

## Conductivity Study On PVDF-HFP / PMMA Electrolytes For Lithium Battery Applications

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**Abstract:** Plasticized polymer electrolyte comprising poly (vinylidene fluoride-co-hexa fluoro propylene), poly (methyl methacrylate), and Lithium per chlorate as the complexing salt with different concentrations of Propylene carbonate has been prepared exhibiting an ionic conductivity of the order of  $10^{-3} \text{ S cm}^{-1}$ . Temperature dependent ionic conductivity seems to obey Vogel Tamman Fulcher relation, and the transport mechanism has been discussed on the basis of free volume theory. The structural elucidations have been ascertained from X-ray diffraction and Fourier transform infrared spectroscopy. Thermal stability of the electrolyte has been asserted based on results from Differential Scanning Calorimetry.

**Key Words:** Polymer electrolyte; PVdF-HFP blend polymer electrolyte; Ionic conductivity; Thermal stability; Lithium per chlorate.

### INTRODUCTION

Polymer electrolytes are of mammoth interest for use in solid state lithium – based batteries, because of their advantage over conventional lithium ion batteries, such as safety, no-leakage of electrolyte, higher energy density and flexible geometry. This allured many researchers on the development of lithium polymer batteries.<sup>1</sup> Conventional poly (ethylene oxide)-based polymer electrolytes are most commonly studied which exhibits conductivity ranging from  $10^{-8}$  to  $10^{-5} \text{ S cm}^{-1}$  at room temperature leading to their exclusion from their practical application at ambient temperature. The development of polymer system with high ionic conductivity is one of the main objectives in polymer research which resulted in blending of polymers, cross linking, insertion of ceramic fillers, plasticization etc.<sup>2</sup> Generally, blending of two polymers not only result in improving the mechanical strength but also helps increasing the conductivity by suppressing the crystallization of polymer chain in any one of the following ways: (i) cross linking (ii) Copolymerization (iii) comb formation and (iv) polymer alloying.<sup>3-5</sup>

The most impressive results have been obtained with a class of copolymers based on poly (Vinylidene fluoride) (PVdF) and hexafluoropropylene (HFP), when compared with poly (Vinylidene fluoride) (PVdF) homopolymer, PVdF-HFP possesses lower crystallinity and higher free volume due to the incorporation of an amorphous phase of hexafluoropropylene (HFP) into the main constituent vinylidene fluoride (VdF) blocks. Iijima,<sup>6</sup> Appetecchi,<sup>7</sup> and Zhou<sup>8</sup> have explored the possibility of using poly (methyl methacrylate) (PMMA) as host for possible electrolytes in lithium batteries. But the poor mechanical strength of plasticized PMMA offset these electrolytes from practical applications. The possibility of enhancing the poor mechanical strength of PMMA electrolytes by blending with PVdF- HFP has also been reported in our previous work.<sup>9</sup>

Improvement in ionic conductivity of polymer electrolytes has been brought by many workers through hybrid films comprising polymer, salt and plasticizer. The plasticizers generally used for these are low molecular weight aprotic solvents having high dielectric constant, low viscosity and high dipole moment such as propylene carbonate.<sup>10</sup> Propylene carbonate has been selected due to its high dielectric constant (64.4), high molecular dipole moment (4.9D). Its high polarity allows it to create an effective solvation shell around lithium ions there by creating a conductive electrolyte.<sup>11</sup> Superiority in ionic conductivity of plasticized polymer electrolytes are the product of accession of plasticizers and implies on their mechanical property by softening the polymer due to their entrapment.<sup>12</sup> The mechanical rigidity could be increased by blending of polymers reported earlier.

In the present work, the effect of plasticizer concentration on the ionic conductivity and thermal stability has been investigated to optimize plasticizer concentration providing maximal conductivity and congenial mechanical stability. In adding aspect PVdF-HFP, PMMA, LiClO<sub>4</sub> at constant ratio being mixed with Propylene carbonate (PC) in different concentrations and were prepared and characterized. The optimization is being substantially ascertained by XRD, FTIR, conductivity and DSC studies.

## EXPERIMENTAL SECTION

### MATERIALS USED

Poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) (average molecular weight  $4 \times 10^5$ ) and poly (methylmethacrylate) (PMMA) (average molecular weight  $12 \times 10^4$ ), Lithium per chlorate (LiClO<sub>4</sub>) and Propylene carbonate (PC) bought from Aldrich, USA were used for the polymer electrolyte preparation.

### PURIFICATION

The materials purchased were annealed at 373K under vacuum ( $10^{-3}$  tor), in LOGITEC, DTC 5050, for 10 h before use except the plasticizing agent PC.

### PREPARATION

The electrolytes were prepared by solution casting technique, by adding appropriate quantities of PVdF-HFP, PMMA, LiClO<sub>4</sub> and PC (Table1) in sequence to pre-distilled acetone (E. Merck, Germany). The solution was subjected to magnetic stirring for 24 h at room temperature for homogeneous mixing and then for 2 h at an elevated temperature (60 °C) before they were cast on finely polished Teflon supports or Teflon covered glass plates. The films were dried in vacuum oven at 333K at a pressure of  $10^{-3}$  Torr for 24 h to evaporate the residual solvents if any. The films thus obtained were dry and free-standing in nature.

### CHARACTERIZATION TECHNIQUES

The phase analysis of the polymer at room temperature was performed with X-ray diffractometer (XRD) [PAN alytical X'pert PRO X-ray diffractometer]. The Fourier transform infrared (FTIR) spectrum was recorded in the range 4000–400 cm<sup>-1</sup> using Jasco FTIR 460 plus (Japan) spectrophotometer.

The conductivity measurements were carried out in a specially designed conductivity jig with the circular films obtained. The electrode-electrolyte contact was given due care by placing the electrolyte film between the stainless steel electrodes with a spring load arrangement. For electrical conductivity measurement, FRA2  $\mu$ AUTOLAB - III, was used with signal amplitude of 10mV in the frequency range 100Hz – 500 kHz. Variation in conductivity with increase in temperature is recorded with in the range 302–373 K. The films were subjected to Differential scanning calorimetric studies using Mettler Toledo DSC 822e with a heating rate of 10 C / min.

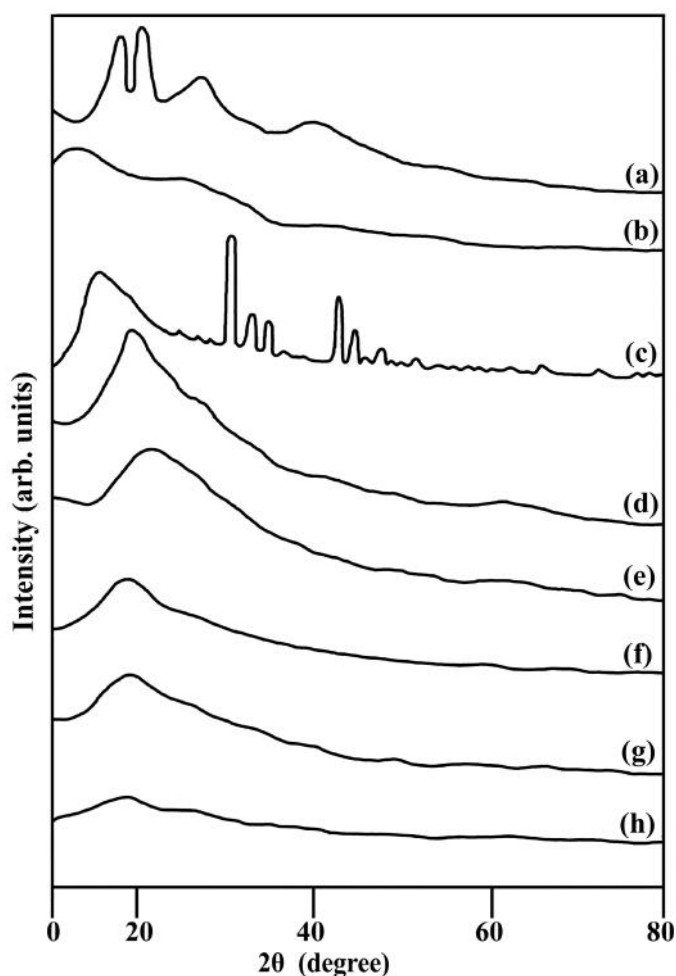
## RESULTS AND DISCUSSION

### X-RAY DIFFRACTION ANALYSIS

X-ray diffraction is propitious in determining the nature of the sample, phase identification, quantitative analysis of a mixture of phases, and physical imperfections, etc.

Amorphous nature of the polymer ordains ionic conductivity in a polymer electrolyte; hence it is necessary to determine the crystalline and amorphous phases of the polymer electrolyte. The X-ray diffraction patterns of pure PVdF-HFP, PMMA, LiClO<sub>4</sub> and the complexes are shown in Fig.1 (a-h), respectively. It is

evident from the Fig. 1(a) that the characteristic diffraction peaks at  $18.09^\circ$  and  $20.47^\circ$  are due to the presence of crystalline PVdF in PVdF-HFP, confirming the partial crystallinity of PVdF-HFP.<sup>13-15</sup> Fig. 1(b) discloses the amorphous phase of pristine PMMA. The presence of sharp diffraction peaks in Fig. 1(c) betokens the crystalline nature of  $\text{LiClO}_4$ . Addition of PC and  $\text{LiClO}_4$  considerably reduces the crystallinity of the polymer which is evident from the absence of the above said crystalline peaks in Fig.1(d-h). Moreover peaks pertaining to  $\text{LiClO}_4$  are not observed indicating that the salt is complexed in the polymer matrix and does not remain as separate phase in the electrolytes. Further the amorphicity of the polymer electrolytes is found to increase with the increase in the concentration of the plasticizer chronologically and highest amorphicity for film  $A_{145}$  consisting 72 wt% PC. This high amorphicity mitigates higher ionic conductivity evidenced in gel polymer electrolytes. A similar observation has been reported by many,<sup>13,16-18</sup> where the authors studied the XRD on PEO, PVC/PMMA, PVdF-HFP and PVA blend electrolytes respectively.



**FIG. 1.** XRD Spectra of (a) PVdF-HFP (b) PMMA (c)  $\text{LiClO}_4$   
 d) PVdF-HFP(24)-PMMA(8)- $\text{LiClO}_4$ (8)-PC(60)  
 e) PVdF-HFP(21.75)-PMMA(7.25)- $\text{LiClO}_4$ (8)-PC(63)  
 (f) PVdF-HFP(19.5)-PMMA(6.5)- $\text{LiClO}_4$ (8)-PC(66)  
 (g) PVdF-HFP(17.25)-PMMA(5.75)- $\text{LiClO}_4$ (8)-PC(69)  
 (h) PVdF-HFP(15)-PMMA(5)- $\text{LiClO}_4$ (8)-PC(72)

## FOURIER TRANSFORM INFRA RED ANALYSIS

Polymer structure and the chemical species could be investigated using FTIR spectroscopy. The infra red spectra of these materials vary according to their composition and may be able to show the occurrence of complexation<sup>19,20</sup> and interaction between the various constituents. The mutual interaction between them generates change in their vibrational modes of the atoms or molecules in material which introduces change in physical and chemical properties of the constituents of the complex.

FTIR spectra of pristine PVdF-HFP, PMMA, LiClO<sub>4</sub>, PC and complexes are shown in Fig. 2 (a-i). The vibrational bands at 1072, 976, 763, 614cm<sup>-1</sup> and bands at 879 and 841 cm<sup>-1</sup> are characteristic of the crystalline phase and amorphous phase of PVdF-HFP<sup>21</sup> respectively. These group frequencies are found to be shifted to the lower side indicating some alteration in their physical property of PVdF-HFP. The vibrational frequency at 1072 and 841 cm<sup>-1</sup> are missing in the complexes indicating the reduction in crystallinity and increase in amorphicity of the complexes. The vibrational frequencies at 1688, 839 cm<sup>-1</sup> are assigned to -CH=CF- skeletal breathing, CH<sub>2</sub> rocking of PVdF-HFP is found to be shifted to lower side hierarchically on subsequent films indicating the increase in polymer – plasticizer interaction with increase of plasticizer content. The vibrational peaks around 3022 and 2980 cm<sup>-1</sup> appears on the addition of LiClO<sub>4</sub> to polymer. These bands are associated with non symmetric and symmetric stretching vibration of CH<sub>2</sub> groups. This appearance is due to the interaction between Li<sup>+</sup> ions and F atoms leading to weakening the interaction between H atoms of CH<sub>2</sub> and F atoms of CF<sub>2</sub>, repercussion of this is evident with the shift of vibration peak at 1403 cm<sup>-1</sup> shifting towards a higher side.<sup>22-24</sup>

The stretching vibration at 720 cm<sup>-1</sup> corresponds to the ring breathing region of PC shifts to lower side upon the addition of LiClO<sub>4</sub> which could be due to the complex formation between salt and polymer. These results are in accordance with observation of Stephan<sup>17,25</sup> and Battisti<sup>26</sup> on the complex formation of PVC/PMMA blend electrolytes with LiClO<sub>4</sub> and LiBF<sub>4</sub> salts, and PAN with LiCF<sub>3</sub>SO<sub>3</sub> respectively.

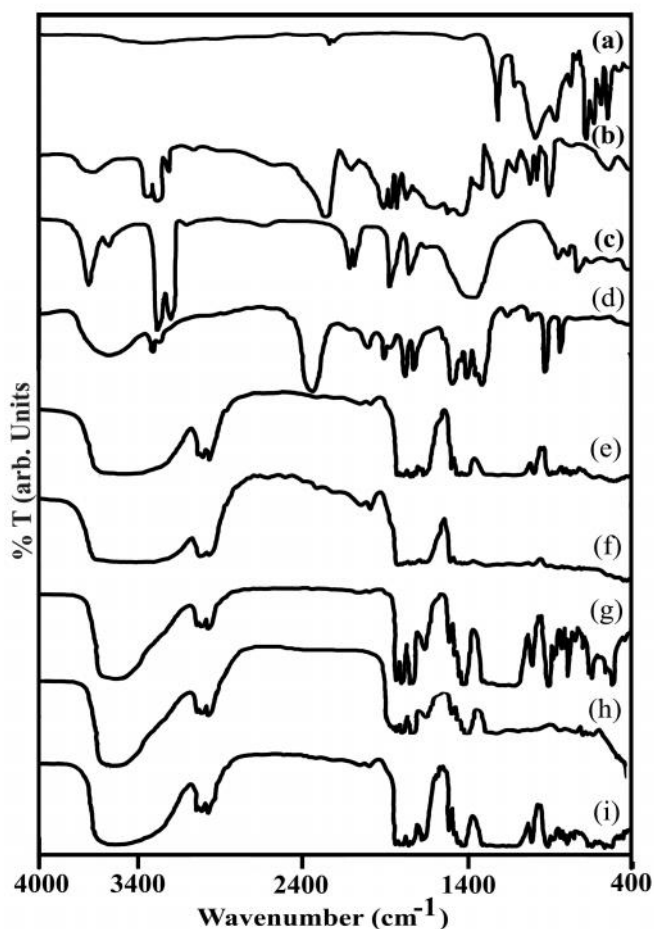
The peaks at 1200 – 1050 cm<sup>-1</sup> are assigned to -C-F and -CF<sub>2</sub>- stretching vibrations. The peak at 881 cm<sup>-1</sup> is assigned to vinylidene group of polymer.<sup>13</sup> This frequency shifts to 873 cm<sup>-1</sup> which could be attributed to ionic association through redissociation of charge accompanying the formation of ionic pairs and aggregates which is in agreement with earlier reports.<sup>13,17,25,26</sup>

The frequencies corresponding to CH<sub>3</sub> asymmetric stretching at 2952 cm<sup>-1</sup>, O-CH<sub>3</sub> deformation at 1451 cm<sup>-1</sup>, CH<sub>2</sub> wagging at 988 cm<sup>-1</sup> and CH<sub>2</sub> rocking at 752 cm<sup>-1</sup> of PMMA are found to be shifted in all the complexes indicating polymer – polymer interaction. The carbonyl group C=O at 1733 cm<sup>-1</sup> of PMMA is shifted to a lower side in the complexes indicating the interaction between the polymer and plasticizer. Further C-C-O bending vibration at 1242 cm<sup>-1</sup> of PMMA, CF<sub>2</sub> bending at 510cm<sup>-1</sup>, CF<sub>2</sub> wagging at 488cm<sup>-1</sup> of (PVdF-HFP), 1097, 712 and 515cm<sup>-1</sup> of LiClO<sub>4</sub> and 2358, 1121 and 534 cm<sup>-1</sup> of PC are found absent in all the complexes. In addition to this some new peaks are observed at 2610, 2488, 2301, 2201 and 1975 cm<sup>-1</sup>. The above analysis establishes the formation of polymer-salt complexes.<sup>2,27</sup>

## CONDUCTIVITY STUDIES

The conductivity studies are performed using ac impedance technique employing FRA2 μAUTOLAB-III to characterize the electrical properties of the material and their interfaces with the electrodes. In the present study, ionic conductivity of PMMA/PVdF-HFP hybrid solid polymer electrolyte films with different concentrations of plasticizer have been analyzed (Table1).

Ionic conductivity of prepared membranes (Table 1) are calculated using the ratio  $\sigma = L / (A \cdot R_b)$ , where R<sub>b</sub> is the bulk resistance recorded from the Nyquist plot, A is the area and L is the thickness of the polymer membrane. The absence of the high frequency semicircular portion (Fig. 3) in the plot concludes that the current carriers are ions, and the total conductivity is solely due to conduction of ions.<sup>28</sup>



**FIG. 2.** FTIR Spectra of (a) PVdF-HFP (b) PMMA (c) LiClO<sub>4</sub> (d) PC (e) PVdF-HFP(24)-PMMA(8)-LiClO<sub>4</sub>(8)-PC(60) (f) PVdF-HFP(21.75)-PMMA(7.25)-LiClO<sub>4</sub>(8)-PC(63) (g) PVdF-HFP(19.5)-PMMA(6.5)-LiClO<sub>4</sub>(8)-PC(66) (h) PVdF-HFP(17.25)-PMMA(5.75)-LiClO<sub>4</sub>(8)-PC(69) (i) PVdF-HFP(15)-PMMA(5)-LiClO<sub>4</sub>(8)-PC(72)

**Table 1:** Conductivity values of PMMA-PVDF-HFP - LiClO<sub>4</sub>-PC systems with different plasticizer concentrations

Sample	Composition (wt%)	Nature of film	Ionic conductivity ( $\times 10^{-3} \text{ S cm}^{-1}$ )				
			302 K (RT)	318 K	333 K	353 K	373 K
A <sub>431</sub>	8-24-8-60	Frangible	0.017	0.033	0.107	0.158	0.195
A <sub>432</sub>	7.25-21.75-8-63	Arid	0.034	0.086	0.286	0.353	0.395
A <sub>433</sub>	6.5-19.5-8-66	Free standing	0.066	0.233	0.512	0.871	1.230
A <sub>434</sub>	5.75-17.5-8-69	Free standing	0.151	0.563	1.000	2.820	3.470
A <sub>435</sub>	5-15-8-72	Jelly	0.355	1.620	4.280	5.800	7.920

The variation of ionic conductivity with the plasticizer content is depicted in Fig. 4. The ratios of PMMA/PVdF-HFP were fixed to 2.5 / 7.5 and salt content at 8 wt% as explained else where.<sup>29</sup> Ionic conductivity results of the prepared polymer electrolytes are in accordance with the results of Rhoo<sup>30</sup> which concedes that conductivity increases with the increase in plasticizer.

The contribution by plasticizer towards the conductivity enhancement can be explained in terms of two factors. A higher percentage of plasticizer would (1) open up the narrow rivulets of plasticizer rich phase for greater ion transport and (2) provide a large free volume of relatively superior conducting phase.<sup>31</sup>

Arrhenius plot of ionic conductivity with various concentration of plasticizer (PC) and fixed ratio of other constituents (Table 1.) are shown in Fig.5. It is conspicuous that at lower concentrations i.e. up to 66%, Arrhenius relation could be applied. This could be due to the hindrance offered to ion transport by PVdF-HFP rich phase, which is attributed to the poorly linked phases between plasticizer-rich and with the other. On increasing the plasticizer content, the volume of the plasticizer rich phase increases ensuing greater connection between domains and thus the ionic transport becomes easier. At higher concentrations of plasticizer, the transport mechanism should be governed by the characteristic of plasticizer rich phase. The liquid-like characteristic of the plasticizer rich phase would be responsible for the VTF relation at higher plasticizer concentration which explains the viscous flow of amorphous materials.<sup>32-34</sup> From Table 1 it is observed that conductivity of the order of  $10^{-3}$  S  $\text{cm}^{-1}$  for film A<sub>434</sub> containing 69% and the increase in conductivity with the increase of temperature, is in agreement with the results others.<sup>25,28,29</sup>

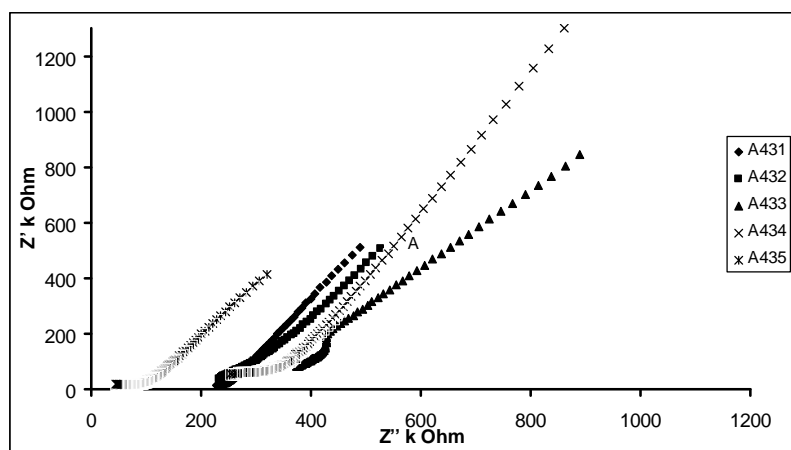


FIG.3. Nyquist plot supporting conductivity due to ion motion

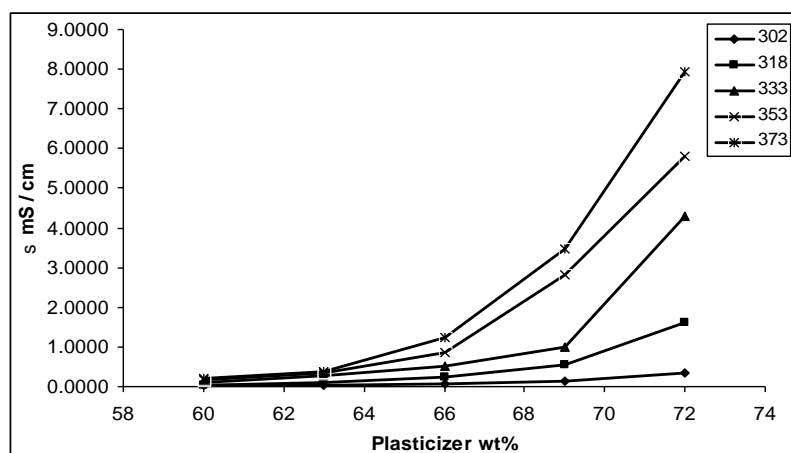
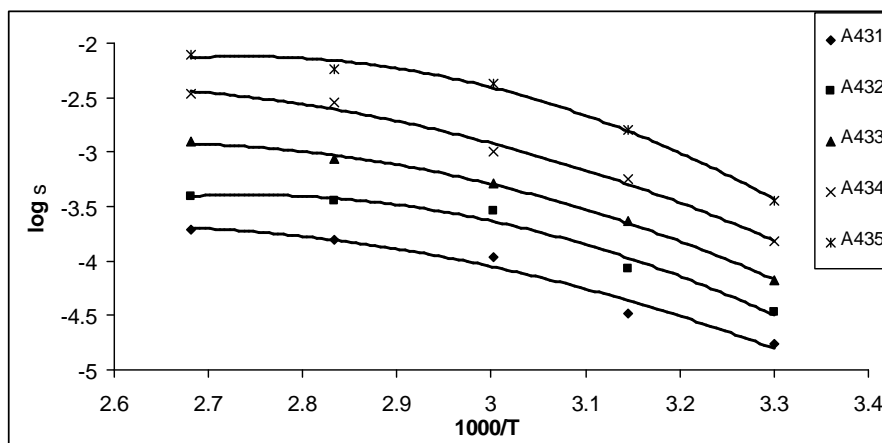


FIG. 4. Variation of ionic conductivity with plasticizer concentration



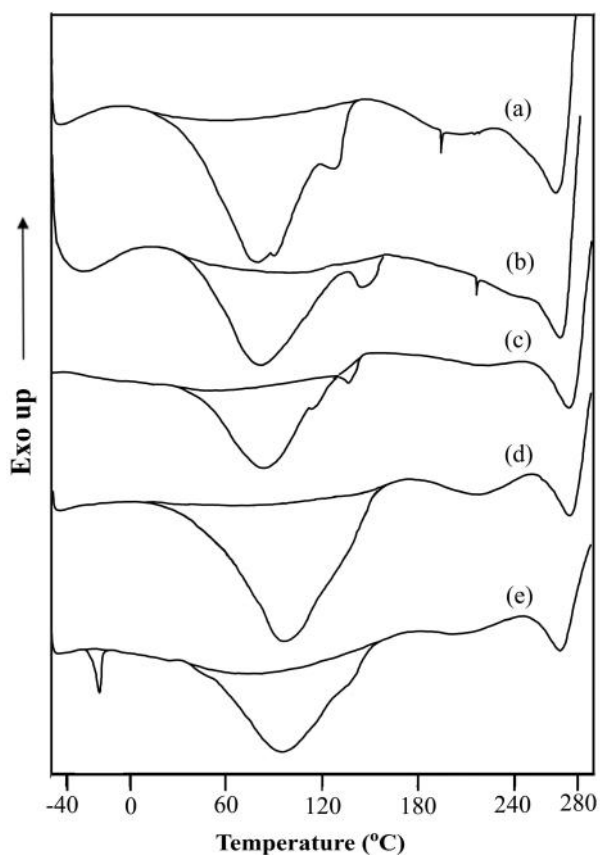
**FIG. 5.** Temperature dependence of ionic conductivity of PVdF – HFP –PMMA –LiClO<sub>4</sub> – PC complexes comprising different plasticizer PC concentrations

### DIFFERENTIAL SCANNING CALORIMETRIC STUDIES

The overall thermal properties of polymer electrolyte systems can be investigated by the Differential Scanning Calorimetric (DSC) technique. The microstructure and morphology of the system is accountable for the important parameters of polymer electrolyte membrane such as the glass temperature ( $T_g$ ), melting temperature ( $T_m$ ) and thermal stability. These parameters will affect the overall separator properties of the electrolyte material when operating in a battery.<sup>35</sup> For compatible polymer blends the glass transition temperature  $T_g$  of the polymer blend is expected to be intermediate between that of the two individual polymers.<sup>36</sup> But in our case it was difficult to find the  $T_g$  of the blended polymer electrolytes PVdF-HFP/PMMA due to the semicrystalline nature of PVdF-HFP and amorphous nature of PMMA. A similar report was published by C-G. Wu.<sup>36</sup> The blend optimization was based on the melting point depression in polymer blends which is an evidence of blend miscibility<sup>8</sup>, which is in accordance to the results already published by Guo.<sup>37</sup> The blending of liquid component decreases the melting point of the polymer membrane (Fig. 6), and is in accordance with the result of H. Ye.<sup>38</sup>

The DSC thermogram of PVdF-HFP/PMMA/LiClO<sub>4</sub> with different concentrations of PC is shown in Fig. 6. In the DSC of PVdF-HFP/PMMA/LiClO<sub>4</sub> the endothermic peak observed at 145°C could be attributed to the melting of crystalline part of PVdF-HFP, on addition of plasticizer the endothermic peak attributed to transition shift was observed to shift to lower temperature region between 90° to 100°C corresponding to different concentrations. A similar result was observed by J.M. Song,<sup>39</sup> where the shift was based on the addition of EC to PVdF-HFP polymer system.

In the Fig. 6, it is found that the melting endothermic peak is broadened and there is a hierarchical decrease in melting temperature indicating decrease in melting point and increase in amorphicity. The blending of the solvents with PVdF-HFP/PMMA must be at molecular level which would have resulted in a highly homogeneous, largely amorphous phase, where the only crystallinity present is the weak crystallinity of the recast PVdF-HFP<sup>40</sup> leading to only one melting point associated with the PVdF-HFP, and no melting point associated with the individual solvents. The broad endothermic peak depicts the transition in the polymer membrane which has an onset around 50°C and endset around 175°C, which indicate the temperature range of optimum usage of the polymer electrolytes.



**FIG. 6** DSC spectra of

- (a) PVdF-HFP(24)–PMMA(8)–LiClO<sub>4</sub>(8)-PC(60)
- (b) PVdF-HFP(21.75)–PMMA(7.25)–LiClO<sub>4</sub>(8)-PC(63)
- (c) PVdF-HFP(19.5)–PMMA(6.5)–LiClO<sub>4</sub>(8)-PC(66)
- (d) PVdF-HFP(17.25)–PMMA(5.75)–LiClO<sub>4</sub>(8)-PC(69)
- (e) PVdF-HFP(15)–PMMA(5)–LiClO<sub>4</sub>(8)-PC(72)

## CONCLUSION

Polymer electrolyte systems comprising PVdF-HFP/PMMA/LiClO<sub>4</sub> at constant ratio and with different PC concentrations have been prepared and subjected to different characterization to confirm the complexation and its electrochemical characteristics. Functional group analysis and interaction of the constituents with each other are ascertained from FTIR studies. The appearance of new peaks along with the changes in the existing peaks in the FTIR spectra confirms the complexation between the individual components. The incorporation of plasticizer (PC) and its amount has been found to influence the ionic conductivity of polymer electrolytes which may be due to lower viscosity, moreover the physical properties of the polymer electrolytes prepared has been ascertained from XRD and DSC. The temperature dependence of ionic conductivity is explained on the basis of free volume model. Hence from the characterizations, polymer electrolyte comprising of PVdF-HFP(75)/PMMA(25)/LiClO<sub>4</sub>(8)/PC(69) having good conductivity and thermal stability is ascertained promising for lithium battery applications.

## REFERENCES

1. Gray, FM; Solid polymer electrolytes-fundamentals and technological applications, first ed.,VCH, London, New York, (1991).
2. Rajendran, S ;Ravi Shanker Babu; Sivakumar, P; J. of memb.sci. 315, 67 (2008).
3. Murata, K.; Izuchi, S.; Yoshihisa, Y. Electrochim. Acta. 45, 1501 (2000).



4. Noda, K; in: Proceedings of the First International Conference on Polymer batteries and Fuel Cells, South Korea, June (2003).
5. Prabakaran, S. R. S.; Micahel, M. S. in: Proceedings of the First International Conference on Polymer batteries and Fuel Cells, South Korea, June (2003).
6. Iijima, T.; Toyoguchi, Y.; Eda, N. *Denki Kagaku*. 53, 619 (1985).
7. Appetecchi, G. B.; Croce, F.; Scrosati, B. *Electrochim. Acta*. 40, 991 (1995).
8. Zhou, YF.; Xie, S.; Ge, XW.; Chen, CH.; Amine, K. *J. Appl. Electrochem*. 34, 1119 (2004).
9. Rajendran, S.; Usha Rani, M. ; Ravi Shanker Babu. *MSAIJ*. 7, 3 (2011).
10. S. Rajendran, Ravi Shanker Babu, P. Sivakumar, *Ionics*. 14, 149 (2008).
11. Doron Aurbach (1999), "Nonaqueous Electrochemistry", (Marcel Dekker, Inc.), p 602.
12. S. Rajendran, V. Shanthi Bama, *J. Non-crystalline solids*. 356, 2764 (2010).
13. Saikia, D.; Kumar, A. *Electrochim. Acta* . 49, 2581 (2004).
14. Abbrent, S.; Plestil, J.; Hlarata, D.; Lindgren, J.; Tegenfeld, J.; Wendsjo, A. *Polymer*. 42, 1407 (2001).
15. Tawansi, A.; Oraby, A.H.; Abdelkader, H.I.; Abdelaziz, M. *J. Magn. Mater.* 262, 203 (2003).
16. Benedict, T.J.; Banumathi, S.; Veluchamy, A.; Gangadharan, R.; Ahamad, A.Z.; Rajendran, S. *J. Power Sources* 75, 171 (1998).
17. Stephan, A.M.; Karan, R.T.; Renganathan, N.G.; Sundaram, V.; Pitchumani, S.; Muniyandi, N.; Gangadharan, R.; Ramamoorthy, P. *J. Power Sources* 81-82, 752 (1999).
18. Rajendran, S.; Uma, T.J. *Power Sources* 87, 218 (2000).
19. Starkey, S.R.; Frech, R. *Electrochim. Acta*. 42, 471 (1997).
20. Fulcher, G.S. *J. Am.Ceram. Soc.* 8, 339 (1925).
21. Li, Z.; Su, G.; Wang, X.; Gao, D. *Solid State Ionics* 176, 1903 (2005).
22. Rajendran, S.; Mahendran, O.; Kannan, R. *Mater. chem. Phys.* 74, 52 (2002).
23. Salami, A.; Yousefi, A.A. *Polym. Test.* 22, 699 (2003).
24. Betz, N.; Bengue, J.; Goncalves, M.; Gionnet, K.; Deleris, G. ; Le Moel, A. *Nucl. Instrum. Methods Phys. Res. Sec. B: Beam Interactions with Materials and Atoms*, 208, 434 (2003).
25. Stephan, A.M.; Premkumar, T.; Renganathan, N.G.; Pitchumani, S.; Thirunakaran, R.; Muniyandi, N. *J. Power Sources* 89, 80 (2000).
26. Battisti, D.; Nazri, G.A.; Klassen, B.; Aroca, R. *J. Phys. Chem.* 97, 5826 (1993).
27. Quist, A.S.; Bates, J.B.; Boyd, G.E. *J. Chem. Phys.* 54, 4896 (1971).
28. Rajendran, S.; Ravi shanker Babu.; Sivakumar, P. *Ionics* 14, 149 (2008).
29. Rajendran, S.; Usha Rani, M.; Ravi shanker Babu. *MSAIJ*. 7, 3 (2011).
30. Rhoo, H.J.; Kim, H.T.; Park, J.K.; Hwang, T.S. *Electrochim. Acta*. 42, 1571 (1997).
31. Ravi shanker Babu, (2008), Ph.D Thesis, Alagappa University, India , p.154.
32. Doremus, R. H. *J. Appl. Phys.* 92, 7619 (2002).
33. Ojovan, M.I.; Travis, K.P.; Hand, R.J. *J. Phys. condens.Matter* 19, 415107 (2007).
34. Ojovan, M.I.; *Adv. in cond. Mat. Phys.* (2008), Article ID 817829, 23 pages doi:10.1155/ 2008/817829.
35. Saikia, D.; Cheng-Yang, Y.W.; Chen, Y.T.; Li, Y.K.; Lin, S.I. *Desalination* 234, 24 (2008).
36. Wu, C.W.; Lu, M.I.; Chuang, H.J. *Polymer* 46, 5929 (2005).
37. Guo, Q.P; Peng, X.S.; Wang, Z.J. *Polymer* 32, 53 (1991).
38. Ye, H.; Xu, J.J. *J. Power Sources* 165, 500 (2007).
39. Song, J.M.; Kang, H.R.; Kim, S.W.; Lee, W.M.; Kim, H.T. *Electrochim. Acta*. 48, 1339 (2003).
40. Baril, D.; Chabre, Y.; Armand, M. B. *J. Electrochem. Soc.* 140, 2687 (1993).

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