}-\text{C}$ symmetric stretching vibrations and shifting with increasing intensity to 875 cm^{-1} , 877 cm^{-1} , 883 cm^{-1} on addition of LiBF₄ salt, EC plasticizer clearly indicates the amorphous nature of polymer and good complexation of polymer-salt-plasticizer and the vibration bands at 1081 cm^{-1} , 1638 cm^{-1} belongs to the asymmetric stretching of BF_4^- ions of inorganic salt [9]. The transmittance peaks at 1060 cm^{-1} , 1078 cm^{-1} , 1178 cm^{-1} indicates CF_2 symmetric stretching and 1228 cm^{-1} asymmetric stretching of PVDF-HFP polymer peaks which is found to be disappeared on addition of EC plasticizer [10, 11]. The reason is because of weak interaction between H atoms of CH_2 groups and F atoms of CF_2 groups. The vibration band peaks formed at the wave number 1397 cm^{-1} , 1404 cm^{-1} corresponds to CH_2 wagging of the polymer PVDF – HFP. Further the absorption peaks at 1641 cm^{-1} , 1645 cm^{-1} , 1648 cm^{-1} corresponds to $-\text{CH}=\text{CF}-$ skeletal breathing of PVDF – HFP polymer [12, 13]. The peaks at 1747 cm^{-1} , 1768 and 1777 cm^{-1} correspond to $\text{C}=\text{O}$ bonds in EC plasticizer and observed that the intensity gradually increases for different concentrations (10 wt% - 40 wt %) of EC plasticizer [14, 15]. The peaks at 3200 cm^{-1} to 2900 cm^{-1} frequencies correspond to $\text{C}-\text{H}$ stretching vibration of PVDF – HFP. These results elucidate that the F- atom of CF_2 group may interacted or coordinates with dissociated Li ion of LiBF₄ salt and indicates the miscibility of three materials PVDF-HFP, LiBF₄ and EC plasticizer. The observed peak at 3400 cm^{-1} and 3616 cm^{-1} of

broad hump is due to OH and –OOH groups. This may be due to highly hygroscopic nature of LiBF₄ salt and Tetrahydrofuran solvent that absorbs moisture from the atmosphere or surroundings.

4.2 D.C. Ionic Conductivity Analysis

The resistance of the polymer films can be calculated with the aid of Ohm's law ($R = \frac{V}{I}$). The DC conductivity of the polymer electrolyte can be calculated using equation 1.

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

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

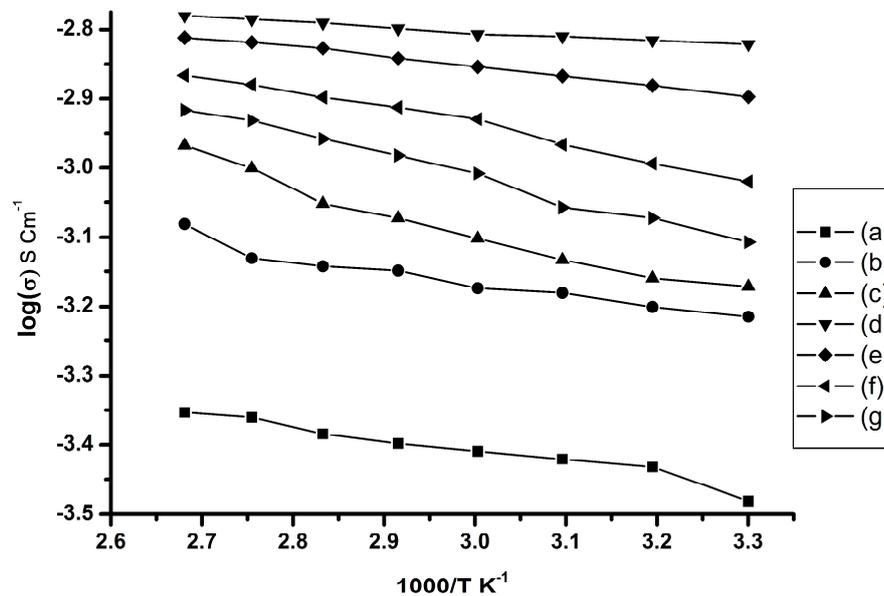


Figure 2. Temperature dependence DC Ionic Conductivity of various concentrations (10 Wt% to 70 Wt %) EC Plasticizer in a polymer-salt matrix electrolyte.

- (a) 80 Wt% PVDF-HFP: 20 Wt % LiBF₄: 10 Wt % EC (b) 80 Wt % PVDF-HFP: 20 Wt % LiBF₄: 20 Wt % EC
 (c) 80 Wt% PVDF-HFP: 20 Wt % LiBF₄: 30 Wt % EC (d) 80 Wt % PVDF-HFP: 20 Wt % LiBF₄: 40 Wt % EC
 (e) 80 Wt % Wt PVDF-HFP: 20 Wt % LiBF₄: 50 Wt % EC (f) 80 Wt % PVDF-HFP: 20 Wt % LiBF₄: 60 % EC
 (g) 80 Wt % PVDF-HFP: 20 Wt % LiBF₄: 70 % EC

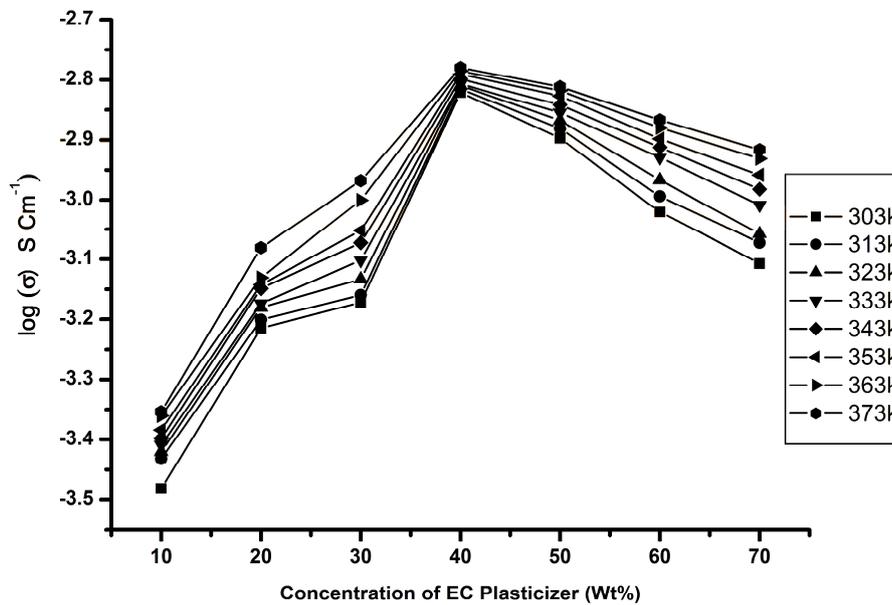


Figure 3: Ionic Conductivity for various concentrations of EC Plasticizer at different temperatures.

Table 1: Ionic Conductivity of various concentrations (10 Wt% to 70 Wt %) 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
80 : 20 : 00	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}	1.90×10^{-8}
80 : 20 : 10	3.30×10^{-4}	3.70×10^{-4}	3.80×10^{-4}	3.90×10^{-4}	4.00×10^{-4}	4.13×10^{-4}	4.36×10^{-4}	4.43×10^{-4}
80 : 20 : 20	6.10×10^{-4}	6.30×10^{-4}	6.60×10^{-4}	6.70×10^{-4}	7.10×10^{-4}	7.20×10^{-4}	7.40×10^{-4}	8.29×10^{-4}
80 : 20 : 30	6.74×10^{-4}	6.92×10^{-4}	7.36×10^{-4}	7.91×10^{-4}	8.46×10^{-4}	8.87×10^{-4}	9.99×10^{-4}	1.077×10^{-3}
80 : 20 : 40	1.51×10^{-3}	1.53×10^{-3}	1.55×10^{-3}	1.56×10^{-3}	1.59×10^{-3}	1.62×10^{-3}	1.64×10^{-3}	1.66×10^{-3}
80 : 20 : 50	1.27×10^{-3}	1.32×10^{-3}	1.36×10^{-3}	1.39×10^{-3}	1.44×10^{-3}	1.49×10^{-3}	1.52×10^{-3}	1.54×10^{-3}
80 : 20 : 60	9.54×10^{-4}	1.01×10^{-3}	1.08×10^{-3}	1.17×10^{-3}	1.22×10^{-3}	1.26×10^{-3}	1.32×10^{-3}	1.36×10^{-3}
80 : 20 : 70	7.82×10^{-4}	8.46×10^{-4}	8.76×10^{-4}	9.81×10^{-4}	1.04×10^{-3}	1.10×10^{-3}	1.17×10^{-3}	1.21×10^{-3}

The ionic conductivity of 80 wt% PVDF – HFP polymer: 20 wt% LiBF₄ salt and different concentrations (10 wt% - 70 wt %) of EC plasticizer was calculated and tabulated in table 1. The corresponding graphs are shown in the figure 2 and figure 3. It is obvious that figure 2 represents the temperature dependence Ionic conductivity with various concentrations of EC plasticizer in polymer-salt matrix. And figure 3 shows the Ionic conductivity for various concentrations of EC plasticizer at different temperatures. The temperature dependence ionic conductivity of the polymer electrolyte follows the Vogel – Tamman – Fulcher (VTF) relation of equation 2.

$$\sigma = \sigma_0 \text{Exp}\left[\frac{-B}{K_B (T-T_0)}\right] \quad (2)$$

‘B’ is the pseudo activation energy for the redistribution of free volume, σ_0 is the maximum ionic conductivity, K_B is the Boltzman constant and T_0 is the reference temperature.

The results show that as temperature increases the ionic conductivity also increases for 10 wt% to 40 wt% plasticizer concentration of polymer – salt – plasticizer matrix. The reason is that plasticizer helps in the dissociation of salt and increases mobility of ions; as the plasticizer decreases viscous nature, increases amorphous nature, increases chain flexibility and segmental motion of the polymer. The plasticizer either permits ions to jump or to move from one site to another in the polymer chain or to the neighbour chain of polymer [16]. As temperature increases, the expansion of the polymer makes the segmental motion of polymer and increases free volume of the polymer [17]. This results either motion of ionic charge from one site to another or provides the path way for the mobility of ions. The highest ionic conductivity of $1.66 \times 10^{-3} \text{ S cm}^{-1}$ for 80 wt% PVDF – HFP polymer: 20 wt% LiBF₄ salt: 40 % EC plasticizer observed at 373 K. It reveals that the addition of EC plasticizer increases the four orders when compared to pure PVDF-HFP and LiBF₄ polymer electrolyte film [18]. Further higher content of 50 wt % of plasticizer, decreases the ionic conductivity due to excess of plasticizer EC results immobility of the polymer chain segments and decreasing the ionic conductivity [19]. The plasticizers ceases the polymer-polymer interaction by occupying in inter and intra chain free volume [20].

5. Conclusions

Plasticized porous gel type polymer – salt electrolyte samples consisting of 80% PVDF – HFP polymer, 20% LiBF₄ salt with various concentrations (10 Wt% - 70 Wt %) of EC plasticizer was prepared using solution casting method. FTIR studies confirm functional groups, interaction between the constituents and complex formation between polymer-salt -plasticizer. It is found that the optimum ionic conductivity of $1.66 \times 10^{-3} \text{ S cm}^{-1}$ was observed for 80 wt% PVDF – HFP polymer: 20 wt% LiBF₄ salt and 40 Wt% of EC plasticizer at 373 K. Results confirm that addition of plasticizer enhances the ionic conductivity to four orders when compared to pure PVDF-HFP with LiBF₄ polymer electrolyte film and temperature dependant ionic conductivity of the polymer electrolyte obeys the Vogel – Tamman - Fulcher (VTF) relationship.

References

- [1] Agarwal R C and Pandey G P 2008 Solid polymer electrolytes: materials designing and all-solid-state battery applications: an overview **41** 223001
- [2] Long M, Wang S, Xiao M and Meng Y 2016 Polymer electrolytes for lithium polymer electrolytes *J. Mater. Chem. A* **4** 10038
- [3] Pu W H, He X M, Wang L, Jiang C Y and Wan, C.R. 2006 Preparation of PVDF-HFP micro Porous membrane for lithium on batteries by phase inversion *J. Membr. Sci.* **272** 11-14
- [4] Noor M M, Careem M A, Majid, S R and Arof A K 2011 Characterization of plasticized PVDF-HFP polymer electrolytes *Material Research Innovations* **15** 157-160
- [5] Shalu, Singh V K and Singh R K 2015 Development of ion conducting polymer gel electrolyte membranes based on polymer PVdF-HFP, BMIMTFSI ionic liquid and the Li-Salt with improved electrical, thermal and structural properties *J. Mater. Chem. C* **3** 7305-7318

- [6] Miao R, Liu B, Zhu Z, Liu Y, Li J, Wang X and Li Q 2008 PVDF-HFP- based porous polymer electrolyte membranes for lithium-ion batteries *J. Power Sources* **184** 420-426
- [7] Sreekanth T, Jaipal Reddy M, Ramalingaiah S and Subba Rao U V 1999 Conducting polymer electrolyte based on poly (ethylene oxide) complexed with NaNO_3 salt –application as an electrochemical cell *J. Power Sources* **79** 105-110
- [8] Angulakshmi N, Thomas S, Nahm K S 2011 Electrochemical and mechanical properties of nanochitin-incorporated PVDF-HFP-based polymer electrolytes for lithium batteries *Ionics* **17** 407-414
- [9] Manoj Kumar V and Amita C 2016 Ion-electron conducting polymer composites: Promising electromagnetic interface shielding material *ACS Appl. Mater. Interfaces* **8** 18450-18461
- [10] Sim L N, Majid S R and Arof A K 2012 Characteristics of PEMA/PVDF-HFP blend polymeric gel Films incorporated with lithium triflate salt in electro chromic device *Solid State Ionics* **209-210** 15-23
- [11] Ataollahi N, Ahmad A, Hamzah H, Rahman M Y A and Mohamed N S 2012 Preparation and Characterisation of PVDF – HFP / MG49 based Polymer Blend Electrolyte *International Journal of ElectroChemical Science* **7** 6693-6703
- [12] Shalu, Chaurasia S K and Chandra S 2013 Thermal Stability, Complexing Behavior and Ionic Transport of Polymeric Gel Membranes Based on Polymer PVDF-HFP and Ionic Liquid, [BMIM] $[\text{BF}_4]$ *J. Phy. Chem. B* **117** 897-906
- [13] Sim L N, Majid S R and Arof A K 2012 FTIR studies of PEMA/PVDF-HFP blend polymer electrolyte System incorporated with LiCF_3SO_3 salt *Vibrational Spectroscopy* **58** 57-66
- [14] Kuo C W, Li W B, Chen P R, Liao J W, Tseng C G and Wu T Y 2013 Effect of Plasticizer and Lithium salt concentration in PMMA based composite polymer electrolytes *Int. J. Electrochem. Sci.* **8** 5007-5021
- [15] Ataollahi N, Ahmad A, Hamzah H, Rahman M Y A and Mohamed N S 2015 Comparative Study of the Properties of Plasticized (PVDF-HFP)-MG49- LiBF_4 Blend Polymer Electrolytes *Russian Journal of Electrochemistry* **3** 227-235
- [16] Ulaganathan M and Rajendran S 2011 Novel Li-ion conduction on Poly(vinyl acetate)-based hybrid polymer electrolytes with double plasticizers *J. Appl. Electrochem* **41** 83-88
- [17] Saikia D and Kumar A 2005 Ionic transport in P(VDF-HFP)-PMMA- LiCF_3SO_3 -(PC +DEC) TiO_2 composite gel polymer electrolyte *European Polymer Journal* **41** 563-568
- [18] Subramania A, Kalyana Sudaram N T and Vijaya Kumar G 2006 Structural and electrochemical properties of micro-porous polymer blend electrolytes based on PVDF-co-PAN for Li ion Battery applications *Journal of Power Sources* **153** 177-182
- [19] Ulaganathan M and Rajendran S 2010 Preparation and characterizations of PVAc/(PVDF-HFP)-based polymer blend electrolytes *Ionics* **16** 515
- [20] Shalu, Chaurasia S K, Singh R K and Chandra S 2013 Electrical, Mechanical, Structural and Thermal Behaviors of Polymeric Gel Electrolyte Membranes of Poly (vinylidene fluoride-co-hexafluoropropylene) with the Ionic Liquid 1-Butyl-3-Methylimidazolium Tetrafluoroborate Plus Lithium Tetrafluoroborate *J. Appl. Polymer Science* **117** 897-906

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Author information

The author declares no competing financial interest.